

**14th International
Symposium on
Metal-Hydrogen Systems:**
Fundamentals and applications

MH2014 Programme and Abstracts

20-25 July 2014
Salford, Manchester, United Kingdom

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Organisation

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G. Walker (co-chair)	University of Nottingham, UK

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Symposium Management

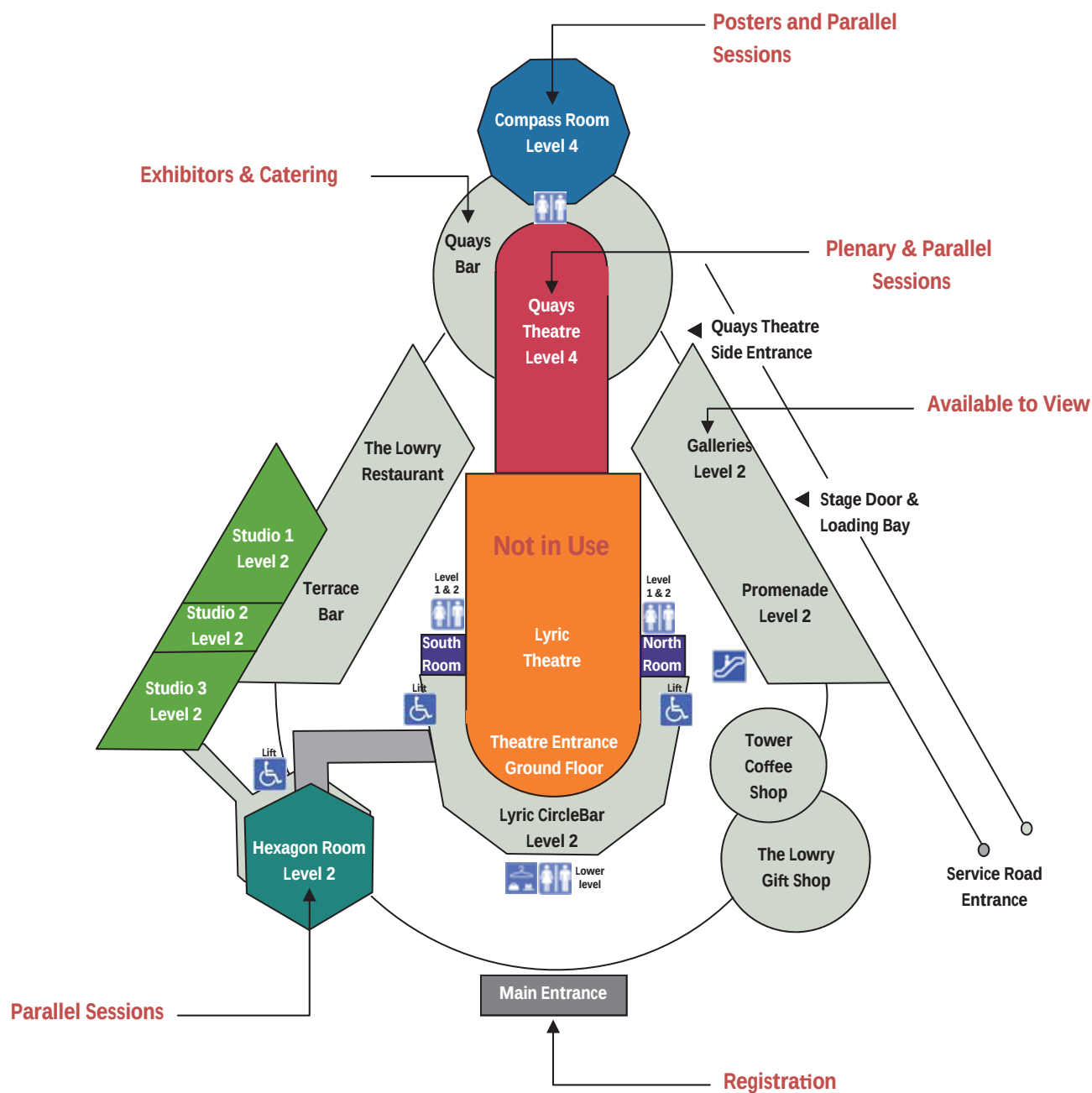
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At a glance timetable

	20 Sunday	21 Monday	22 Tuesday	23 Wednesday	24 Thursday	25 Friday
8:30 AM		Registration	Registration	Registration	Registration	
9:00 AM		Registration	Plenary 2 (9.00am-9.40am)	9.00am-10.30am Parallel Sessions WeOQ-093-WeOQ-096;WeOH-101- WeOH-104;WeOD-109-WeOD- 112;WeOC-117-WeOC-120	Plenary 4 (9.00am-9.40am)	9.00am-10.40am Parallel Sessions FrOQ-169-FrOQ-172;FrOH-177- FrOH-180
9:30 AM		Registration/Opening (9.30am- 9.40am)	Plenary 2 (9.00am-9.40am)	9.00am-10.30am Parallel Sessions WeOQ-093-WeOQ-096;WeOH- 101-WeOH-104;WeOD-109-WeOD- 112;WeOC-117-WeOC-120	Plenary 4 (9.00am-9.40am)	9.00am-10.40am Parallel Sessions FrOQ-169-FrOQ-172;FrOH-177- FrOH-180
10:00 AM		Plenary 1 (9.40am-10.20am) - Quays Theatre	Plenary 3 (9.40am-10.20am)	9.00am-10.30am Parallel Sessions WeOQ-093-WeOQ-096;WeOH- 101-WeOH-104;WeOD-109-WeOD- 112;WeOC-117-WeOC-120	Plenary 5 (9.40am-10.20am)	9.00am-10.40am Parallel Sessions FrOQ-169-FrOQ-172;FrOH-177- FrOH-180
10.20am		BREAK (10.20am-11.00am)	BREAK (10.20am-11.00am)	BREAK (10.30am-11.00am)	BREAK (10.20am-11.00am)	BREAK (10.40am-11.00am)
11:00 AM		11.00am-12.30pm Parallel sessions MoOQ-001-MoOQ-004;MoOH- 013-MoOH-016;MoOD-025-MoOD- 028;MoOC-037-MoOC-040	11.00am-12.30pm Parallel Sessions TuOQ-049-TuOQ- 052;TuOH-061-TuOH-064, TuOD- 073-TuOD-076,TuOC-085-TuOC- 088	11.00am-12.30pm Parallel Sessions WeOQ-097-WeOG- 100;WeOH-105-WeOH108;WeOD- 113-WeOD-116;WeOC-121-WeOC- 124	11.00am-12.30pm Parallel Sessions ThOQ-125-ThOQ- 128;ThOH-137-ThOH-140;ThOD- 149-ThOD-152;ThOC-161-ThOC- 164	11.00am-12.40pm Parallel Sessions FrOQ-173-FrOQ- 176;FrOH-181-FrOH-184
12:30 PM		Lunch & Exhibition (12.30pm- 2.00pm)	Lunch & Exhibition (12.30pm- 2.00pm)	Packed Lunch & Excursion	Lunch & Exhibition (12.30pm- 2.00pm)	12.40pm Closing Session, Prizes and Handover: Quays Theatre
1:30pm						Lunch & Departure
2:00 PM	Registration (2pm-8pm)	2.00pm-3.30pm Parallel Sessions MoOQ-005-MoOQ-008;MoOH-017- MoOH-020; MoOD-029-MoOD- 032;MoOC-041-MoOC-044	2.00pm-3.30pm Parallel Sessions TuOQ-053-TuOQ-056;TuOH-065- TuOH-068;TuOD-077-TuOD- 080;TuOC-089-TuOC-092	Excursion	2.00pm-3.40pm Parallel Sessions ThOQ-129-ThOQ-132;ThOH-141- ThOH-144;ThOD-153-ThOD- 156;ThOC-165-ThOC-168	
3:30 PM	Registration (2pm-8pm)	BREAK (3.30pm-4.00pm)	BREAK (3.40pm-4.00pm)	Excursion	BREAK (3.40pm-4.00pm)	
4:00 PM	Registration (2pm-8pm)	4pm-5.30pm Parallel Sessions MoOQ-009-MoOQ-012;MoOH- 021-MoOH-024;MoOD-033-MoOD- 036;MoOC-045-MoOC-048	4.00pm-5.30pm Parallel Sessions TuOQ-057-TuOQ-060;TuOH-069- TuOH-072;TuOD-081-TUOD-084	Excursion	4.00pm-5.30pm Parallel Sessions ThOQ-133-ThOQ-136;ThOH-145- ThOH-148;ThOD-157-ThOD-160	
5:30 PM	Registration (2pm-8pm)			Excursion		
6:00 PM	Registration (2pm-8pm) Welcome Reception (6pm-8pm)		6.00pm-8.00pm Poster TuP-001- TuP-115 and Exhibition: Compass Room		6.00pm-8.00pm Poster ThP-001- ThP-129 and Exhibition: Compass Room	
6:30 PM	Registration (2pm-8pm) Welcome Reception (6pm-8pm)	Welcome Reception at Manchester Museum of Science and Industry	6.00pm-8.00pm Poster TuP-001- TuP-115 and Exhibition: Compass Room		6.00pm-8.00pm Poster ThP-001- ThP-129 and Exhibition: Compass Room	
7:30 PM	Registration (2pm-8pm) Welcome Reception (6pm-8pm)	Welcome Reception at Manchester Museum of Science and Industry	6.00pm-8.00pm Poster TuP-001- TuP-115 and Exhibition: Compass Room	Conference Dinner - Manchester United Football Club	6.00pm-8.00pm Poster ThP-001- ThP-129 and Exhibition: Compass Room	

Floor map of the Lowry



Awards

The MH2014 organising committee will present MH2014 Student Poster Awards for excellent POSTER presentations by participants under 35 years of age that have been recommended by the MH2014 Committee. The award winners will be announced during Friday's closing session and presented with a prize.

Instructions for Applicants for the MH2014 Poster Awards:

1. All poster presentations are scheduled to take place on either Tuesday or Thursday
2. Applicants should put their poster on display at 5pm on the day of their poster session
3. Applicants should stand next to their poster from 6pm-8pm of the poster session for discussion with the reviewers

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Technical Programme

MONDAY July 21st					
Registration					
Opening					
9.40	Chair: Gavin Walker Plenary 1: Quays Theatre Hydrogen as the basis for a sustainable energy economy Andreas Züttel				
10.20	Break				
	Quays Theatre Chair: Radovan Cerny	Hexagon Chair: Bjorgvin Hjorvarsson	Deck 1 Chair: Astrid Pundt	Compass Chair: Daniel Fruchart	
11.00	MoOQ-001 Invited F2 Reversible Hydrogen Activation in Molecular Complexes: Approaches to Catalysis and Energy Storage Using Amine Boranes Tom Autrey	MoOH-013 Invited M2 Novel Complex Hydrides for Hydrogen Storage and Related Structural Studies Hui Wu	MoOD-025 Invited A5 The Use of Hydrogen to Separate and Recycle NdFeB Magnets from Electronic Waste Allan Walton	MoOC-037 Invited M1 Improvement of Activation and Re-hydrogenation Behaviors of TiFe Etsuo Akiba	
11.30	MoOQ-002 Contributed F5 Femtosecond Spectroscopy on Complex Hydrides Andreas Borgschulte	MoOH-014 Contributed F5 Tuning Thermodynamics by Finite Size Maximilian Wolff	MoOD-026 Contributed F1 Where is the critical point of the Pd-D ₂ system? Evan Gray	MoOC-038 Contributed A1 Hydrogen Storage in Metal Hydrides and Complex Hydrides: Differences, Challenges and Advantages Inga Bürger	
11.50	MoOQ-003 Contributed M2 Investigating and Understanding Ionic Ammine Materials Martin Jones	MoOH-015 Contributed F4 Origin of the Huge Asymmetry in Ab- and Desorption Kinetics of Hydrogen in Capped Films Ronald Griessen	MoOD-027 Contributed F1 In-situ studies of hydrogen loading and unloading in single palladium nanocrystals Andrea Baldi	MoOC-039 Contributed F6 Size Reduction in Mg and Mg rich Intermetallics for Hydrogen Storage Tayfur Ozturk	
12.10	MoOQ-004 Contributed M2 Complex Transition Metal Hydrides Incorporating Covalent and Ionic Hydrogen Terry D. Humphries	MoOH-016 Contributed M1 Probing the cerium / cerium hydride interface using nanoindentation Martin Brierley	MoOD-028 Contributed F5 Lattice Expansion of Palladium-Hydrogen (Pd-H) : a Critical Review of Dimensional Measurements Nicolas Armanet	MoOC-040 Contributed M1 Searching out the hydrogen absorption / desorption limiting reaction factors: strategies allowing to increase kinetics Ali Zeaiter	
12.30	Lunch and Exhibition				
	Quays Theatre Chair: Bjorn Hauback	Hexagon Chair: Petra de Jongh	Deck 1 Chair: David Book	Compass Chair: E.Akiba	
14.00	MoOQ-005 Invited A4 High throughput computational characterization of hydrogen solubility and diffusion in intermetallics and complex metal hydrides David Sholl	MoOH-017 Invited F4 Functionalized Mesoporous Carbon Supports for Hydrogen Storage: A First-principles Study of Surface Interactions with Complex Hydrides Eric Maizoub	MoOD-029 Invited A4 Hydrogen Purification for Cost-effective Fuel Cell Power Zheng Xiao Guo	MoOC-041 Invited A6 Development of Thermal Batteries Based on Metal Hydrides: Opportunities and Challenges Zak Fang	

14.30	MoQ-006 Contributed M2 Theoretical Exploration and Syntheses of Complex Transition Metal Hydrides with High Gravimetric Hydrogen Density Shigeyuki Takagi	MoOH-018 Contributed A5 Mesoscale Microstructural Computational Simulation of Hydrogen Permeation Test to Calculate Grain Boundary Diffusivity Sathiskumar Jothi	MoOD-030 Contributed A4 Pd-Cu-M: Alloys for Hydrogen Separation Membrane Shahrouz Nayeibossadri	MoOC-042 Contributed A1 Lightweight aluminium based storage tank system with Ti-doped Na ₃ AlH ₆ for hydrogen and heat storage Michael Felderhoff
14.50	MoQ-007 Contributed M2 Optimized Complex Hydride Powder from High-Throughput Screening Jean-Philippe Soulie	MoOH-019 Contributed A6 Pressure and Temperature influence in a MgH ₂ Numerical Model Alistair Stuart	MoOD-031 Contributed A4 High Hydrogen Flux through Bare Vanadium Membrane without Pd Overlayer Hiroshi Yukawa	MoOC-043 Contributed A1 Comparative Analysis of the Efficiencies of Hydrogen Storage Systems Utilising Solid State H Storage Materials Michael Lototsky
15.10	MoQ-008 Contributed M2 The Destabilization of Complex Hydrides with Metal Sulfides Drew Sheppard	MoH-020 Contributed M2 Tuning the Stability of Ca(BH ₄) ₂ by the Inclusion of Additives: A Computational Study Elisa Albanese	MoOD-032 Contributed M1 Alloys Based on 5 Group Metals for Hydrogen Purification Membranes Serik Kozhakhmetov	MoOC-044 Contributed M1 Can new Mg-rich phases in RE-TM-Mg (RE = Rare-Earth, T = Transition metal) systems be good candidates for hydrogen storage? Jean-Louis Bobet
15.30	Break			
	Quays Theatre Chair: Craig Jensen	Hexagon Chair: David Sholl	Deck 1 Chair: Xiao Guo	Compass Chair: Jose Bellosta von Colbe
16.00	MoOQ-009 Invited M2 Enthalpy-Entropy Compensation Effect in the Alkali Silanides Series: MSiH ₃ (M = K, Rb, Cs) Raphael Janot	MoOH-021 Invited F1 Thermodynamic Modelling of Metal-Hydrogen Systems Using the Calphad Method Jean-Marc Joubert	MoOD-033 Invited A4 Ni-Nb-Zr Amorphous Alloy Membranes for Separation of Hydrogen from CO ₂ and Other Gases Danesh Chandra	MoOC-045 Invited A1 Solid State Hydrogen Tank Coupled with High Temperature PEM: From Materials to APU Application Marcello Barrico
16.30	MoOQ-010 Contributed M2 Thermodynamics and Crystal Structures of the Alkali Silanides MSiH ₃ (M=K, Rb, Cs) Jean-Noël Chotard	MoOH-022 Contributed F1 Thermodynamics of Borohydrides-based Materials Coupling ab-initio and Calphad Methods Eugenio R. Pinatel	MoOD-034 Contributed M1 Engineering Hydrogen Separation Membrane Alloys: An Optical Approach Ruud Westerwaal	MoOC-046 Contributed A1 Integrated System Of Fuel Cell And Hydride Tank Paola Rizzi
16.50	MoOQ-011 Contributed M2 Reversibility of Complex Hydrides Under High Pressure Conditions Anna-Lisa Chaudhary	MoOH-023 Contributed F1 Self-amplified Site Occupancy Transition of Hydrogen in V studied from Density Functional Calculations Robert Johansson	MoOD-035 Contributed F2 Mechano-chemical coupling effects during hydriding of nanocrystalline metallic thin films Joris Proost	MoOC-047 Contributed A1 Modelling the Thermal Management of a Solid State Hydrogen Store Based on Magnesium Hydride Christopher Bennett
17.10	MoOQ-012 Contributed M1 Lithium Hydride Stabilised Nanoparticles and its Hydrogen Storage Properties Lei Wang	MoOH-024 Contributed F1 First Principles Calculations on (La-Mg)-Ni Hydrides Jean-Claude Crivello	MoOD-036 Contributed M1 Influence of Microstructure and Mechanical Stress on Behavior of Hydrogen in Thin Pd Films Marián Vlček	MoOC-048 Contributed A1 An Improved Model for Metal-Hydrogen Storage Tanks Shahrzad Mohammadshahi
18.30	Welcome Reception at Manchester Museum of Science and Industry			
20.30	Free time in Manchester for dinner			

TUESDAY July 22nd					
Time	Registration				
09.00	Chair: Andreas Zuetzel Plenary 2: Quays Theatre UK Hydrogen and Fuel Cell Research - an overview Nigel Brandon				
09.40	Plenary 3: Quays Theatre Cool Hydrides! Shin-ichi Orimo				
10.20	Break				
	Quays Theatre Chair: Shin-ichi Orimo	Hexagon Chair: Dag Noreus	Deck 1 Chair: Bill David	Compass Chair: Ronald Griessen	
11.00	TuOQ-049 Invited M1 Structure-Properties Relationship in Nanostructured Mg-Based Hydrides for Energy Storage Volodymyr Yartys	TuOH-061 Invited A3 Role of RE composition on the performance of working metal-hydride electrodes in Ni-MH alkaline batteries Michel Latroche	TuOD-073 Invited F4 On the role of size, shape and composition in metal nanoparticle - Hydrogen interactions Christoph Langhammer	TuOC-085 Invited A6 The use of metal hydrides in hydrogen sensors and detectors Bernard Dam	
11.30	TuOQ-050 Contributed M1 SPD processed Mg-based materials to build up reactive microstructures enabling fast hydrogen sorption kinetics Daniel Fruchart	TuOH-062 Contributed A3 Past, Present, and Future of Metal Hydride Alloys in Nickel-Metal Hydride Batteries Kwo Young	TuOD-074 Contributed M1 Synthesis, Characterization and Hydrogen Sorption Properties of Mg-Ti based Nanoparticles and Nanocomposites Marco Calizzi	TuOC-086 Contributed A6 Metal Hydride Based Eye-readable and Color Tunable Detectors for Chemical and Biomedical Hydrogen Sensing Applications Peter Ngene	
11.50	TuOQ-051 Contributed M1 Kinetics Enhancement, Thermodynamics Tailor and Thermal Conductivity Study in Mg-based Hydrogen Storage Materials Huaiyu Shao	TuOH-063 Contributed A3 Influence of Kinetics of Hydrogen Transport in a Metal Hydride Anode on the Discharge Properties of the Electrodes of the Ni-MH Batteries Igor Gabis	TuOD-075 Contributed M2 Low Temperature Hydrogen Cycling and Modified Thermodynamics of Spark Discharge Generated Fluorite Cubic Mg-Ti Hydride Nanoparticles Stephan W.H. Eijt	TuOC-087 Contributed A6 Large Pressure Range Optical Hydrogen Sensing Materials Christiaan Boelsma	
12.10	TuOQ-052 Contributed M1 Stability of Magnesium for Elevated Temperature Cycling as a Thermal Storage Medium for Concentrated Solar Power Applications Andrew Patman	TuOH-064 Contributed A3 Influence of alloy stoichiometry, surface- and heat treatment on NiMH cells made by atomised as well as reused alloys from spent batteries. Dag Noréus	TuOD-076 Contributed F6 Destabilization of Mg hydride in the Mg-Ti system Kohta Asano	TuOC-088 Contributed A6 Hydrogen gas collection System Using Mg Catalyzed with Niobium Oxide Satoshi Hino	
12.30	Lunch and Exhibition				
	Quays Theatre Chair: Sabrina Sartori	Hexagon Chair: Paul Anderson	Deck 1 Chair: Vlad Antonov	Compass Chair: Richard Chahine	
14.00	TuOQ-053 Invited F2 The Size Dependence of Reactivity and Hydrogen Mobility for Carbon-Supported MgH ₂ Particles Petra de Jongh	TuOH-065 Invited A3 Borohydrides continue to surprise: A different outlook on their properties Rana Mohtadi	TuOD-077 Invited F8 The Synthesis and Characterisation of Novel Metal Hydrides Eugene Gregoryanz	TuOC-089 Invited F2 Spontaneous Dehydrogenation Reactions Elsa Callini	

14.30	TuOQ-054 Invited M1 Recent progress in enhanced hydrogen storage of MgH ₂ Min Zhu	TuOH-066 Invited A3 Fast Ionic Conduction in Complex Hydrides Motoaki Matsuo	TuOD-078 Invited F8 High pressure and temperature formation of graphene hydride Dean Smith	TuOC-090 Invited A1 Practical Hybrid High-Pressure / Sorbent Hydrogen Storage Systems Incorporating Nanoporous Material Tim Mays
15.00	TuOQ-055 Contributed F4 Anti-Oxidized Mg for a Variety of Applications Shigehito Isobe	TuOH-067 Contributed A3 Metal hydride electrode for Metal Hydride-Air Secondary Battery Tomoya Matsunaga	TuOD-079 Contributed F8 Pressure Effect on Hydrogen Tunneling and Vibrational Spectrum in alpha-Mn Alexander Kolesnikov	TuOC-091 Contributed A5 Stress Generation of Hydride Graphite Composites Associated with Cyclic Hydrogenation Felix Heubner
15.20	TuOQ-056 Contributed M1 Synthesis and Hydrogen Storage Properties of Nanostructured Mg-based Alloys Xingguo Li	TuOH-068 Contributed A3 Mg catalysed with TiF ₃ as anode in a Ni-MH battery Fokko Mulder	TuOD-080 Contributed F8 In Situ Neutron Diffraction Measurement on Deuterization Process of Iron at High Pressure and High Temperature Akihiko Machida	TuOC-092 Contributed M2 Initial Step of Hydride Formation in Single Crystalline Gadolinium Thin Films and Islands Studied on the nm-Scale Sara Wanjelik
15.40	Coffee Break			
	Quays Theatre Chair: Bernard Dam	Hexagon Chair: Rana Mohtadi	Deck 1 Chair: Vlad Yartys	Compass
16.00	TuOQ-057 Invited F1 The Interpretation of Experimental Polycrystalline Coherent Inelastic Neutron Scattering (poly-CINS) from Magnesium Deuteride Daniel Roach	TuOH-069 Invited A3 Metal hydride as anode material for all-solid-state Li-ion batteries Takayuki Ichikawa	TuOD-081 Invited F8 Aluminum-based Interstitial Hydride, Al ₂ CuH _x Hiroyuki Saitoh	
16.30	TuOQ-058 Contributed M1 Correlation between microstructural and mechanical behavior of nanostructured MgH ₂ upon hydrogen cycling Patricia de Rango	TuOH-070 Contributed A3 Hydrides as negative electrode for lithium-ion batteries: A review of this challenge for hydrogen storage and Li-ion technologies Liwu Huang	TuOD-082 Contributed F2 A kinetics investigation of MgH ₂ formation/decomposition in Mg-Ti layers and MgO-Mg thin films José Francisco Fernandez	
16.50	TuOQ-059 Contributed M1 Coating of Magnesium Spheres for Thermal Energy Storage Applications Priyen Mistry	TuOH-071 Contributed A3 Nanoconfined hydrides as anode material for Li-ion batteries Yassine Oumellal	TuOD-083 Contributed F8 A family of high pressure synthesized MgTM ₂ H ₆ (TM=Zr, Nb) hydrides Dag Noréus	
17.10	TuOQ-060 Contributed M1 The effect and optimization of microstructure on the hydrogenation of Mg/Fe thin film multilayers Lennard Mooij	TuOH-072 Contributed A3 H ₂ thermal desorption and hydride conversion reactions in Li cells of TiH ₂ /C nanocomposites Francesco Maria Vitucci	TuOD-084 Contributed M1 Effect of the rare earth on the structural and hydrogen storage properties of A ₂ Ni ₇ (A = Y or Gd) Veronique Charbonnier	
18.00	Poster and Exhibition: Compass Room			
20.00	Free evening			

WEDNESDAY July 23rd					
Time	Registration				
	Quays Theatre Chair: Michael Hirscher	Hexagon Chair: Dan Bull	Deck 1 Chair: Evan Gray	Compass Chair: Steve Bennington	
09.00	WeOQ-093 Invited A1 State of the Art and Needs of Hydrogen Adsorption Storage Systems Richard Chahine	WeOH-101 Invited M3 Nitrogen Based Materials for Hydrogen Storage Ping Chen	WeOD-109 Invited F1 On site occupation and diffusion of H in transition metals Björgvin Hjörvarsson	WeOC-117 Invited A1 Engineering technologies for fluid chemical hydrogen storage systems Bart van Hassel	
09.30	WeOQ-094 Contributed M4 Hydrogen interaction with nanoconfined materials Claudia Zlotea	WeOH-102 Contributed M2 Probing Reversibility in the Li-N-H Hydrogen Store by in situ X-Ray Powder Diffraction Josh Makepeace	WeOD-110 Contributed M1 Degradation in the reversible hydrogen storage capacity of V-based bcc alloys: what is the origin and how to improve it? Hyunjeong Kim	WeOC-118 Contributed M3 Reverse Engineering the Chemistry for High Capacity Chemical Hydrogen Storage Solutions Tom Autrey	
09.50	WeOQ-095 Contributed M4 Quantum Dynamics of Hydrogen Molecules trapped inside Nanocavities in different solid Water Structures Lorenzo Ulivi	WeOH-103 Contributed M2 Structure Solution of New Imide and Mixed Imide-Amide Compounds for Hydrogen Storage Materials Emilio Napolitano	WeOD-111 Contributed M1 Total Scattering Investigations of the Local Structure in Fe-containing hydrides of bcc-alloys Magnus H. Sørby	WeOC-119 Contributed M3 Ionic Liquid Borohydride - A Liquid Phase Chemical Hydrogen Storage Material Theo Friedrich	
10.10	WeOQ-096 Contributed M4 Synthesis of Cr-MOF Derived Porous Carbon for Hydrogen Storage Applications Henrietta Langmi	WeOH-104 Contributed M2 Phase space investigation of lithium amide halides Rosalind Davies	WeOD-112 Contributed M1 Defect studies of H ⁺ implanted Niobium Ivan Prochazka	WeOC-120 Contributed M2 Hydrogen Rich Nickel Boride as Catalyst for the Recycling of Spent Ammonia Borane Florian Mertens	
10.30	Coffee Break				
	Quays Chair: Takayuki Ichikawa	Hexagon Chair: Ping Chen	Deck 1 Chair: Jean-Marc Joubert	Compass Chair: Ralph Janot	
11.00	WeOQ-097 Invited M4 Recent Progress in Hydrogen Storage on MOFs Michael Hirscher	WeOH-105 Invited F1 Hydrogen storage: imides, amides and ammonia Bill David	WeOD-113 Invited F1 Proving the Contact Rules for Phase Regions: Implications to Phase Diagrams of Metal-Hydrogen Systems Vladimir E. Antonov	WeOC-121 Invited M2 Control of Dehydrogenation / Rehydrogenation Reaction of Metal Borohydride-based Composites Young Whan Cho	
11.30	WeOQ-098 Contributed M4 Direct observation of Pd(H ₂) at ambient temperature on single atoms of Pd supported on a metal-organic framework Petra Szilagyi	WeOH-106 Contributed M2 Effect of Lithium Ion Conduction on Hydrogen Desorption of LiNH ₂ -LiH Solid Composite Tengfei Zhang	WeOD-114 Contributed M1 Structure and properties of hydrides of gamma-U alloys Ladislav Havela	WeOC-122 Contributed M2 New method of synthesis of dead-mass free mixed-cation borohydride materials for hydrogen storage applications Tomasz Jaron	
11.50	WeOQ-099 Contributed M4 Ultradense Hydrogen Physisorption in the Porous Magnesium Borohydride Nikolay Tumanov	WeOH-107 Contributed M2 New insights upon desorption process of the Mg/K amide system Sebastiano Garroni	WeOD-115 Contributed F4 Hydride Initiation Experiments using Spherical Uranium Powders George Powell	WeOC-123 Contributed M2 Quantitative spectra-structure relation for borohydrides Vincenza D'Anna	

12.10	WeOQ-100 Contributed M4 Ceramic on Metal Type Hydrogen Storage Composites and Their Applications Nobuyuki Nishimiya	WeOH-108 Contributed M2 Effects of Doping the Li-Mg-N-H System with CaCl_2 and CaBr_2 Rachel Bill	WeOD-116 Contributed F4 The influence of vacuum annealing on the uranium-hydrogen reaction and the progression from nucleation to growth mechanisms John Knowles	WeOC-124 Contributed M2 Spectroscopic and Structural Characterization of gamma- $\text{Mg}(\text{BH}_4)_2$ Thermal Decomposition: Vacuum vs. Hydrogen Atmosphere Jenny G. Vitillo
12.30	Packed Lunch and Excursion			
19.30	Conference Dinner			

Afternoon excursion



MH2014 Conference Dinner



Time	THURSDAY July 24th				
	Registration				
09.00	Chair: Tim Mays Plenary 4: Quays Theatre Hydrogen storage research and development efforts supported by the U.S. Department of Energy Ned Stetson				
09.40	Plenary 5: Quays Theatre Planck Sorption Cryocoolers - A Very Successful Metal Hydride Technology for Space Exploration Robert C Bowman Jr				
10.20	Coffee Break				
	Quays Theatre Chair: Cladia Weidenthaler	Hexagon Chair: Marcello Baricco	Deck 1 Chair: Robert Bowman	Compass Chair: John Knowles	
11.00	ThOQ-125 Invited M2 Rare-earth borohydrides – structures and thermal properties Bjørn C. Hauback	ThOH-137 Invited A1 Tank design challenges and optimization for metal hydride based hydrogen storage Jose Bellosta van Colbe	ThOD-149 Invited F3 NMR in NaH: The Effects of Added NaOH Mark Conradi	ThOC-161 Invited F7 Hydrogen Isotope Separation for Fusion Power Applications Robert Smith	
11.30	ThOQ-126 Contributed M2 Borohydrides: Stabilizing Light Metal Frameworks Radovan Cerny	ThOH-138 Contributed A1 Modelling Around the Design of a Hydride Hydrogen Tank for Heavy Applications Olivier Guilla	ThOD-150 Contributed F4 In-situ TEM Observation on Hydrogenation of Mg-Ni Films Deposited by Magnetron Sputtering Junko Matsuda	ThOC-162 Contributed F7 Computational study of helium bubble release from titanium tritide surface under different temperatures Li Liang	
11.50	ThOQ-127 Contributed M2 Crystal Structures and Decomposition Properties of Hydrogen-Rich $Al(BH_4)_3 \cdot NH_3BH_3$ Complex Iurii Dovgaliuk	ThOH-139 Contributed A5 Measure of the hydride breathing while cyclically absorbing and desorbing hydrogen Vasile Iosub	ThOD-151 Contributed F4 In-situ STM and XRD studies on the Coherency state of Hydride Precipitation and Growth in Nb Thin Films Vladimir Burlaka	ThOC-163 Contributed F7 Helium 3 Retention In Tritium Storage Materials Sylvain Challet	
12.10	ThOQ-128 Contributed M2 Towards Hydridic Nanoporous Frameworks: the First Imidazolate – Borohydride Compound Li_2ImBH_4 ($Im=[C_3H_3N_2]$) Fabrice Morelle	ThOH-140 Contributed A5 High-Resolution In-Operando Neutron Radiography and Tomography of Hydride-Graphite Composites Kai Herbrig	ThOD-152 Contributed M1 Closing the Pressure Gap in X-Ray Photoemission Spectrometry for the Study of Hydride-Forming Compounds Renaud Delmelle	ThOC-164 Contributed F7 Quasi-elastic neutron scattering studies of the hydrogen / deuterium diffusion process in palladium Simon Steel	
12.30	Lunch and Exhibition				
	Quays Theatre Chair: Tom Autry	Hexagon Chair: Alberto Albinati	Deck 1 Chair: Keith Ross	Compass Chair: Ian Morrison	
14.00	ThOQ-129 Invited M2 Mechanistic Studies of the Reversible Hydrogenation of Boranes to Borohydrides under Moderate Conditions Craig Jensen	ThOH-141 Invited M4 Neutron studies of hydrogen adsorption in porous materials Craig Brown	ThOD-153 Invited F3 Nuclear Magnetic Resonance Studies of Atomic Motion in Borohydride-Based Materials Alexander Skripov	ThOC-165 Invited F7 Hydrogen Isotope Separation in Nanoporous Framework Materials Hyunchul Oh	

14.30	ThOQ-130 Invited M3 Octahydrotriborates ($B_3H_8^-$): Synthesis and Hydrogen Storage Zhenguo Huang	ThOH-142 Invited F1 High throughput Inelastic Neutron Scattering, from fiction to reality A. J. Timmy Ramirez-Cuesta	ThOD-154 Invited F3 Probing Hydroborate Polyanion Reorientations via Quasielastic Neutron Scattering Terrence J. Udovic	ThOC-166 Invited F7 Hydrogen isotope separation in metal-organic frameworks: Insights from theory Thomas Heine
15.00	ThOQ-131 Contributed M2 A series of novel metal borohydride ammoniates Lars H. Jepsen	ThOH-143 Contributed M2 Mechanochemical synthesis of hydrides followed in situ by X-ray diffraction Yaroslav Filinchuk	ThOD-155 Contributed F3 Quasielastic neutron scattering on $Mg(BH_4)_2$ Luca Silvi	ThOC-167 Contributed F7 Reversible Isotope Exchange Reactions in $Ca(BH_4)_2$ Manish Sharma
15.20	ThOQ-132 Contributed M2 Thermal decomposition of a $NaZn_2(BH_4)_5 + MgH_2$ composite Daniel Reed	ThOH-144 Contributed F1 Diffraction Profile Broadening Owing To Vacancies In $LaNi_5$: Simulations And In-Situ Neutron Diffraction Timothy Webb	ThOD-156 Contributed F3 Probing Molecular Dynamics of Metal Borohydrides on the Surface of Mesoporous Scaffolds by Multinuclear High Resolution Solid State NMR Son-Jong Hwang	ThOC-168 Contributed F7 Isotope effect on magnetic and structural properties of $Y_{1-y}Gd_yFe_2(H_2D_{1-z})_{4.2}$ compounds Valerie Paul-Boncour
15.40	Coffee Break			
	Quays Theatre Chair: Young Wan Cho	Hexagon Chair: Craig Buckley	Deck 1 Chair: Kuriyama Nobuhiro	Compass
16.00	ThOQ-133 Invited M2 Hydrogen storage in Ammine metal borohydrides Xuebin Yu	ThOH-145 Invited M1 Tailoring the Hydrogen De-sorption Thermodynamics of VH_2 by Various Alloying Additives Sanjay Kumar	ThOD-157 Invited A5 Hydrogen diffusion and interaction with microstructure of the duplex stainless steels Dilson Silva dos Santos	
16.30	ThOQ-134 Contributed M2 Reactivity of the different magnesium borohydride polymorphs Voraksmy Ban	ThOH-146 Contributed F1 Effect of Solid Solution Hardening by Interstitial Elements on Hydrogenation Properties of V Based BCC Alloys Kouji Sakaki	ThOD-158 Contributed A5 Effects of Hydrogen and Helium on Swelling in Electron-irradiated Pure FE Naoyuki Hashimoto	
16.50	ThOQ-135 Contributed M2 Additives in magnesium borohydride: local structure and effect on reversibility Olena Zavorotynska	ThOH-147 Contributed A6 Niche Applications of Metal Hydrides and Related Thermal Management Issues Mykhaylo Lototsky	ThOD-159 Contributed A5 Multiscale multiphysics atomistic-meso-continuum critical dislocation method for hydrogen embrittlement Sathiskumar Jothi	
17.10	ThOQ-136 Contributed A1 Study on the effects of repeated hydrating and dehydrating reactions on compacted ball milled Mg-based powders Amelia Montone	ThOH-148 Contributed A6 Numerical Study on a Two-Stage Metal Hydride Hydrogen Compression System Evangelos Gkanas	ThOD-160 Contributed M1 Hydrogen-induced defects and multiplication of dislocations in Palladium Jakub Cizek	
18.00	Poster and Exhibition: Compass Room			
20.00	Free evening			

FRIDAY July 25th				
Time	Quays Theatre Chair: Craig Brown	Hexagon Chair: Martin-Owen Jones	Deck 1	Compass
09.00	FrOQ-169 Invited M2 Core-shell hydride nanoarchitectures: Design and hydrogen behaviour Francois Aguey-Zinsou	FrOH-177 Invited M1 In Pursue of Light Intermetallic Hydrides Isaac Jacob		
09.30	FrOQ-170 Invited F3 Hydrogen Pipe Diffusion in Palladium: First Principles, Kinetic Monte Carlo, and Experiments Dallas Trinkle	FrOH-178 Invited M2 Expanding Complex Aluminum Hydrides Towards Heavier Group I and II Family Members Claudia Weidenthaler		
10.00	FrOQ-171 Contributed F5 Hydrogen Absorption Properties of $\text{Pd}_{0.75}\text{Mo}_{0.25}$ Solid Solution Alloy Tomoe Yayama	FrOH-179 Contributed F3 Experimental and numerical modelling studies of the kinetics of hydrogen evolution from zirconium hydride Mingwang Ma		
10.20	FrOQ-172 Contributed M1 Superior effect of Ni-substitution on the hydrogenation kinetics of $\text{Mg}_6\text{Pd}_{1-x}\text{TM}_x$ (TM = Ag, Cu, Ni) pseudo-binary compounds José Francisco Fernandez	FrOH-180 Contributed F3 Hydrogen Accumulates in and UH_3 Precipitates at Carbides in Uranium Supersaturated in H and C Wigbert Siekhaus		
10.40	Coffee Break			
	Quays Theatre Chair: Ned Stetson	Hexagon Chair: Terence Udovic	Deck 1	Compass
11.00	FrOQ-173 Invited A1 Hydrogen Storage: From Academia to Market Stephen Bennington	FrOH-181 Invited M2 Interactions of C_{60} with Metal Hydride Systems Ragay Zidan		
11.30	FrOQ-174 Invited A6 Metal Hydride Heat Storage Prototype for Concentrating Solar Thermal Power Mark Paskevicius	FrOH-182 Invited F4 Structure Determination of Metal- C_{60} Nano-composites Sabrina Sartori		
12.00	FrOQ-175 Contributed A6 Material Development for Metal Hydride Thermal Energy Storage Systems for Future Concentrating Solar Power Plants Claudio Corgnale	FrOH-183 Contributed M1 Investigation of the hydrogen distribution inside a storage tank by in situ Neutron Radiography of a hydrogen storage tank Stefan Börries		

12.20	FrOQ-176 Contributed A1 Metal Hydride Hydrogen and Heat Storage Systems as Enabling Technology for Spacecraft Applications Ronald Pawelke	FrOH-184 Contributed M1 Cycle Stability of Gas Atomised Alloy Electrodes Mariana Spodaryk		
12.40	Closing Session, Prizes and Handover: Quays Theatre			
13.30	Lunch and Departure			

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Tuesday

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Code	Topic	Presenter	Title
TuP-001	M3	Jianwei Ren	Shaped Chromium-based Metal-Organic Frameworks (Cr-MOFs) for Hydrogen Storage Applications
TuP-002	M3	Bin Hong Liu	Catalyzed Hydrogen Storage Reaction of $2\text{LiH} + \text{MgB}_2$
TuP-003	M3	Yuki Nakagawa	Investigation of dehydrogenation processes of ammonia borane and metal hydride composites
TuP-004	M3	Bao Zhang	Hydrogen storage properties and microstructural evolution of the mixtures $\text{MgH}_2\text{-Li}_3\text{N}$ with different ratios
TuP-005	M3	Taihei Aoki	Thermodynamics of ammine complex of Metal Halide and Borohydride
TuP-006	M3	Chiara Milanese	Hydrogen Storage Properties of Transition Metals Decorated Li-Fullerides
TuP-007	M3	Sheng Guo	Direct Hydrogenation of Li-Mg Alloy by High-energy Reactive Milling
TuP-008	M3	Tom Wood	Producing Hydrogen from Ammonia Using Sodium Amide
TuP-009	M3	Didier Blanchard	A Class of Superior Ammonia Storage Materials Based on Solid Solution Barium Strontium Chloride Salts
TuP-010	M4	Andrew Goudy	Comparative Studies of Sticking Efficiencies in Gas Adsorptions Analysis on Selected Metal Organic Frameworks
TuP-011	M4	Darryl Pyle	Hydrogen Adsorption Characteristics of Magnesium Combustion Derived Graphene at 77 and 293 K
TuP-012	M4	Hirokazu Kobayashi	Hydrogen-storage Properties of Pd Nanocrystals covered with Metal-organic Framework
TuP-013	M4	Zeric Hulvey	Neutron Diffraction of Hydrogen Adsorption in Metal-Organic Frameworks at High Pressures
TuP-014	M4	Israel Savaris	Morphological Studies on the Formation of TiO_2 Nanotubes Arrays: Improvements in the Photocatalytic Response for Hydrogen Production
TuP-015	M4	Stephen Lyth	Hydrogen Storage on Defective Graphene Foam
TuP-016	M4	Christos Tampaxis	Hydrogen storage properties of Pd-doped thermally oxidised single wall carbon nanohorns
TuP-017	M4	Ezgi Dundar-Tekkaya	The Effect of Pd Loading on the Hydrogen Storage Capacity of Templated Porous Carbon Structures Grown in MCM-41
TuP-018	M4	Yinghe Zhang	Hydrogen storage properties of nanostructured graphite-based materials
TuP-019	M4	Ian Morrison	Hydrogen Interaction with MOF-5 using Dispersion Corrected DFT for a Correct Interpretation of Rotational Inelastic Neutron Spectra

Code	Topic	Presenter	Title
TuP-020	A1	Mykhaylo Lototskyy	Distributed "Hybrid" MH-CGH ₂ System for Hydrogen Storage and its Supply to LT PEMFC Power Modules
TuP-021	A1	Tai Sun	The Integrated Metal Hydride System for the Application of Fuel Cell
TuP-022	A1	Jürgen Danzberger	Surface Modification of Mg Materials based on Ultra Violet Imprint Lithography for Faster Kinetics in H ₂ De- and Absorption
TuP-023	A1	Shahrzad Mohammadshahi	Optimization of Cooling Fins for Metal-Hydrogen Storage Tanks
TuP-024	A1	Satya Sekhar Bhogilla	Performance Analysis of Metal Hydride Based Hydrogen Storage Tanks with Various Heat Exchange Options
TuP-025	A1	Oliver Metz	Metal hydride Tank Designs for in situ Neutron Radiography (NR) and Tomography (NCT) Experiments
TuP-026	A1	Maximiliano Melnichuk	Characterization of a thermally optimized hydride container
TuP-027	A1	Djafar Chabane	Metal hydrides for optimal hydrogen storage system of fuel cell electrical vehicles
TuP-028	A1	Tatsuya Fuura	Development of hybrid hydrogen tank
TuP-029	A1	Prakash C Ghosh	Transient modeling and simulation of hydrogen supply from a metal hydride tank
TuP-030	A1	Giovanni Capurso	Static and Dynamic Performance Tests on Room Temperature Hydride Tank
TuP-031	A3	Hiroshi Inoue	High Capacity Hydrogen Storage Alloy Negative Electrodes for Use in Nickel-Metal Hydride Batteries
TuP-032	A3	Youhei Ariga	Electrochemical Properties of Ti ₄₉ Zr ₂₆ Ni ₂₅ -XPdX Quasicrystals Produced by Mechanical Alloying
TuP-033	A3	Koji Kawahito	Electrochemical charge-discharge properties of MgH ₂ via LiBH ₄ solid electrolyte
TuP-034	A3	Ihor Zavaliy	Phase-Structural and Electrochemical Properties of the R ₂ Mg(Ni,Co) ₉ -Based Electrode Materials for Ni-MH Batteries
TuP-035	A3	Zhou Peng Li	Porous carbon as anode and cathode catalyst supports for direct borohydride fuel cell
TuP-036	A3	Judith Monnier	Characterisation Of Corrosion Products Of (La, Mg) ₂ Ni ₇ -Type Hydrogen Storage Alloys For Nickel-Metal Hydride Batteries And Influence Of Magnesium
TuP-037	A3	Berke Piskin	Development of CaNi ₅ Compounds for Metal Hydride Batteries
TuP-038	A4	Kazuhiro Ishikawa	Effects of Surface Oxidation on Hydrogen Permeability of Nb-TiNi Two-phase Alloy
TuP-039	A4	Myung Jin Lee	Synthesis and Evaluations of hydrogen permeability on TCN-Ni composite membranes by sol-gel process

Code	Topic	Presenter	Title
TuP-040	A4	Yoshihide Saeki	Relationship between Microstructure and Hydrogen Permeability in Nb-TiNi Alloys
TuP-041	A4	Shahrouz Nayeboossadri	Zr-Based Amorphous Hydrogen Separation Membranes Fabricated by Magnetron Sputtering
TuP-042	A4	Yuki Nakamura	Alloying effects on hydrogen permeability of V without Pd overlayer
TuP-043	A4	Fatih Pişkin	Combinatorial Thin Film Membranes for Hydrogen Separation
TuP-044	A4	Naser Al-Mufachi	Effects of Thin Film Pd Deposition on the Hydrogen Permeability of Rolled Pd60Cu40 Membranes
TuP-045	A5	Nikolay Anfilov	APPLICATION OF METAL HYDRIDES AS BLOWING AGENTS FOR METAL FOAM MANUFACTURING
TuP-046	A5	Ekaterina Stepanova	Effect of Hydrogen on the Structural and Phase State and Deformation Behavior of the Ultrafine-Grained Zr-1Nb Alloy
TuP-047	A5	Victor Kudiiarov	Influence of surface structure on hydrogen interaction with Zr-1Nb alloy
TuP-048	A5	Evgeniy Merson	Application of Acoustic Emission Method for Investigation of Hydrogen Embrittlement Mechanism in the Low-Carbon Steel
TuP-049	A6	Ferry Anggoro Ardy Nugroho	PdAu Alloy Nanoparticles for Nanoplasmonic Hydrogen Sensing
TuP-050	A6	Kouji Sakaki	Development of Hydrogen Storage Alloys for a Soft Actuator Device in Medical Rehabilitation
TuP-051	A6	Minako Hosono	Development of a Hand-Size Soft Actuator Utilizing Hydrogen Storage Alloy
TuP-052	A6	Satoshi Akamaru	Sensing of hydrogen in gas phase using ferromagnetic Pd-Co alloy
TuP-053	A6	Theo Friedrich	Hydrogen Production, Storage and Purification using the Steam Iron Process
TuP-054	A6	Inga Buerger	Investigation of Long Term Cycle Stability – First Results of metal hydride composites
TuP-055	F1	Hoda Emami	Investigating the effect of severe plastic deformation on the hydrogenation properties of TiFe for stationary applications
TuP-056	F1	Kazutoshi Miwa	Ab-initio Molecular Dynamics Simulations with Fractional Atomic Occupation Numbers
TuP-057	F1	Stepan Lushnikov	Interaction of V-M (M-Cu, Co and W) alloys with hydrogen under high pressure
TuP-058	F1	Stepan Lushnikov	Interaction of V _{1-x} Mn _x (x=0.1-0.3) alloys with hydrogen under high pressure
TuP-059	F1	Elena Anikina	Calorimetric study of hydrogen interaction with Sm ₂ Fe ₁₇
TuP-060	F1	Naoki Fukumuro	Hydrogen-Induced Superabundant Vacancies in Electrodeposited Fe-C Alloy Films

Code	Topic	Presenter	Title
TuP-061	F1	Andrey Lider, Viktor Kudiiarov	Hydrogenation-induced Microstructure Changes in Titanium
TuP-062	F1	Toyoto Sato	Synthesis, Crystal Structure and Dehydrogenation Reaction on a Mixed Alkali and Alkaline-earth Metal Alanate $\text{LiCa}(\text{AlH}_4)_3$
TuP-063	F1	Mark Conradi	Fluorite MgD_2 in a MgD_2 - TiD_2 Composite
TuP-064	F1	Stuart Campbell	Improving the connection between neutron scattering and computational modeling
TuP-065	F1	Stuart Campbell	Mantid - Data Reduction and Visualization
TuP-066	F1	Julien François	Kinetics and Thermodynamics of Hydrogen Sorption as Studied by Hyphenated Calorimetric and Volumetric Techniques
TuP-067	F1	Sotirios Droulias	Tailoring the Properties of Metal Hydrates through Superlattice Growth.
TuP-068	F1	Kazutaka Ikeda	In-situ Diffraction Measurements of Hydrogen Storage Materials by High-Intensity Neutron Total Diffractometer, NOVA
TuP-069	F2	Ko Tamehiro	A Study on Hydrogen Absorption and Desorption Kinetics of Hydrogen Storage Alloys at Temperatures from 77K to 298K.
TuP-070	F2	Shinnosuke Tokuhira	Effects of CsOH Pretreatments on the Hydrogen Absorption Kinetics of a Mn-Ni Based Hydrogen Storage Alloy
TuP-071	F2	Hitoshi Inokawa	Catalysis of Thermally Stable Nickel Nanoparticles for Ammonia Decomposition
TuP-072	F2	Miranda Camping	The desorption of hydrogen from uranium hydride
TuP-073	F2	Daiju Matsumura	Observation of Dynamic Structure during Hydrogenation Reaction for Pd Nanoparticles by using Real-Time-Resolved X-ray Absorption Fine Structure Spectroscopy
TuP-074	F2	Helen Fell	The Hydriding Kinetics of Cerium and Reaction Site Morphology
TuP-075	F3	Olga Babanova	Nuclear Magnetic Resonance Study of Atomic Motion in New Bimetallic Perovskite-Type Borohydrides $\text{RbCa}(\text{BH}_4)_3$ and $\text{CsCa}(\text{BH}_4)_3$
TuP-076	F3	Konstantin Klyukin	Ab initio simulation of hydrogen mobility in hcp, bcc, fcc magnesium lattice
TuP-077	F3	Hideaki Iwaoka	Effect of Grain Boundaries on Hydrogen Diffusion in Ultrafine-Grained Palladium
TuP-078	F3	Yolanda Sadikin	Structural Analysis of Possible Lithium Migration Paths in Borohydrides
TuP-079	F3	Hiroshi Ogawa	Atomistic Simulation of Hydrogen Dynamics near Dislocations in Vanadium Hydrides

Code	Topic	Presenter	Title
TuP-080	F3	Alexey Volodin	Hydrogen Diffusion in La _{1.5} Nd _{0.5} MgNi ₉ Alloy Electrodes of the Ni-MH Battery
TuP-081	F3	Sveinn Ólafsson	Conductivity of H and D Rydberg matter condensed on ultrathin metal films.
TuP-082	F3	Alicja Klimkowicz	Chemical Diffusion and Surface Exchange in Ln-Ba-Sr-Co-Fe Perovskite System in Hydrogen- and Oxygen-containing Atmospheres
TuP-083	F3	Anna Vyvodtceva	Nuclear magnetic resonance study of hydrogen diffusion in the transitial metal alloys lattice
TuP-084	F3	Shun Dekura	Study on the States of α -phase Palladium Hydride by in situ Solid-State ¹ H NMR Measurement Under Controlled Hydrogen Gas Pressure
TuP-085	F3	Asuka Suzuki	Analysis of hydrogen mobility in Nb-based alloy membrane in view of new description of hydrogen permeability based on hydrogen chemical potential
TuP-086	F3	Wen Huang	Diffusion of Hydrogen in Nano-confined Vanadium film
TuP-087	F4	Allan Abraham Bustria Padama	Hydrogen Atom Absorption in Pd(110) Surface
TuP-088	F4	Shigehito Isobe	Theoretical and experimental synthesis of hydrogenated iron clusters over graphene
TuP-089	F4	Abel Salam Awad	Hydrogen production from hydrides : microwaves and hydrolysis methods
TuP-090	F4	Ryota Gemma	Atom Probe Tomography (APT) Analysis of Deuterium-loaded V/Cr Thin Films
TuP-091	F4	Luke Hughes	Buckling of Mg films due to hydrogenation stress and its effect on sorption behaviour
TuP-092	F4	Hiroyuki T. Takeshita	Effect of Particle Size on Dehydrogenation of MgH ₂
TuP-093	F4	Yeuda Greenbaum	Minimally strained hydride nucleation on a strained Gd/W(110) surface
TuP-094	F4	Shunsuke Kato	In Situ XPS Investigation of a Platinum Catalyst Supported on Ceria Nanocubes under a Hydrogen Atmosphere
TuP-095	F5	Daniel Sethio	Computational Study of Spectroscopic Properties of Different Borohydride Species
TuP-096	F5	Takayoshi Ishimoto	Composition dependence of H storage capacity for Rh-Ag alloy
TuP-097	F5	Daniel Azofeifa	Parametrization of the dielectric function of Pd thin films as function of film thickness, temperature and hydrogen absorption
TuP-098	F5	Daniel Azofeifa	Hydrogen concentration and dielectric function of nanostructured Pd thin films calculated from optical transmission

Code	Topic	Presenter	Title
TuP-099	F6	Dalin Sun	Formation of Mg ₂ Ni with enhanced kinetics: Using MgH ₂ instead of Mg as a starting material
TuP-100	F6	Alexander Surrey	Multi-Slice Simulations for In-situ TEM Studies of Nanostructured Magnesium Hydride at Elevated Hydrogen Pressures of 1 bar
TuP-101	F6	Colin Webb	The Effect of Uncertainties and Calibrations on Hydrogen Uptake Measurements
TuP-102	F6	Stephan W.H. Eijt	Monitoring vacancies, nanopores and metal-to-insulator transitions in Mg-Ti films and Mg hydride nanoparticle layers using positrons
TuP-103	F6	Boris Tarasov	Synthesis of Hydrides by Interaction of Intermetallics with Ammonia
TuP-104	F7	Yuji Kunisada	Delocalized Adsorption States of Hydrogen Isotopes on fcc-Fe(111) Surfaces
TuP-105	F7	Mathieu Segard	³ He NMR measurements on palladium samples aged under tritium
TuP-106	F7	František Lukáč	Stress Release during Cyclic Loading of Thin Palladium Films
TuP-107	F7	David Wilkinson	H/D exchange in micron powder Pd H/D measured using neutron diffraction
TuP-108	F7	Simon Owens	Kinetics of hydrogen isotope exchange over solid storage media
TuP-109	F7	Marek Tkacz	Low Temperature Raman Measurements of AlH ₃ and AlD ₃ Systems
TuP-110	F7	Ian Robinson	Monte Carlo Simulations of Hydrogen Isotopes in Palladium
TuP-111	M1	Vasilii Tihonov	Analysis of Hydrogen Isotope Mixed Gas at High Pressure Using Raman Spectroscopy
TuP-112	F8	Valérie Paul-Boncour	Properties of ZrNi ₅ hydride and deuteride synthesized under high deuterium pressure
TuP-113	F8	Valentina Degtyareva	Crystal Structure of the Gold Hydride
TuP-114	F8	Naruki Endo	Hydrogenation of CsCl-type AlTM (TM = Fe, Co, Ni) alloys at high pressures and high temperatures
TuP-115	F8	John Proctor	Solubility of hydrogen in Zircaloy-4 nuclear fuel cladding

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Code	Topic	Presenter	Title
ThP-001	M1	Jin Nakamura	Preparation of cost-effective hydrogen storage materials for on board application
ThP-002	M1	Colin Webb	The Effect of Carbon Additives on the Hydrogen Uptake of Light Metals
ThP-003	M1	Sergey Mitrokhin	Effects of Scaling in Metal Hydride Materials for Hydrogen Storage and Compression
ThP-004	M1	Jean-Benoît Denis	Influence of impurities on the performance of a metal hydride
ThP-005	M1	Ulrich Ulmer	Development of low-cost hydrogen storage materials – intrinsic effects of low-purity raw materials
ThP-006	M1	Vaclav Paidar	The effect of internal hydrogen pressure on the energetics of hydrides
ThP-007	M1	Pavel Fursikov	Experimental and Quantum Chemical Studies of Hydrogen Interaction with Nanostructured Composites and Clusters based on Light Metals
ThP-008	M1	Akihiko Machida	In-situ and time-resolved measurements on hydrogen absorption/desorption processes of hydrogen absorbing alloys using synchrotron radiation x-rays
ThP-009	M1	Nor Diana Zulkifli	Hydrogen Storage Properties in Pd-based Nanoalloys
ThP-010	M1	Oksana Melikhova	Effect of hydrogen on generation of lattice defects in shock-loaded Pd
ThP-011	M1	Arnaud Fabre	Static and dynamic response of a Pd-coated microcantilever exposed to hydrogen
ThP-012	M1	Martin Deutges	In-situ Nanoindentation of Palladium-Hydrogen Alloys
ThP-013	M1	Tatsuki Tsutsumi	Theoretical analysis for interface interaction and hydrogen absorption of Pd@HKUST-1 hybrid material
ThP-014	M1	Hang Liu	Hydrogen sorption behaviour of carbon-supported Pd nanoparticles
ThP-015	M1	Kenji Iwase	Crystal structure and hydrogen absorption-desorption property of Gd ₂ Ni ₇ with Ce ₂ Ni ₇ -type structure
ThP-016	M1	Stephen Blaxland	Simulating the Surface Stress Effects due to the Initiation and Growth of Uranium Hydride
ThP-017	M1	Sergey Mitrokhin	Influence of Hydrogen and Mechanochemical Activation on the Properties of Nd-Fe-B- and Sm-Fe-N-Type Magnetic Materials
ThP-018	M1	Petr Hruška	Investigation of nanocrystalline and epitaxial Gd films loaded with hydrogen
ThP-019	M1	Hui Wang	Enhanced joint catalysis of YH ₂ /Y ₂ O ₃ on dehydrogenation of MgH ₂
ThP-020	M1	Krystyna Giza	Preparation and Electrochemical Properties of La ₂ (Ni,Co,M,Mg) ₁₀ (M=Al or In) hydrogen storage alloys

Code	Topic	Presenter	Title
ThP-021	M1	Juliusz Skoryna	XPS Studies of Nanocrystalline $\text{La}_x\text{Ni}_{1-x}$ and $\text{LaNi}_{5-x}\text{Al}_x$ ($x = 0.2, 0.5, 1$)
ThP-022	M1	Evangelis KouloukakisGeorge Karagiorgis	Composition changes of structural and hydrogenation properties of ZrM_2 type intermetallics for high pressure hydrogen storage applications
ThP-023	M1	Silvie Maskova	Impact of hydrogen absorption on crystal structure and magnetic properties of $\text{RE}_2\text{T}_2\text{X}$ compounds
ThP-024	M1	Fahim Karimi	Structural impacts of Transition Metal Fluorides on the Reactive Hydride Composites (RHC)
ThP-025	M1	Chul Kim	Deuterium Exchange Dynamics in $\text{Zr}_2\text{NiD}_{4.8}$ Studied by ^2H MAS NMR Spectroscopy
ThP-026	M1	Schweke Danielle	Preferred Hydride Growth Orientations on Oxide-coated Gadolinium Surfaces
ThP-027	M1	Marie Trynogga	Investigation of Crack Formation in High-purity Iron
ThP-028	M1	Xin Xiao	Hydrogen in V: isotope effects and site occupancy
ThP-029	M1	Thu Trang Trinh	Apparatus for In-situ Defect Analysis (AIDA) - Investigations on $\text{Fe}_{60}\text{Al}_{40}$ Phase transition
ThP-030	M1	Dariusz Rusinek	Structural properties of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17-x}\text{Mn}_x$ alloys and its deuterides
ThP-031	M1	Anahit Aleksanyan	Formation in Ternary Ti-V-Mn Alloy in the Hydride Cycle, Their Interaction With Hydrogen
ThP-032	M1	Maxim Tsarev	IMPEDANCE SPECTROSCOPY FOR CHARACTERIZATION OF OXIDIZED TITANIUM HYDRIDE POWDERS
ThP-033	M1	Kaveh Edalati	Hydrogen Storage in Nanostructured TiFe Processed by High-Pressure Torsion
ThP-034	M1	Hyunjeong Kim	Reduction and Unusual Recovery in the Reversible Hydrogen Storage Capacity of $\text{V}_{1-x}\text{Ti}_x$
ThP-035	M1	Chaoling Wu	Decaying Behavior of $\text{V}_{40}(\text{TiCr})_{51}\text{Fe}_{8}\text{Mn}$ Hydrogen Storage Alloy with Different Particle Sizes
ThP-036	M1	Itoko Saita	Improvement in Cyclic Stability and Resistance to Water Impurity in Hydrogen of TiFe-Based Alloy by V Substitution
ThP-037	M1	Juliusz Skoryna	Modification of Interlayer Exchange Coupling in Fe/V/Fe Trilayers Using Hydrogen
ThP-038	M1	Lydia Pickering	Ti-V-Mn Based Metal Hydrides for Hydrogen Compression Applications
ThP-039	M1	Alexander Rokhmanenkov	Simulation of behavior hydrogen in titanium hydrogen systems TiH_x
ThP-040	M1	Kandavel Manickam	Effect of Non-stoichiometry on AB_2 - type Alloys for Improved Hydrogen Storage Properties

Code	Topic	Presenter	Title
ThP-041	M1	Alexey Postnikov	A STUDY OF SURFACE OF TITANIUM TARGETS FOR NEUTRON GENERATORS
ThP-042	M1	Rolando Pedicini	Interesting Hydrogen Storage Capability in Manganese Oxide
ThP-043	M1	Tomoki Tominaga	HREM Observation and High-Pressure composition Isotherm Measurement of Ti ₄₅ Zr ₃₈ Ni ₁₇ Quasicrystal Powders Synthesized by Mechanical Alloying
ThP-044	M1	Yanghuan Zhang	The hydrogen storage performance of LaMg ₁₁ Ni+x%Ni (x = 100, 200) alloys prepared by mechanical alloying
ThP-045	M1	Koji Tanaka	Formation Mechanism of Micro/nano-structures through Competitive Reactions in Mg/Cu Super-laminate Composites during Initial Hydrogenation
ThP-046	M1	Peipei Liu	Microstructures and Hydrolysis Behaviors of Mg-Ca Hydrides Synthesized by Different Ball-milling Processes
ThP-047	M1	Haizhen Liu	Mg-Al-H Hydrogen Storage Systems: Preparations, Reaction Mechanisms and Hydrogen Desorption Properties
ThP-048	M1	Annalisa Paolone	Study of the hydrogenation/dehydrogenation process in the Mg-Ni-C-Al system
ThP-049	M1	Gulhan Cakmak	Hydrogen Decrepitation of Mg Rich Intermetallics
ThP-050	M1	Liuzhang Ouyang	The Phase Transition and Hydrogen Storage Properties of Mg ₁₇ Ba ₂ compound
ThP-051	M1	Yanshan Lu	Novel Mg-In-Ni Ternary Alloys for Reversible Hydrogen Storage
ThP-052	M1	Valérie Paul-Boncour	Structure and Hydrogen Storage Properties of the NdMgT ₄ (T=Co, Ni) Compounds
ThP-053	M1	Valérie Paul-Boncour	Hydrogen Storage Properties of the RE ₄ MgCo (RE=Y, Nd, Tb) Compounds
ThP-054	M1	Volodymyr Yartys	HYDROGEN ASSISTED PHASE TRANSITION IN A TRIHYDRIDE MgNi ₂ H ₃ SYNTHESISED AT HIGH H ₂ PRESSURES: THERMODYNAMICS, STRUCTURE AND CHEMICAL BONDING
ThP-055	M2	Nils Bergemann	Thermodynamic Properties of Borohydrides Destabilized by Hydrides of Mg-TM Alloys
ThP-056	M2	Valérie Paul-Boncour and Ihor Zavaliy	The Mg ₂ Ni _{1-x} CoxHy (0 < x < 1) Hydrides Obtained by Reactive Milling
ThP-057	M1	Yujie Lv	Effects of Cu on microstructural evolution and hydrogen storage properties of the Mg ₇₇ Ni _{20-x} CuxLa ₃ (x=0, 5, 10) alloys
ThP-058	M1	Xuanli Luo	Microstructure evolution and hydrogen storage properties for Mg-Zn-Y ternary alloy
ThP-059	M1	Anshul Gupta	Enhanced hydrogen storage properties in Mg-based hybrids synthesized by severe plastic deformation

Code	Topic	Presenter	Title
ThP-060	M1	Yongtao Li	Structural Rearrangement of Mg-containing Superlattices for Superior Hydrogen Storage
ThP-061	M1	Hyeon Man Shin	Evaluations of hydrogenation properties on MgHx-transition metal fluoride composites by planetary ball milling
ThP-062	M1	Huai-Jun Lin	Hydrogen Storage Property of MgH ₂ Doped with Ce-fluorides
ThP-063	M1	Wei Liu	Size Effects on the Hydrogen Storage Properties of Mg Nanoparticles Synthesised by Eletroless Reduction Method
ThP-064	M1	Eki Setijadi	Magnesium Hydrides Nano-objects: Novel Physical and Hydrogen Storage Properties Relationships
ThP-065	M1	Jacques Huot	Effect of Rolling Atmosphere on Sorption Kinetics of MgH ₂
ThP-066	M1	Ying Wang	Different catalytic effects of Ti-based compounds on dehydrogenation properties of MgH ₂
ThP-067	M1	Luis Miguel Sanz Moral	MgH ₂ Pd Nanoparticles Embedded in Silica Aerogel Monoliths
ThP-068	M1	Nataliya Skryabina	Impact of Severe Plastic Deformation and Additives on the Stability of MgH ₂
ThP-069	M1	Miriam Rueda Noriega	Micronized MgH ₂ and MgO by Supercritical Anti Solvent process
ThP-070	M1	Nataliya Skryabina	Electrocatalytic Activity of Mg in Hydrogen Evolution Reaction
ThP-071	M1	Claudia Vargas	Magnesium hydride - Magnesium nanoparticles confined in carbon aerogels
ThP-072	M1	Xuezhong Xiao	Rapid Dehydrogenation of Chemically-Synthesized MgH ₂ Nanocomposites
ThP-073	M1	Andreas Grill	Hydrogen Storage Properties of Mg and Mg-alloys after Severe Plastic Deformation
ThP-074	M1	Pragya Jain	Catalytic Effect of MgF ₂ on hydrogenation properties of MgH ₂
ThP-075	M1	Ewelina Kosciuczyk	MgH ₂ destabilization by the anodic porous alumina impregnation
ThP-076	M2	Yongan Liu	Hydrogen generation from Mg-hydride system
ThP-077	M2	Shivani Agarwal	Effect of ZrCrCo alloy on hydrogen storage properties of Mg
ThP-078	M1	Zhjie Cao	Dual-tuning Effects of In, Al and Ti on the Dehydrogenation Thermodynamic and Kinetic Properties of MgH ₂ using DBDP Milling
ThP-079	M1	Akito Takasaki	Hydrogen Sorption Properties of Magnesium Hydride Catalized Multiply with Carbon and Silicon
ThP-080	M1	Jordan Guichard	Hydrolysis Mechanism of Lithium Hydride
ThP-081	M1	Chubin Wan	Synthesis and Characterization of LiBH ₄ confined in Mg-Coated Mesoporous Carbon for Reversible Hydrogen Storage

Code	Topic	Presenter	Title
ThP-082	M1	Christos Paterakis	Alkali metal borohydride/ LiH composites for Energy Storage Applications
ThP-083	M1	Binayak Roy	Effect of Ni- alloys on thermal decomposition of ammonia borane
ThP-084	M2	Hai-Wen Li	A Novel Synthesis Process of Anhydrous Alkali Metal Dodecaborate $M_2B_{12}H_{12}$ ($M = Li, Na, K$) Using Decaborane $B_{10}H_{14}$
ThP-085	M2	Lixin Chen	Synergetic Effect of Nano-confinement and Nano-catalysis for the Reversible Hydrogen Storage of $LiBH_4$
ThP-086	M2	Elsa Roedern	Thermal decomposition of $Mn(BH_4)_2 - M(BH_4)_x$ and $Mn(BH_4)_2 - MH_x$ composites with $M = Li, Na, Mg$ and Ca
ThP-087	M2	Bjarne R. S. Hansen	Nanoconfinement of $LiBH_4$ - KBH_4 Eutectic Composite Systems
ThP-088	M2	Yijing Wang	Synthesis of Trimetallic Core-Shell Catalysts for Hydrolytic Dehydrogenation of Ammonia Borane
ThP-089	M2	Arndt Remhof	Revisiting the Role of Dodecaborates
ThP-090	M2	Kasper Møller	Bimetallic Borohydrides Synthesized from $Sr(BH_4)_2$ and Alkali Metal Borohydrides
ThP-091	M2	Elisabeth Grube	Investigation Of γ - $Mg(BH_4)_2$ -X Composites, $X = LiH, NaH, CaH_2, MgH_2$
ThP-092	M2	Yigang Yan	Synthesis and Stability of Dodecaborates $M(B_{12}H_{12})_n$ ($M = Mg, Y$)
ThP-093	M2	Asem Ampoumogli	Hydrogen Desorption and Cycling Properties of Eutectic Borohydrides - Mesoporous Carbons Composites
ThP-094	M2	Oliver Deavin	Investigation into the destabilisation of $LiBH_4$ with $CaNi_5$
ThP-095	M2	Mykhaylo Lototskyy	Magnesium-Based Hydrogen Storage Nanomaterials Prepared by High Energy Reactive Ball Milling in Hydrogen at the Presence of Mixed Titanium – Iron Oxide
ThP-096	M2	Morten Brix Ley	Electrochemical performance of $LiM(BH_4)_3Cl$ ($M = La, Ce, Gd$)
ThP-097	M2	Nicholas Stadie	Supercritical Nitrogen Processing: a Route to Clean Hydrogen Storage in γ - $Mg(BH_4)_2$
ThP-098	M2	Jianmei Huang	Improving dehydrogenation of $LiBH_4$ via modification with poly(methylmethacrylate)
ThP-099	M2	Yuting Wang	Study on dehydrogenation kinetics of $LiBH_4$ via confinement in modified carbon nanotubes
ThP-100	M2	Guanqiao Li	Dehydriding Property of Metal Borohydrides Combined with Mg_2FeH_6
ThP-101	M2	Rapee Goslawit-Utke	Destabilization of $LiBH_4$ by nanoconfinement in PMMA-co-BM polymer matrix for reversible hydrogen storage
ThP-102	M2	Yohei Ito	Cycle Durability and Factors Disturbing Rehydrogenation for $LiBH_4$ - MgH_2 -Al Composites

Code	Topic	Presenter	Title
ThP-103	M2	Mingxia Gao	Improved Hydrogen Storage properties of $\text{Ca}(\text{BH}_4)_2 + \text{LiBH}_4$ composite motivated by LaMg_3 alloy
ThP-104	M2	Karol Fijalkowski	$\text{M}(\text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3)$ – the missing link in the mechanism of thermal decomposition of light alkali metal amidoboranes
ThP-105	M2	Yushi Chen	Hydrogen desorption properties of a LiBH_4 - C_{60} composite
ThP-106	M2	Wan Si Tang	Altering the Structural Properties of $\text{A}_2\text{B}_{12}\text{H}_{12}$ Compounds via Cation and Anion Modifications
ThP-107	M2	Wojciech Wegner	Mechanochemical synthesis of new rare-earth borohydrides.
ThP-108	M2	Morten Brix Ley	New eutectic $x\text{LiBH}_4 - 1-x\text{KBH}_4$ ($x = 0.7 - 0.75$)
ThP-109	M2	Payam Javadian	Hydrogen storage properties of nanoconfined $\text{LiBH}_4\text{-NaBH}_4$
ThP-110	M2	Jalaal Hayes	Hydriding and Dehydriding Kinetics of RbH-Doped $2\text{LiNH}_2/\text{MgH}_2$
ThP-111	M2	Yongfeng Liu	Mechanistic investigations of the high-temperature failure of K-based additives for $\text{Mg}(\text{NH}_2)_2\text{-}2\text{LiH}$ systems
ThP-112	M2	Antonio Santoru	Synthesis, characterization and reaction kinetics on the K/Mg amides-based system
ThP-113	M2	He Fu	In situ hybridization of $\text{LiNH}_2\text{-LiH-Mg}(\text{BH}_4)_2$ nano-composites for enhanced hydrogen storage properties
ThP-114	M2	Matthew Howard	Hydrogen Storage Properties and Ionic Conductivity in Lithium nitride Bromide Systems
ThP-115	M2	Peter Bramwell	Preparation of Carbon Supported Lithium Amide
ThP-116	M2	Ping Li	Catalytic Effects of ZrC Additions on the Hydrogen Storage Properties of LiAlH_4
ThP-117	M2	Mariam Meggouh	Assessing the Performance of Sodium Aluminium Hexahydride as a Hydrogen Storage Material for an Al-alloy Based Tank.
ThP-118	M2	Marc Segales	Enhanced Dehydrogenation in LiAlH_4 via Nanoconfinement in Porous Carbons
ThP-119	M2	Daniel Krech	Direct Mechanochemical Synthesis of the Complex Aluminum Hydrides of Rb and Cs
ThP-120	M2	Trang Nguyen	Hydrogen Release and Uptake in the Li-Zn-N System
ThP-121	M2	Dag Noréus	Rb_3AlD_6 an unusual alanate featuring an interstitial hydrogen atom position in addition to a well ordered octahedral AlD_6 complex and 3 disordered complexes

Code	Topic	Presenter	Title
ThP-122	M2	Alberto Albinati	Inelastic Neutron Scattering Studies on Water Exposed Sodium Alanate: Is "S105" Relevant to Enhanced Hydrogen Cycling Kinetics?
ThP-123	M1	Hai-Wen Li	Composites of Light-metal Amides and Hydrides as Hydrogen Storage Systems
ThP-124	M1	Seda Dolukhanyan	Synthesis of Niobium Aluminides Using Hydride Cycle Method
ThP-125	M2	Philippe Mauron	Hydrogen Sorption in Metal Intercalated Fullerenes
ThP-126	M2	Ankur Jain	Catalytic Modification in Hydrogenation properties of KSiH ₃
ThP-127	M2	Li Li	Enhanced Catalytic Effects of Co@C Additive on Dehydrogenation Properties of LiAlH ₄
ThP-128	M2	Vadim Efimchenko	Hydrogen Solubility in Silica and Silicate Compounds
ThP-129	M2	Andrew Kirk	Raman spectroscopy and imaging of lithium hydride and corrosion products

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Abstracts

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Hydrogen as the basis for a sustainable energy economy

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The storage of renewable energy is the greatest challenge for the transition from the fossil era to a sustainable future. The world economy is growing due to the spreading industrialisation and global population will saturate at approx. 10 billion people in 2050. Due to the economic growth worldwide the energy demand will tripple in the coming 35 years. This is only possible if renewable energy i.e. solar energy becomes the major source of energy and if the materials cycles will be closed in the near future. During the last century the industrialized parts of the world operated based on mining resources and depositing waste with the consequence of a global shortage in resources (Fig. 1).



Fig. 1 Open cycle established during industrialization (left) and closed cycle based on renewable energy and complete recycling of materials, i.e. no deposition (right)

Hydrogen produced from renewable energy leads to a closed cycle, because the water released from the combustion condenses in the atmosphere. The challenge in the large scale application of hydrogen is the storage with a high gravimetric and volumetric density. Based on today's knowledge a hydrogen storage is limited to about 20 mass% and 70 kg/m³. Therefore the maximum energy density of hydrogen based energy storage is limited to approx. 50% of the energy density in fossil fuels. The main reason is that the host material of the hydrogen storage is not oxidized in the combustion. In order to achieve a comparable energy density of fossil fuels, hydrogen has to be stored in hydrocarbons (synthetic fuels), where the CO₂ is extracted from the atmosphere. The latter requires energy in order to increase the concentration from 400 ppm to pure CO₂, corresponding about 5% of the heating value of the hydrocarbon. However, the process working close to the thermodynamic limit is not known yet. Furthermore, the reduction of CO₂ to hydrogen is based on the Sabatier to Methane or on the reversed water gas shift reaction and Fischer-Tropsch synthesis to an unspecific hydrocarbon. The surface of metal hydrides can offer new reaction paths and catalytic centers with atomic hydrogen.

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UK Hydrogen and Fuel Cell Research - an overview

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The presentation will discuss the drivers for the development and deployment of hydrogen and fuel cell technologies in the context of future UK low carbon energy systems. Current research in the field within the UK will be discussed, and future research priorities will be explored.

Cool Hydrides ! - Research Topics and Trends in Japan -

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The significance of the research on materials containing hydrogen has increased rapidly and extensively due to the consideration of hydrogen as a future energy source/carrier. Accumulation of knowledge of hydrogen behavior in metallic, inorganic, and polymer-like materials is vital in order to develop hydrogen production, storage, and transportation technologies. Besides the practical aspects, fundamental studies of hydrogen in materials are indispensable to understand the intrinsic properties of the materials, and in many cases, to modify/improve their properties.

In this presentation, some selected research topics and trends currently underway in Japan will be discussed:

- Commercialization of fuel cell vehicles planned in the next year, and on-going improvements of related infrastructures and legal systems.
- Focused research on liquid-state hydrides (ammonia and methylcyclohexane (MCH), etc.) as hydrogen/energy carriers.
- Research progress in solid-state hydrides, especially using advanced neutron and synchrotron beam techniques, combined with high-pressure technique.
- Recent studies on iron-hydrogen systems in both materials science (hydrogen embrittlement/storage) and earth science.
- Multiplicity of complex hydrides, including all-solid-state battery device studies and applications.
- New phenomena observed in hydrogen-doped materials; superconductivity and electronic properties.

These topics above will provide vital information for promoting the mutual exchange of ideas among researchers and expanding the possibilities of future collaborations.

Hydrogen Storage Research and Development Efforts Supported by the U.S. Department of Energy - Invited

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The U.S. Department of Energy supports the research and development of technologies to improve and promote the overall efficiency and sustainability of energy generation and utilization. Within the Office of Energy Efficiency and Renewable Energy and the Advanced Research Projects Agency-Energy, research into metal-hydrogen systems remains a subject of critical importance given the technological relevance that this class of materials continues to demonstrate. Metal hydride research is being supported to develop advanced hydrogen storage for both transportation and portable applications and for the emerging area of thermal energy storage. Significant efforts have recently been supported on complete system modeling and engineering, see figure 1, allowing for the identification of minimum material level performance metrics to meet system performance targets. Improvements to metal hydride battery technologies for transportation are still being sought. Also, in recognition of the near-term emergence of commercial fuel cell passenger vehicles that will rely on 700 bar compressed hydrogen stored in carbon fiber composite overwrapped pressure vessels, the hydrogen storage program also supports efforts to improve overall system performance and costs. This work includes efforts on improved carbon fiber composites, system design and balance-of-plant components, where hydrogen embrittlement is an important topic. An overview will be presented that covers the goals of the programs, the research projects supported and current the status of the work.

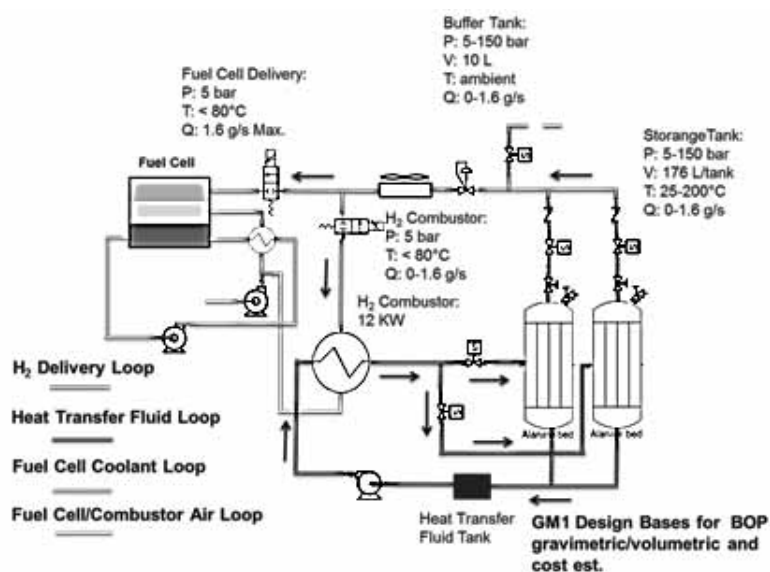


Figure 1: Baseline schematic of a metal hydride system for automotive use. [1]

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Planck Sorption Cryocoolers - A Very Successful Metal Hydride Technology for Space Exploration

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The European Space Agency (ESA) Planck spacecraft completed its scientific mission [1,2] to measure the anisotropy of the cosmic microwave background (CMB) in October 2013. Two fully redundant sorption cryocoolers, operating nominally at 18 K by the continuous formation of liquid H₂, provided 1 W cooling to the radiofrequency and infrared detectors of the two science instruments [1,3] starting in May 2009. These two coolers were originally required to provide a total on-orbit operational lifetime of 36 months. The actual flight duration using the two coolers was 52 months [2].

Each Planck Sorption Cryocooler (PSC) contained six individual compressor sorbent beds [4] filled with LaNi_{4.78}Sn_{0.22} to provide high-pressure (~30 bar) hydrogen gas to a Joule-Thomson (J-T) expander and to absorb low-pressure (~0.3 bar) gas from liquid hydrogen reservoirs that were cooled to ~18K. Thermal control of the hydrogen storage sorbent beds was managed by closed-cycle Gas Gap Heat Switches (GGHS) with small hydride actuators [4,5] containing ZrNiH_x. The GGHS enabled on/off heat conduction ratios >200, reducing of nominal input power to each sorbent bed by ~80% over a lifetime exceeding 20,000 heating/cooling cycles without the use of any moving parts.

Long-term performance of the hydride beds was limited by degradation of the LaNi_{4.78}Sn_{0.22} hydride [6] during its temperature cycling between ~270 K and ~450 K as well as gas accumulation in the GGHS primarily from H₂ permeation through the walls of the high-pressure hydride bed [5]. An overview of the engineering issues addressed during the design and fabrication of the hydride sorbent and GGHS beds for the PSC will be reviewed along with a summary of the extensive laboratory testing of hydride degradation during thermal cycling and aging. The predictions from this preflight testing are compared to the performance observed during the Planck Mission [6]. Finally, lessons learned from this project and recommendations for future applications will be presented.

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Reversible Hydrogen Activation in Molecular Complexes: Approaches to Catalysis and Energy Storage Using Amine Boranes

Tom Autrey*

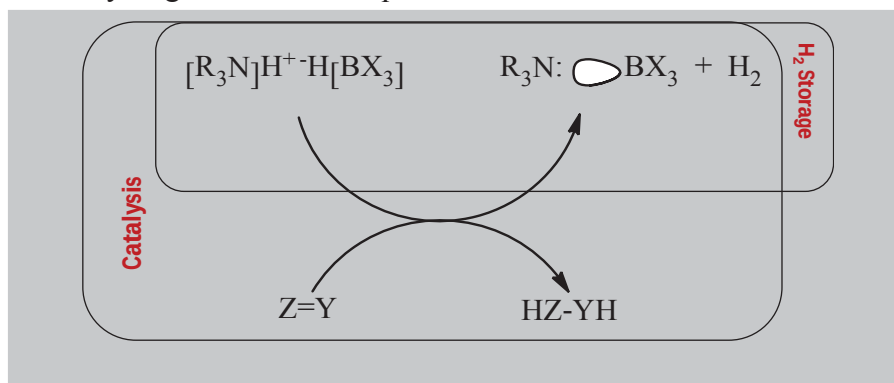
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Novel approaches for activating hydrogen are needed to increase efficiency and decrease costs in energy-intensive industrial processes. Amine boranes have the potential to provide unique solutions to two seemingly different applications: (i) catalytic hydrogenation, critical to many industrial processes, ranging from upgrading crude oil to carbon dioxide reduction, and (ii) hydrogen storage, a potentially critical solution to storing energy from intermittent renewable sources such as wind and solar.

In this presentation the relationship between hydrogen storage and catalysis is discussed. The work starts with the pedagogical example of ammonia borane and ammonium borohydride in hydrogen storage and extends to more complex amine borane structures that provide the ability to tune thermodynamics. We describe our recent efforts using a combination of experimental and computational approaches to gain insight into structure and reactivity of molecular complexes composed of Lewis acid Lewis base functionality to understand the mechanism of heterolytic activation of molecular hydrogen [1-4].

Scheme 1. Reversible activation of hydrogen is a goal in both hydrogen storage and in catalysis. The presentation will elaborate on the critical connections between amine boranes for hydrogen storage and amine boranes in catalysis. The catalysts can be used to activate molecular hydrogen to store in liquid carriers.



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Femtosecond spectroscopy on complex hydrides

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In borohydrides, a reduced charge δ on the $(\text{BH}_4)^{\delta-}$ ion is predicted to affect its structure by forming a pair from the four hydrogen atoms, which diverges from the boron, and a pair of hydrogen, which approaches to it [1]. Furthermore, the charge transfer from the cation to the $(\text{BH}_4)^{\delta-}$ ion determines the stability of the borohydride. Apart from equilibrium properties, the distortion is proposed to be the precursor of the decomposition reaction. To prove this hypothesis, we need to probe the atomistic motion of the phase transition in real time, i.e. on a femto second time scale.

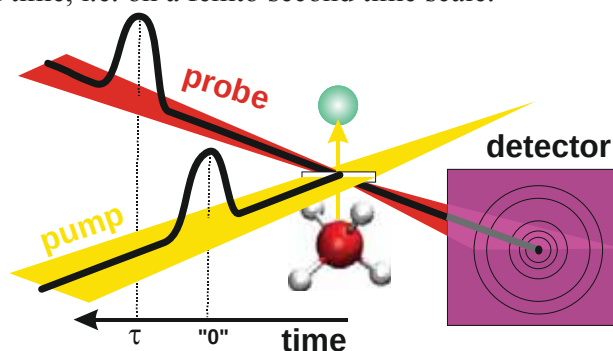


Figure 1. Sketch of a pump-probe setup.

We will present recent pioneering femto second experiments on the archetypical hydrides LiH, LiBH₄, and NaBH₄. The ultimate target of determining the mechanism of the sorption process on the femto-second scale is not yet achieved. However, the results at hand give insights into the nature of borohydrides that are inaccessible via other methods: anharmonicity and vibrational lifetimes from infrared pump-probe and 2D spectroscopy [2], and the charge transfer between ions in the ionic systems and their atomic motions induced by an electric field from fs X-ray powder diffraction [3,4,5].

Exciting physics is discovered – e.g. the charge transfer in the ostensibly simple compound LiH is determined by strong electron correlations [4]. Furthermore, we observe asymmetric transient charge changes on the H-atoms within the distorted BH₄ tetrahedron of LiBH₄ [5] being a possible precursor of its decomposition.

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Investigating and Understanding Ionic Ammine Materials

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Ammonia has been promoted as a viable candidate as an indirect hydrogen fuel vector, due to its high hydrogen content (17.8 wt%) and its ability to store 30% more energy per liquid volume than liquid hydrogen [1]. Ammonia can be safely stored in very high gravimetric and volumetric density in solid state halide materials [2-3], for example, at 109 gL⁻¹ for Mg(NH₃)₆Cl₂ compared to 108 gL⁻¹ for liquid ammonia. These solid state ammonia coordination complexes, known as ammines, have attracted much recent attention (for examples see [4-5] and references there within) with a view to their use as solid state ammonia and/or hydrogen storage materials. Solid state materials undergo considerable changes in structure and dielectric properties on coordination of ammonia due to changes in metal coordination environment and the presence of a partially hindered rotor.

We are interested in understanding the physical properties that determine the strength of ammonia binding within solids and the effect of ammonia coordination on structure [6]. To investigate these we have developed a new sample environment for use on the Polaris neutron diffractometer that allows the simultaneous characterisation of structure and dielectric properties whilst measuring ammonia uptake through mass flow measurements and out-gas mass spectroscopy. The combination of these characterisation techniques allows us to correlate the structure and coordination environment with dielectric properties, measure the kinetics of ammonia uptake and develop a greater understanding of ammonia absorption processes. Here we discuss our recent research on group 1 and group 2 halide ammines, expound a simple ionic model that can be used to predict absorption and desorption temperatures and describe the results of our preliminary multi-characterisation experiments on the Polaris diffractometer at the ISIS neutron spallation facility.

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Complex Transition Metal Hydrides Incorporating Covalent and Ionic Hydrogen

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A new class of quaternary group eight complex transition metal hydrides ($\text{Na}_2\text{Mg}_2\text{TD}_8$ ($T = \text{Fe}, \text{Ru}$)) has been synthesised and their structures determined by combined synchrotron radiation X-ray and powder neutron diffraction. These hydrides are scientifically of interest and can be considered as a link between ionic and complex hydrides in terms of incorporating mixed covalent and ionic hydrogen bonding character. This structural survey has been complemented with a topological analysis of the calculated electron distribution, employing high-level periodic calculations.

These novel isostructural complex transition metal hydrides crystallise in the orthorhombic space group *Pbam* and have been determined to incorporate independently coordinated ionic and covalent hydrogen (Figure 1). The octahedral complex transition metal hydride moiety is surrounded by a cubic array of four Mg^{2+} and four Na^+ (Figure 1a), forming distinct 2D layers (Figure 1c). An intriguing feature of these materials is the distorted octahedral coordination of the isolated D^- anions by four Na^+ and two Mg^{2+} counterions (Figure 1b), which form face-sharing layers between the transition metal containing layers. Density of state (DOS) calculations determined the specific bonding characteristics of the two types of hydrogen, indicating that a strong mixing of Fe states is observed for octahedrally coordinated hydrogen only.

Financial support from JSPS KAKENHI Grant Number 25220911 and Integrated Project of ICC-IMR of Tohoku University is gratefully acknowledged, as well as the use of SR16000 supercomputing resources at the Center for Computational Materials Science of the Institute for Materials Research, Tohoku University.

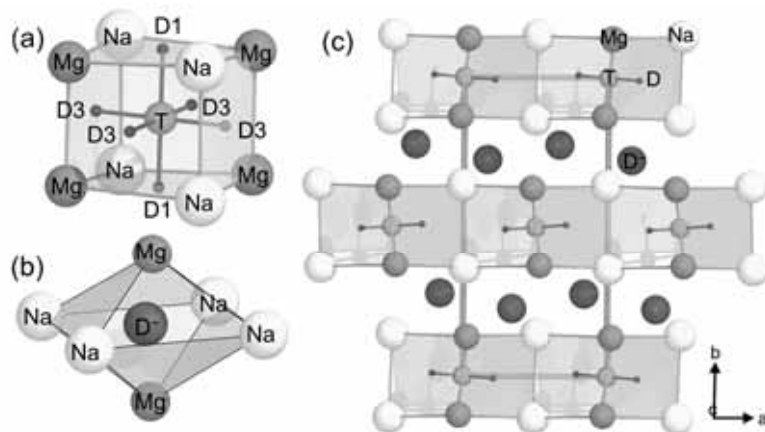


Figure 1. Structure of $\text{Na}_2\text{Mg}_2\text{TD}_8$ ($T = \text{Fe}, \text{Ru}$); (a) Coordination of the $[\text{TD}_6]^{4-}$ unit, (b) coordination of the D^- octahedra and (c) structure viewed down the *c* axis.

**High Throughput Computational Characterization of Hydrogen
Solubility and Diffusion in Intermetallics and Complex Metal Hydrides
(invited)**

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First principles calculations are able to give quantitative information about the thermodynamics of hydrogen solubility in metals and the rates of hydrogen diffusion. We have used these methods to systematically examine large libraries of materials for applications involving high temperature hydrogen purification using metal membranes and high temperature tritium capture using metal hydrides as getters. We will describe results from a library of over 1000 intermetallics that enormously expands the available information about interstitial hydrogen in these materials. We will also describe results that develop phase diagrams for a comprehensive collection of complex transition metal hydrides and use these results to predict the existence of a variety of materials that have not been previously reported.

Theoretical Exploration and Syntheses of Complex Transition Metal Hydrides with High Gravimetric Hydrogen Density

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Hydrogen displays a variety of bonding schemes in hydrides, and understanding them is indispensable for the development of novel hydrides for application use, such as hydrogen storage materials and fast ionic conductors. We are currently focused on the covalently bonded hydrogen to the transition metal elements in complex hydrides, and are searching for new materials with high gravimetric hydrogen density using first-principles calculations.

Iron primarily forms a tetravalent $[\text{FeH}_6]^{4-}$ complex anion with six octahedrally coordinating hydrogen atoms, yielding several complex hydrides normally with divalent alkaline earth cations. Related to this family, we recently synthesised the complex hydride, Li_4FeH_6 , on the basis of first-principle prediction [1,2]. This hydride is the first material containing $[\text{FeH}_6]^{4-}$ stabilised by only the lightest alkali metal element, lithium, and has the highest gravimetric hydrogen density of 6.7 mass% observed in the transition metal based complex hydrides.

In addition to the recently discovered hydride, we predicted the formation of the hypothetical Li_3FeH_7 , with a greater gravimetric hydrogen density of 8.4 mass% [3]. Besides the high hydrogen density, it is of scientific interest as the complex hydride contains a pentagonal bipyramidal $[\text{FeH}_7]^{3-}$ complex anion that features the unusual sevenfold coordination of iron (Figure 1). We found that the D_{5h} symmetry of the ligand enables the formation of strong covalent bonds between iron and hydrogen through ligand-field effects, stabilizing the sevenfold coordination.

This work was supported by JSPS KAKENHI Grant Number 25220911 and 25420725. We gratefully acknowledge the use of SR16000 supercomputing resources at the Center for Computational Materials Science of the Institute for Materials Research, Tohoku University.

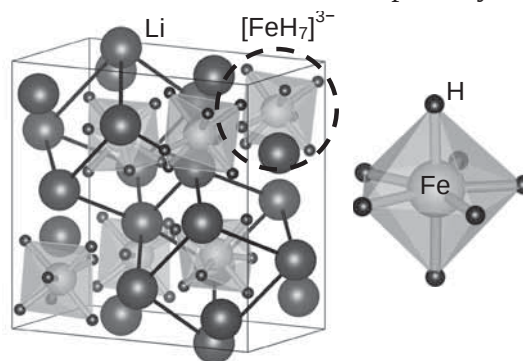


Figure 1. Structure of hypothetical complex hydride Li_3FeH_7 containing the pentagonal bipyramidal $[\text{FeH}_7]^{3-}$ anion that features the unusual sevenfold coordination of Fe.

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Optimized Complex Hydride Powder From High-Throughput Screening

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Hydrogen storage materials with high reversible gravimetric capacity, working under mild conditions are required for future, mobile hydrogen energy systems. A rapid throughput capability will accelerate the identification and development of such candidate materials. Thin film synthetic and screening methodologies provide an ideal route to combinatorially identify new materials, and provide a speed of analysis that is outside the reach of conventional bulk chemical methods.

The synthesis, screening and optimisation of the Mg-B-Ti hydride system [1] using a Physical Vapor Deposition system (PVD) have previously been reported [2]. A series of lead compositions were identified within the Ti doped Mg-B hydride system. Maximum capacity of the material is close to 10.6 wt.%, onset desorption temperature is at around 260 °C, presence of B-H bonding was shown by Raman and re-absorption was possible under moderate conditions (10 bar H₂ at RT).

Scale-up of these lead compositions was carried out by reactive planetary ball-milling of MgH₂ and B with a range of Ti-based compounds, under 100 bar of hydrogen. Although a single-phase material has not yet been produced, the composition and ball-milling conditions have not yet been fully optimized. The most recently produced Mg-based ternary hydride powder samples exhibited a reversible capacity of 5.3 wt% and a 110 °C reduction in hydrogen desorption temperature dependant on the preparation route (analysed by PCT and TGA, see Figure 1).

An approach to discover a Mg-B-TM-H (TM = different transition metals) compound in order to reach at least 8 wt.%, with an onset temperature of 80-100 °C and accelerated hydrogen sorption kinetics, will be discussed.

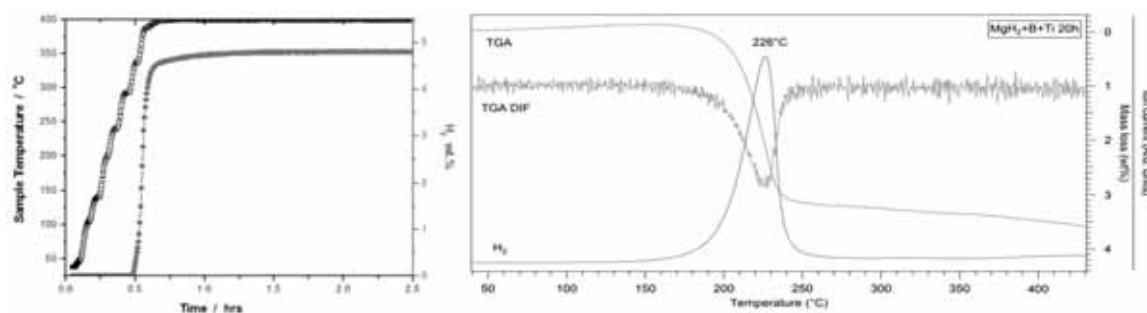


Figure 1: PCT (left) and TGA (right) for the latest Mg-B-Ti produced

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The Destabilization of Complex Hydrides with Metal Sulfides.

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Thermodynamic calculations suggest that alkali metal complex hydrides can undergo single step hydrogen release when destabilized with metal sulfides.¹ By forming M_2S (where $M = Li, Na, K$) as one of the desorption products instead of MH , the hydrogen capacity remains high while the volumetric hydrogen capacity is higher than the pure complex hydrides.

Temperature Programmed Desorption Mass Spectrometry (TPD-MS), *in-situ* Synchrotron X-ray Diffraction and hydrogen sorption measurements were performed on a number of complex hydrides mixed with various metal sulfides. All of the systems studied to date show complex decomposition pathways not predicted by thermodynamic calculations with a number of previously unknown phases.

In some systems, Temperature Programmed Photographic Analysis (TPPA) showed massive changes in sample morphology during hydrogen release (Figure 1). The decomposition pathways, hydrogen reversibility and the implications of morphology changes during hydrogen desorption will be discussed.

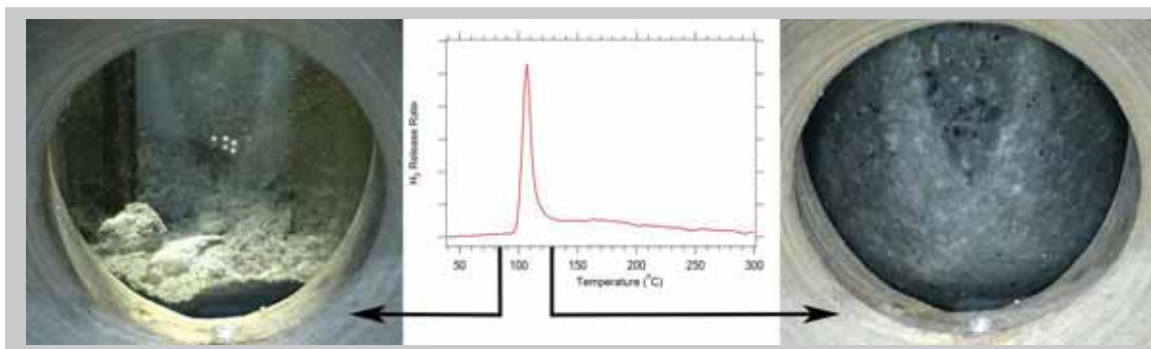


Figure 1. Temperature Programmed Photographic Analysis of $2NaAlH_4 + Al_2S_3$ heated at $2^\circ C/min$.

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Enthalpy-Entropy Compensation Effect in the Alkali Silanides Series: MSiH_3 ($M = \text{K}, \text{Rb}, \text{Cs}$) - INVITED

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The alkali silicides MSi ($M = \text{K}, \text{Rb}, \text{Cs}$) form a family of Zintl phases, with Si being present as isolated $[\text{Si}_4]^{4-}$ tetrahedra (iso-electronic with P_4 molecules) counter-balanced by M^+ cations in the crystal structures. If these compounds are quite well known, they have been only very recently investigated as possible hydrogen storage materials [1], although the corresponding MSiH_3 silanides were also reported. The MSiH_3 silanides are usually prepared by wet chemical reactions between the alkali metal M and silane SiH_4 .

In our group, we have investigated the direct hydrogenation of the MSi Zintl phases and studied the equilibrium, both by experimental measurements and DFT calculations, between MSi and the corresponding hydride counterpart MSiH_3 . We have shown that the $\text{KSi}/\alpha\text{-KSiH}_3$ system allows the reversible storage of 4.3 wt.% H_2 with very suitable thermodynamic properties [1], namely a 1 bar equilibrium pressure at about 440 K (cf. Figure 1). The hydrogenation properties of the heavier MSi Zintl phases ($M = \text{Rb}, \text{Cs}$) have been also determined. An enthalpy-entropy compensation effect is observed in the MSiH_3 series [2]: bigger is the alkali cation, more is the hydride stable (larger ΔH) and less is the $[\text{SiH}_3]^-$ anionic group mobile in the hydride (larger ΔS) (cf. Figure 2).

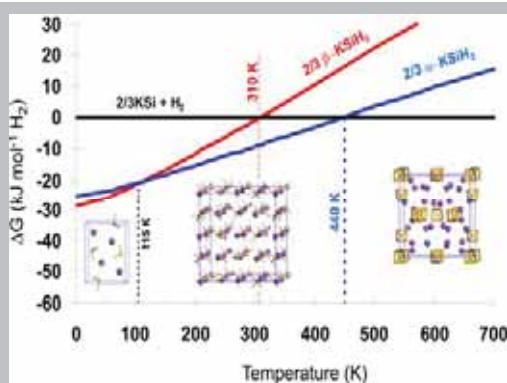


Figure 1. Stability domains for $\beta\text{-KSiK}_3$, $\alpha\text{-KSiH}_3$ and KSi phases

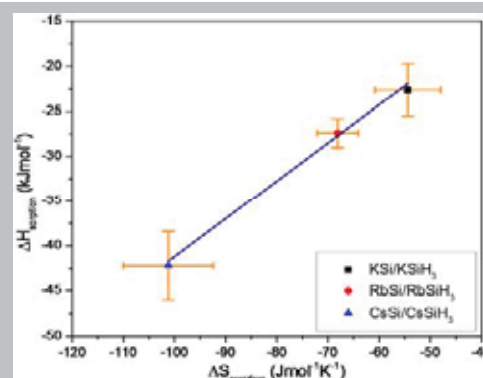


Figure 2. Linear enthalpy-entropy compensation for the MSi/MSiH_3 equilibria

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Thermodynamics and Crystal Structures of the Alkali Silanides MSiH_3 ($\text{M}=\text{K}, \text{Rb}, \text{Cs}$)

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Following our work on the direct hydrogenation of Zintl phase KSi [1] leading to the reversible alkali silanide $\alpha\text{-KSiH}_3$, we extended our investigation to the thermodynamic stability and crystal structures of the other MSiH_3 alkali silanides ($\text{M}=\text{Rb}, \text{Cs}$) using combined experimental and theoretical studies. Under mild conditions (*ca* 50 bar H_2 at 100°C) MSi Zintl phases ($\text{M}=\text{K}, \text{Rb}, \text{Cs}$) can absorb 3 H/f.u. corresponding to hydrogen contents of 4.3, 2.6 and 1.85 wt% H_2 , respectively (figure 1).

With the three alkali metals, a structural transition between a high ($\alpha\text{-MSiH}_3$) and a low temperature form ($\beta\text{-MSiH}_3$) is observed around 270 K. The complete crystal structures of those six phases have been fully solved using neutron powder diffraction (NPD) on deuterated samples [2]. For the first time, the crystal structures of $\beta\text{-RbSiH}_3$ and $\beta\text{-CsSiH}_3$ are reported showing a monoclinic distortion of the $\beta\text{-KSiH}_3$ orthorhombic unit cell (figure 2). The Si-H bonding in the α - and $\beta\text{-MSiH}_3$ phases will be detailed thanks to the NPD results as well as infrared spectroscopy. The temperature-dependency of the $[\text{SiH}_3]^-$ anionic group mobility will be especially discussed in correlation with the unusual thermodynamic properties encountered for the $\text{MSi}/\alpha\text{-MSiH}_3$ equilibrium.

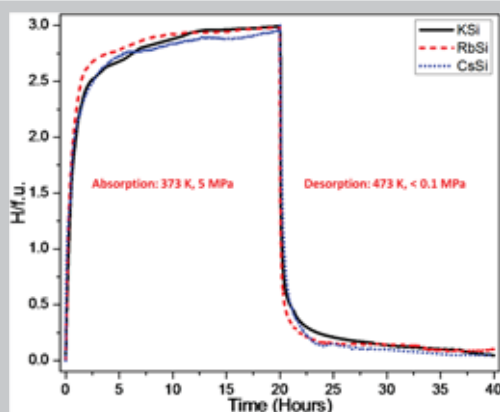


Figure 1. Kinetic absorption/desorption curves for the MSi Zintl phases ($\text{M}=\text{K}, \text{Rb}, \text{Cs}$)

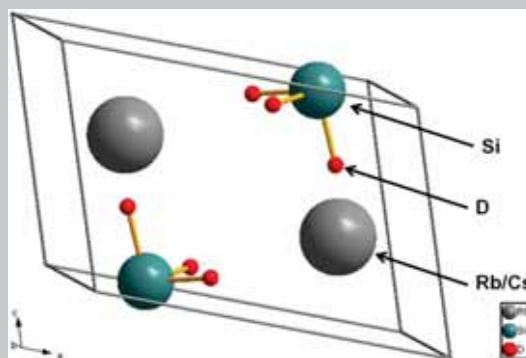


Figure 2. Crystal structures of the $\beta\text{-RbSiH}_3$ and $\beta\text{-CsSiH}_3$ silanides

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Reversibility of Complex Hydrides Under High Pressure Conditions

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Metal borohydride complexes have high gravimetric hydrogen densities and are therefore attractive candidates for hydrogen based energy systems. Practical use of these complex hydrides has not yet become commercially viable due to the high thermal stability and often non-reversibility. Theoretical calculations show that when metal borohydrides such as $\text{Ca}(\text{BH}_4)_2$, $\text{Mg}(\text{BH}_4)_2$ and LiBH_4 are combined with other compounds, thermodynamic equilibrium is significantly reduced[1, 2].

Presented here are mixtures of $\text{Ca}(\text{BH}_4)_2$, $\text{Mg}(\text{BH}_4)_2$ and LiBH_4 with either Sc or Si based compounds. These mixtures were ball milled and the sorption behaviour was characterised. X-ray diffraction, Sieverts apparatus, differential scanning calorimetry, thermogravimetric analysis and mass spectroscopy was done to observe the structure and behaviour of the borohydride mixes before and after the reaction.

Reversibility issues were recently addressed with a study that shows that high pressure can be used to overcome kinetic barriers to achieve direct absorption in an otherwise thermodynamically viable system[3]. This principal is also used here for pressures up to 1 kbar of hydrogen, 300°C. High pressure synchrotron experiments, differential scanning calorimetry and X-ray diffraction were used to observe changes in crystal structure and composition after all of the rehydrogenation attempts of the metal borohydride mixtures.

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Lithium Hydride Stabilised Nanoparticles and its Hydrogen Storage Properties

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Despite of the fact that lithium hydride (LiH) has the highest gravimetric content of hydrogen (12 mass%) of any metal hydride, it is generally not of interest for hydrogen storage. This is because of its high thermodynamic stability which requires 650°C for hydrogen desorption [1]. Furthermore, the direct reaction of Li metal and H₂ also needs 700°C at atmospheric pressure for an effective conversion[1] or 500 bar H₂ pressure under at room temperature [2].

In our work, by effectively utilising a nanosynthesis strategy, we have synthesised LiH nanoparticles (size range of 5-20 nm, Figure 1) under mild conditions in the presence of a surfactant. To further stabilise these LiH nanoparticles, they were coated with a nickel shell. Analysis by thermal gravimetry coupled with mass spectrometry revealed low H₂ desorption temperature for this new material starting from 100°C (Figure 2). This shows the possibility of modifying the properties of LiH to some extent. Furthermore, some reversibility was achieved. This finding is likely due to nanosize effects imparting shorter hydrogen diffusion distance hence easier hydrogen desorption.

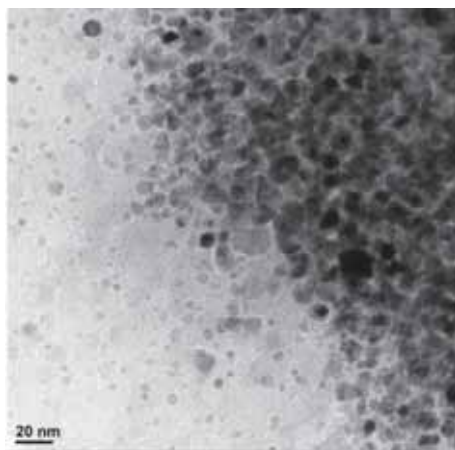


Figure 1. Image of LiH @ Ni nanoparticles

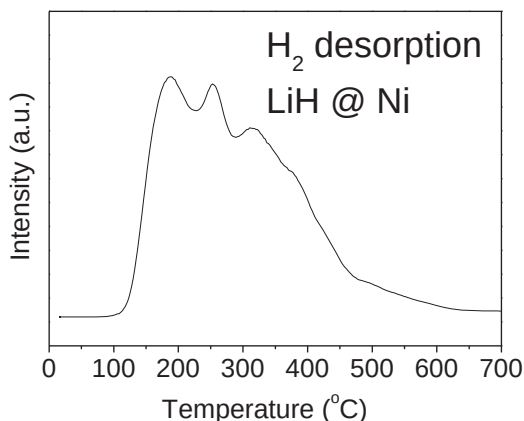


Figure 2. H₂ desorption from LiH @ Ni

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Novel Complex Hydrides for Hydrogen Storage and Related Structural Studies (Invited)

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Successful development of hydrogen as an energy carrier will simultaneously reduce the dependence on fossil fuel and emissions of greenhouse gases and pollutants. This is especially critical in this century with increasing concerns about energy security and global warming. One of the major challenges to widespread use of hydrogen is the lack of storage materials with suitable on-board operating capacities and properties for fuel-cell vehicular applications. In this talk, I am going to present our recent work on developing novel high-hydrogen-capacity complex metal hydrides and chemical hydrides for hydrogen storage. Particularly, I will discuss our efforts to rationally search for $H^{\delta+}/H^{\delta-}$ co-existing B-N compounds, including metal amidoboranes ($M-NH_2BH_3$)^{1,2}, borohydride ammonia borane complexes ($MBH_4-NH_3BH_3$)³ and metal hydrazinoboranes ($MN_2H_3BH_3$)⁴. These materials exhibit remarkable dehydrogenation performances compared to conventional metal hydrides. The talk will focus on the structural studies of these materials, highlighting various aspects of crystal structure determination and crystal chemistry. The rich information obtained from the structural analysis and its implications for hydrogen storage will also be discussed.

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Tuning thermodynamics by finite size

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Using hydrogen as a future energy carrier in mobile applications faces several challenges. The gravimetric density needs to be high and the kinetics need to allow reversible charging and uncharging at close to ambient conditions. On route, which attracted considerable attention recently, to achieve these goals is the use of finite sized materials. The idea behind this approach is to influence the thermodynamics of the hydrogen uptake and release and by this tailor the properties of materials to become optimized for specific applications.

However, unraveling the finite size scaling of thermodynamic properties in metal hydrides is challenging since it is difficult to exclude other physical parameters. For example, it is known that changes in the strain state of a material have significant influence on the hydrogen uptake [1]. Furthermore, when discussing finite size effects the proximity of a boundary manifesting in a depletion region needs to be considered [2]. To unambiguously determine finite size effects on hydrogen uptake, all other effects, like the boundary condition and strain state, need to be taken into account.

We show that for thin layers of vanadium grown epitaxial on magnesium oxide and sandwiched between iron the effects of proximity and changes in strain can be separated from finite size effects. Moreover, due to the tetragonal distortion of the vanadium unit cell the hydrogen atoms always occupy the octahedral sites even for the lowest concentration implying a coherent disorder to order transition. We report a linear inverse size dependence of the critical temperature of hydride formation which is explained by the absence of nearest neighbors and the presence of dead layers at the vanadium boundaries combined with a lattice gas model [3]. The scaling behaviour shows that finite size effects change the thermodynamic properties only when the nano-meter length scale is approached.

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Origin of the huge asymmetry in ab- and desorption kinetics of hydrogen in capped films

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In many situations, hydrogen ab- and desorption in nano-sized metals is of great interest. Very often small particles are (naturally) coated with an oxide layer or capped with a suitable layer. This is for example the case in experiments involving thin films where the caplayer is chosen so as to facilitate the catalytic splitting of the H₂ molecules and to protect the film from oxidation (for example during hydrogenographic investigations [1]). In such samples the hydrogen absorption is always found to be order(s) of magnitude faster than the desorption.

In this talk, I present a model that reproduces accurately the *time dependence* of the hydrogen ab- and desorption in typical samples: Palladium (Pd) capped yttrium, magnesium, MgTi, and platinum (Pt) capped yttrium nanoantennas for active plasmonics [2]. The model, which is a further development of the one developed by Borgschulte et al. [3], takes into account dissociation at the surface, absorption in subsurface sites, and subsequent diffusion through caplayer and underlying sample. In several cases it leads to analytical expressions that are useful for the interpretation of the experimental results and the determination of the rate limiting processes in hydrogen ab- and desorption.

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Probing the cerium/cerium hydride interface using nanoindentation

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The surface of cerium metal has been observed to degrade in the presence of low pressures of hydrogen [1], forming surface hydride species. Previous work has been carried out to establish the kinetic parameters of the growth of hydrides [2, 3]; and anisotropic growth kinetics have been identified which results in an oblate hemispherical hydride morphology [3].

The mechanical properties of hydrides have been modelled, indicating that non-spherical hydrides should only occur in the case where the hydride is softer than the surrounding material [4]. This work aims to investigate the mechanical properties of a surface cerium hydride to test those modelling results.

Surface cerium hydrides were grown on cerium metal at 10 mbar and analysed in cross-section (Figure. 1) using nanoindentation. The nanoindenter used was a cube-corner diamond on a stainless steel cantilever in a Veeco Enviroscope AFM system allowing the cerium and cerium hydride to be probed at high spatial resolutions, whilst maintaining vacuum.

The work demonstrates that the cerium hydride is harder than the cerium metal by a ratio of 2.5, and identifies the presence of a zone of work hardened material in the cerium metal surrounding the hydride (Figure 2).

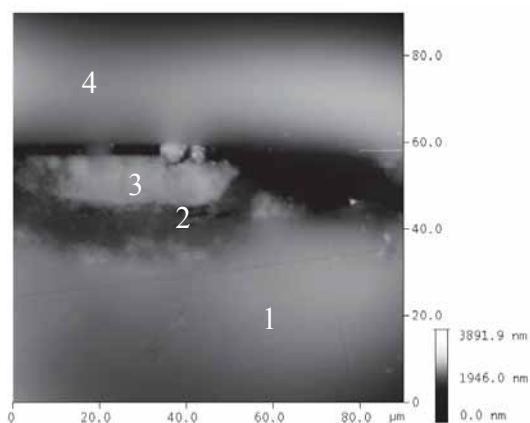


Figure 1. AFM image of a cerium hydride in cross-section, 1) parent Ce metal, 2) adherent hydride, 3) reoxidised hydride, 4) epoxy resin.

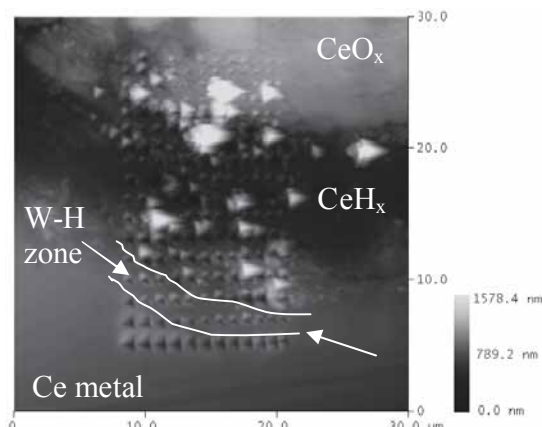


Figure 2. Nanoindentations across cerium/cerium hydride interface. The presence of a work-hardened zone in the metal is indicated.

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Functionalized Mesoporous Carbon Supports For Hydrogen Storage Materials: A First-principles Study Of Surface Interactions With Complex Hydrides

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Abstract

Significant research has been conducted on nanoconfinement of hydrides in framework materials, mainly metal organic frameworks and nano-structured carbons. Mesoporous carbon frameworks provide a high surface area and reasonably large pore volume for containment of complex hydrides. The advantages are two-fold. First, the frameworks possess a large surface area that may provide significant support for membrane-bound catalysts. Second, the support confines the hydride and may mitigate safety issues such as rapid reaction with oxygen and water in the event of a containment failure. The pyrolysis of phenolic resins results in a combination of sp²-bonded carbon networks and also defects. The degree of each depends strongly on the synthesis temperature of these carbons and provides a degree of control over the surface characteristics and functionalization properties. We present results for small clusters of LiBH₄ in contact with pristine graphitic carbon, which has sp²-bonded sheets, and may be modeled using graphene. We illustrate through first-principles calculations both with and without van der Waals corrections that small clusters of LiBH₄ are predicted to wet these carbon sheets only when there are defects present. We also discuss doping of the framework, and illustrate the concept and benefits of changing the local electronic structure of the carbon surface by substitution with electron deficient boron and electron rich nitrogen.

Mesoscale microstructural computational simulation of hydrogen permeation test to calculate the intergranular/grain boundary diffusivity

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The hydrogen induced intergranular embrittlement has been identified in aerospace components such as combustion chambers made of electrodeposited polycrystalline nickel [1]. So it is important to quantify the hydrogen diffusion coefficient of intergranular grain boundary(GB) in polycrystalline nickel to understand the metal susceptibility to hydrogen induced intergranular fracture. It is well know that the effective diffusion coefficient of hydrogen has been experimentally determined using electrochemical permeation tests and on the hand it needs lots of effect to measure the intergranular GB diffusion coefficient of hydrogen in polycrystalline material experimentally [2]. This made the authors develop an approach to calculate the intergranular GB hydrogen diffusivity using finite element (FE) computational analysis. First, the microstructural representative volume element (RVE) meso scale model has been developed based on the parameters (i.e such as grain size, volume fraction of grain and GB) collected from electron backscattering diffraction (EBSD) analysis. Second, the effective diffusivity was computed as a function of grain size and GB volume fraction using FE microstructural homogenisation technique. Third the homogeneous model have been developed and applied in order to simulate the hydrogen diffusion permeation test by implementing the computed effective diffusivity. Fourth code has been developed in order to find the unknown GB diffusivity by varying its value and fitting the results of experimentally measured permeation curves with the simulated curves.

Keywords

Intergranular/Grain boundary diffusivity; Polycrystalline pulse plated nickel; Hydrogen induced intergranular embrittlement; microstructural homogenization technique; electrochemical permeation test; Finite element analysis;

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Pressure and Temperature influence in a MgH_2 Numerical model.

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MgH_2 is a promising candidate for thermal energy storage, TES, in the context of concentrated solar power, CSP. This is due to the temperatures of suitable plateau pressures of MgH_2 being commensurate with the operational temperatures of the solar field parabolic collectors and the steam raising plant, combined with its low cost and high enthalpy. Investigation into the performance and viability of MgH_2 based TES is being conducted using numerical models. Simulations of this kind are reliant upon accurate representation of material properties and kinetics. In particular consideration must be given to the influence of temperature and pressure on the rate of reaction in order to attain numerical models with a workable level of accuracy [1].

The influence of pressure and temperature on the rate of reaction was investigated using 0.2 g sample of Mg powder. Isothermal kinetic data was collected at the reference temperatures of 330, 350 and 390 °C. To isolate the pressure influence component of the reaction the isothermal data was collected for incremental changes in the ratio of initial pressure to equilibrium pressure [2,3]. A linear model of the pressure influence was obtained, Figure 1, from which the constants, activation energy and activation volume were derived. The inclusion of an activation volume distinguishes this method from the normal practice employed where temperature and pressure influences are the product of two separate functions. Here a combination of Arrhenius and Eyring type equations allows temperature and pressure influences to be represented by a single rate expression.

To explore the validity of this approach the resulting rate expression was implemented in a 3-D numerical model and solved using COMSOL Multiphysics 4.3. Further empirical data was collected for a sample of Mg powder where the reaction parameters of temperature and pressure were transient. Comparison of experimental with predicted data indicates that this approach improves the level of confidence that can be placed in the prediction of high temperature hydride reactions using numerical methods.

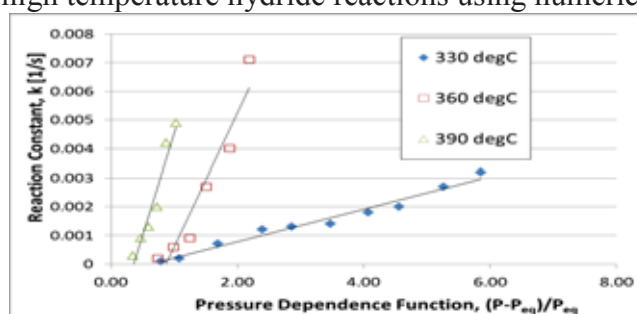


Figure 1. Isothermal Hydrogenation Kinetics for MgH_2 Powder.

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Tuning the Stability of $\text{Ca}(\text{BH}_4)_2$ by the Inclusion of Additives: A Computational Study

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Metal borohydrides (MBHs) are considered as promising hydrogen storage materials because of their high weight percent of hydrogen (up to 20.8 wt%). Unfortunately, they found limited applicability because of various drawbacks. The MBHs are either thermodynamically too stable or kinetically too slow (e.g. alkali, alkaline earth); on the other hand, they can be unstable and irreversible (e.g. transition metals). Several strategies have been proposed to improve the kinetics and the thermodynamics of the hydrogenation/dehydrogenation reaction. Among them, the inclusion of additives in the BHs structure appears to be one of the more effective because it reduces the activation barrier of the hydrogenation process and then the H_2 desorption starting temperature [1].

In the present work, we studied the inclusion of Ni^{2+} ions at the surface of $\beta\text{-Ca}(\text{BH}_4)_2$, which is one of the most interesting systems because of its high H_2 wt% (11.6 wt%), by using quantum-mechanical methods. Calculations were carried out with periodic density functional theory (DFT) calculations employing the PBE-D* (i.e. PBE augmented with the Grimme's DFT-D2 empirical dispersion correction, as modified for solids) functional as implemented in the CRYSTAL code [2].

As a first stage, we modeled various surfaces of $\text{Ca}(\text{BH}_4)_2$ and evaluated their relative stability in order to predict the most stable one. To simulate the surfaces, the so-called slab model approach was used [3]. The (001) surface was predicted to be the most stable one. The inclusion of Ni^{2+} as additive was then investigated. Two different molar concentrations were simulated by substituting Ca^{2+} with Ni^{2+} at the top most layer of the (001) surface. The structural deformation and the qualitative information provided by the electrostatic potential maps of the surface have been analyzed. The distortion from the ideal T_d symmetry of BH_4 ion and its destabilization (25 kJ/mol) due to the decreasing of the charge transfer from the cation (i.e. Ca and Ni) to the BH_4 ion are likely responsible of the decrease of the activation energy for H_2 release. As pictorially shown in the scheme in Figure 1. The effect of other additives (Co, Cu,...) is under investigation. The research leading to these results has received funding from the E.U. project BOR4STORE.

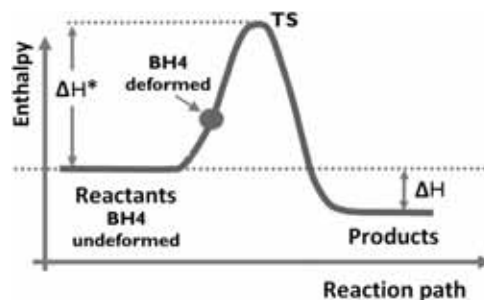


Figure 1. Simplified scheme of the energy as a function of reaction pathway.

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Thermodynamic Modelling of Metal-Hydrogen Systems Using the Calphad Method

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The Calphad (CALculation of PHase Diagrams) method is an extensively used semi-empirical technique for phase diagram calculation and modelling. It consists in describing the Gibbs energies of the different phases present in a system by adjusting parameters in order to fit the known experimental data.

When experimental data is missing, DFT calculations may be a great help to estimate enthalpies of formation, energy of mixing or vibrational entropies.

The two merits of the Calphad method are:

- to obtain reliable self-consistent thermodynamic description of given simple systems
- to be able to combine simple systems in order to obtain predictions of phase equilibrium in multi-component systems

In this presentation, the basics of the Calphad method will be presented. It will be shown how this method may be applied specifically to metal-hydrogen systems in order to get better knowledge of the phase diagrams and thermodynamic behaviour of these systems. The application to several specific binary systems will be shown. Finally, the predictive aspect will be demonstrated.

Thermodynamics of Borohydrides-based Materials Coupling ab-initio and Calphad Methods

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Thermodynamic requirements (such as a value around 35 kJ mol_{H₂}⁻¹ for the dehydrogenation enthalpy) are a key aspect in the selection of appropriate materials for hydrogen storage applications. Modern modelling techniques, especially ab initio ones, showed the ability to correctly predict the stability of the different phases involved in the dehydrogenation reactions. Nevertheless, using exclusively these techniques, it is difficult and computationally demanding to understand how the system evolves when conditions (temperature and pressure) are modified. This, instead, can be easily obtained coupling first principle calculations with the Calphad approach [1].

In the present work, developed in the framework of the Bor4Store european project, experimental data and new ab initio calculations performed with the Crystal code [2] have been used as input for the thermodynamic description of several borohydride based systems: LiBH₄, NaBH₄, Ca(BH₄)₂ and Mg(BH₄)₂. The presence of species containing B₁₂H₁₂⁻ anions has been studied thanks to data provided only by ab initio calculations.

Thermodynamic databases obtained with this method have been employed to predict equilibrium phases, calculate phase diagrams (as shown in Figure 1) and other data useful for the interpretation of experiments. Indeed it has to be underlined that using this approach it is possible to compare the different experiments and obtain a clear picture of the accuracy for the available data.

Competitive reactions bringing to undesired products have been evidenced and a satisfactory agreement between experiments and calculations has been achieved.

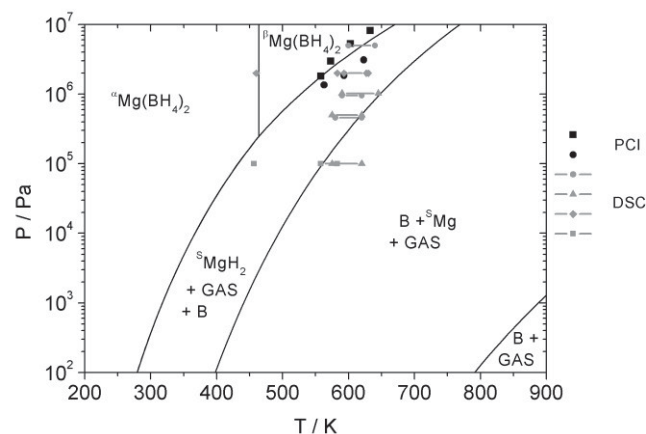


Figure 1. Calculated phase diagram for Mg(BH₄)₂ composition when MgB_n and MgB₁₂H₁₂ are rejected. Experimental data from literature are reported for comparison.

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Self-amplified Site Occupancy Transition of Hydrogen in Vanadium Studied from Density Functional Calculations

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The site occupancy of hydrogen atoms in strained body-centered cubic vanadium is investigated using density functional theory. Predominant occupancy of either the tetrahedral or the octahedral interstitial sites results from the different effect by the strain state of the material. Interstitially absorbed hydrogen will itself give rise to local strain fields in the material. For large enough hydrogen concentrations, the sum of these local strain fields will combine to give rise to a change in volume which in turn alters the energetic landscape of the absorbed hydrogen.

We predict that a change in site occupancy from tetrahedral to octahedral will occur at a critical strain at which the energetics of hydrogen site occupancy becomes equal (Figure 1). We also predict hysteresis behavior in the site occupancy during the loading and unloading of hydrogen in the system (Figure 2). This phenomenon has been experimentally observed [1] and theoretical calculations [2] that will be presented provide an atomistic insight to the underlying process.

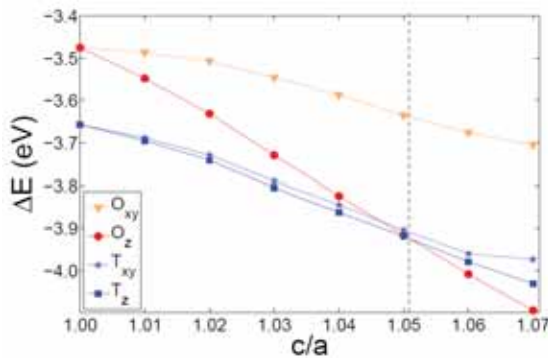


Figure 1. Relative energies of hydrogen occupying one of the four different interstitial sites in bcc vanadium as a function of an externally applied global uniaxial lattice strain c/a .

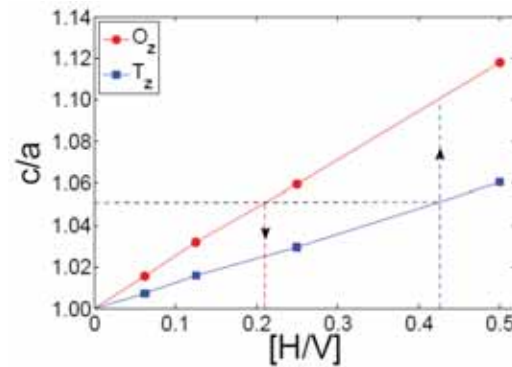


Figure 2. The uniaxial lattice strain c/a for exclusive occupation of either T_z or O_z sites resulting from varying the concentration of hydrogen $[H/V]$.

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First Principles Calculations on (La-Mg)-Ni Hydrides

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Between interstitial metal hydrides, such as LaNi_5H_y , and ionic complex hydrides, as Mg_2NiH_4 , the whole family of (La,Mg)-Ni hydrides exists, exhibiting intermediate electronic properties. Using Density Functional Theory (DFT) calculations, a systematic investigation of the electronic properties of these $(\text{La,Mg})\text{Ni}_x\text{H}_y$ hydrides was performed.

We previously showed that the intermetallics (La,Mg)Ni_x compounds, based on the frame of $x=(5n+4)/(n+2)$ phases described by Khan [1], are stable by the stacking of $n \times [\text{LaNi}_5] + [\text{LaMgNi}_4]$ layers of Haucke and Laves phases, respectively, with Mg atoms filling only half sites of the later [2].

In the present work, focus is made on the calculated preferential H sites. A systematic comparison between geometrical and chemical arguments, leads to a general rule which governs the stability of the hydrides of the (La-Mg)-Ni compound family.

As an example, the $(\text{La,Mg})_2\text{Ni}_7\text{H}_y$ hydrides are fully presented. An analysis of their electronic structure and charge transfer is proposed. Crystallographic features and possible ordered hydride description are compared with available experimental data (Figure 1). Moreover, an investigation of the recently discovered MgNi_2H_3 hydrides will be discussed in terms of stability and electronic structure [3].

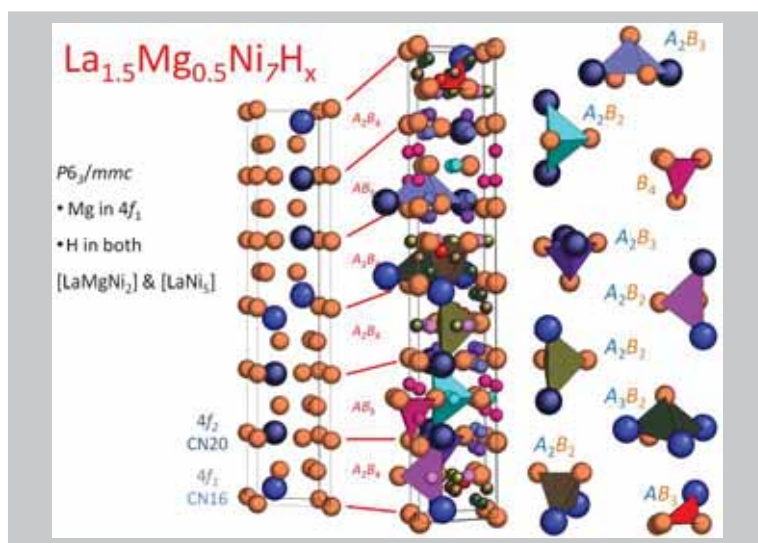


Figure 1. $\text{La}_{1.5}\text{Mg}_{0.5}\text{Ni}_7$ hydride structure from Ref. [4].

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The Use of Hydrogen to Separate and Recycle NdFeB Magnets from Electronic Waste

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Rare earth metals have been identified by the EU, US and Japan as being at greatest supply risk of all materials for clean energy technologies. Neodymium and dysprosium, which are both employed in neodymium iron boron magnets (NdFeB), have been highlighted in particular. Recycling of scrap NdFeB-based magnets contained within waste electronics could provide an additional and secure supply of these materials. In this work, hydrogen has been used as a processing gas to break down sintered NdFeB-based magnets contained within hard disk drives (HDDs) into a demagnetised hydrogenated powder. The powder is then extracted mechanically from the devices and is processed further to produce a powder with <330ppm of Ni contamination. The extracted powder can be re-processed in a number of ways, either directly from the magnet alloy by re-sintering, by the Hydrogenation, Disproportionation, Desorption, Recombination process (HDDR), or by re-melting; or by chemical extraction of the rare earth elements from the alloy. The advantages and disadvantages of these processes are discussed in the latter part of this paper.

Where is the critical point of the Pd–D₂ system?

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Beyond the critical point of a two-phase system, the two phases are indistinguishable. In the metal-hydride context, a path exists between the distinguishable low-temperature/pressure phases via the supercritical region of the phase diagram, along which the two phases seamlessly interchange. The Pd–H₂/D₂ system exhibits this property owing to the miscibility gap between the pure solid-solution (α) and hydride (β) phases. The phase transformation exhibits hysteresis in the sub-critical region of the phase diagram. There is a large body of existing literature on Pd–H₂/D₂ that strongly suggests a nexus between hysteresis, bistability (coexisting α and β phases) and dislocation generation, but does not clearly indicate how hysteresis arises.

An *in-situ* x-ray structural investigation of Pd–H₂ by Maeland and Gibb [1] revealed that above 308°C the hydride was single phase and below 308°C the α and β phases coexisted. This critical temperature was within error of that at which hysteresis was believed to disappear [1], as expected if hysteresis accompanies the discontinuous phase transformation. Wicke and Blaurock [2] investigated pressure hysteresis around the critical point and concluded that hysteresis disappeared at 291°C in Pd–H₂ and 283°C in Pd–D₂, thus raising a question about the true critical temperature.

Here we present the results of an experiment to study the supercritical region of the Pd–D₂ system using high resolution *in-situ* neutron diffraction. Figure 1 shows that at 322°C, well above the proposed critical temperature of 283°C [2], two phases coexist, with elastic accommodation of their differing lattice parameters revealed as a spread of intermediate *d* spacings. The same effect was observed, less markedly at 342°C.

Comparing our results with those of Wicke and Blaurock [2], the presumed nexus between criticality and hysteresis is clearly false.

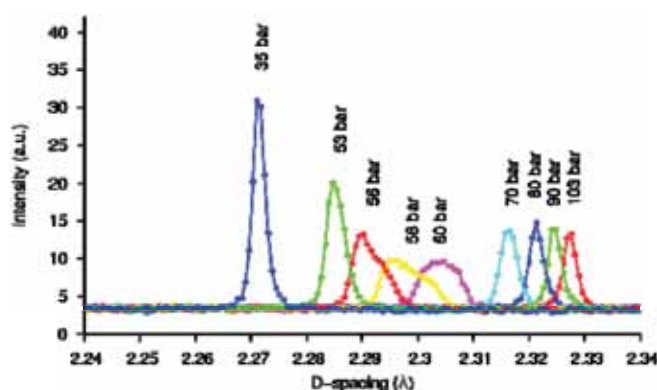


Figure 1. (111) diffraction peaks for Pd–D₂ at increasing pressures, at $T = 322^\circ\text{C}$.

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***In-situ* studies of hydrogen loading and unloading in single palladium nanocrystals**

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Many energy and information storage processes, such as hydrogen storage, battery charging, and memory switching, rely on phase changes of nanostructured materials in reactive environments. Compared to their bulk counterparts, nanostructured materials appear to exhibit faster charging and discharging kinetics, an extended life cycle, and size-tunable thermodynamics [1-3].

However, in ensemble studies of these materials, it is often difficult to discriminate between intrinsic size-dependent properties and effects due to sample size and shape dispersity. Studies of hydrogen absorption in individual nanoparticles so far have been limited to evaporated nanostructured, with thermodynamics heavily influenced by the elastic interaction with the substrate [4,5].

Here, we present the first direct measurement of hydrogen absorption and desorption in individual colloidally-synthesized palladium nanocrystals, with sizes ranging from 29 nm down to 13 nm. Our approach is based on *in-situ* electron energy-loss spectroscopy (EELS) in an environmental (scanning) transmission electron microscope. By constructing single-particle pressure – energy-loss isotherms, we find that hydrogen intercalation in Pd nanocrystals is regulated by the coherent elastic coupling between the alpha and beta phases of PdH_x [6,7]. Such coupling results in an energy barrier that cannot be overcome by thermal fluctuations, suppressing coexistence of alpha and beta phases in equilibrium. Consequently, hydrogen loading and unloading isotherms are characterized by abrupt phase transitions and macroscopic hysteresis gaps [8]. These findings are in contrast with ensemble measurements of Pd nanoparticles, in which sloped H₂ loading/unloading isotherms suggest a thermally-driven nucleation of the hydride phase [9]. Furthermore, we find that surface energy plays a critical role in determining the energetics of the hydrogen absorption process.

Our results highlight the importance of single-particle approaches to the characterization of nanostructured metal hydrides.

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Lattice Expansion of Palladium-Hydrogen (Pd-H) : a Critical Review of Dimensional Measurements

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Since the work of Peisl in 1978 [1] about Pd-H lattice expansion by change of volume $\frac{dV}{V_0}$ with measurements of lattice parameter $\frac{da}{a_0}$ and length $\frac{dl}{l_0}$ [1,2], no update has been made with dilatometric results $\frac{dl}{l_0}$. The present paper propose to review dilatometric results for Pd-H and report unexpected expansion rate from papers published between 1869 to 2014.

Data were obtained during hydrogenation of bulk samples (wires, rods, disks, foils, bars) by electrochemistry or by gas absorption, as received or annealed, at room temperature or temperatures above T_c .

It is shown that apart from the results of Ribaupierre et al. [2], all the available results show surprisingly low rate of expansion (up to one order of magnitude), very different from what is expected [1]. The expansion behavior is not linear and shows different slopes depending on the area. When other dimensions were measured on a same sample, some investigators report different expansion rates depending on the dimensions (length, width, thickness) showing a clear anisotropic behaviour.

Possible explanations of these results are reviewed and discussed. Finally, the reliability of dilatometry as a relevant tool for lattice expansion measurements is questioned.

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Hydrogen Purification for Cost-Effective Fuel Cell Power

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Hydrogen and fuel cells (HFCs) offer multiple advantages as power systems, such as low urban pollution / CO₂ emission, quiet operation, low self-discharge, high energy density and extended driving ranges for vehicles. The technology simultaneously addresses many of the major energy and environmental challenges, and shows the flexibility to integrate the diverse/intermittent renewable energy sources that are increasingly installed across Europe and emphasized in EU “Horizon 2020”. It is estimated that the HFC market could reach \$3 billion with hydrogen demand from fuel cells > 140 million kg in 2030. However, the technology needs to be economically competitive with other fuel systems, e.g. gas turbines for balancing electrical grids, Li-ion batteries for domestic storage, and high-compression-ratio diesel engines for transport. Two important factors contributing to the elevated costs of HFCs are: the additional cost of high-purity H₂ needed to extend asset lifetime, especially when the H₂ is generated from diverse sources or supplied by an on-board hydride/hybrid tank; and the cost associated with the limited lifetime of HFCs due to impurity built-up or catalytic poisoning. Therefore, low-cost and in-line H₂ purification and impurity monitoring are crucial for the reduction of H₂ fuel costs and fuel-cell running cost due to extended lifetime of the fuel cell stacks.

This presentation comparatively examines the issues of H₂ purification at source and in-line to reduce H₂ fuel cost for HFCs, and other ways of hybridizing HFCs and monitoring H₂ impurities to reduce FC capital costs, cell maintenance costs and extend the lifetime of HFCs. How different types of membranes can be developed to meet such requirements.

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Pd-Cu-M (M= Y, Ti, Zr, V, Nb, and Ni) Alloys for Hydrogen Separation Membrane

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Palladium-copper (Pd-Cu) alloys are of potential interest for use as hydrogen separation membranes because they are lower in cost and more chemically resistant than the commercially available Pd-Ag membranes [1-2]. However, their hydrogen permeability and chemical stability needs to be further improved. In this work, self-supported fcc Pd-Cu-M (M= Y, Ti, Zr, V, Nb, and Ni) ternary alloys were studied as potential hydrogen purification membranes. The effects of small additions of these elements on the structure, hydrogen solubility, diffusivity, and permeability were examined. Structural analyses by XRD showed fcc phase for all alloys with induced textures from cold rolling. Heat treatment at 650 °C for 96 h led to the re-orientation in all alloys except Pd-Cu-Zr alloy exhibiting structural stability as a result of Zr addition. Hydrogen solubility was almost doubled in the ternary alloys containing Y and Zr compared to Pd_{65.1}Cu_{34.9} binary alloy at 300 °C. It was noted that hydrogen diffusivity is decreased upon additions of these elements compared to Pd_{65.1}Cu_{34.9} binary alloy, with Pd-Cu-Zr alloy showing the lowest hydrogen diffusivity. However, the comparable hydrogen permeability of Pd-Cu-Zr alloy with the corresponding binary alloy, as well as its highest hydrogen permeability amongst the studied ternary alloys at temperatures higher than 300 °C suggested that hydrogen permeation of these alloys within the fcc phase is mainly dominated by hydrogen solubility [3]. Hydrogen flux variations of all ternary alloys were studied and compared with Pd_{65.1}Cu_{34.9} binary alloy under 1000 ppm H₂S+H₂ feed gas. The marked effect of Zr addition for improving the resistance to the sulphur poisoning was observed and attributed to the less favourable H₂S-surface interaction and more importantly to the structural stability of the Pd-Cu-Zr alloy delaying the bulk sulphidation. Therefore, to the best of our knowledge, Pd-Cu-Zr alloys may offer new potential hydrogen purification membranes with improved chemical stability and hydrogen permeation compared to the binary fcc Pd-Cu alloys.

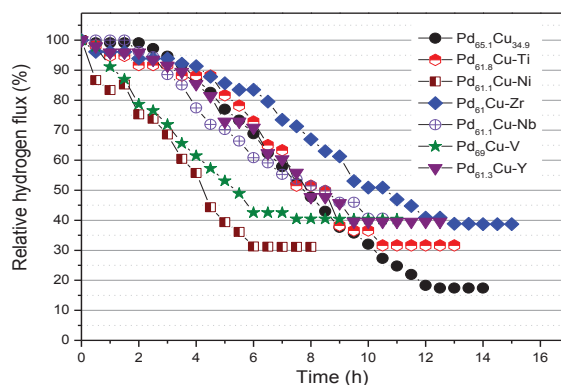


Figure 1. Poisoning of Pd_{65.1}Cu_{34.9} and ternary Pd-Cu-M (M= Y, Ti, Zr, V, Nb, and Ni) alloys at 450 °C. The feed gas contains 1000 ppm H₂S+H₂.

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High hydrogen flux through bare vanadium membrane without Pd overlayer

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Hydrogen permeable alloy membranes are important materials for hydrogen separation and purification technologies. Group 5 metals, (i.e., V, Nb and Ta), are promising metals for non Pd-based alloy membranes, because of their lower cost and higher hydrogen permeability than currently used Pd-based alloys. For such non Pd-based alloy membranes, the Pd overlayer on their surfaces are still considered to be essential to obtain practical hydrogen flux through them [1]. However, if such Pd/(V, Nb, Ta)/Pd composite membrane is operated at high temperature, a significant degradation of the hydrogen permeability readily occurs due to the formation of intermetallic compounds, e.g., Pd₃Nb, at the Pd/base-metal interface [2].

In this study, the hydrogen permeability of bare V membranes without Pd overlayer has been investigated. The time dependence of the hydrogen flux through pure V membrane with different membrane thickness, L , is shown in Fig.1. It is found that the pure V membranes exhibit excellent hydrogen permeability even without Pd overlayer. The hydrogen fluxes are almost constant at least more than 8 hours, so the membranes without Pd overlayer possess good durability. As shown in Fig.2, there is a linear relationship between the hydrogen flux and the inverse of the membrane thickness, indicating that the diffusion limiting hydrogen permeation reaction takes place following Fick's law even without Pd overlayer on the surface.

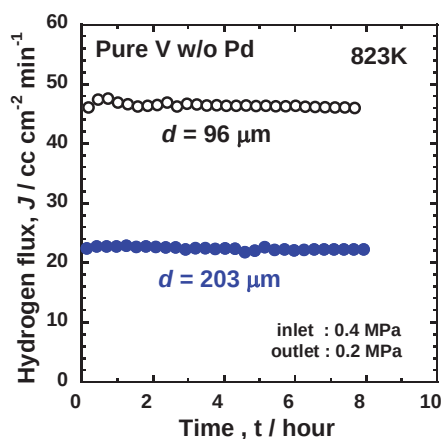


Fig.1 Time dependent of the hydrogen flux for pure V membrane without Pd overlayer at 823K.

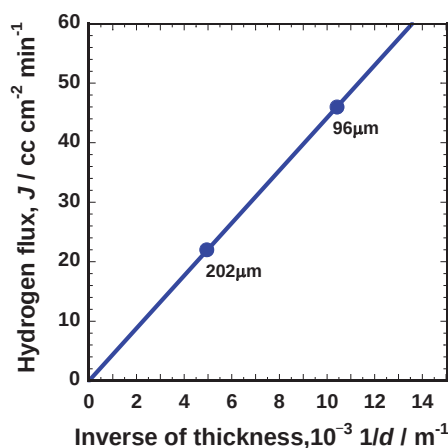


Fig.2 Correlation between hydrogen flux and inverse of sample thickness for pure V membrane without Pd overlayer at 823K.

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Alloys Based on 5 Groupe Metals for Hydrogen Purification Membranes

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The problem of creating alloys not containing palladium for hydrogen purification is still vital from the scientific and technological point of view. Group V metals were selected because of their high solubility of hydrogen (higher than palladium). Besides they are promising materials for the membrane separation of hydrogen from gas mixtures.

The properties of alloys based on vanadium, niobium and tantalum were investigated and their compositions with titanium nickelide [1,2] and NbTa alloys were compared known from the available literature data. The main criterion for comparison is the specific permeability of hydrogen; however, the factors affecting the membrane manufacturing technology, such as specifics of melting and heat treatment, possibility of producing foil by milling, resistance to leaks due to the formation of hydride phases at quenching were also taken into account.

In addition, effect of the membrane surface state (surface coating with non-metallic impurities such as carbon and oxygen) on the kinetics of the penetration process during interaction of hydrogen with membrane-based alloys of Group V metals were studied.

Research was conducted by hydrogen penetration technique adapted for high values of flows, SEM, X-ray diffraction to determine the phase composition, metallographic analysis, and mechanical testing. It was established that alloys V-(TiNi) and Ta-Nb demonstrated the most specific to hydrogen permeability comparable with palladium. Ta-Nb alloy was proven to be more convenient in terms of technology. It is quite ductile and is easily rolled, while alloy V-(TiNi) has a high hardness.

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Improvement of Activation and Re-hydrogenation Behaviors of TiFe

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After the earthquake of eastern Japan on 11th March 2011, stationary energy storage attracts more attention than before. Especially, fluctuating renewable energy is expected to be stored in a form of hydrogen. In order to apply hydrogen storage materials for stationary applications, cost-effective, long-life and room temperature working materials are indispensable.

TiFe [1] seems to be ideal for such applications but it has a critical issue to be solved before fabricating the device [2]. That is activation behavior. TiFe needs treatments for activation under hydrogen pressure of over 3 MPa at higher than 673 K [2].

In this work we have solved the activation issue using quite different ways: one is to give huge strain to the materials using High Pressure Torsion (HTP) technique [3] and another is to add the third elements those are cost-effective and rich in resource.

Both methods successfully solve the issue. Without pretreatment that cannot be applied for commercial applications, the materials are activated easily.

Using the HPT technique, even under 6 GPa pressure pressing a quarter of turn is enough for activation of TiFe [4]. Once TiFe is activated, degradation was not observed in several cycles. After the exposure to air for a few months HTP'ed TiFe absorbs hydrogen without severe pretreatment. The mechanism is proposed [5].

Adding the third element is also very effective for activation. Considering the Clark number that is the rate of existence in the earth crust, we selected oxygen that is one of the richest elements on the earth. There has been intensive work on oxygen addition from fundamentals to materials development [6]. We carefully selected chemical composition of Ti-Fe-O alloys using a matrix of Ti to Fe ratio and oxygen content. The optimum compositions of the Ti-Fe-O alloys are proposed and the mechanism is considered.

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Engineering Hydrogen Separation Membrane Alloys An Optical Approach

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There is an increasing need for reducing the emission of greenhouse gasses and thus for technologies which are able to decarbonize fuels in pre-combustion capture processes. By separating the hydrogen from the carbon containing fuel stream, the hydrogen can be used as a clean fuel. A very promising technique to separate the hydrogen is based on dense metal alloy membranes. These membranes are generally Pd based due to its (in principle) infinite selectivity towards H₂ and high hydrogen permeability. However, the use of pure Pd is intrinsically related to several limiting issues. Higher temperatures increase the mobility of Pd and thereby results in grain coarsening, a mechanism responsible for pinhole formation in the membrane. In addition, Pd undergoes a phase transition upon hydrogenation below 573 K from a low hydrogen concentration α -phase to a high hydrogen concentration β -phase resulting in a 10% volume expansion. This effect is undesired since it results in the failure of the membrane in the case of a reactor start-up/shut-down cycle. A possible solution to these detrimental effects is by alloying the Pd with other metals. One of the most promising alloys is Pd-Cu based which has a suppressed α - β phase transition. Although Pd-Cu alloys have been investigated for many years, the Pd-Cu phase diagram has been reported only for higher temperatures and it still remains unclear how the different phases and microstructures contribute to the overall permeability and stability.

We will show that by using a newly developed optical combinatorial technique [1] combined with structural characterization techniques we are able to relate the permeation to the specific structural properties of the membrane layer. Furthermore, we find that the earlier extrapolations of the high temperature phase diagram, as reported in literature, do not directly apply to our thin film based membrane layer. Surprisingly we find that the pure fcc and bcc phases have very low permeability values whereas the mixed bcc-fcc phase region shows the highest permeability (14.2×10^{-9} mol/msPa^{0.5}). This mixed phase is characterized by a high Pd content fcc and low Pd content bcc phase. We argue that this high permeation is due to the heterogeneous grain boundary diffusion and depends strongly on the micro-structure of the alloy, which is most prominent in the mixed bcc/fcc compositional range. In addition, by tuning the specific structure of this alloy we are able to improve the hydrogen permeability by at least one order of magnitude resulting in a huge cost benefit for actual applications.

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Mechano-chemical coupling effects during hydriding of nanocrystalline metallic thin films

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One of the challenges for gaining a more fundamental understanding of the behaviour of hydrogen in nanocrystalline metals is the quantification in real-time of the amount and rate of hydrogen uptake and release. In this respect, we recently developed a new experimental technique for studying the hydriding behaviour of metallic thin films in-situ, based on high resolution curvature measurements [1]. In the thin film geometry, such curvature changes during hydriding arise from the constrained volume expansion upon interaction of hydrogen with the metallic thin film. The use of thin film model systems was also shown to allow more easily to separate the different rate-controlling steps involved during hydriding. In the current paper, we extend this work to address specific mechano-chemical coupling effects during hydriding, and illustrate how these may lead to significant improvements in both hydrogen storage capacity as well as uptake and release rate. In the case of room temperature hydriding of nanocrystalline thin films for instance, a first characteristic regime was observed at the beginning of hydrogen uptake, the kinetics of which are significantly enhanced by the presence of pre-existing tensile internal stresses in the film. Based on such in-situ curvature data, we have been able to quantify the effect of such pre-existing internal stresses on relevant kinetic and thermodynamic hydriding parameters for a number of tailored nanocrystalline thin film microstructures. These include the equilibrium H-concentration, the alpha to beta phase transition, and the hydrogen ad- and absorption velocities. Our findings finally resulted in the construction of a self-consistent kinetic model [2], able to describe the different rate-controlling steps encountered during the complete hydriding cycle of nanocrystalline metallic thin films, as well as their sensitivity to internal stress.

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Influence of Microstructure and Mechanical Stress on Behavior of Hydrogen in Thin Pd Films

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Hydrogen absorption and hydride formation in metals is of great interest due to its use for hydrogen storage in bulk materials and sensor applications in thin metal films. Pd films can be used as a model system to examine influence of microstructure and stress on hydrogen absorption. In this work we study Pd films with thickness 500 nm prepared by cold cathode beam sputtering on substrates with different binding strengths. Nanocrystalline films were deposited on sapphire, silicon and polystyrene at room temperature and epitaxial film was sputtered on sapphire substrate at 500 °C. The films were loaded with hydrogen up to hydrogen concentration of 1.0 H/Pd. Hydrogen loading was performed electrochemically in a galvanic cell filled with electrolyte consisting of a mixture of phosphoric acid and glycerol. Hydrogen concentration introduced into the sample was calculated from the transported charge using the Faraday's law of electrolysis.

Development of lattice constant with increasing hydrogen concentration and phase transition of Pd to Pd hydride were investigated by in-situ X-ray diffraction using synchrotron radiation (see Fig. 1). Measurement of electromotive force was used to determine actual hydrogen concentration in the sample and to monitor desorption of hydrogen from the film during measurement. Microstructure and mechanical stress in the films influence the width of the coexistence region of the α -phase and Pd hydride (α' -phase). Films deposited on substrates with low binding strength (i.e. polystyrene) exhibit properties closer to the bulk Pd while films deposited on hard substrates with high bonding strength (i.e. sapphire) show greater deviation from the bulk behavior.

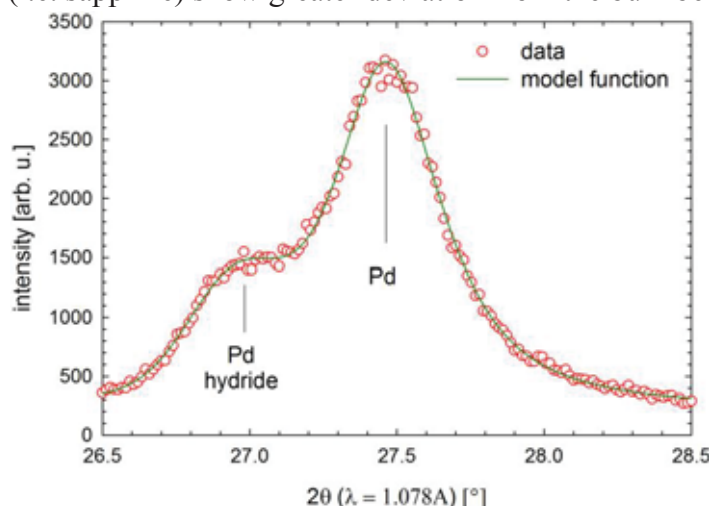


Figure 1. X-ray diffraction profile of (111) reflection measured on 500 nm thick Pd film deposited on silicon at room temperature electrochemically loaded to $c_H = 0.5$ H/Pd.

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Improvement of Activation and Re-hydrogenation Behaviors of TiFe

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References

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Hydrogen Storage in Metal Hydrides and Complex Hydrides: Differences, Challenges and Advantages

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Starting in the 1970s, metal hydrides (MeH) have been widely studied [1] and discussed as materials for hydrogen storage or for the utilization in thermal heat pumps. As these materials show very high reaction rates even at low temperatures, very fast charging times can be reached, e.g. for H₂ fuelling. Furthermore, very high thermal power densities can be achieved for heat pumps. However, due to the low gravimetric storage capacity, these materials never reached commercialization except for niche applications.

From 1997 [2], complex hydrides (CxH) have been studied as promising hydride materials, as they show the potential to significantly increase the hydrogen storage density. However, in these materials H₂ is stored by a conversion reaction leading to kinetic limitations for charging that prevented them so far from technical applications.

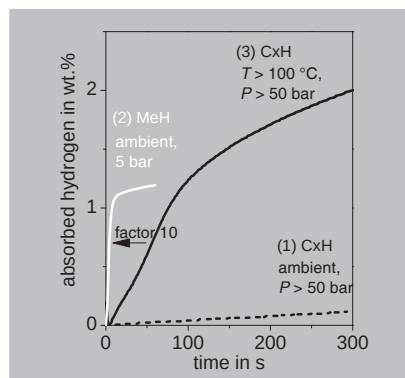


Figure 1. Comparison of storage capacity and reaction rate for CxH and MeH.

In this presentation a short overview of the two different material classes will be given. As the focus is on the intrinsic differences of the materials, it is especially emphasized which application is most suitable for each material class, e.g., preheating devices or gas storage. One application that is presented in detail is the combination of a complex hydride with a metal hydride in one storage tank, as it has been studied in the EU-project SSH2S¹. Here, the high reaction rates of the metal hydride are used to initiate the reaction from room temperature, while at high temperatures the large storage capacity of the complex hydride can be used [3]. The presented results focus on the scale-up in the development of such a combination reactor from 50 g to 680 g and 6.8 kg of hydride material.

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¹ SSH2S, Solid State Hydrogen Storage to System. (FP7/2007-2013, grant agr. no. 256653.)

Size Reduction in Mg and Mg rich Intermetallics for Hydrogen Storage

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With a view to develop efficient hydrogen storage materials, we investigated size reduction in Mg and Mg rich intermetallics through a number of means. First, size reduction in Mg was investigated by milling. In addition to the conventional milling, powders were also milled with MgH₂ addition or by predeforming the powders by ECAP. These enable the production of particles down to approximately 10 µm in size. An alternative and more efficient mean in obtaining a size reduction is to synthesize hydrogen storage alloys directly from their oxides. In this process, oxides mixed and sintered at the required stoichiometry are deoxidized in a molten salt yielding a porous residue where the particles are of 1-3 µm. The fabrication of particles less than a micron in size normally require gas-phase synthesis, although such particles may also be fabricated via hydrogen decrepitation treatment or through reactive milling. An innovative method in gas-phase synthesis is to process hydrogen storage alloys via thermal plasma. Here the precursor powder is fed to thermal plasma where it evaporates and then condenses further down in the reactor into powders of extremely small size. Pure metals less than 100 nm can be produced quite successfully, but intermetallics e.g. Mg₂Ni of similar sizes can also be obtained by injecting Mg and Ni in carefully controlled position within the plasma. Mg nanoparticles as small as 6-8 nm can also be produced by co-feeding Mg and methane into the plasma where nanoparticles are embedded in graphitic matrix.

Searching out the hydrogen absorption/desorption limiting reaction factors: strategies allowing to increase kinetics

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Hydrogen gas has become one of the most promising energy carrier. Main breakthrough concerns hydrogen solid storage, specially based on intermetallic material use. Regarding the raw material abundance and cost, the AB type alloy FeTi [1] is an auspicious candidate to store hydrogen. Its absorption/desorption kinetics is a basic hindrance to common use, compared with more usual hydrides.

First, discussions based on literature help us identifying the successive steps leading to metal hydriding, and allow to introduce the physical parameters which drive or limit the reaction. This analysis leads us to suggest strategies in order to increase absorption/desorption kinetics.

Attention is then paid to a thermodynamics model [2], allowing to describe a macroscopic solid storage reactor. Thus, we can achieve a simulation which describes the overall reaction inside the hydrogen reactor and, by varying the sub-mentioned parameters (thermal conductivity, the powder granularity, environment heat exchange...), we attempt to hierarchy the reaction limiting factors. These simulations are correlated to absorption/desorption experiments for which pressure, temperature and hydrogen flow are recorded.

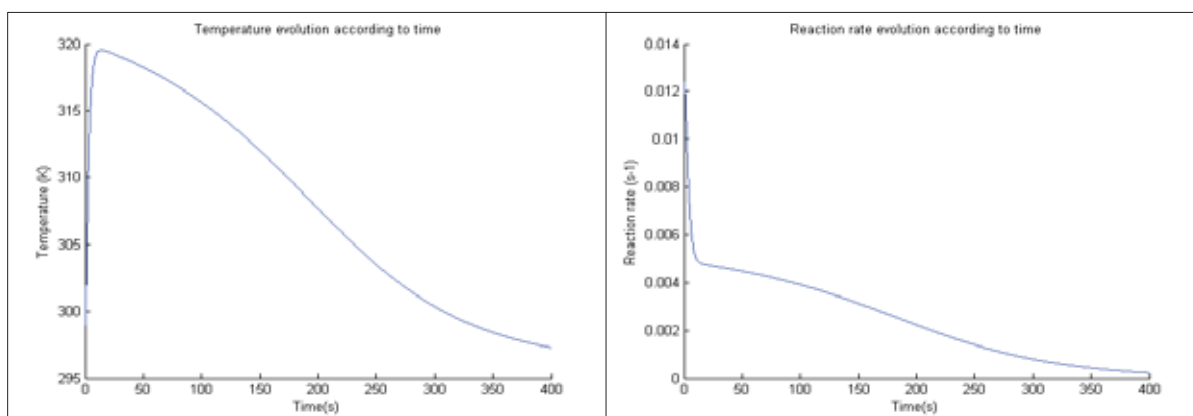


Fig.1: Typical results from the simulated absorption reaction:
Temperature evolution (left), Reaction rate (right)

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Development of Thermal Batteries Based on Metal Hydrides: Opportunities and Challenges (Invited)

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Among many potential applications of metal hydrides, heat pumps and thermal energy storage that have been discussed since 1970's. The fundamental principles of those thermal energy applications are inherent in the reversible hydrogenation and dehydrogenation reactions that are exothermic and endothermic respectively. With the ever increasing demand for more energy and the effects of fossil energy sources on climate changes, there are considerable renewed interests on using metal hydrides for thermal energy storage and the so-called "thermal battery" applications.

"Thermal battery" is a subset of the thermal energy storage technologies that implies an energy storage system that can store as well as provide energy for service as does an electrical battery. Similar to an electrical battery that supplies electricity from stored electrochemical energy, a thermal battery would supply heat or cold from stored thermal energy. In most cases, a battery should also be able to be charged and discharged cyclically. These requirements for performance dictate that metal hydrides, i.e. the reactions between metal and hydrogen must meet certain characteristics including energy density, kinetics, thermal conductivity, cycle stability, cost and availability. This presentation will discuss the concept of metal hydride thermal batteries based on advanced magnesium hydride paired with transition metal hydride. Potential applications in transportation vehicles (EV) and space heating and air conditioning will be discussed. Before thermal batteries could become a reality, however, considerable research is still needed to engineer and customize properties of metal hydrides to meet the challenges of thermal energy applications.

Light weight aluminium based storage tank system with Ti-doped Na_3AlH_6 for hydrogen and heat storage

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Solid state hydrogen storage in complex aluminium hydrides was in the focus of research for mobile applications over the last two decades, but these material are also of interest for stationary hydrogen and heat storage combined with fuel cell systems. For the use in stationary systems the hydrogen capacity is not the most important aspect of interest. The overall performance of the whole storage system (tank design and storage material) combined with e.g. a HT-PEM fuel cell had to be optimized. Compared to NaAlH_4 (5.5 wt. % H_2) the hexahydride Na_3AlH_6 can store only 3 wt. % H_2 , but the equilibrium pressure at a temperature of 160 °C is only 8 bar and hydrogen is released during one decomposition step. This lower equilibrium pressure offers the possibility to construct much lighter aluminium alloy based tank systems (Figure 1) in comparison to the normally used steel tanks. The operating temperature of 160 °C for Na_3AlH_6 fits perfect to the requirements of a HT-PEM fuel cell.

The description of a light weight aluminium-based tank system, the optimization of the storage material Na_3AlH_6 and the performance of the whole system will be presented. The use of the system for the decoupling of the energy and heat production of a HT-PEM fuel cell will be discussed.



Figure 1. Aluminium based storage tank system with heat exchange units (inner volume 3.1 L, can be filled with 1.9 kg Ti-doped Na_3AlH_6)

Comparative Analysis of the Efficiencies of Hydrogen Storage Systems Utilising Solid State H Storage Materials

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Comparative evaluation of the performances of hydrogen stores accommodating solid H storage materials should include the data on their reversible hydrogen storage capacity, packing density of the material, operating pressures and temperatures, and heat effects of hydrogen uptake and release. We have performed analysis of the systems accumulating 5 kg H in a containment of cylindrical geometry filled with a solid H storage material. All main types of the practically important materials, including such hydrides and reactive hydride composites as AlH_3 , MgH_2 , “low-temperature” (inter)metallic hydrides, NaAlH_4 , $\text{LiBH}_4 + \text{MgH}_2$, and MOFs have been evaluated. The analysis yielded gravimetric and volumetric H storage capacities and energy efficiency of hydrogen stores (see Figure). We conclude that the weight efficiency of hydrogen stores at the system level, apart from the gravimetric H storage capacity of the material, is greatly affected by its packing density, as well as the pressure-temperature conditions which determine type, size and wall thickness of the containment.

The energy consumption of hydrogen storage required for (i) cooling (MOF) or heating (all other) of the H storage material and the containment from ambient conditions to the operating temperature, and (ii) removal of H absorption heat (MOF), or supply of H desorption heat (other materials) at the operating temperature was also analysed. It appears that materials with low heat effects of H exchange and requiring a minimum deviation of the operation from the ambient conditions should be targeted in the course of the development of the new hydrogen stores as yielding the best energy efficiency.

On the basis of the performed estimations, the potential of different solid-state materials accommodated into hydrogen stores has been evaluated.

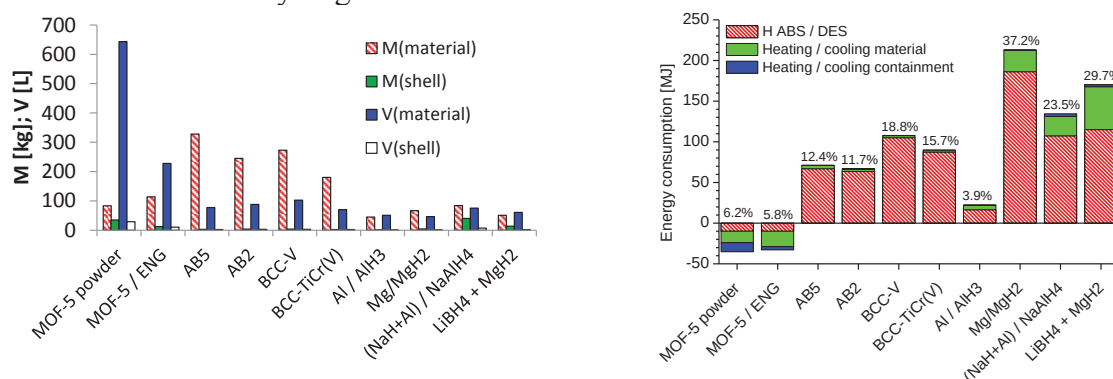


Figure 1. System volume and weight (left), and energy consumption for hydrogen stores (right; negative and positive values correspond to the cooling and heating, respectively) in containers accommodating 5 kg of stored hydrogen, filled with various hydrogen storage materials. The materials for the containers are plastic composite (MOFs and “low-temperature” MH) or stainless steel (“high-temperature” MH). The bar labels on the right correspond to the energy consumption in % of heating value of the stored hydrogen.

Can new Mg-rich phases in RE-TM-Mg (RE = Rare-Earth, T = Transition metal) systems be good candidates for hydrogen storage?

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Metal hydrides are good candidates for safe hydrogen storage. However, the gravimetric capacity is often the main drawback. Magnesium allows to reach a capacity of 7.6wt.% but at high temperature (i.e. 300°C) and with poor sorption kinetics. The discovery of new candidates is then a great challenge for the solid state chemists. The Mg-rich part of the RE-TM-Mg diagram (RE = Rare-Earth, TM = Transition metal) was investigated in order to highlight the existence of new composition with potential high hydrogen sorption properties.

During the last 3 years, several new compounds have been discovered. We will focus on only three new compositions : one (LaCuMg₈) derived from a known structure, another one (Gd₁₃Ni₉Mg₇₈) based on a random distribution of atoms in a FCC packing and a last one (NdNiMg₅) crystallizing in an original and new structure.

LaCuMg₈ [1] crystallizes in the La₂Mg₁₇ structure type (S.G. P6₃/mmc) with the lattice parameters $a = 10.1254(2)$ and $c = 10.0751(2)$ Å. For Gd₁₃Ni₉Mg₇₈[2], the determination of the structural parameters is more complex because of the difficulty to obtain a well-crystallized sample. TEM allows to highlight an average cubic structure with lattice parameter $a = 4.55$ Å with a modulation along both **a*** and **b*** axis. NdNiMg₅[3] crystallizes with an unusual structural type (SG : Cmc₂m, $a = 4.4799(2)$, $b = 9.9827(3)$, $c = 13.7854(10)$ Å). Its structure is made of infinite layers of Mg atoms which form blocks stacked along the c axis. These blocks, with a close-packed array of Mg atoms, are separated by infinite NiNd layers. In the NiNd layer the Ni and Nd atoms form an ordered graphite-type network.

Unfortunately, hydrogenation of these three new Mg-rich phases led to their decomposition. Nevertheless, the subsequent cycling of the various MgH₂ (combined with Mg₂Cu or Mg₂Ni and REH_x) present very good kinetics.

Finally, some other properties like magnetic and mechanical ones will be discussed briefly to open new applications areas.

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Solid State Hydrogen Tank coupled with High Temperature PEM: from materials to APU application

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The main objective of this work is to develop a solid state hydrogen storage tank fully integrated with a fuel cell and to demonstrate its application on a real system.

The synthesis of materials has been performed by ball milling, firstly in a laboratory scale and then scaled-up. The selected complex hydride material ($2\text{LiNH}_2\text{-}1.1\text{MgH}_2\text{-}0.1\text{LiBH}_4\text{-}3\text{ wt\% ZrCoH}_3$) was characterized by suitable thermodynamic and kinetic properties (e.g. ΔH_{hydr} about 40 kJ/mol_{H₂}) and resistance to cycling. The characterisation has been performed by a combination of structural (XRD), volumetric (PCI) and spectroscopic (ATR) experimental techniques.

A new two-materials concept has been developed for the tank, combining hydrogen sorption properties of complex hydrides and metal hydrides (i.e. LaNi_5 -based intermetallic compound). In particular, thanks to a careful control of thermal exchanges, synergic effects have been obtained, promoting fast hydrogen sorption reactions. Fluidodynamic modelling of different tank concepts, as well as the experimental validation of the models in a lab-scale tank, drove the development of a prototype tank optimized for use with the selected materials. A total amount of 6 kg of hydride materials has been used for the tank.

The results have been used to integrate the tank with a High Temperature Polymer Electrolyte Membrane (HT-PEM) Fuel Cell (1 kW_{el}). A suitable thermal exchanger between the tank and the fuel cell have been set up at temperatures around 160-180 °C. The integrated system has been installed into an Auxiliary Power Unit (APU) for an Iveco Daily full electric vehicle. Performances of the integrated systems will be described. Finally, a critical techno-economic assessment and a Life Cycle Analysis have been performed in order to evaluate a possible scale-up of developed system.

The work has been performed in the frame of SSH2S project, supported by Fuel Cells and Hydrogen Joint Undertaking of the European Commission.

Integrated System Of Fuel Cell And Hydride Tank

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In the framework of an Italian Regional Project, an integrated system of fuel cell and hydride tanks was developed, mainly designed for stationary applications.

The work was focused on different aspects related to the construction of the tank and to its integration with a PEM fuel cell.

In detail:

1) it was first of all necessary to identify metal hydrides with absorption / desorption characteristics adequate to the working conditions of the system (i.e. 60°C and 1 atm). Materials already available on the market (AB2 and AB5 type) were selected for this application and they were characterized in order to assess operating performance in real conditions. $\text{LaNi}_{4.8}\text{Al}_{0.2}$ was finally selected for the tank, being competitive both for the absorption / desorption characteristics and prices on the market.

2) a careful analysis of the absorption/desorption characteristics was made on commercial $\text{LaNi}_{4.8}\text{Al}_{0.2}$ made by different producers, in order to identify the more reliable material on the market. Moreover, a quality control procedure was optimised in order to check the reproducibility of absorption/desorption characteristics of different alloy batches of the same producer.

3) stainless steels were used for the construction of the tank, due to their compatibility and resistance to pressure, together with copper elements that improve the heat exchange between the external and internal part of the tank;

4) for the integration of the tank with the fuel cell, it was developed a system enabling the delivery of a constant flow of hydrogen to the fuel cell.

The performances of the integrated system were tested in different working conditions, in order to evaluate its reliability, efficiency and durability. The system can operate for about 6 hours, giving an average power of 0.76 kW and delivering a total of 4.8 kWh of electricity. To deliver this energy the system consumed about 3120 Nl of H_2 . Demonstration in real applications will be shown.

Modelling the Thermal Management of a Solid State Hydrogen Store Based on Magnesium Hydride

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Magnesium hydride is a promising candidate for solid state storage of hydrogen due to its high gravimetric capacity of 7.6wt%. During both hydrogenation and dehydrogenation the rate limiting factor is heat transfer through the hydride bed. Increasing the heat transfer rate is an important design goal in order to optimise metal hydride based storage systems. There are several methods which can be employed to improve the thermal properties of the bed material; however these will normally result in a weight penalty for the system.

This work presents 2D and 3D computational models which have been developed incorporating highly accurate thermal and geometric properties for the bed material. There is a marked improvement, in agreement between simulated and experimental results, by applying measured material properties for thermal conductivity and particle geometry in hydrogenated and dehydrogenated states to a COMSOL model. The characterisation of thermal conductivity and particle geometry involved taking measurements under a range of conditions: varying temperature, system gas (Helium, Argon, Air and Hydrogen) along with measurements while the material is hydrogenated and dehydrogenated. It has been found that assuming identical particle geometry and size between hydrogenated and dehydrogenated states is incorrect, post dehydrogenation particle size increased by 28% and shape function altered by 10%. Prior to these measured properties being applied an average discrepancy of 10% was seen between experimental and simulated data, post application the discrepancy falls to 2.6%. Figure 1 shows the agreement of bed temperature between simulated and experimental results for a magnesium hydride bed during dehydrogenation.

This is a significant refinement on previous work in the literature which assumes constant material properties for hydrogenated and dehydrogenated material states.

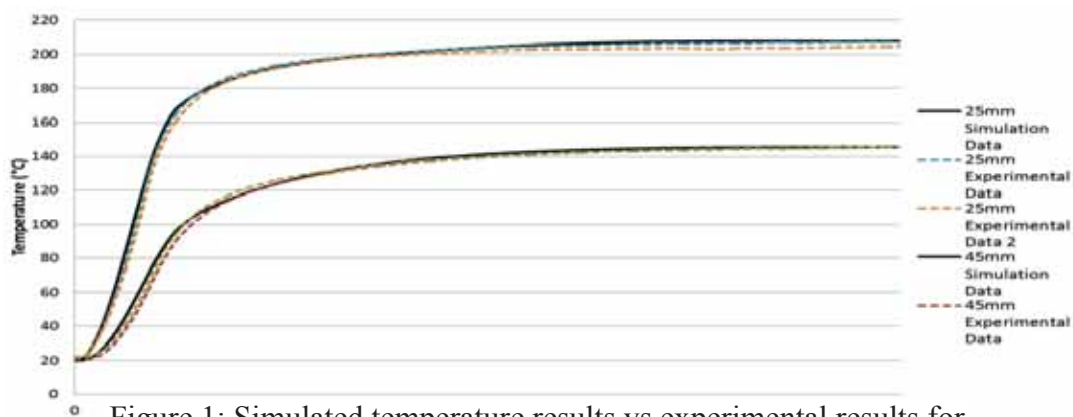


Figure 1: Simulated temperature results vs experimental results for dehydrogenation of magnesium hydride

An Improved Model for Metal- Hydrogen Storage Tanks

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Metal hydrides as a class of solid-state materials have been the subject of intensive research since the 1970's. They are of great interest for hydrogen storage in stationary or portable applications. Some of these, such as LaNi_5 and other AB5 intermetallics have excellent characteristics (good cyclability, high volume density and relatively good kinetics) that make them attractive as storage media. The exothermic absorption of hydrogen and endothermic desorption makes heat management an important part of any real metal-hydrogen storage system. The design of such a system must therefore be based on a credible modelling of the heat and mass flow. The Hardy and Anton model [1, 2] is a comprehensive and reliable model for metal hydride tanks, however, some realistic features such as the volume change of metal/metal hydride particles and pressure changes during hydrogen uptake and discharge have not been incorporated. Moreover, hydrogen was assumed to be an ideal gas, however at the operating conditions of pressure and temperature, the compressibility of hydrogen should be included.

This work presents the results of a more realistic intermetallic-hydrogen storage tank model, using the COMSOL software package taking into account practical conditions such as:

- 1- including the compressibility of hydrogen gas
- 2- the difference between equilibrium pressure for hydrogen absorption and desorption
- 3- the dependence of equilibrium pressure on concentration

In this model, the effects of system variables such as temperature, pressure and hydrogen concentration distribution on the amount of stored hydrogen, hydriding and dehydriding rates and their interaction are investigated. The results are compared to any experimental results as well as the predictions of Hardy and Anton's model.

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Structure-Properties Relationship in Nanostructured Mg-Based Hydrides for Energy Storage

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LaNi₃ hybrid layered structure can be selectively modified by Mg, with Mg atoms entering the AB₂ Laves slabs only (LaNi₂ → MgNi₂) and a maximum Mg solubility reaching LaMg₂Ni₉. Hydrides in the LaNi₃-H₂ easily become amorphous / decompose to form LaH_{3-x}. We have synthesized a corresponding monoclinic interstitial hydride LaNi₃H_{2.9} only at subzero temperatures and low H₂ pressures. La in La_{3-x}Mg_xNi₉-based can also be substituted by Nd and Pr; in the corresponding (La,Pr,Nd)_{3-x}Mg_xNi₉ (*PuNi*₃ type) hydrides Mg, Pr and Nd significantly affect all important features of the hydrogenation process, including crystal structures, H storage capacities, and thermodynamics allowing improved capacity and high energy density performance of H stores and anodes of the rechargeable Ni-MH batteries. Studies of the structure-properties relationships in the (La,Pr,Nd)_{3-x}Mg_xNi₉H₁₀₋₁₃ hydrides synthesised during interactions of intermetallics with gaseous hydrogen or deuterium revealed: a) Caused by magnesium change of the mechanism of the hydride formation from anisotropic to isotropic exposition takes place; b) A nearly equal distribution of H atoms within the REMgNi₄ and RENi₅ layers is observed; c) Preferred filling of the Mg- and Ni-surrounded sites within the REMgNi₄ layers of the Mg-rich hydrides; d) Local hydrogen ordering with the H-sublattice built from MgH₆ octahedra and NiH₄ tetrahedra and a directional metal-hydrogen bonding; e) Desorption pressures change by a factor of 1000, from 0.01 bar to 20 bar H₂, by modifying the Mg content. Significant lowering of the thermodynamic stability follows even a small increase in magnesium content in La_{3-x}Mg_xNi₉ from x = 1.0 to 1.1-1.2 and a replacement of La by Pr and Nd. As example, for Nd₂MgNi₉H₁₂ ΔH_{des} = 29 kJ/mol H₂ while for La₂MgNi₉H₁₃ ΔH_{des} = 36 kJ/mol H₂ (See PC diagrams in the Figure). A partial substitution of Mg for RE allows the electrochemical discharge capacity of the (La,Pr,Nd)_{3-x}Mg_xNi₉ hydrides to become 25% greater than that of the commercial AB₅-type based electrodes and reaching 400 mAh/g. A crucial

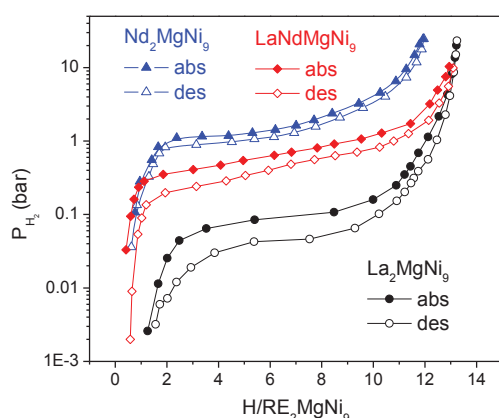


Figure. P-C diagrams for the RE₂MgNi₉-H₂ systems measured at 20 °C.

issue is in synthesis of the materials with high degree of homogeneity of the (La,Pr,Nd)_{3-x}Mg_xNi₉ type intermetallics. This has been achieved by choosing a correct synthesis route, optimising appropriate content of Mg in the initial mixtures, time and temperature of the homogenisation process and, also, by using a rapid solidification process to synthesise the alloys in one step by quenching the melt. Microstructural and phase-structural composition will be discussed as related to their performance as metal hydride anodes studied at high discharge current densities.

SPD processed Mg-based materials to build up reactive microstructures enabling fast hydrogen sorption kinetics

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Pure Mg, Mg-alloys (AZ31, AZ91 and ZK60) as well as Mg-Ni composites, in form of either fully bulk pieces or compressed powders (from particles or atomized spheres) were submitted to one or several successive of SPD treatments. Equal Channel Angular Pressing (ECAP) treatments were operated from room temperature up to 300°C, Fast Forging (FF) was operated as well at various temperatures up to ~ 400°C and Cold Rolling (CR) treatments were operated at room temperature only.

The microstructure of the resulting materials was analyzed by XRD, SEM, micrograph and X-ray texture analyses. Some TEM characterizations were done as well. Then the materials were submitted to hydrogenation/dehydrogenation processes by using H₂ pressurized autoclaves (typically and subsequent Pressure-Composition- Temperature (PCT) measurements. The absorption/desorption kinetics of the H/D reaction were recorded to be compared to some of our reference Mg-based materials as besides processed by energetic Ball-Milling. Quite various kinetics H/D reactivity were pointed out, the main parameters to account for when nano structuring Mg-based compounds are the initial morphology of the precursor and the type of applied SPD process. Also, adding a few % of Ni-μm powders to Mg or MgH₂ leads to quite better reactivity profit made with the formation of binary Mg-Ni based precipitates.

The present work was supported by a grant of the Ministry of Education and Sciences of the Perm Region C-26/211 as well as the French Carnot Institut "Energie du Futur".

Kinetics Enhancement, Thermodynamics Tailor and Thermal Conductivity Study in Mg-based Hydrogen Storage Materials

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Mg-based nanostructure materials with crystallite size ranging from 5 to 300 nm, were synthesized by various techniques (ball milling, catalyzed solution synthesis, hydrogen plasma metal reaction). The hydrogen sorption kinetics may be drastically enhanced by nanostructure and catalyst. However, the desorption thermodynamics including enthalpy change and entropy change does not vary with the grain size in this range¹. However, it was found that kinetics difference may affect thermodynamic performance (plateau pressure values and step numbers) based on our recent PCT measurements².

From the study of the above Mg-based hydrogen storage materials as well as micrometer scale ones³, thermal conductivity in nanostructure samples besides the thin film sample is low (table 1), compared to micrometer scale materials because heat conduction by electron/phonon transfer is greatly scattered due to more boundaries and interfaces in nanostructure materials. Based on this work, some new ideas of development of future Mg-based hydrogen storage materials which may show fast kinetics and good cycle ability as well as high thermal conductivity will be discussed in this paper.

Table 1. Kinetics and thermal conductivity of various Mg-based materials.

Sample	325 mesh Mg	Mg single crystal (0001)	Mg nanoparticles	Mg ₅₀ Co ₅₀ nanocrystalline sample	Pd capped Mg thin film
Thermal conductivity (W/m/K)	10.42	168	4.985	0.432	82
Hydrogen absorption kinetics	poor	poor	good	superior	superior

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Stability of Magnesium for Elevated Temperature Cycling as a Thermal Storage Medium for Concentrated Solar Power Applications

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Magnesium is an ideal candidate for concentrated solar power thermal energy storage devices. However, such applications operate at temperatures of 400 °C, approaching 80% of the melting point (T_m) of Mg. This could lead to sintering of the Mg based powder beds, reducing the hydrogenation kinetics and capacity of the material. In order to address this, we have investigated a potential method of fabricating a Mg based thermal storage medium which maintains both a high hydrogen capacity and fast reaction kinetics when tested at 400 °C.

The form of the fabricated material renders it easily handleable, and a comprehensive study of both the mechanism behind its formation and its behavioural characteristics is underway. Work has included investigating the ease of re-activating the material after passivation in air for several weeks, together with assessing the effects of annealing the material in its metallic state at 400 °C for six hours. This latter test represents a shortened simulation of store operation during the period in which total heat absorption has occurred, but the material remains exposed to the maximum input temperature. Detrimental sintering of the storage medium is expected to be most prominent during this time.

Figure 1 (left) gives hydrogen capacity as a function of time recorded during re-activation of the specimen at 400 °C under 40 bar H_2 and shows that maximum theoretical capacity was reached within three hours. Hydrogen uptake immediately prior to and directly after annealing at 400 °C for six hours is presented in Figure 1 (right). The two curves indicate that the annealing process did not detrimentally impact the hydrogenation characteristics of the material.

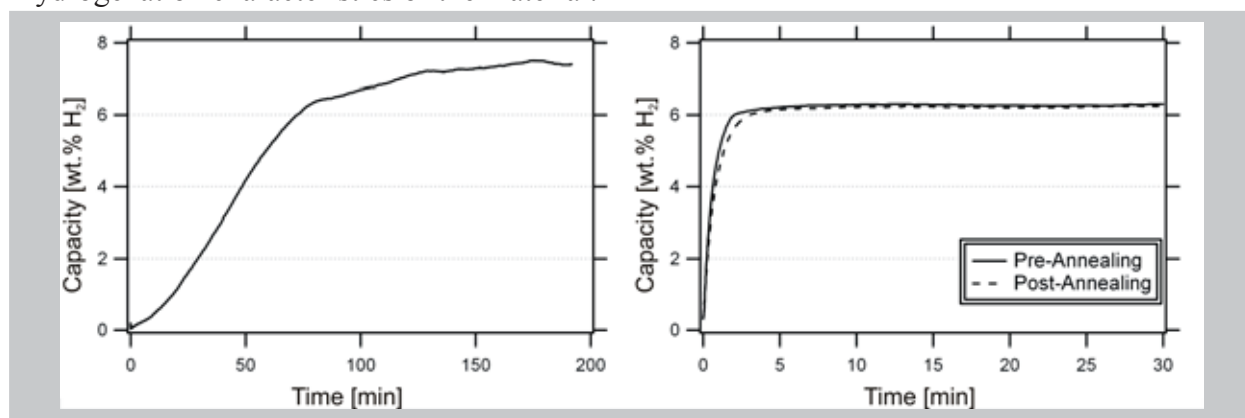


Figure 1. Hydrogen capacity versus time for re-activation of the passivated sample (left), together with uptake curves recorded before and after annealing at 400 °C for six hours in the metallic state (right).

The Size Dependence of Reactivity and Hydrogen Mobility for Carbon-Supported MgH₂ Particles - INVITED

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Nanostructured metal hydrides, for instance MgH₂ based, are of potential interest for solid state hydrogen storage [1], but also for other applications such as rechargeable batteries and hydrogenation catalysts. Our group was the first to report a strategy to prepare carbon supported nanoparticles by simply mixing MgH₂ with a porous carbon support, and heating the mixture to above the melting point of magnesium [2]. It is known that particle size can have a strong impact on hydrogen sorption properties, but more detailed insight has been hampered by the great challenge to prepare small and well-defined light metal hydride particles. .

I will first discuss recent progress in the preparation of supported MgH₂ nanoparticles. We identified vapour-phase transport (at temperatures below the melting point of Mg) to be able to transport Mg from larger crystallites to small nanoparticles being formed inside the carbon support at higher loadings than previously possible, and I will discuss the possible origin of this counter-intuitive effect. Furthermore we were able to vary in a controlled manner the MgH₂ particle size between 6 and 20 nm by adjusting the support porosity, which allowed us to measure the size-dependent hydrogen absorption and desorption rates, and attain information about the rate limiting factors in these processes. The fast hydrogen sorption was maintained during cycling of the material, showing the ability of the carbon support to stabilize the small nanoparticles. The size-dependent hydrogen kinetics were for the first time corroborated by intrinsic hydrogen dynamics data obtained by solid state ¹H NMR. [3].

Interestingly we could exploit the reactivity of the pore confined MgH₂ nanoparticles to selectively let them react for instance with B₂H₆ under mild conditions to form magnesium boron hydrides. Hydrogen release from the confined magnesium boron hydrides starts just above the synthesis temperature of 120 °C. The addition of Ni facilitates reaction to proceed readily at temperatures as low as 30 °C. Furthermore by Ni addition and tuning the synthesis temperature, the product distribution can be steered towards Mg(BH₄)₂ and other magnesium boron hydrides. This shows the suitability of the method to selectively form pore-confined complex metal hydrides [4].

I will spend the last part of my presentation on an outlook to the future of supported metal hydride nanoparticles research also for other applications such as for selective hydrogenation catalysis and for all-solid state rechargeable batteries, highlighting some first results in these fields.

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Recent progress in enhanced hydrogen storage of MgH_2 -Invited

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As a type of potential high-capacity hydrogen storage materials, Mg and Mg-based alloys have attained sustaining research interest over last two decades. Herein we demonstrate our latest effort in dual-tuning the thermodynamics and kinetics properties of magnesium base hydrides by innovative method.

Novel processes are adopted to synthesize efficient nano-catalysts with fine distribution on the surface of MgH_2 . For example, by chemical reaction between Mg powder with TiCl_3 in THF solution^[1], we achieve remarkable enhancement in dehydrogenation of MgH_2 by a nano-coating of multi-valence Ti-based catalysts (Figure 1a). The MgH_2 -coated Ti based system can start to release H_2 at about 175°C and release 5 wt% H_2 within 15 min at 250°C . To realize massive production of Mg based hydrides doped with nanocatalysts, a simple method is developed to induce symbiotic $\text{CeH}_{2.7}/\text{CeO}_2$ catalyst. The method is to thermally activate the Mg-Ce-Ni amorphous alloy under different hydrogen pressure, and then manually oxidize it, which dramatically reduce the desorption temperature of MgH_2 by $\sim 200^\circ\text{C}$.

Based on previous successful preparation of $\text{Mg}(\text{In})$ binary solid solution alloy for reversible hydrogen storage^[2], ternary Mg-In-Y, Mg-In-Al, and Mg-In-Ni alloys are further explored, the solid solubility limit, hydriding reaction mechanism and hydrogen storage properties are systematically investigated. It is found that some Mg-In-Al and Mg-In-Ni alloys show improved thermodynamic properties and full de-/hydriding reversibility, but with different reaction mechanism. Two new phases were identified in the de-/hydrided products of a Mg-In-Ni alloy (Figure 2). In addition, plasma-assisted ball milling is used to prepare $\text{Mg}(\text{In})\text{-MgF}_2$ composite and $\text{Mg}_2\text{In}_{0.1}\text{Ni}$ solid solution, both of which show great improvement in not only thermodynamics but also kinetics^[3].

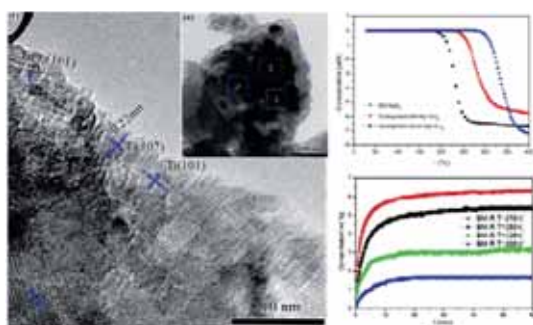


Figure 1. Mg particle with a nano-coating of Ti catalysts shows excellent dehydrogenation properties

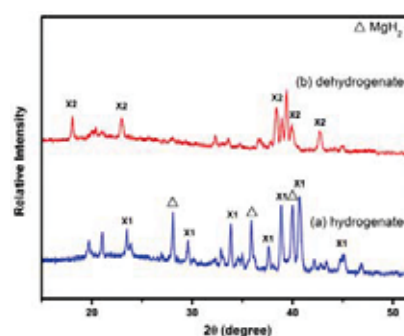


Figure 2 Reversible phase transformation of a ternary Mg-In-Ni alloy

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Anti-Oxidized Mg for a Variety of Applications

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Mg can be considered as a promising hydrogen storage material due to its high hydrogen capacity, however Mg has sluggish reaction kinetics and unsuitable thermodynamics for on-board. So far, a lot of research on Mg to improve the properties has been reported. By adding a small amount of Nb₂O₅, the reaction kinetics is drastically improved, that is Mg can absorb 4 mass% hydrogen within a few tens of seconds at room temperature [1, 2]. Now, we are trying to develop this Mg added with Nb₂O₅ (labelled as "activated-Mg") for not only hydrogen storage but also a variety of applications such as hydrogen sensor and hydrogen trapping system. For those applications, it is necessary to avoid the oxidation of activated-Mg. Recently Ki-Joon Jeon reported PMMA can be used for avoiding the oxidation of Mg [3]. In this research, activated-Mg ball-milled with PMMA (labelled as "PMMA-Mg") was synthesized and its hydrogen storage properties were investigated. The results showed PMMA-Mg was stable in air, and was able to absorb hydrogen at 200 °C under 1.0 MPa H₂. Figure 1 and 2 show the TEM image and hydrogen absorption curve of PMMA-Mg, respectively. Further, the onset of hydrogen absorption was around 80 °C.

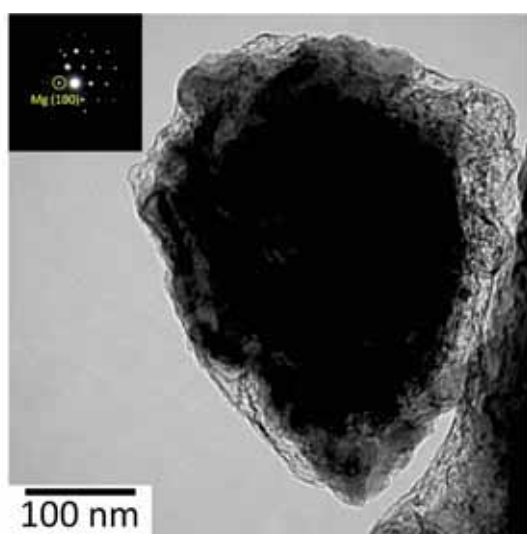


Figure 1 TEM image of PMMA-Mg

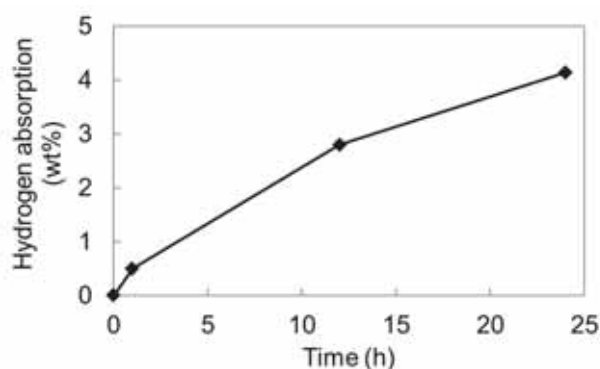


Figure 2 Hydrogen absorption curve of PMMA-Mg

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Synthesis and Hydrogen Storage Properties of Nanostructured Mg-based Alloys

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Mg-based alloys are promising novel solid-state hydrogen storage materials currently under investigation due to their high hydrogen capacity, low specific weight and abundance. However, the major problem of magnesium as a rechargeable hydrogen carrier system is its slow reaction rate and high sorption temperature. Nanostructure of samples provides a way overcoming the thermodynamic and kinetic barriers associated with the Mg-based alloys, and recently receives great attention.

We developed a method to prepare ultrafine Mg nanoparticles around 40 nm by acetylene plasma, which is a revised approach for the traditional hydrogen metal plasma reaction. During the preparation, the growth of the Mg nanoparticles was confined by the carbon from the decomposition of acetylene. The Mg particles size exhibited a clear decreasing trend with increasing acetylene fraction in the plasma. Due to the short diffusion distance and large specific surface area, the kinetics of hydrogenation and dehydrogenation of the small Mg nanoparticles were improved. From the equilibrium plateau pressures of the absorption and desorption isotherms, the enthalpy and entropy of the reaction were deduced, which were significantly reduced compared to the commercial magnesium.

The reaction between reactive metals and water is very convenient for on-site hydrogen generation. Mg is extensively studied for this purpose due to its high hydrogen carrying capacity (8.3%), moderate reactivity and low cost. Recently we found that H_2 generation from the reaction between Mg nanoparticles and water can be significantly promoted by low cost chlorides. The promotion effect exhibits strong correlation with the OH affinity of the corresponding cation. This interesting observation offers a simple and effective solution to portable H_2 generation under mild conditions.

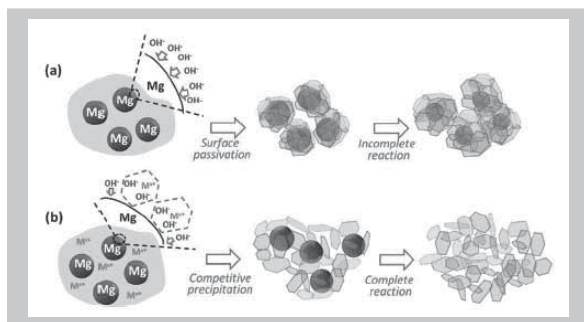


Figure 1. Schematic illustration of the mechanism of the Mg-H₂O reaction, without (a) and with (b) cations with high affinity to OH in the solution.

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An experimental/computational investigation of the vibrational properties of the powder MgD₂ system, using coherent inelastic neutron scattering*.

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Currently the only available methods of directly investigating the dynamics of nanomaterials are more or less limited to IR and Raman and density of states measurements using incoherent inelastic scattering. We have developed a methodology for the direct interpretation and analysis of coherent inelastic scattering from polycrystals, which contains information about the spatial separation of atoms taking part in a particular mode of vibration i.e. Q dependent scattering analogous to dispersion curves in single crystals. As the scattering from experimental has to be averaged over all possible orientations of the crystalline structure, the data so obtained is difficult to interpret directly and hence requires a combined modelling-experimental approach. We have so far published a brief account of the software modelling technique [1] combined with model simulations of poly-CINS scattering from polycrystalline aluminium [2] that established that effective lattice dynamics models may be fitted to experimental data

Presented here will be an overview of the modelling and analysis methodology used to interpret the very complex one-phonon scattering features obtained from experimental magnesium deuteride measurements on the MARI spectrometer. This process has resulted in a temperature-dependent semi-empirical force constant model, based initially on a 0K DFT calculation and then fitted to Q-dependent features in the poly-CINS data set using GULP [3]. The results of a pending paper presenting this modelling process are presented and discussed.

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* *Invited presentation*

Correlation between microstructural and mechanical behavior of nanostructured MgH_2 upon hydrogen cycling

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Reversible hydrogen storage in magnesium hydride is the most suitable solution for stationary applications, which require large-scale storage systems with an expected lifetime exceeding 5000 hydrogen cycles. Highly reactive nanostructured powders are produced on a large scale by co-milling MgH_2 with transition metals. These powders present a very stable weight capacity upon cycling. However, the MgH_2 grains tend to recrystallize and to induce a progressive swelling of the composites. This could drastically reduce the lifetime stability of the MgH_2 tanks.

The purpose of this study is to quantify and understand this irreversible phenomenon, through correlations with microstructural evolutions. In-situ dilatometry measurements are performed on samples prepared with different additives. The irreversible phenomenon increases progressively up to about 50 cycles where swelling is stabilised. Granulometry measurements show a bi-modal distribution of the as-milled powders. Upon cycling, we observe the coalescence of the “small” MgH_2 particles, which tend to create large agglomerates and results - again after about 50 cycles - in mono-disperse powders. This behaviour induces an increase in porosity, which explain the progressive swelling of the composites. The maximum of deformation strongly depends of the additive. A relaxation of the maximum strain is observed after 50 cycles for vanadium whereas it remains constant for Ti-V-Cr. This could be correlated to the ability of the fine additive particles to prevent the motion of the grain boundaries, then to limit the agglomeration of MgH_2 particles

The present study is supported by the Carnot Institute “Energies du Futur”

Magnesium Spheres for Thermal Energy Storage Applications

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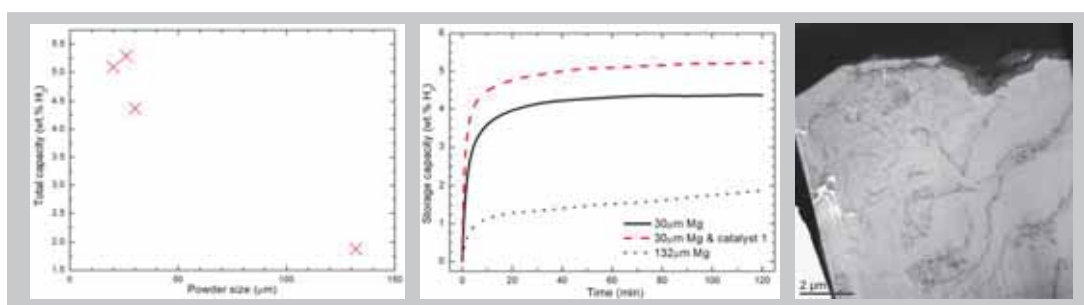
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Magnesium is an ideal candidate for CSP thermal energy storage devices. Previous research predominantly focused on catalyst addition through a number of different processing routes, such as ball milling, or the production of thin film multilayer structures. In this work a catalyst was added to spherical particles of Mg, of mean particle size from 20 - 132 μm , by a commercial scale up route capable in the first instance of modifying a few kg of material in each batch. Hydrogen storage capacity and kinetics of hydrogenation were tested at 400°C.

Figure 1 illustrates the expected reduction of capacity with increasing sphere size after 120 min hydrogenation cycles. As anticipated, Figure 2 highlights the reduction in hydrogenation kinetics with increasing sphere size when comparing the 15th cycle. The addition of up to 2 wt.% catalyst resulted in additional capacity compared to the sphere without the catalyst. Since Mg and the catalyst are mutually insoluble at these temperatures, this was then attributed to possible mass transport reordering of the structure during the volume expansion and contraction of the spheres during cycling. More detailed examination by cross-section TEM shows evidence of catalyst pathways extending into the sphere, as shown by the sample in Figure 3 which was taken after only 18 cycles. The effect of cycling on capacity was also examined up to 200 cycles. When a catalyst addition was applied to the spherical structures an initial improvement in capacity was observed within the first 15 cycles. Subsequently, a capacity drop of 13% occurred up to 150 cycles followed by stability for the remaining cycles. This was attributed to the initial effect of sintering which appears to stabilise capacity.

These results show the potential of the catalyst additions to improve such structures such as in improved capacity when cycled at 400°C.



Left: Figure 1. Effect of sphere size on storage capacity. Middle: Figure 2. Hydrogenation kinetics for as received 30 μm Mg, 132 μm Mg and catalysed 30 μm Mg after 15 cycles at 400°C. Right: Figure 3. Cross-section TEM of post cycling catalysed 30 μm Mg showing diffusion pathway formation.

The effect and optimization of microstructure on the hydrogenation of Mg/Fe thin film multilayers

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Nanoconfined magnesium hydride can be simultaneously protected and thermodynamically destabilized when interfaced with materials such as Ti [1] and Fe. We study the hydrogenation of thin layers of Mg (<14 nm) nanoconfined in one dimension within thin film Fe/Mg/Fe/Pd multilayers by the optical technique Hydrogenography. The hydrogenation of nanosized magnesium layers in Fe/Mg/Fe multilayers surprisingly shows the presence of multiple plateau pressures, whose nature is thickness dependent. In contrast, hydrogen desorption occurs via a single plateau which does not depend on the Mg layer thickness. From structural and morphological analyses with X-ray diffraction/reflectometry and cross-section TEM, we find that the Mg layer roughness is large when deposited on Fe and furthermore contains high-angle grain boundaries (GB's). When grown on Ti, the Mg layer roughness is low and no high-angle GB's are detected. From a Ti/Mg/Fe multilayer, which has a flat Mg/Fe interface and little or no GB's, we find that MgH₂ is indeed destabilized by the interface with Fe, and more than in Mg/Ti. Both the ab- and desorption plateau pressures are increased by a factor two compared to the hydrogenation of Mg within Ti/Mg/Ti multilayers. We hypothesize that the GB's in the Fe/Mg/Fe multilayer act as diffusion pathways for Pd, which is known to greatly alter the hydrogenation behavior of Mg [2,3].

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Role of the rare earth composition on the performance of working metal-hydride electrodes in Ni-MH alkaline batteries

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Beside Li-ion batteries, Ni-MH ones remain very attractive due to their good efficiency, high safety and low cost. Accordingly, they are today developed for ground transportation in HEV vehicles and wireless tramways. To reach the continuously increasing demand in energy density, new intermetallic alloys with higher capacity are developed for the negative electrode. Hydride forming compounds based on the R -Mg-Ni ternary system (R : Rare earth) with crystallographic phases of AB_3 , A_2B_7 and A_5B_{19} types show enhanced performances. These compounds can be described as the growth along the c axis of two different sub-units $[AB_5]$ and $[A_2B_4]$, where A is a rare earth or an alkali earth metal and B is a transition metal, forming either a rhombohedral $3R$ ($R\bar{3}m$) or hexagonal $2H$ ($P6_3/mmc$) structure [1, 2]. The A_2B_4 sub-unit has the advantage to allow the substitution of heavy rare earth atoms by light metal ones such as magnesium. The crystal structures of several hydrides of the Mg-containing La-based compounds were characterized by neutron powder diffraction, including $La_2MgNi_9D_{13}$ [3] and $La_{1.5}Mg_{0.5}Ni_7D_{9.1}$ [4]. The Mg substitution improves the properties of the compound and allows to reach capacities higher than 400 mAh.g⁻¹. In the present work, various compositions in the AB_3 system with A : La, Nd, Mg; B : Ni have been investigated by in situ neutron diffraction on working electrodes. From the diffraction data (Figure), valuable information can be obtained regarding the phase transformation, the correlation between solid-gas and electrochemical capacities, the kinetics and the reversibility of these systems.

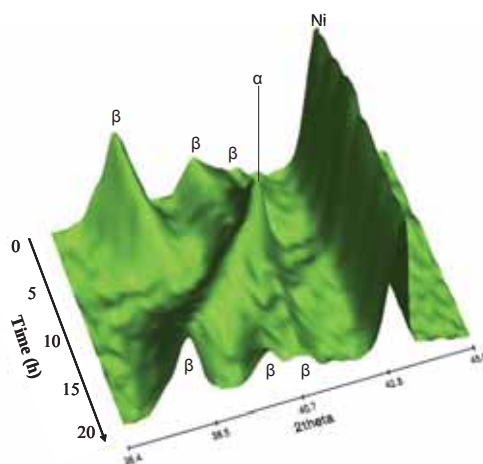


Figure: ND pattern evolution as function of the charge and discharge state for the La_2MgNi_9 electrode at 150 mA.g⁻¹. Labels alpha and beta stand for the metal and hydride phases respectively.

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Past, Present, and Future of Metal Hydride Alloys in Nickel-Metal Hydride Batteries

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One of the key applications for metal hydride (MH) alloys is the nickel-metal hydride rechargeable battery (Ni/MH) [1]. In the past five decades, MH alloys have been studied specifically for their electrochemical applications, and in a recent review article, their current research status has been updated to reflect the progress made in the field and to address the evolving needs of the markets [2]. The discharge capacities of a few MH alloys are compared in Figure 1. Each high-capacity MH candidate proposed as a replacement for AB₅ has characteristics unique to each alloy, requiring careful cell-design considerations to incorporate the material into the Ni/MH battery.

The current Ni/MH battery available on the market demonstrates a cycle life > 6,000 and discharge rates up to 60C, providing performance advantages to a wide-range of applications. However, improvement in the energy density of Ni/MH is needed for further product development. The US Department of Energy has granted \$4 million geared to stimulate breakthroughs in this area [3], and the technical hurdles and proposed approaches to achieving higher Ni/MH energy densities using leading-edge MH alloys will be discussed in this presentation.

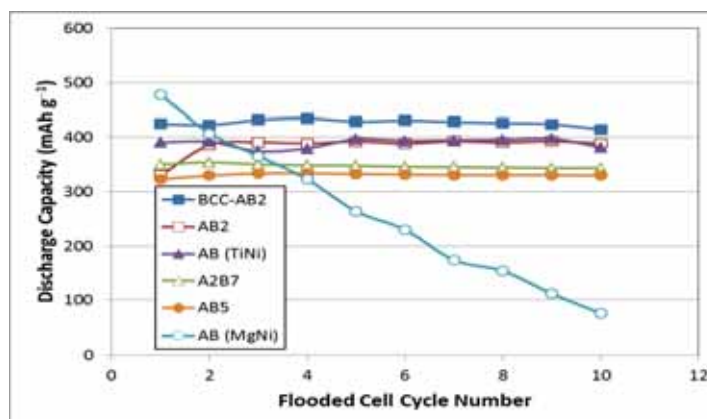


Figure 1. Comparison of discharge capacities in feature MH alloys for Ni/MH batteries

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Influence of Kinetics of Hydrogen Transport in a Metal Hydride Anode on the Discharge Properties of the Electrodes of the Ni-MH Batteries

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In present work, a theoretical model has been developed for the description of the electrochemical discharge process in metal hydride anodes of nickel-metal hydride (NiMH) batteries at various current densities. The model considers the assembly of spherically shaped metal hydride particles where the process of electrochemical discharge is fitted using a shrinking core model, with an H storage alloy shell growing inside the particle by decreasing the internal metal hydride core volume. The model has been tested for the La_2MgNi_9 -based anode material having an electrochemical discharge capacity of 400 mAh/g and a hydrogen storage capacity of 13 at.H/f.u. It allows to quantitatively describe kinetic behaviors for the electrode at various applied current densities (Figure) and to estimate the diffusion coefficient of hydrogen and equilibrium content of H in the solid solution domain of hydrogen in La_2MgNi_9 . The discharge is described by considering a boundary-value problem of hydrogen transport from the hydride core to the boundary metal-electrolyte. Solution of this problem yields the interrelation between

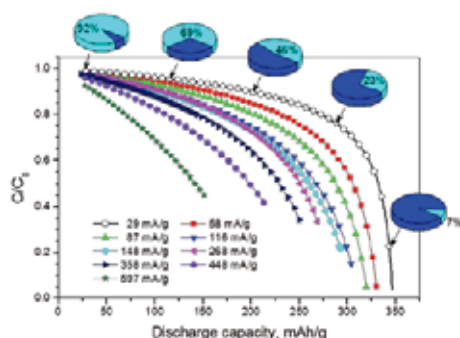


Figure.

Modelling of the discharge curves for a MH anode at various current densities. The calculated ratio between the volume of the MH core (cyan) and the volume of the H solid solution (blue) is shown, with the amount of MH changing from 92 % in a nearly completely charged electrode to 7 % at the end of the discharge.

the potential and concentration of hydrogen at a boundary metal-electrolyte. Eventually, current densities are related to the voltage, with a Tafel shift accounted for, based on the known hydrogen concentration and hydrogen flux through the discharging metal hydride particles. Importantly, shift of the potential was found to be proportional to the concentration of hydrogen in the solid solution; such important observation has not been reported in the reference literature earlier. A natural assumption of interdependance of the Fermi energy, concentration of dissolved hydrogen and equilibrium voltage of the electrode at various current densities is currently under investigation for the model MH electrode materials.

The proposed model has a general applicability and can be used for the optimization of other electrode materials for NiMH rechargeable batteries at high current densities.

Influence of alloy stoichiometry, surface- and heat treatment on NiMH cells made by atomised as well as reused alloys from spent batteries.

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Dag Noréus

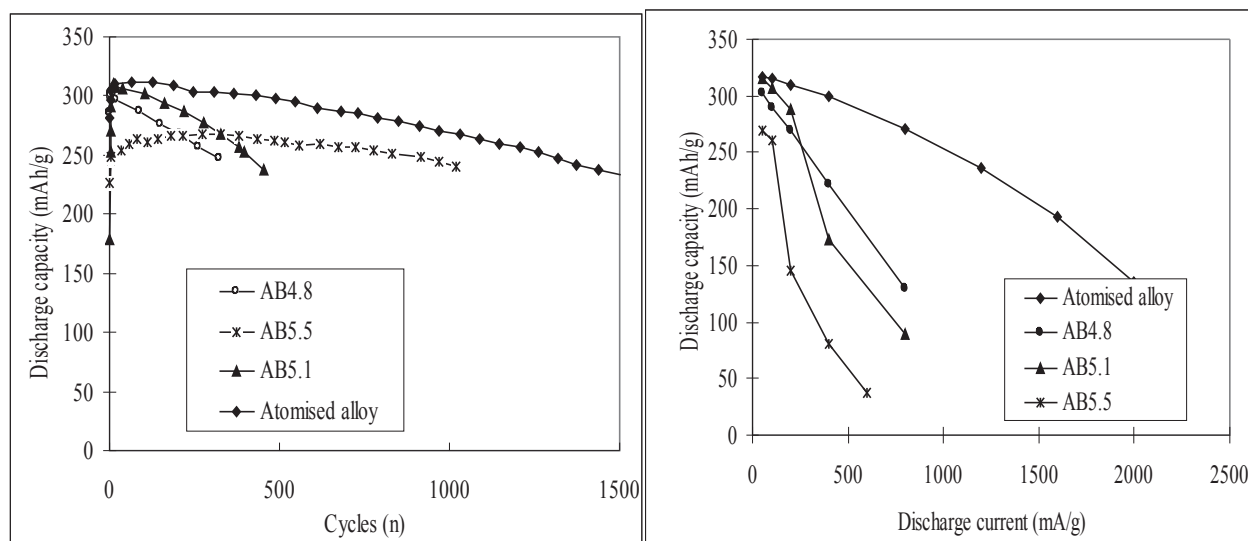
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Abstract

Different AB₅ alloy production methods have been tested in NiMH cells. A new rapid quenching method was implemented leading to a very homogeneous alloy composition and microstructure. These were compared with alloys made by conventional casting and by melt spinning. In all three cases an annealing treatment of the alloys was needed in order to achieve good electrochemical cycle stability. This is interesting, since the rapid quenched alloys had no macro-inhomogeneity and the melt-spun alloys had a very homogeneous composition and a flat pressure plateau already before the heat treatment. This indicates that factors other than homogeneity are important for a long cycle life. The rate capability and cycle life of the atomised alloys were found superior to those of the conventionally cast and melt-spun alloys. The discharge capacity of an atomised alloy with the standard composition $\text{MmNi}_{3.6}\text{Co}_{0.7}\text{Mn}_{0.4}\text{Al}_{0.3}$ had 80% of its initial after 1500 cycles at 80% DOD. Three compositions corresponding to AB_{4.8}, AB_{5.1} and AB_{5.5} were tested. AB_{5.5} had the longest cycle life and AB_{4.8} the shortest. For high rate properties the situation was reversed. Best high rate properties had AB_{4.8} and the slowest AB_{5.5}. Interestingly the atomised alloy was superior in both aspects.

A La-rich mischmetal content gave a higher capacity but a shorter cycle life. The opposite was found for a Ce-rich mischmetal.

During cycling, both capacity and rate capability of an alloy decrease. The decline of performance can be reversed by rinsing the alloy in a boiling KOH solution. Particularly interesting is that the high rate capability of NiMH cells made by a recycled La-rich mischmetal-based alloy was dramatically improved by this reactivation as well as recombination reactions during overcharge and overdischarge.¹



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Borohydrides continue to surprise: A different outlook on their properties

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Abstract

For over more than a decade, borohydrides have attracted interests as hydrogen storage materials due to superior gravimetric and volumetric densities of hydrogen. However, several challenges that hamper their utilization remain. These are primarily related to undesired thermodynamic properties, sluggish kinetics and complex reaction pathways during hydrogen release/uptake[1]. Recently, motivated by the thermal stability and a presumed robustness of the BH_4^- anion against electrochemical reduction, we proposed magnesium borohydride as an electrolyte for rechargeable magnesium batteries[2]. Owing to a high volumetric capacity (3833 mAh cm^{-3} vs. 2046 mAh cm^{-3} for Li), absence of dendrites formation and lower cost of Mg metal (about 10 times cheaper than Li), rechargeable magnesium batteries have been receiving increased attention. One major challenge facing these batteries is related to the electrolytes as they are restricted to a handful of corrosive Grignard/organohalo -magnesium reagents and complexes. Electrolytes based on conventional inorganic and ionic Mg salts, were found unsuitable due to electrochemical instability in the reducing environment of the Mg anode[3]. We found that magnesium borohydride could withstand this highly reducing environment making it the first and only example of an inorganic, relatively ionic and halide free salt reported to date that could function as an electrolyte in a Mg battery. A new family of highly performing electrolytes based on this finding has also been proposed [4]. Here, we will explain our design strategies, discuss fundamental properties obtained from systematic spectroscopic and electrochemical studies and share up-to-date results related to these new promising systems.

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Fast Ionic Conduction in Complex Hydrides

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Complex hydrides has been attracting much attention not only as hydrogen storage materials but also as solid-state fast ionic conductors. As we have reported, LiBH₄ exhibits lithium fast ionic conduction accompanied by the structural transition (more than 1×10^{-3} S/cm over 390 K), which opened up research on lithium ionic conduction in complex hydrides [1]. Then, we have worked on the design of lithium fast ionic conductors in LiBH₄-based, LiNH₂-based, and LiAlH₄-based complex hydrides [2]. It has been recently reported that the complex hydrides can be used as electrolytes in all-solid-state lithium rechargeable batteries [3, 4].

These findings suggest that ionic conduction of the other cation such as Na⁺, K⁺ and Mg²⁺ may also occur in complex hydrides because they are composed of various combinations of the above-described metal cations and complex anions. In fact, Na₂(BH₄)(NH₂) obtained in the NaBH₄–NaNH₂ system exhibits the sodium fast ionic conductivity of 2×10^{-6} S/cm at RT because of the specific antiperovskite-type structure with vacancies on the Na⁺ site [5]. Just recently, Na₂B₁₂H₁₂ was found to exhibit high ionic conductivity on the order of 0.1 S/cm above its order-disorder phase-transition at about 530 K [6]. Finally, recent progresses on magnesium fast-ionic conduction in complex hydrides are to be briefly explained.

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Metal hydride electorode for Metal Hydride-Air Secondary Battery

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In order to increase the cruising range of plug-in hybrid vehicles or electric vehicles, high energy density secondary battery is strongly expected. MH-air battery is expected as a promising option[1][2]. Energy density of an MH-air battery strongly depends on the capacity of the negative electrode, because there is no limitation on the capacity of the positive electrode. In other words, a high capacity metal hydride for negative electrode is very important to improve the performance of an MH-air battery.

BCC type hydrogen storage alloys have hydrogen storage capacities for a maximum around 4.0 mass% H_2 (1061mAh/g), though effective capacity as electrode material is limited at present. In this work, various compositions of BCC type hydrogen storage alloys are investigated in order to obtain a high capacity electrode material to apply for MH-air battery.

Many compositions of BCC type hydrogen storage alloys were prepared by arc-melting. The alloys after cooling were crushed into small particles. The particles were mixed with Ni powder, polyvinyl alcohol, carboxymethylcellulose and ion-exchanged water in order to make pastes. The pastes were coated on a porous Ni (size:30mm*40mm) as a current collector to make electrodes. The electrodes were tested in 6M KOH electrolyte with a NiOOH counter electrode. Hydrogen storage capacities of the alloys were evaluated by PC isotherm measurement. Morphologies of the alloys were observed by SEM and TEM.

For most of the alloys, the main phase was confirmed to be BCC by XRD analysis. Electrochemical properties of the alloys varied drastically depending on the composition. Hydrogen storage property of the alloys seems to be an important factor, but not sufficient for good electrochemical performance. By SEM-EDX analysis, TiNi alloys were observed as grain boundary phases for most of the electrochemically active alloys. The TiNi phase on the surface probably enhances electrocatalytic activity[3][4].

This research is partly supported by Advanced Low Carbon Technology Research and Development Program(ALCA) of Japan Science and Technology Agency (JST).

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Mg catalysed with TiF_3 as anode in a Ni-MH battery

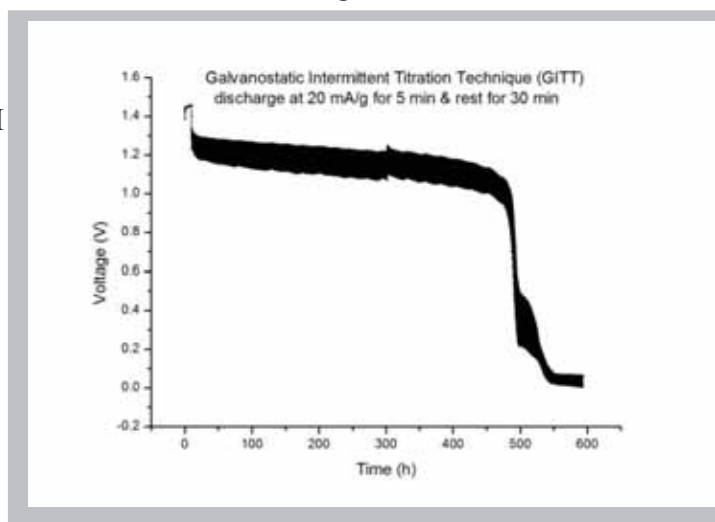
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The facile storage of hydrogen gas in magnesium hydride is greatly enhanced when catalysts and nanostructuring is applied. An example is the catalyst TiF_3 which enables relatively low temperature H_2 absorption (down to -10°C) and desorption ($150 - 200^\circ\text{C}$). [1] For practical applications the gas pressure is still low at these temperatures, however. For application in a Ni-MH battery the low internal pressure is a requirement. For this reason the Mg-0.05TiF_3 material was tested as anode against a conventional Ni(OH)_2 cathode. The material was synthesized using ball milling and subsequent desorption. A Ni metal powder was mixed in the desorbed sample as inert conductive medium to enhance the electrical conductivity. The reaction taking place at the anode during charge is: $\text{Mg} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{MgH}_2$, while at the cathode protons are extracted from nickel hydroxide in the reaction: $\text{Ni(OH)}_2 \rightarrow \text{NiOOH} + \text{H}^+ + \text{e}^-$. For Mg based materials the H insertion during charge at RT is slow and the extraction of H during discharge is even slower or impossible. Here we show that applying the catalyst TiF_3 can lead to a large reversible capacity of $> 1300 \text{ mAh/g}$ of Mg in a massive compacted pellet pressed from the catalysed and nanostructured material.[2] Such capacity corresponds to an average composition of approximately $\text{MgH}_{1.2}$. The kinetics of the proton insertion is rapid during charge but still slow during discharge, necessitating a Galvanostatic Intermittent Titration Technique (GITT) to observe the sloping plateau at $\sim 1.22 \text{ V}$.

Further characterisation of the material was performed using XRD, TEM and MAS ^1H and ^{19}F NMR to elucidate the environment of F and H in (partly) charged materials.[3] The conclusion is that the MgF_2 observed in diffraction is actually a defect rich MgF_{2-x} in the proximity of MgO , while TiH_{2-x} has, judged from the absence of a metallic ^1H Knight Shift, very small dimensions and is in contact with the Mg.

Figure 1. Discharge plateau of hydrogen loaded $\text{MgH}_2 + 0.05 \text{ TiF}_3$ in a Ni-MH battery.



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Metal hydride as anode material for all-solid-state Li-ion batteries (invited)

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Effects of metal oxide additives on anode properties of magnesium hydride (MgH₂) have been investigated by means of all solid-state lithium-ion battery, where MgH₂ actually has a high potential as the anode material, showing 2038 mAh·g⁻¹ as the theoretical capacity by following reaction, $\text{MgH}_2 + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Mg} + 2\text{LiH}$ [1]. All solid-state cell brings us strict analyses to approach the mechanism why some differences are obtained with the different additives. In this work, Nb₂O₅ and Al₂O₃ as typical two different additives were attempted, where Nb₂O₅ and Al₂O₃ reveal, respectively, the best and no catalytic effect on hydrogen storage properties of MgH₂[2].

Figure shows the charge-discharge curves of MgH₂ anode with no, Nb₂O₅ and Al₂O₃ additives at the temperature of 100 °C. In the cases of both profiles with and without Nb₂O₅, the plateaus corresponding the insertion are located at around 0.43 V. On the other hand, MgH₂ anode with Al₂O₃ shows 0.48 V of slightly higher plateau voltage than the others. With respect to the extraction profiles, the anode capacity massively changes with the different additives, and it increases in order of no, Nb₂O₅ and Al₂O₃ as the additives. Because the transfer of hydrogen atoms from Mg to Li phases could be important factor deduced from the reaction equation, it is thought that the catalyst for hydrogen storage properties plays an important role. However, Al₂O₃ plays much important role in the charge-discharge reactions even though it does not show any catalytic effect in the hydrogen desorption properties of MgH₂.

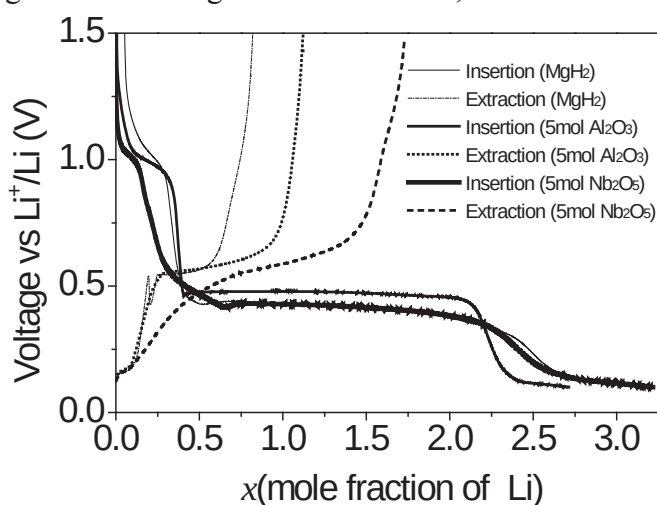


Fig. Charge-discharge curves of MgH₂ anode with no, Al₂O₃ and Nb₂O₅ additives at 100 °C

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Hydrides as negative electrode for lithium-ion batteries: A review of this challenge for hydrogen storage and Li-ion technologies

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The use of metal hydrides (MH) for lithium-ion technology, coupling the advantages of high weight capacity of MH electrodes with the high energy density of Li-ion batteries, has been first presented in 2008 as a new concept for mobile and stationary applications [1], and subsequently explored by several academic and industrial research teams [2-5].

For instance, amongst hydrides, MgH_2 is especially promising with a substantial experimental reversible capacity of 1480 mAh/g (four times that of Li/C electrodes), the smallest measured conversion electrode polarization ($<0.2\text{V}$) at an average potential of 0.5V vs. $\text{Li}^+/\text{Li}^\circ$ which is appropriate as a negative electrode compound. Although hydrides are very interesting from a fundamental point of view, drastic technological improvement is needed for practical applications to enhance conversion process efficiencies $\text{MH}_x + x\text{Li}^+ + x\text{e}^- \rightleftharpoons \text{M} + x\text{LiH}$ [1-3, 6]. The goal is to overcome the limitations due to the poor electronic conductivity of LiH and the electrode volume variation during lithium extraction.

Herein, the current state of the research on the conversion process with hydrides is presented and discussed, through different examples from binary, ternary and complex hydrides. It appears that the development of high capacities hydrides anode should be inspired by the emergent Si nano research prospects, i.e.: Si carbon nano fibers, nano confined, Si carbon composites, Si nano wires or Si-carbon-CMC mixture. The sharing of the knowledge of both hydrogen storage and Li anode communities seems here one of the suitable route to success in in this new research topic.

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Nanoconfined hydrides as anode material for Li-ion batteries

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The use of hydrides as anode materials for lithium ion batteries has been demonstrated according to a conversion mechanism, where the hydride MH_x reacts with lithium ions to form at the end of a discharge metal/alloy M and the lithium hydride LiH : $MH_x + x Li^+ + x e^- \rightleftharpoons M^0 + xLiH$ [1,2]. Among all metal hydrides, MgH_2 ($MgH_2 + 2 Li^+ + 2 e^- \rightleftharpoons Mg^0 + 2LiH$) has the highest gravimetric capacity (2038 mAh/g).

The present work reports on the electrochemical conversion reaction of nanoconfined Mg-based hydrides into porous carbons. The use of nanoparticles leads to faster lithium/hydrogen diffusion and to a better electronic conductivity within the composite electrode, thereby a lower cell polarization and the whole improvement of the electrochemical behaviour are expected. Our synthesis route allows the formation of Mg-based nanoparticles with a range size of 5-10 nm via *in situ* hydrogenation of organometallic Mg-based precursor in the carbon porosity [3].

The effect of the Mg loading ratio (15, 25, 50 and 70 wt.%) and the textural properties of several carbon hosts (surface area and pore size distribution) on the Mg-based particle size distribution has been investigated.

The electrochemical performance of all hybrids has been tested as negative electrode material in Li-ion batteries. Our results show that these nanoconfined materials have promising discharge/charge capacities and cycle life (figure 1 and 2).

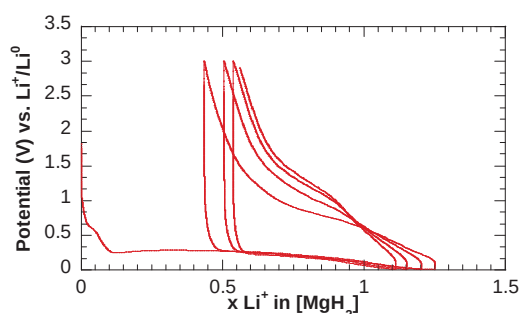


Figure 1: Potential/composition profile of MgH_2 50wt%/Li cell

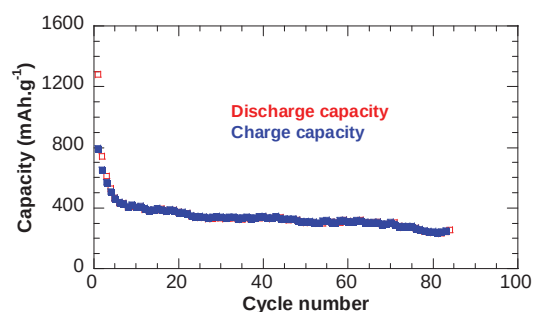


Figure 2: Charge (full square)/discharge (open square) capacities vs. cycle number

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H₂ thermal desorption and hydride conversion reactions in Li cells of TiH₂/C nanocomposites

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Lithium ion batteries are currently used as power sources for wireless telephones, laptops and other portable electronic devices: this mobile market is rapidly expanding due to the worldwide demand. Hydrides can theoretically operate in a rechargeable lithium cell through a conversion process (hydride conversion reaction, HCR) according to the scheme: $M_xM'_yH_z + z e^- + zLi^+ = M_xM'_y + z LiH$, where e^- and Li^+ are the electron and the lithium ion, respectively.[1] In the HCRs the metallic hydride gives hydrogen atoms to Li, forming Me nanoparticles surrounded by LiH: these processes are theoretically capable to disclose outstanding improvement in the negative electrode specific capacity [2]. However only few studies describe HCR processes, mainly for MgH₂. [1, 2] In the present study we present our recent results about the use of TiH₂/carbon nanocomposites as active material in lithium cells.

Several TiH₂/C composites have been prepared by means of a mechanochemical route by varying the carbon/hydride ratio, the milling time and the shacking sequence. Materials have been characterized by X-ray diffraction, Raman spectroscopy, transmission electron microscopy and tested in electrochemical cells versus lithium metal in EC:DMC LiPF₆ electrolyte by galvanostatic cycling (GC).

The same samples studied in lithium cells have been also investigated by thermogravimetry and mass spectrometry in order to highlight the various steps of the dehydrogenation induced by thermal treatments. A parallelism between the dehydrogenation steps induced by the thermal treatments and the HCR reaction steps in lithium batteries is here sketched for the first time.

Thermal dehydrogenation processes are altered depending on the mechanochemical treatment of the sample: apparently prolonged carbon milling decreases the hydrogen content of the hydride, likely producing volatile hydrocarbons. On the other hand, mechanical milling has negligible effects on the GC performances of the materials in lithium cells. This is in contrast with results on MgH₂ where mechanical mixing with amorphous carbon enhances battery performances.[2]

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On the Role of Size, Shape and Composition in Metal Nanoparticle - Hydrogen Interactions

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We have over the last years established localized surface plasmon resonance (LSPR) based optical spectroscopy as efficient tool to investigate the interaction of hydrogen with well-defined nanoparticles at the ensemble and even the individual nanoparticle level. [1] Our characterization approach allows us to work with well-defined nanoparticle systems in terms of their size, shape and composition due to the required very small amounts of sample. On the example of Palladium (Pd) I will report on our recent efforts to investigate in detail the role of particle size in the sub-10 nm range on the hydride formation thermodynamics. Surprisingly, we find no significant size-effects even for the smallest particle sizes and explain our finding by a compensation effect between lattice strain and increasing importance of subsurface sites. [2] To address a second important parameter for nanoparticle systems, I will also summarize our results on the role of nanoparticle shape and exposed surface facets in the hydride formation process in shape-selected and surfactant free Pd nanoparticles. [3]

Relying on the LSPR phenomenon we have also devised several strategies for all-optical hydrogen sensors. Here I will report on our recent developments towards self-referenced hydrogen sensors using polarized light (Figure 1) [4], and I will demonstrate the use of AuPd alloy nanoparticles for hysteresis-free plasmonic all-optical hydrogen sensing.

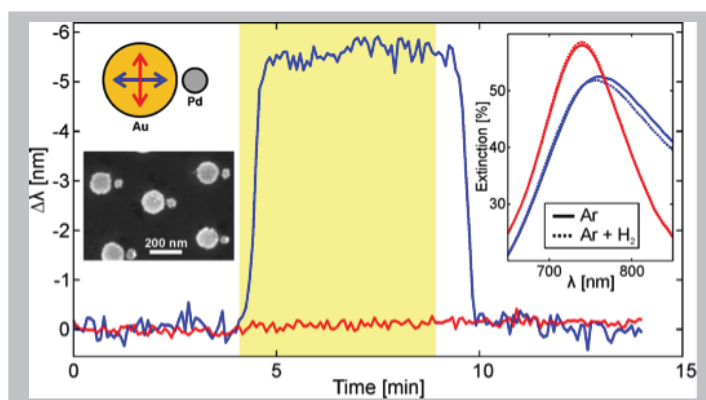


Figure 1. Plasmonic Au-Pd heterodimers for self-referenced optical hydrogen sensing.

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Synthesis, Characterization and Hydrogen Sorption Properties of Mg-Ti based Nanoparticles and Nanocomposites

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In the field of solid state hydrogen (H) storage, magnesium (Mg) is widely known to be an element of interest because it is abundant, low-cost, light and its hydride (MgH₂) stores large quantities of H. However, MgH₂ is too stable for H desorption close to ambient conditions and suffers from slow kinetics. Magnesium hydride's performances can be improved by adding a transition metal catalyst and/or reducing the crystallite size down to the nanoscale.

In this work, we selected titanium (Ti), a cheap transition metal which is known to improve both the dissociation of H₂ molecules and the diffusion of H atoms in the material [1].

For the synthesis of nanostructured Mg-Ti, we used a bottom-up physical vapor deposition technique, the Inert Gas Condensation (IGC) [2], employing a modified set-up that also allows *in situ* hydrogenation and compaction of the collected nanoparticles, resulting in the formation of a Mg-Ti-H nanocomposite.

A complete morphological and structural characterization was carried out by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) analyses before and after H-sorption cycles. In the as-prepared samples, metastable Mg-Ti alloy nanoparticles were observed despite the complete immiscibility of Mg and Ti.

Hydrogen storage properties such as capacity, kinetics, enthalpy of hydride formation and cycling stability were investigated with a Sievert apparatus and a High Pressure Differential Scanning Calorimeter (HPDSC).

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Low Temperature Hydrogen Cycling and Modified Thermodynamics of Spark Discharge Generated Fluorite Cubic Mg-Ti Hydride Nanoparticles

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Spark discharge generation (SDG) is an interesting and very flexible new method to synthesize metal hydride nanoparticles and nanocomposites [1-3]. We recently showed that spark discharge generation is very attractive for producing Mg-Ti nanocomposites with a primary particle size of 10-20nm [3]. Upon hydrogenation, the Mg-Ti nanocomposite transforms into the fluorite cubic $\text{Mg}_{1-y}\text{Ti}_y\text{H}_x$ phase instead of the commonly observed rutile MgH_2 phase, and exhibits promising hydrogen storage properties. This opens up a way for up-scaling the production of this interesting hydrogen storage material previously identified in thin films. A significantly less negative enthalpy of formation of the hydride is observed in our Sievert's measurements. The hydrogenation plateau pressures were substantially higher than those for bulk MgH_2 in the low temperature range from 150°C to 250°C (Figure 1). Plausible mechanisms for the modified thermodynamics are discussed, including the effects of interfaces and lattice strains. These mechanisms all rely on the finely interdispersed nanocomposite character of the samples achieved by spark discharge generation, and which is preserved by grain refinement [4]. Finally, Mg-Ti-H nanoparticles synthesized *in-situ* in the spark discharge generator showed hydrogen desorption at a remarkable low-temperature of ~100 °C in our thermal desorption spectroscopy studies, reversible during hydrogen cycling.

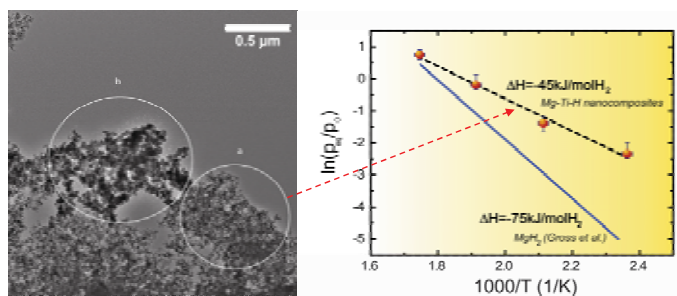


Figure 1. Less negative enthalpy of hydride formation of Mg-Ti-H nanocomposites [3].

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Destabilization of Mg hydride in the Mg-Ti system

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Often Mg is reported as one of the most attractive hydrogen storage materials due to its high volumetric and gravimetric storage capacity. However, the MgH₂ phase is too stable to desorb hydrogen at ambient pressure and temperature because of the large negative enthalpy for hydride formation of $-74 \text{ kJ mol}^{-1}\text{-H}_2$. Therefore destabilization of the Mg hydride phase is necessary for stationary and onboard storage applications. One of the possible ways is to synthesize Mg based alloys. Recently, Mg-Ti alloys and hydrides have been synthesized by means of for example magnetron sputtering [1] and ball milling [2] methods. Hydrides of Mg-rich Mg_xTi_{1-x} ($0.55 \leq x \leq 0.87$) thin films locally segregated into a Mg matrix and nanometer-sized Ti domains within a large coherent grain which had an FCC structure [1]. The formation of nanometer-sized Mg domains possibly reduces the stability of the Mg hydride phase because of the interface energy effect between Mg and Ti domains [3]. In the present work, we synthesized Ti-rich Mg_xTi_{1-x} ($x \leq 0.5$) thin films to destabilize the Mg hydride phase by reducing the size of Mg domains.

A Mg_{0.25}Ti_{0.75} thin film covered with a Pd capped layer was hydrogenated at room temperature. X-ray diffraction showed that the hydride consists of single FCC phase. This agrees well with hydride of Mg_{0.25}Ti_{0.75} powder synthesized by ball milling [2]. However, positron Doppler broadening spectroscopy of the thin film revealed that Mg domains with a size of $\sim 1 \text{ nm}$ are formed in a Ti matrix. The pressure-transmission isotherms (*PTI*'s) of Mg_xTi_{1-x} ($x \leq 0.5$) gradient thin film after three cycles of the hydrogenation and dehydrogenation showed the plateau regions, which are mainly due to hydride formation and dissociation of Mg domains. The Ti matrix has been hydrogenated by the cycles before the *PTI* measurements and that is not dehydrogenated in the given temperature and pressure. The equilibrium hydrogen pressure of the plateau regions observed in the hydrogenation and dehydrogenation processes increased with the Ti content. This indicates that hydride of Mg domain is destabilized for compositions with a smaller Mg fraction. In conclusion, we have shown the possibility to destabilize the Mg hydride phase by forming nanometer-sized Mg domains in the Mg-Ti system.

This work was supported by FY 2013 Researcher Exchange Program between the Japan Society for the Promotion of Science (JSPS) and the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

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The Synthesis and Characterisation of Novel Metal Hydrides

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Hydrogen is known to form compounds with many elements in the periodic table. Among those, the metal hydrides are of particular interest due to their application in hydrogen storage for fuel cells or heat storage for solar energy industry. Also in fundamental science metal hydrides become increasingly important due to their relevance to the study of the behaviour of pure hydrogen at extreme conditions and as materials with potentially interesting properties. Extreme conditions, namely high pressures and/or temperatures could facilitate the chemical reactions between elements, which would not happen otherwise.

High pressure as a general route to material synthesis has been used in the past to obtain hydride phases of most transition metals under thermodynamic equilibrium conditions. However, in most of the cases, the pressure of the synthesis was mostly limited to about 15-20 GPa. Using diamond anvil cell technique together with synchrotron x-ray diffraction spectroscopy, we have synthesised the novel hydrides of platinum, tungsten and iridium (PtH, WH and IrH₃) at pressures ranging from 25 to 120 GPa. By combining the experimental data with *ab-initio* calculations we demonstrate that the novel hydrides possess a wide variety of interesting properties such as unusual stoichiometry, formation of nano-crystalline material and high bulk moduli.

High pressure and temperature formation of graphene hydride (invited)

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The interaction between graphene and hydrogen (H) and deuterium (D) is of great interest to development of graphene-based technologies, including hydrogen storage, high-performance composite materials and especially electronics – where graphene's extremely high carrier mobility remains unexploited due to the lack of intrinsic band gap in the material. By chemical functionalisation with H, there is potential to open a bandgap in graphene with control over its properties.

Partial hydrogenation of graphene has been achieved by direct exposure to atomic H at ambient conditions [1, 2], but it is believed that this technique only yields at 10% H coverage [3]. Electron diffraction studies of hydrogenated graphene [1] show contraction in the lattice parameter, suggesting that in-plane compressive strain in graphene might facilitate the reaction.

We present a new technique for activating the reaction of H/D with graphene – combined high pressures and temperatures. Graphene samples on copper foil have been subjected to pressures of 7 GPa and temperatures up to 200°C in H₂ and D₂ atmospheres in a diamond anvil cell. The Raman spectrum of the graphene was observed before and after the process to monitor the extent of the hydrogenation and changes characteristic of a change in bonding from sp² (planar as in graphene) to sp³ (diamond or methane-like) hybridisation are observed. Figure 1 shows the appearance of the carbon D peak after 2p_z orbitals in graphene have formed covalent bonds with hydrogen during high-pressure heating. A variety of pressure-temperature combinations have been employed in an attempt to find the necessary conditions for hydrogenation/deuteration and to maximise the extent of the reaction and it has been shown that the reaction will not take place at ambient temperature, even under pressures up to 9 GPa.

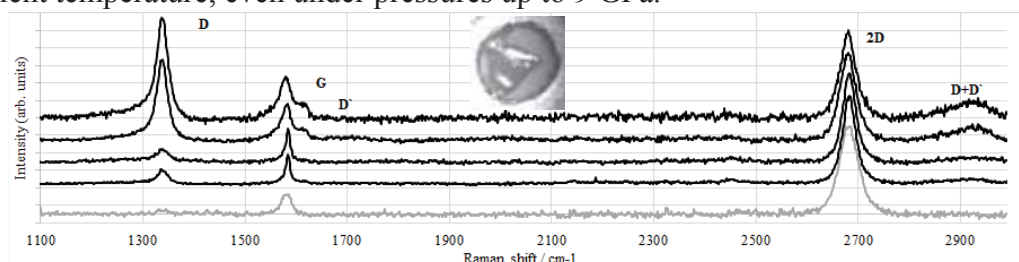


Figure 1: D peak enhancement in graphene following treatment at 7 GPa pressure and 200°C temperature. (inset) Graphene sample inside DAC pressure chamber.

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Pressure Effect on Hydrogen Tunneling and Vibrational Spectrum in α -Mn

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The solubility of hydrogen in α -Mn reaches a few atomic percent under high hydrogen pressures [1]. A neutron diffraction study showed that hydrogen forms an unusual sublattice in α -MnH_{0.07} and occupies the 12e-type positions arranged in dumb-bells 0.68 Å long [2,3]. In the inelastic neutron scattering (INS) spectra of α -MnH_{0.07} and α -MnD_{0.05}H_{0.005} [2–4], pronounced peaks were observed at 6.3 and 1.6 meV, respectively. The behaviour of the temperature and momentum transfer dependences of the peaks led us to the conclusion [4] that these peaks originated from splitting of the vibrational ground states of H and D atoms due to their tunneling between the 12e positions inside dumb-bells.

The present paper reports on the effect of pressure on the tunneling and vibrational spectra of hydrogen in α -MnH_{0.07} studied by INS with the use of the CNCS and SEQUOIA spectrometers at the Spallation Neutron Source in Oak Ridge. Pressurising the sample in a clamped piston-cylinder Ni-Cr-Al pressure cell to 16.7 kbar and 22.3 kbar at 1.5 K is shown to shift the hydrogen tunneling peak to higher energies by 0.6 and 0.77 meV. Correspondingly, the increase in splitting of the vibrational ground state of H atoms is as large as 10 and 12% compared to the ambient pressure value of 6.3 meV. The energies of the fundamental hydrogen vibrations measured in the range 50–200 meV also rise with pressure, but their increase is less pronounced and only reaches 1–2%. The estimated Grüneisen parameter varies between 0.6 and 1.0 for the fundamental modes, and equals to about 7.0 for the tunneling mode.

The observed pressure effects can be understood assuming that the potential well for the H atoms in α -Mn becomes overall steeper, while the potential barrier in the direction of tunneling decreases.

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***In Situ* Neutron Diffraction Measurement on Deuterization Process of Iron at High Pressure and High Temperature**

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Structural studies of metal hydrides have been performed under high pressure and high temperature conditions, where hydrogen fluid turns chemically reactive and reacts even with metals and alloys inert against hydrogen at ambient conditions. Iron hydride FeH_x , is thermodynamically stable only at high hydrogen pressure of several GPa. In-situ x-ray diffraction measurements of Fe-H system have been carried out to investigate pressure-temperature phase diagram [1, 2], formation of the superabundant vacancies [3], etc. Three hydride phases, bcc- FeH_x ($x < 0.05$), dhcp- FeH_x ($x \sim 1$), and fcc- FeH_x ($x = 0-1$) were confirmed at 300–2000 K and 0–20 GPa. However, *in situ* neutron diffraction measurement on their deuterides have not been reported yet. For dhcp- FeD_x quenched at 90 K and ambient pressure, deuterium composition and site occupancy were determined by neutron diffraction measurement [4], while for fcc- FeD_x unquenchable, the crystal structure including deuterium positions and composition remains unknown.

A high pressure neutron diffractometer, PLANET, constructed at Materials and Life Science Experimental Facility at J-PARC, enables us to perform *in situ* neutron diffraction measurements on deuterization process of metals at high pressure and high temperature. With PLANET, the deuterization process of iron was investigated at a pressure of ~ 7 GPa and temperatures up to about 1000 K. This *in situ* measurement was successfully made using a deuterization reaction cell developed for neutron diffraction measurement. Diffraction profiles were measured by every two minutes accumulation during heating. We observed the bcc-fcc transition of pure iron around 800 K and successive deuterization of fcc-Fe around 870 K. The diffraction profile of fcc- FeD_x showed gradual but significant change in reflection intensity owing to interstitial-site occupation by absorbed deuterium atoms as the deuterization reaction proceeded.

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Aluminum-based Interstitial Hydride, Al_2CuH_x (invited)

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Aluminum-based interstitial hydride has not been reported so far, whereas complex aluminum hydrides have been synthesized and investigated. In the present study, we demonstrate the formation of Al_2CuH_x ($x \sim 1$) interstitial hydride by a hydrogenation reaction of Al_2Cu alloy under high pressure and high temperature [1].

The starting material was ground Al_2Cu alloy powder. The sample was pressurized to 10 GPa at room temperature and then was heated up to 900°C in hydrogen fluid. High-pressure and high-temperature conditions were generated using a cubic-type multi-anvil high-pressure apparatus. Structural changes of the sample were monitored by *in-situ* synchrotron radiation X-ray diffraction technique at BL14B1 at SPring-8.

Figure 1 shows synchrotron radiation X-ray diffraction profiles taken at 10 GPa. Al_2Cu alloy first decomposed into Al_2Cu_3 and pure aluminum at 880°C, and the hydrogenation reaction started upon lowering the temperature to 800°C. The formed hydride was recovered at ambient conditions and characterized by powder X-ray diffraction measurement. The interstitial nature of the hydride, as well as its crystal structure and thermodynamical stability, will be presented.

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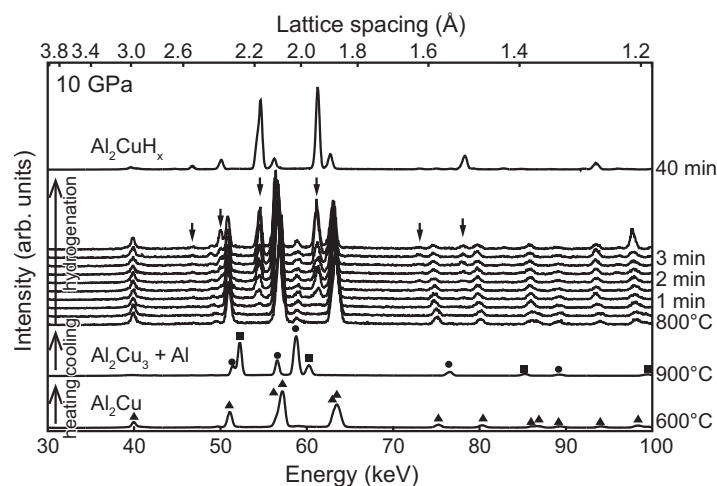


Figure 1. Synchrotron radiation X-ray diffraction profiles taken at 10 GPa. Bragg peaks with triangles, circles, and squares were from Al_2Cu , Al_2Cu_3 , and pure aluminum, respectively. Arrows indicate Bragg peaks from the formed hydride.

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A kinetics investigation of MgH_2 formation/decomposition in Mg-Ti layers and MgO-Mg thin films.

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The use of thin films for the investigation of kinetics of hydride formation have advantages and drawbacks compared to their bulk counterpart. Main advantages are the well defined geometry and experimental conditions and, also, the short experimental time to perform the measurements. For the drawbacks, the main problem is related to the interaction between the film and the substrate and the mixing between the layers that compose the film. For instance, in a recent publication [1], we have shown the problem of interaction of Mg films with quartz substrates due to the formation of Mg_2Si -MgO phases. In this investigation, we try to obtain stable and robust MgH_2 layers by two different approaches. On one hand, we have prepared Pd capped Ti-Mg-Ti thin film sandwiches on glass substrates by electron beam evaporation. The Mg and Pd layers were fixed to 100 and 10 nm, respectively. Two different Ti layer thicknesses of 10 and 25 nm were investigated. On the other hand, 250 nm Mg films were prepared by the same technique onto quartz substrates previously covered with 100 nm MgO layer. The films were characterized by profilometry, glancing angle X-Ray Diffraction, Raman spectroscopy and RBS-ERDA techniques. The hydride formation/decomposition was investigated with a technique that allows following the Mg- MgH_2 transformation “optically”, by means of an optic microscope comprising a high temperature chamber working under inert or reactive atmosphere. During the experiments, transmitted or reflected light and optical photographs are taken along the phase transformation. The results are analyzed on the light of the Johnson-Mehl-Avrami kinetic model in order to get further insight of the process of nucleation, the morphology and dimensionality of the growing phase and, also, the rate of growing of MgH_2 /Mg nuclei (Fig.1).



Figure 1. Optical microscopy image showing incipient growth of abundant MgH_2 nuclei in Mg-Ti layers at 120°C under a H_2 -pressure of 10 mb.

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A family of high pressure synthesized MgTM_2H_6 (TM=Zr,Nb) hydrides where structure and stability were studied by combining x-ray diffraction and DFT calculations

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Abstract

When working with synthesizing members in a series of high pressure synthesized Mg-rich $\text{Mg}_{6-7}\text{TMH}_{12-16}$ (TM= Ti, Zr, Hf, V, Nb and Ta) hydrides, a new family of similar hydrides was found. These hydrides are based on non-miscible metals. The presence of hydrogen is needed to keep the metals together, and only partial release of hydrogen is possible in order to make the reactions reversible.^{1,2} Such systems can anyhow be interesting for hydrogen storage due to the low atomic weight of magnesium.

Hydrogen positions could not be determined by neutron diffraction, as only minute sample amounts were available. The metal atom positions could be established by x-ray powder diffraction. Hydrogen atom positions were determined by calculating formation energy of possible hydrogen sites in the metal atom framework of the high pressure synthesized structures of MgZr_2H_6 and MgNb_2H_6 . The hydrides were found to be described in the $R\bar{3}m$ space group with unit cell axes $a = 3.3592(2) \text{ \AA}$, $c = 25.131(3) \text{ \AA}$ and $a = 3.2901(9) \text{ \AA}$, $c = 23.09(1) \text{ \AA}$, respectively. The hexagonal cell contains three formula units. Different structural models were calculated with density functional theory for the zirconium containing hydride. By correlating all possible combinations of hydrogen sites in the MgZr_2 lattice, the measured lattice parameters and refined metal atom atomic positional parameters could be reproduced. The hydrogen atoms were found to fully occupy an octahedral site coordinating 3 Mg- and 3 Zr-atoms, a tetrahedral site coordinating pure 4 Zr atoms and another tetrahedral site coordinating 3 Mg- and 1 Zr-atoms. The stability of the MgZr_2H_6 structural phase is further discussed via chemical potential equilibrium diagram and phonon calculations.

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Effect of the rare earth on the structural and hydrogen storage properties of A_2Ni_7 ($A = Y$ or Gd)

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Ni-MH batteries stay attractive in many application domains such as hybrid or electric vehicles and photovoltaic energy storage. In these batteries, the hydride-forming intermetallic compounds are used as active materials for negative electrode. To meet the continuously increasing demand in energy density, the development of new intermetallic alloys with higher capacity is necessary. Recently, some research groups have reported that the A_2Ni_7 ($A = La, Mg$) compounds present interesting discharge capacity (400 mAh/g) and relative good cycle life [1]. In order to improve the performance of these materials, some new compounds such as Gd_2Ni_7 and Y_2Ni_7 should be investigated. In the present work, Gd_2Ni_7 and Y_2Ni_7 compounds have been synthesized by induction melting. X-ray diffraction and EPMA indicate that both compounds were successfully synthesized. Their hydrogenation properties and electrochemical performance will be studied.

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The use of metal hydrides in hydrogen sensors and detectors.

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With the increasing number of hydrogen applications, the need for safety sensors and detectors increases. The current generation of hydrogen sensors is large in size and generally relies on an electrical readout at the area of measurement. We developed a series of new hydrogen detectors and detectors based on the optical changes in metal hydrides on hydrogenation.

Optical fiber based threshold *detectors* using metal-hydride based sensing layers at the top of an optical fiber. To detect hydrogen we use a thin layer- e.g. a Magnesium-Titanium alloy- deposited at the end of an optical fiber. At a well-defined hydrogen pressure this switchable mirror transforms into a highly absorbing state (picture at the left). This defines the threshold pressure of the sensor. The change in reflection is measured by shining a red diode from the other end of the fiber and measure its reflection by a photo-detector. To protect the Mg-Ti against oxidation and to facilitate its hydrogenation at room temperature, this detection layer is covered by Pd. The detector is highly selective for hydrogen. However, Pd is poisoned by strongly absorbing species such as H₂O, CO and H₂S. Thus, we have developed various protection layers to use the sensor in various gaseous and liquid environments.

To make optical fiber based hydrogen *sensors* we need metal hydrides showing a continuous change in optical properties with hydrogen concentration. One possibility is to choose materials with a critical temperature below room temperature. This is possible in Pd alloys, such as the Pd₈₅Ta₁₅ alloy. In addition, we have developed Mg-based alloys showing a much higher contrast over a much larger pressure range.

We also explore eye-readable hydrogen tape sensors. Here we simply deposit the optical detection layer on a piece of (plastic) tape and cover it with a thick layer of Pd. Upon hydrogenation, color changes are induced due to interference, when viewed from the substrate side. Taking advantage of the reversible changes in optical properties of an Y thin film upon exposure to H₂, we detect the presence of hydrogen in concentration range between 5 and 100 ppm H₂ in a step-wise fashion. The nature of the color change is a function of the layer thickness. This device can possibly be used in biochemical/biomedical H₂ sensing applications such as breathe hydrogen tests for the detection of lactose intolerance.

Metal Hydride Based Eye-readable and Color Tunable Detectors for Chemical and Biomedical Hydrogen Sensing Applications

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There is a growing need to develop inexpensive, reliable and very sensitive hydrogen sensors for various applications such as safety detection in hydrogen fuel cell vehicles and generators, nuclear reactors, coal mines, space applications, medical diagnostics and many industrial chemical manufacturing processes. Current H_2 sensors generally have limitations related to costs, speed of operation and cross-sensitivity towards other gases. Therefore they are not suitable for applications such as biochemical and biomedical H_2 sensing where low H_2 concentrations need to be detected in the presence of other gases such as oxygen and/or water.

Here we will show the realization of a new, simple and sensitive metal-hydride based device that indicates the presence of H_2 at certain well-defined pressures merely by a reversible and tunable change in color as shown in figure 1. The reversible and eye-readable color change circumvents the need for additional readout devices, thus making it a very low-cost H_2 indicator. We will show how the thermodynamics and kinetics of hydrogen sorption in the metal hydride sensing layer, the color change and selectivity in the presence of other gases, can be tailored using techniques such as alloying and electronic modification of the surface by polymer films. A highly interesting feature of our proposed H_2 detector is that it can respond to very low H_2 concentrations (0.1% H_2) even in the presence of O_2 and H_2O and is thus potentially suitable for many applications ranging from a simple safety indicator which can warn people of the presence of H_2 at concentrations as low as 5 ppm (simply by a reversible change in color), to biochemical/biomedical applications such as breath hydrogen test for the diagnosis of lactose intolerance and fructose malabsorption[1].

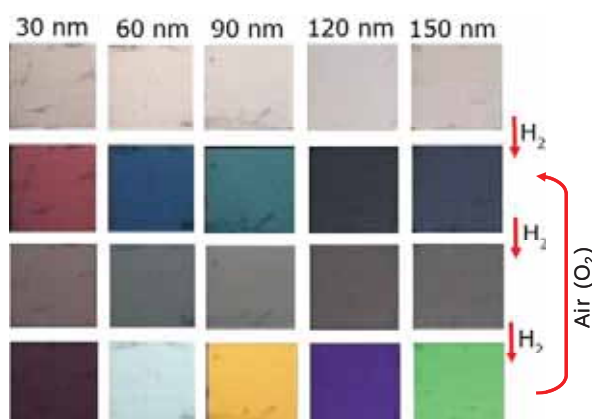


Figure 1. Eye-readable and color tunable hydrogen detector

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Large Pressure Range Optical Hydrogen Sensing Materials

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In a sustainable economy with hydrogen as a major energy carrier, a sensitive hydrogen sensor is indispensable. Current available detectors are mainly catalytic resistors or electrochemical devices. Since hydrogen detection often takes place in gas mixtures that can form explosive mixtures, the presence of electric leads can result in unsafe situations. Using optical-fiber sensors, the readout can be separated from the sensing points (no electric contacts). Therefore fiber-optical-sensors are ideal for continuous sensing in small spaces, which are unreachable or unsafe for catalytic resistors or electrochemical devices.

In literature usually two classes of optical hydrogen sensing materials are reported. The first class consists of Pd-based compounds. These compounds show fast and reversible kinetics and are very stable, but the optical contrast is rather low with a small detectable range of partial hydrogen pressure ($10^3 - 10^5$ ppm) [1,2]. In addition, Pd-based compounds show a (suppressed) hysteresis between hydrogen absorption and desorption. The second class consists of Mg-based compounds where the optical contrast is superior compared to Pd-based compounds, but the detection range spans also only two orders of magnitude ($10^1 - 10^3$ ppm) [3]. Furthermore, Mg-based compounds exhibit a large hysteresis, limiting the possibility to monitor fluctuations in hydrogen concentration by means of Mg-based compounds.

Here we introduce a new class of hydrogen sensing materials. This class consists of a wide-range of different compounds, all with a well-defined relation between optical response and the applied hydrogen pressures over a very large range of at least 4 orders of magnitude. First results show that we are able to detect hydrogen at partial pressures as low as a few ppb up to a hundred ppm. Therefore with these compounds we can detect hydrogen concentrations that are a factor 10 000 or even a factor 1 000 000 lower than detectable with resp. Mg-based and Pd-based compounds. In addition, the compounds show a high stability upon cycling with good kinetics.

In contrary to Pd- and Mg-based systems, we found that these compounds are hysteresis free; there is no difference between the absorption and desorption curves. These compounds exhibit a second-order phase transition, meaning that there are no mechanical issues when exposing them to hydrogen. This means that these compounds have the potential to be used for continuous monitoring of hydrogen in situations where little hydrogen is involved.

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Hydrogen gas collection System Using Magnesium Catalyzed with Niobium Oxide

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A hydrogen gas collection system using hydrogen storage materials is proposed in this study. In case of hydrogen leakage, the system works as a safety apparatus which can prevent hydrogen explosion by collecting hydrogen gas without electric power supply. The composite of magnesium powder with 1 mol% niobium oxide (activated-Mg), which can absorb hydrogen at room temperature[1], was tested for this system. ~10 g of activated-Mg was placed in a closed container (8L) to imitate the hydrogen collection system placed in a room at a small scale. The atmosphere inside the container was controlled (mixture of hydrogen/nitrogen/oxygen) and change in concentrations of hydrogen gas in the container was monitored. After hydrogen gas introduction in the N₂-filled container at room temperature, the activated-Mg absorbed hydrogen gas of low concentration (< 4 vol.%) as shown in the Figure. It is suggested that the hydrogen gas collection system using the activated-Mg has capability to maintain hydrogen concentration in a room below lower explosion limit.

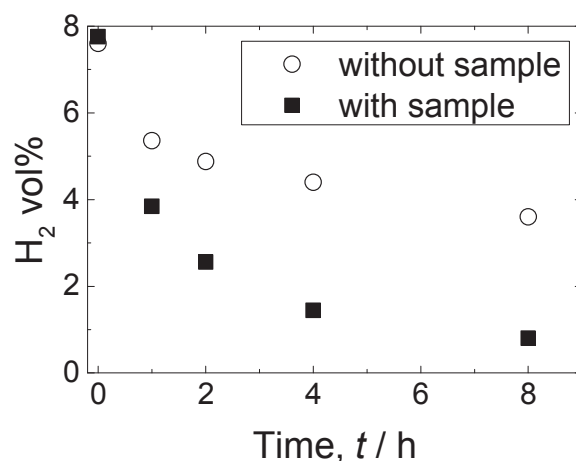


Figure. Change in hydrogen gas concentrations in a container as a function of time.

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Spontaneous Dehydrogenation Reactions - Invited

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Several new transition metal borohydrides e.g. $\text{Ti}(\text{BH}_4)_3$ have been synthesized and the dehydrogenation reaction was investigated in view of the thermodynamics and intermediate products formed by means of thermo gravimetry, mass spectroscopy and IR-spectroscopy. The hydrogen desorption kinetics was analyzed and the intermediate products were identified.

The new compound $\text{Ti}(\text{BH}_4)_3$ was synthesized by the metathesis reaction and reactive milling. The intermediates and/or products formed during the hydrogen desorption reactions are thermodynamically unstable. Their characterization and measurement as a function of time and temperature is a key challenge to understand the reaction mechanisms and the upscaling [1].

We analysed the formation of intermediate species, studying LiBH_4 , one of the materials with the highest gravimetric hydrogen density considered for hydrogen storage. The following reaction was investigated:



The identification and characterization of $\text{Ti}(\text{BH}_4)_3$ is a technical issue because it is extremely reactive in air, spontaneously decomposes within few hours at room temperature and is volatile. Therefore, different in situ techniques i.e. thermogravimetric balance, mass and IR-spectroscopy were combined in order to determine the thermodynamics of the reaction, the emitted and the intermediate products. [2]

We found that the metathesis product, $\text{Ti}(\text{BH}_4)_3$, decomposes into diborane, hydrogen and solid residues. Therefore it is an intermediate phase in the dehydrogenation reaction of TiCl_3 added LiBH_4 . $\text{Ti}(\text{BH}_4)_3$ is stable at room temperature for few hours and therefore its detection is possible [3]. This species, under these experimental conditions, does not catalyze the decomposition reaction of LiBH_4 . These findings open a new perspective in the research of additives to destabilize complex hydrides.

Several intermediate species have been theoretically predicted but never experimentally shown: $\text{V}(\text{BH}_4)_3$ or $\text{Zn}(\text{BH}_4)_2$. The spontaneous release of gas species from the products of the reaction of LiBH_4 with ZnCl_2 , and VCl_3 , will be analyzed. A comprehensive bulk, surface and gas phase analysis of the reactions products and eventually formed intermediate species will be presented, pointing out the route towards the control of spontaneous dehydrogenation reactions and the stabilization of the intermediate species.

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**Practical Hybrid High-Pressure / Sorbent Hydrogen Storage Systems
Incorporating Nanoporous Materials
(Invited)**

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Our research vision is to provide design and operation principles for hybrid adsorption / high-pressure hydrogen gas containment in sustainable energy systems, especially low carbon vehicles [1, 2]. The key questions we are addressing are whether and how such hybrids may enhance capacity and/or lead to less demanding storage conditions compared with state-of-the-art pressurised tanks to 70 MPa operating at ambient temperature. This will be of interest across academic and industrial communities involved in hydrogen energy especially as road vehicles fuelled by hydrogen approach commercialisation. We adopting a novel and ambitious approach, combining adsorption science with practical storage solutions, that is designed to lead to a second stage of hydrogen storage technologies even as the first stage is still in progress.

En route to the final goal of a practical adsorbent / pressurised hydrogen gas storage system, several key aspects are being investigated to generate new knowledge and understanding of materials, design and performance. Accordingly, our linked research objectives are:

- (i) To produce a range of nanoporous materials and structures to integrate into Type IV hydrogen storage tanks.
- (ii) To study and understand the nature of sorbent integration on the mechanical and thermal properties of tank materials.
- (iii) To produce design and operation principles for hybrid storage tanks based on results and insights from objectives (i) and (ii).

This presentation will cover all these aspects, with a focus on nanoporous carbon sorbents.

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Stress Generation of Hydride Graphite Composites Associated with Cyclic Hydrogenation

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The development of safe and efficient hydrogen storage applications is a precondition to establish a hydrogen-based energy cycle. Compacted metal-hydride graphite composites offer especially high volumetric hydrogen storage densities and absorption rates at a low loading pressures and, thus, with a corresponding low hazard potential [1, 2]. The volume expansion of the material during hydrogen absorption is an important fact and has been examined in microscopic and macroscopic scale [3, 4]. To avoid any damage in state-of-the-art storage vessels, the expansion of the storage material is compensated using only partially filled pressure vessels which in turn reduces the volumetric storage density by up to 30% [5]. It is possible to utilize the porosity of these composites to compensate the expansion of the material which leads to increased volumetric storage densities. Thus, it is necessary to consider an additional stress introduced on the reactor wall during construction.

This contribution reveals influences on the stress generation of hydride-graphite composites with limited expansion during hydrogen (ab-) desorption. An interstitial alloy (TiMn₂-based) was mixed with expanded natural graphite (ENG) and compacted with up to 300 MPa under inert atmosphere. The stresses evolving during hydrogenation were monitored using a specially designed measuring cell and commercially available pressure-sensitive films (cf. Figure 1). Influences like pellet geometry, ENG fraction, porosity, anisotropy and hydrogen content on these stresses were considered. From the results, it is possible to deduce design criteria which allow to optimize a hydride based hydrogen storage system according to its volumetric and gravimetric hydrogen storage density. Furthermore, pressure-stress-isotherms similar to pressure-composition isotherms can be derived which allow to quantify the stresses occurring at a given hydrogen load.

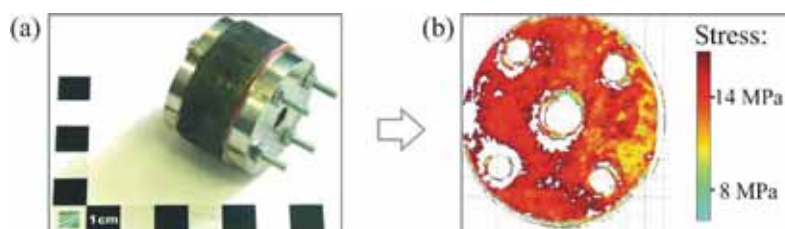


Figure 1: (a) Designed clamp to limit the expansion while hydrogenation; (b) Spatial evaluated pressure sensitive foil after cyclic hydrogen uptake.

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Initial Step of Hydride Formation in Single Crystalline Gadolinium Thin Films and Islands Studied on the nm-Scale

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The initial steps of hydrogen absorption in gadolinium systems are investigated by means of scanning tunneling microscopy (STM) under ultra high vacuum conditions. Gadolinium is grown on a W(110) substrate. Depending on the preparation conditions smooth films or islands can be obtained.

Clean and well ordered Gd surfaces exhibit a highly localized surface state near the Fermi edge. Exposure to low amounts of hydrogen (1-2 L) on thin films leads to adsorption and as a consequence to a suppression of the surface state. This change in the electronic structure results in a voltage dependent corrugation in STM measurements which changes sign at 0.8 V. But no other changes can be observed until the hydrogen dosage is increased. Then small discs with a diameter of a few nm and a height of one atomic step appear. The discs form chains with clearly preferred directions. A triangular shaped structure is observed together with the discs. Areas completely transformed to hydride also appear. At the same time the reappearance of the surface state can be observed, which indicates the diffusion of hydrogen into the bulk material. The formation of the hydrides significantly depends on the quality of the surface and the hydrogen partial pressure.

The absorption process in islands was also investigated and is compared with the behavior in thin films.

All measurements are performed at room temperature. By increasing the temperature changes of the different modifications can be observed up to that point which they vanish at.

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State of the Art and Needs of Hydrogen Adsorption Storage Systems (Invited)

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R&D efforts are being directed toward improving the efficiency and economics of hydrogen storage systems to make hydrogen fuel cells competitive, and enable larger than 500 km driving ranges for a wider variety of transportation applications. The majority of today's fuel cell vehicles rely on high-pressure tanks rated at 350 or 700 bar for onboard storage of hydrogen gas. One of the pursued alternatives is cryosorption on nanoporous materials (such as activated carbon, polymers, and metal organic frameworks) due to its inherent reversibility, cyclability, and fast kinetics.

While advanced sorption material development is generally directed toward increasing the activity of surface area and hence the excess gravimetric energy density and/or the temperature of operation; hydrogen storage systems need to simultaneously satisfy a set of technical requirements including but not limited to: usable gravimetric and volumetric energy densities, min/max pressure and temperature operability, well to power plant efficiency; acceptable thermal loads and dormancy, charging/discharging rates; and fuel purity.

We present a set of cascading computing tools that enables a preliminary performance assessment of the storage system based on the knowledge of the basic crystal structure of the constituent adsorbent material. It bridges the gap between materials development and system analysis. Moreover, when it is applied backward it helps orienting materials optimization. We will give an example of its application on a metal organic framework.

Hydrogen interaction with nanoconfined materials

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Camelia Matei-Ghimbeu² and Cathie Vix-Guterl²

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The present work reports on an emerging route towards improving the properties of solid-state hydrogen storage materials by nanoconfinement of metal/hydride particles into porous scaffolds.[1,2] Among different design approaches, the confinement of nanoparticles into porous scaffolds allows easy handling and prevents coalescence of the particles.

The synthesis and hydrogen sorption properties of hybrid materials containing different nanoconfined hydrides (MgH_2 , Mg_2NiH_4 and Mg_2CoH_5) within the pores of carbon hosts are reported. The effect of different confining carbon hosts and metal loading on the fundamental and hydrogen sorption properties of Mg-based nanoparticles will be addressed. Experimental results revealed that the hydrogen sorption properties, such as desorption kinetics, are significantly enhanced by nanoconfinement. Ultrasmall MgH_2 nanoparticles (particle size distribution within 2-10 nm and average size ~ 4 nm) have a maximum desorption rate at 150 K below the temperature of bulk material (Figure).[2]

In addition, the nanoconfinement suppresses the polymorphic transition from cubic high temperature to monoclinic low temperature structure in the complex hydride Mg_2NiH_4 , which preserves the cubic structure at room temperature.[3]

The nanoconfinement strategy holds promise for enhanced hydrogen storage properties and opens the route to a better understanding of the underlying nanochemistry.

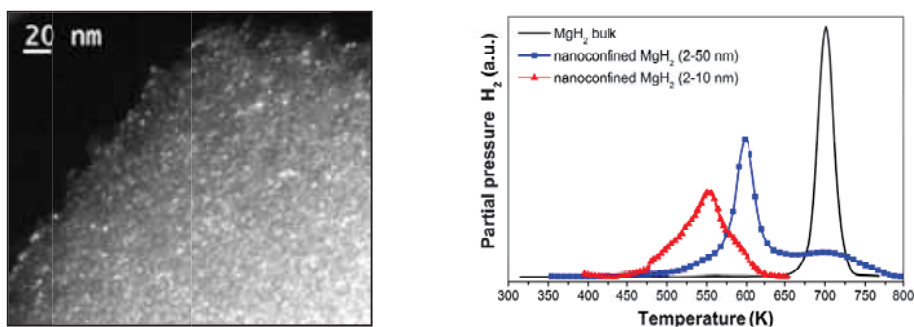


Figure. Left: TEM image of ultrasmall MgH_2 nanoparticles embedded into a porous carbon host. Right: thermo-desorption spectra of nanoconfined MgH_2 with different particle size distributions (2-10 nm and 2-50 nm) compared to bulk material (Heating rate = 10 K min^{-1}).

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Quantum Dynamics of Hydrogen Molecules trapped inside Nanocavities in different solid Water Structures

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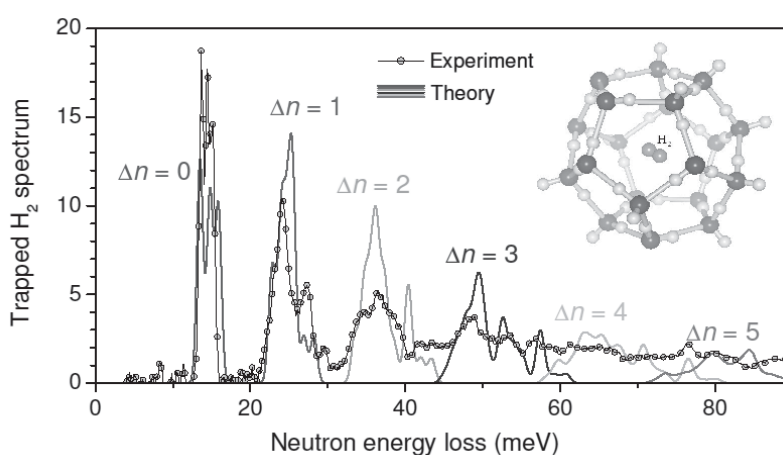
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Hydrogen gas and water may form clathrates hydrates either together with some help substance (binary clathrates) or at higher pressure, without it (simple clathrates). The confinement of the hydrogen molecules in the two types of clathrates is substantially different: in binary clathrates hydrogen singly occupies the smaller dodecahedral cages, while in simple clathrates also the larger cages (hexakaidecahedral) are filled with more than one (up to four) hydrogen molecule.

The dynamics of the molecules trapped in the two kind of cages is qualitatively different. Recent inelastic neutron scattering (INS) spectra of binary hydrogen clathrates (single occupation of dodecahedral cages) agree well with a rigid-cage, five dimensional quantum simulation, which account for the effects of the anisotropy, angular and radial, of the host cage (see figure). On the contrary, the INS spectrum of the hydrogen molecules in the large cages of cubic simple clathrates presents a very different shape, without sharp bands. Finally, the spectrum of the hexagonal clathrate compares much less favorably with the theory, probably due to the lack of a precise knowledge of the structure of the crystal.

The Raman spectra reveal details of the interaction of the H_2 molecule with the cage, and of the different number of molecules in the cages. An interesting effect, seen by Raman measurements in hydrogen clathrates at 20 K, is the different rate of conversion from *ortho*- H_2 to *para*- H_2 for molecules caged alone or in larger number in the same cage.



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Synthesis of Cr-MOF Derived Porous Carbon for Hydrogen Storage Applications

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Over the recent years, applications of porous metal-organic frameworks (MOFs) in hydrogen storage have received increasing attention in the scientific community [1]. Conversion of organic moiety in MOFs to porous carbon, as well as the use of MOFs as a template during the production of highly porous carbonaceous material have also been demonstrated to lead to enhancement of hydrogen storage capacity of the MOFs [2]. Most of the studies in this case have mainly focused on the use of Zn-based MOFs. In this work Cr-based MOF was used as a precursor and as a template for generation of MOF-derived carbons. In the first instance, the MOF sample was subjected to thermal treatment in a tube furnace to generate the carbonaceous material. In the second instance, the MOF sample was used as a template, in which case, furfural alcohol and ethylene gas were employed as the second and third carbon precursors. Various characterization techniques such as XRD, SEM, TGA as well as surface areas and hydrogen storage measurements were used to investigate the properties of the generated porous carbons.

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Recent Progress in Hydrogen Storage on MOFs (Invited)

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The field of coordination polymers or framework materials has tremendously grown, since the stability of these structures could be shown after removal of the solvent molecules, exhibiting a nanoporous framework with ultra-high porosity and large specific surface area [1-3]. Different classes of these novel highly porous structures, e.g., metal-organic frameworks (MOFs), zeolitic imidazolate frameworks (ZIFs) or covalent organic frameworks (COFs), have been extensively studied for applications in gas storage. Beside their large surface area, these crystalline frameworks possess well defined pore sizes having a uniform distribution.

Typically, the interaction of the adsorbent and hydrogen molecules is simply governed by van der Waals forces and therefore high storage capacities can only be achieved at low temperatures. As known from activated carbons, the maximum hydrogen uptake at high pressure and 77 K shows an almost linear correlation with the specific surface area even for these nanoporous framework materials consisting of various other elements than carbon [4]. Furthermore, frameworks possessing smaller pores show typically a higher heat of adsorption. Both, maximum hydrogen storage capacity and heat of adsorption have to be considered to optimize the materials for their potential application [5]. The presentation will give a short overview and explain a new method to determine experimentally the maximum gravimetric and volumetric hydrogen storage capacity for monoliths of porous materials in one isothermal measurement [6].

Finally, the talk will review the many attempts carried out for enhancing the interaction between the hydrogen molecule and the adsorbent. A critical assessment of the results published in literature shows that none of the promising results could be independently reproduced [7,8]. Metal doping of the framework leads in many cases to an enhancement, which can be explained by chemisorption of hydrogen, however, at ambient temperature the total storage capacity is very small and below any technological relevance [9,10].

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Direct observation of σ -Pd(H₂) at ambient temperature on single atoms of Pd supported on a metal-organic framework

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Kubas-type complexes represent a desirable option for hydrogen storage as their typical enthalpies of formation are close to 15-30 kJ mol⁻¹, allowing for ambient-condition operation. [1] Despite the promising computational results, direct observation of these materials in the solid state has been hindered by the fact that such interaction only occurs on single metal atoms or small clusters [2], which are unstable. [3]

In this work, the synthesis of Pd stabilised as single atoms on a metal-organic-framework (MOF) scaffold is presented. Most importantly, the ambient-temperature hydrogen capacity of the MOF was found to increase upon the introduction of single atoms of Pd.

Using temperature-programmed desorption spectroscopy and *in-situ* Raman spectroscopy we were able to demonstrate that this increase was primarily due to the σ -Pd(H₂) Kubas complex, thereby providing the first spectroscopic evidence for its formation at ambient-temperature.

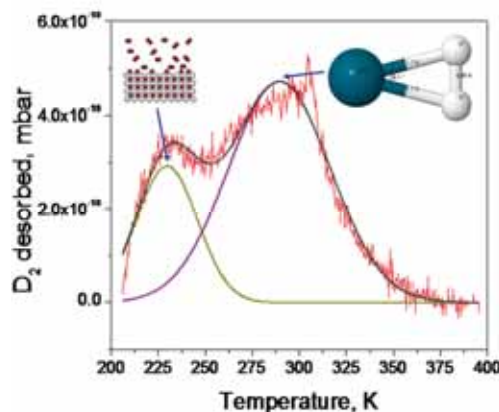


Figure 1. Temperature-programmed desorption spectrum of D₂ from a MOF containing single atoms of Pd near ambient temperature, displaying the desorption sites assigned.

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Ultradense Hydrogen Physisorption in the Porous Magnesium Borohydride

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Recently the first porous hydride, $\gamma\text{-Mg}(\text{BH}_4)_2$, featuring so-called "borohydride framework" and capable to store reversibly guest species was discovered [1]. This example clearly shows that the covalently bound hydride anions, such as borohydride, can act as directional ligands, capable to form molecular and polynuclear complexes, as well as framework structures typically occurring in classical coordination chemistry. Various small molecules are reversibly absorbed in $\gamma\text{-Mg}(\text{BH}_4)_2$.

In this work we show that molecular hydrogen and nitrogen have different adsorption sites in $\gamma\text{-Mg}(\text{BH}_4)_2$, leading to different capacities on saturation and to different H_2 and N_2 BET areas. Only up to 0.66 N_2 molecules are adsorbed per Mg atom, but the saturation capacity is double (1.33 per Mg) for the smaller hydrogen molecule. Moreover, at higher pressures, the second hydride phase $\gamma\text{-Mg}(\text{BH}_4)_2 \cdot 2.33\text{H}_2$ forms with unprecedented hydrogen content of ~22 weight %. The density of molecular hydrogen adsorbed into the pores (0.144 g/cm^3) is twice (!) higher than in liquid hydrogen (0.071 g/cm^3), having no analogues among other porous systems.

On the technical side, we will illustrate how *in-situ* diffraction at neutron and synchrotron sources allows to follow adsorption isobars, aiming for extraction of isosteric heats of adsorption directly from diffraction data, as well as for clarifying the microscopic mechanisms in terms of guest-host and guest-guest interactions. Using powder neutron diffraction data from freshly prepared $\gamma\text{-Mg}({}^{11}\text{BD}_4)_2$ sample we reliably determined position and amount of adsorbed hydrogen that coincide with synchrotron powder diffraction data and BET experiments.

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Ceramic on Metal Type Hydrogen Storage Composites and Their Applications

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Metal decorated nanocarbons have been studied as high surface area hydrogen storage materials, and on the other hand most of metal catalysts have been composed on ceramic supports. Those materials can be classified as metal on ceramic composites, and have enhanced hydrogen capacity and proper catalytic activity, respectively.

Reversed construction of composites, that is, ceramic formation on metals and alloys, for example, imparts water resistance to hydrogen storage materials [1]. If the ceramic shells have some functions, the composites would have novel functions, other than the protective effect, based on cooperative effects of ceramic shells and metallic cores. Another unknown effect would be incubation of peculiar materials through inclusion of reaction fields. Ceramic on metal type composites were thus investigated with conscious emphasis on hydrogen storage in the present work.

A Laves phase alloy, ZrVFe, successfully occluded hydrogen from gas mixtures of hydrogen and oxygen as well as hydrogen, carbon dioxide and steam, generated by water electrolysis and biological fermentation, respectively, when the alloy was encapsulated in tetraethoxysilane-derived shells. Particularly, in the latter case, hydrogen was yielded several times as much as in the absence of the alloy. The hydrogen selective membrane on ZrVFe would have shifted the equilibrium or accelerated the kinetics of fermentation. Other examples comprising reactive separation membranes are in progress.

Chemical vapor deposition (CVD) of ethanol on Fe-Ni-Cr powdery mixtures gave carbon on metal type composites, which occluded hydrogen under 0.7 MPa during cooling cycle from 623 K to room temperature. The temperatures where hydrogen release was significant were drastically lowered by manual milling as shown in Figure 1. Since the released amount of hydrogen largely increased, formation of good absorbers at the boundary of carbon and metals was plausible. The incubating effect is now under verification.

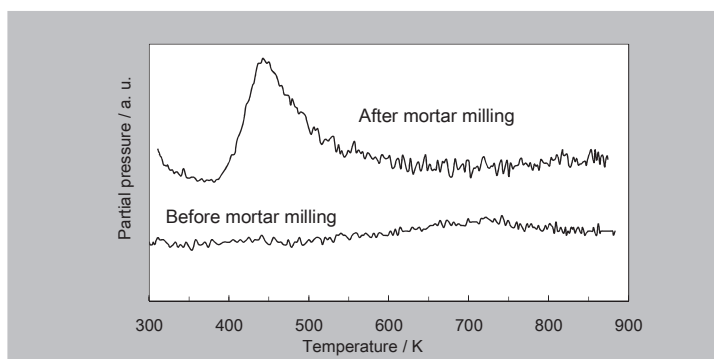


Figure 1. Temperature programmed desorption of hydrogen from the CVD composite.

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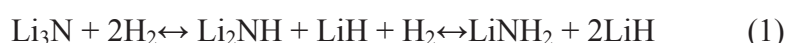
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Nitrogen Based Materials for Hydrogen Storage

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N can bond with hydrogen forming NH₃, amines, amides, imines, and imides etc. Nitrides (M₃N_x), imides (M₂(NH)_x) and amides (M(NH₂)_x), where x is the valence of M, are the examples showing continuous replacement of M by H in the Metal-N-H system. Li₃N, as an example, absorbs H₂ following the reaction 1 giving rise to Li₂NH-LiH and LiNH₂-2LiH in a stepwise manner. Such a reversible reaction, can desorb/absorb ~10.5 wt% H₂ under moderate conditions.^[1]



Comparatively, the M-N-H system has three distinct features:

1. It contains non-metallic elemental N;
2. The fully hydrogenated material is a composite of amide and hydride; H₂ generation relies on the chemical interaction of the corresponding components;
3. Both protic hydrogen (H^{δ+} in amide) and hydridic hydrogen (H^{δ-} in LiH) co-exist.

Efforts in materials development based on the M-N-H system mainly devote to thermodynamic alteration through compositional change and to kinetic improvement through introduction of catalytic additives. The target of achieving room temperature operation encourages considerable activities recently especially on the Mg(NH₂)₂-LiH composite.^[2]

Compared with those inorganic N-based hydrides, organic amines, especially primary amines, remain essentially untouched. The thermal decomposition of amines usually leads to the cracking of C-N or C-C bond rather than coordinative cleavage of C-H and N-H bonds. Our recent research demonstrates that upon replacing hydrogen from primary amines by Li, a variety of lithiated amines can be formed, which, interestingly, decompose to hydrogen endothermically at temperatures around 170 degree C.^[3] Characterization on the structural information and kinetics reveal that hydrogen desorption is via direct breaking of C-H and N-H bonds following the alpha-beta elimination mechanism, which may be mediated by Li through forming LiH intermediate. The endothermicity in dehydrogenation and the relatively high hydrogen content enable this newly developed lithiated amines potential hydrogen carriers.

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Probing Reversibility in the Li-N-H Hydrogen Store by *in situ* X-Ray Powder Diffraction

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Facile reversibility of hydrogen storage has been an elusive goal among most complex hydride materials, and yet is an indispensable requirement for on-board systems. The lithium amide – lithium hydride (Li-N-H) system is a canonical hydrogen store primarily because of the moderate conditions under which it is reversible (<10 bar H₂). While its relatively high temperature of operation currently prevents commercial application, developing an understanding of the physical processes which underpin its reversibility will inform our exploration of complex hydrides more generally.

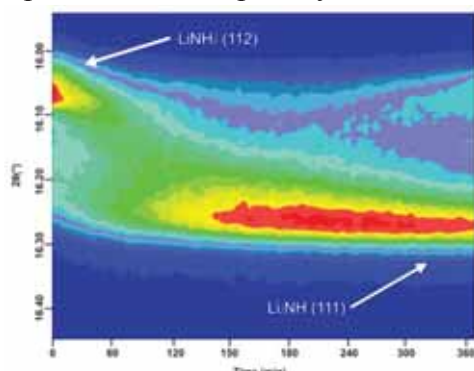


Figure 1 – Contour plot of a section of the diffraction data for the dehydrogenation of the Li-N-H system

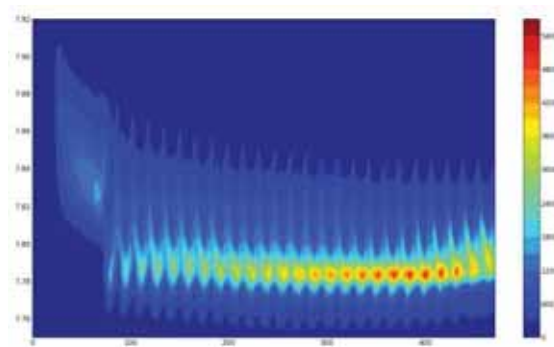


Figure 2 – Contour plot of a section of the diffraction data for 26 hydrogenation/dehydrogenation cycles of the Li-N-H system

Here, we report our examinations of the Li-N-H system, studied using *in situ* synchrotron X-ray powder diffraction. This work ranges from analyzing individual hydrogen storage and release cycles, observing the formation of non-stoichiometric intermediates of the form Li_{1+x}NH_{2-x} as the reaction progresses (Figure 1) [1], to tens of cycles in which subtle changes are observed with variation in the hydrogenation gas stream composition (Figure 2), echoing previous results[2]. Rietveld analysis of these data allows for the extent of reaction to be followed, and for the extraction of kinetic data which shows the variation with variable temperature and hydrogen pressure. Furthermore, differences in the kinetic and thermodynamic stabilities of the non-stoichiometric phases are observed, pointing to factors underlying the reversible nature of the reaction, and the limitations of that reversibility.

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Structure Solution of New Imide and Mixed Imide-Amide Compounds for Hydrogen Storage Materials

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In the field of solid-state hydrogen storage the alkali amides and alkaline-earth analogues show remarkable reversibility in terms of hydrogen release and up-take processes[1]. As these systems also exhibit promising hydrogen mass and volume ratios, further investigations into the significant structural modifications occurring both at macrostructure to atomic scale level were undertaken. The formation of new unknown phases during intermediate steps of the absorption/desorption reaction pathways hinder the understanding of the basic mechanisms of the reaction kinetics. The combination of neutron powder diffraction data with the so called *ab-initio* processing methods[2] is uniquely suited to achieve unambiguous structure solution of these new compounds. The new crystal structures solved by this method will be able to shed light on the atomic interactions especially concerning the hydrogen atoms.

A detailed discussion of the crystal structures will be provided, as well as detailed information on the methodology of the structure solution of MgNH magnesium imide and KMg(NH)(NH₂) mixed imide-amide compounds[3, 4], which made use of both conventional X-ray diffraction and neutron diffraction patterns, the latter obtained from deuterated specimens.

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Phase space investigation of the lithium amide halides.

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Lithium amide has been shown to release up to 6.5 wt% of hydrogen reversibly on reaction with lithium hydride,^[1] often accompanied by ammonia release. It has been seen that doping LiNH_2 with LiCl , LiBr and LiI forms the amide halides, such as $\text{Li}_4(\text{NH}_2)_3\text{Cl}$, $\text{Li}_7(\text{NH}_2)_6\text{Br}$ and $\text{Li}_3(\text{NH}_2)_2\text{I}$. These amide halides not only release hydrogen more rapidly on heating with LiH than LiNH_2 itself, but also exhibit a suppression of ammonia release to below detection level.^[2]

As replacement of NH_2^- ions by heavier halide ions increases the weight of the material, the lower limit of halide content was investigated using powder X-ray diffraction. This paper investigates the phase space for each of these halide systems, examining the structural changes that occur as the halide level is changed.

It was found that the $\text{Li}_3(\text{NH}_2)_2\text{I}$ structure was unable to accommodate any variation in stoichiometry, with the starting materials present in the product at other reactant ratios and the lattice parameters remaining unchanged (Figure 1, left).

In contrast, some non-stoichiometry was accommodated in $\text{Li}_7(\text{NH}_2)_6\text{Br}$, shown by a decreasing unit cell volume (Figure 1, right). However, with the starting material LiBr present in the product at all non-stoichiometric ratios, the exact degree of the non-stoichiometry accommodated within the structure has been difficult to determine.

For the amide chloride $\text{Li}_4(\text{NH}_2)_3\text{Cl}$, the phase space was investigated for both one and twelve hour reaction times and a range of non-stoichiometric phases were observed, including a new phase with the stoichiometry $\text{Li}_7(\text{NH}_2)_6\text{Cl}$.

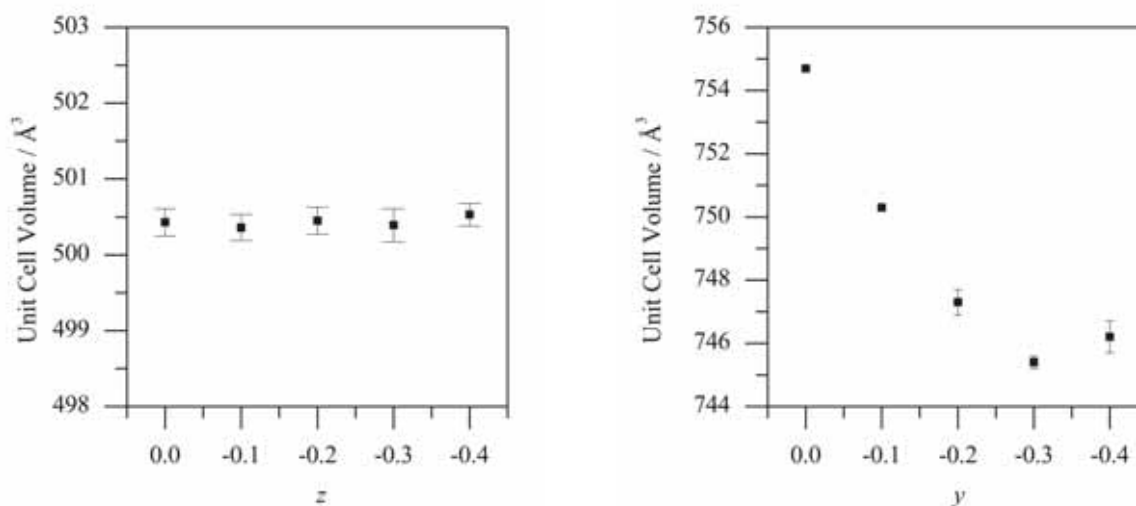


Figure 1: Graph of unit cell volume against halide content for $\text{Li}_3(\text{NH}_2)_{2-2z}\text{I}_{1+z}$ (left) and $\text{Li}_7(\text{NH}_2)_{6-y}\text{Br}_{1+y}$ (right).

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Hydrogen storage: imides, amides and ammonia

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Despite intensive research over the past decade, the discovery of a reversible lightweight hydrogen storage material has remained an elusive goal. While di-hydrogen bonded hydrides, such as ammonia borane, ammonium borohydride and the various amidoboranes, can release a high wt% of hydrogen often at modest temperatures, they are, at best, difficult to cycle and are usually irreversible. Protic hydrides, such as the alanates and amides, are generally easier to cycle although rehydrogenation pressures can be high. The best reversible systems are often associated with high ionic conductivity where the bulk ionic motion facilitates hydrogen uptake and release.

In this talk, I will briefly discuss our in-situ synchrotron X-ray powder diffraction studies of lithium imide and amide^[1] and highlight the importance of lithium ion mobility and the mediating role of ammonia in the facile reversibility of this system. If one reconsiders this system in reverse – i.e. the mediating role of the amide in ammonia decomposition – then it is possible to access all 17.8wt% of the hydrogen in ammonia. I will present our recent results^[2] that show that ammonia may be effectively and efficiently decomposed through the concurrent stoichiometric decomposition and regeneration of sodium amide via sodium metal. As an abundant and inexpensive material, the development of NaNH₂-based ammonia cracking systems may promote the utilisation of ammonia for sustainable energy storage purposes.

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Effect of Lithium Ion Conduction on Hydrogen Desorption of LiNH_2 - LiH Solid Composite

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Li-N-H system is an attractive hydrogen storage material, which can be reversible and desorb a large amount of hydrogen (6.5 wt. %).^[1] At the same time, some of the authors have proposed in their reports that the reaction based on Li^+ migration across reactive interfaces between the LiH particles and the LiNH_2 particles.^[2] Based on these results, we report another feasibility study of adding LiTi_2O_4 as catalyst in the Li-N-H system showing the better desorption kinetics and the purer product gas, due to the increasing of the lithium ion mobility.^[3] Figure 1 presents that the Li^+ interstitial combines with Li vacancy to form an intermediate product $\text{Li}_1\text{LiNH}_2^+$, which could release the H^+ and react with H^- from LiH to generate H_2 gas during dehydrogenation. This study not only demonstrates an important direction in which to search for the reaction mechanism in complex hydrides but also introduces a novel way to target catalyst into solid-state-reaction.

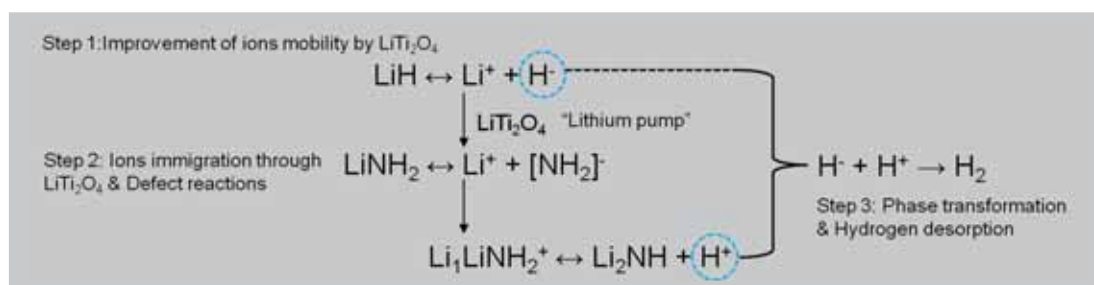


Figure 1. Formula representation of the direction of the Li^+ immigration through different solid phase.

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New insights upon desorption process of the Mg/K amide system

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In the field of the hydrogen-based fuel cells technology, large interest is addressed towards a class of materials defined as multicomponent systems. Among them, great attention is now devoted to systems based on metal amides, due to their high hydrogen gravimetric densities and good reversibility [1]. However, although the very promising thermodynamic properties of these systems are close to the target for practical applications, i.e. the desorption enthalpy is in the range 15–25 kJ mol⁻¹, the release of hydrogen can be achieved only after long time due to the severe kinetic barrier of the sorption reactions. It has been shown that potassium-based compounds can act as good additives for many metal amide systems, improving the sorption kinetic properties [2]. In particular, P. Chen et al. proved that the reaction between magnesium and potassium hydride takes place already at 120–150 °C and it is characterized by the formation of potassium-magnesium tetramide, magnesium imide, and potassium-magnesium amide/imide phases [3]. Although the main sorption steps are well known, the detailed picture of the phase evolution during the desorption of the K₂Mg(NH₂)₄/Mg(NH₂)₂ system is not yet reported. Moreover, some thermodynamic aspect of the processes and the chemical nature/crystallographic structure of an unknown K-Mg-N phase need to be investigated.

In this study, a detailed interpretation of the in-situ synchrotron-XRD data, combined with sorption-calorimetric experiments and mass spectrometry measurements, were performed with the aim to provide an exhaustive description of the Mg/K-amides decomposition pathway. The preparation of the potassium/magnesium amide system was performed by mechanochemical reaction under reactive atmosphere, starting from the corresponding hydride species. The desorption process of the powder mixture takes place at around 150 °C with the evolution of hydrogen (and ammonia traces). At higher temperature, Mg(NH₂)₂ and K₂Mg(NH₂)₄ react forming the K-Mg imide-amide phase KMg(NH)(NH₂), which decomposes around 330 °C to magnesium nitride. Side reactions among the unreacted MgH₂, KNH₂ and MgNH also occur during the desorption step. Finally, the catalytic role of the K-based phases in the mixture is also discussed.

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Effects of doping the Li-Mg-N-H system with CaCl_2 and CaBr_2

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Several groups have looked at doping the Li-Mg-N-H system with borohydride compounds such as NaBH_4 which creates additional Mg vacancies¹ and LiBH_4 in catalytic and stoichiometric amounts². The latter provided an alternative route for dehydrogenating through in-situ formation of $\text{Li}_4\text{BH}_4(\text{NH}_2)_3$ and subsequently helped to seed the $\text{Li}_2\text{Mg}(\text{NH})_2$ product³. Li *et al.*⁴ investigated the benefits of combining Ca^{2+} and $[\text{BH}_4]^-$ by doping the Li-Mg-N-H system with 10-30 mol% of $\text{Ca}(\text{BH}_4)_2$. It was proposed that simultaneous kinetic and thermodynamic improvements could be made by introducing calcium borohydride into the system due to Ca^{2+} and $[\text{BH}_4]^-$ ions. The rates of de- and rehydrogenation were vastly improved and the dehydrogenation onset temperature was lowered.

The in-situ identification of the fast-lithium ion conductor $\text{Li}_4\text{BH}_4(\text{NH}_2)_3$ as a key intermediate in the desorption process was especially interesting. It has previously been reported that the addition of halides may produce a kinetic improvement by increasing lithium ion mobility⁵. An isostructural phase to $\text{Li}_4\text{BH}_4(\text{NH}_2)_3$ is $\text{Li}_4(\text{NH}_2)_3\text{Cl}$, which has been found to possess comparable ion mobility.

Initial research has compared the effects of doping with varying amounts of CaCl_2 and CaBr_2 against the pristine Li-Mg-N-H system. Figure 1 shows a preliminary Kissinger's plot, which was used to estimate the activation energies⁶ of 3 ball milled systems. Doping with 15 mol% CaCl_2 gave an estimated 7% decrease of activation energy of compared to the control. The E_a of a sampled doped with 15 mol% CaBr_2 was reduced by around 15%.

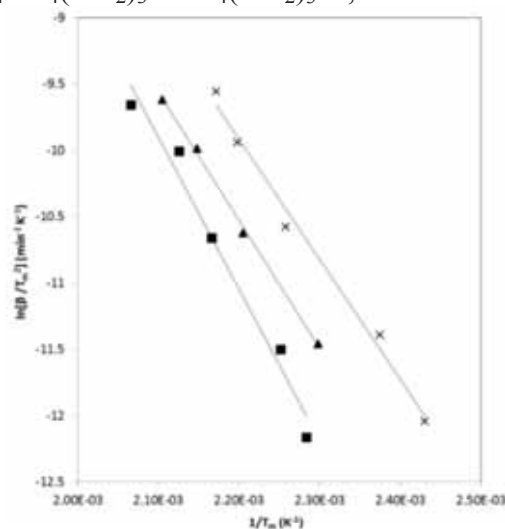


Figure 1: Kissingers Plot showing ball milled control sample $2\text{LiNH}_2\text{-MgH}_2$ (■) and samples doped with, 15 mol% CaCl_2 (▲) and 15 mol% CaBr_2 (X)

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On site occupation and diffusion of H in transition metals

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Abstract

The transition metals can be viewed as the archetype for investigations of hydrogen uptake and diffusion. The early work was predominantly performed using bulk materials, both single crystals and polycrystalline powder. The experimental investigations were therefore restricted with respect to the strain state of the investigated materials. Recent development within thin film technology has opened completely new avenues with respect to investigations on the influence of confinement and stress. For example, the strain state of single crystals can be altered over a significant range, allowing the exploration of the influence of biaxial and tensile strain on hydrogen uptake and diffusion. This, in combination with significant improvements on the theoretical side has allowed for a direct comparison between first principle calculations and experiments, on both thermodynamic and dynamic processes. Here we will discuss the influence of biaxial strain on both the site occupancy and diffusion of hydrogen using Nb and V as examples.

Degradation in the reversible hydrogen storage capacity of V-based bcc alloys: what is the origin and how to improve it?

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Vanadium-(V) based body-centered cubic (bcc) alloys are promising materials for on board application due to their ability to reversibly absorb and desorb a large amount of hydrogen at ambient conditions. For a practical use, reduction in high-cost V content is highly desirable but it often leads to poor cyclic stability, that is to say, the reversible hydrogen storage capacity gradually decreases as the hydrogen absorption and desorption process is repeated. Although excellent cyclic stability is one of prerequisites for practical application, the mechanism behind degradation in the reversible hydrogen storage capacity of V-based bcc alloys during hydrogen cycling has not been fully elucidated yet.

To tackle this problem, we have investigated the development of structural defects and disorders in $V_{1-x}Ti_xH_2$, $x=0, 0.2$, and 0.5 during the first 15 hydrogen absorption and desorption cycles using the atomic pair distribution function (PDF) analysis [1] of synchrotron X-ray total scattering data obtained at BL22XU at SPring-8 in Japan [2]. While pure vanadium ($x=0$) shows no significant change in the PDF, $V_{1-x}Ti_x$ alloys subject to several hydrogen absorption and desorption cycles display fast decaying of the PDF profile due to a progressive increase in the PDF peak width with interatomic distance r . This r -dependent PDF peak broadening effect becomes stronger with cycle number. Molecular dynamics (MD) simulations show that dislocations are responsible for such broadening and the effect becomes stronger with increase in dislocation density. Based on our experimental data and MD simulation results we found a close correlation between reduction in the reversible hydrogen storage capacity of $V_{0.8}Ti_{0.2}$ and increase in dislocation density.

Our results above suggest that dislocation plays an important role in degradation in the reversible hydrogen storage capacity of V-based bcc alloys during hydrogen cycling and to improve their cyclic stability, we need to restrain the formation of dislocation. Based on these basic research results, we have attempted various ways to improve the cyclic stability of V-based bcc alloys. In this presentation, we will introduce one of the ways showing promising results [3].

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Total Scattering Investigations of the Local Structure in Fe-containing hydrides of bcc-alloys

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Body-centered cubic (bcc) alloys with compositions Ti-V-M (M = Cr, Mn, Fe, Co or Ni) have decent hydrogen capacities (2-3 wt.%) as well as suitable thermodynamics and kinetics for hydrogen storage purposes [1]. Vanadium costs about 300 Euro/kg, about 10 times more than most other first row transition metals, which is a severe limitation for utilization of Ti-V-M bcc alloys for hydrogen storage. A possible workaround is to utilize much cheaper ferrovanadium alloys ($\text{FeV} = \text{Fe}_{\sim 0.2}\text{V}_{\sim 0.8}$) instead (about 30 Euro/kg). The reduction in price comes at the cost of lower hydrogen capacity. Kinetic and thermodynamic properties are also altered; however sometimes in a favorable way [2-4].

The crystallographic average structures of Ti-FeV-M-hydrides are very simple with the metal atoms distributed over the same crystallographic sites (bcc or fcc depending on the hydrogen content) and hydrogen typically in partially filled tetrahedral sites. The high degree of atomic disorder makes it challenging to understand structure-property relations by regular powder diffraction or computational methods alone. Still, such relations are crucial to understand in order to intelligently improve the properties of these alloys.

Total neutron and X-ray scattering experiments coupled with pair-distribution function (PDF) analysis and Reverse Monte Carlo modelling are powerful tools to extract information about short-range atomic order in hydrides [5-8]. Such measurements have been performed at ISIS (UK) and SNBL (ESRF, France), respectively, on a series of bcc-hydrides with V, Fe, Ti, Cr and/or Nd and different hydrogen loadings. The obtained structural information is presented with special emphasis on the local structure around Fe which is essential to understand the effects of substituting expensive vanadium with inexpensive ferrovanadium.

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Defect studies of H⁺ implanted Niobium

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Niobium is an important construction material for high temperature technology. It is used also in advanced fission and fusion reactors and for superconducting rf cavities in particle accelerators. Niobium is known as an exothermal hydrogen occluder. Absorbed hydrogen in Nb is very mobile even at low temperatures around 60 K. Mobile hydrogen atoms are able to scan a large volume in Nb sample and interact with lattice defects. It is known that hydrogen is trapped at open volume defects like vacancies, dislocations, grain boundaries etc. However, the knowledge about hydrogen interaction with defects is still limited and detailed investigations on atomic scale are highly desirable. Hydrogen interaction with irradiation-induced defects is especially important in the view of Nb applications.

The aim of the present work was characterization of defects in Nb specimens implanted with H⁺ ions. Implanted ions create a lot of defects (vacancies and interstitials) and hydrogen is incorporated into the specimens at the same time. Hence, H⁺ implanted specimen represents an appropriate system for investigations of hydrogen interaction with defects. Defect studies were performed by three complementary techniques of positron annihilation: (i) positron lifetime (LT) spectroscopy was employed for identification of defects in implanted specimens and estimation of defect concentration, (ii) local chemical environment of defects in implanted specimens was characterized by coincidence Doppler broadening (CDB), and (iii) variable energy positron annihilation spectroscopy (VEPAS) was used for defect depth profile studies.

The virgin Nb sample exhibits a single component spectrum with lifetime of 128 ps which agree well with the calculated lifetime of free positrons in Nb. It testifies that the concentration of defects in the virgin sample is very low and the sample can be considered as a defect-free material. The sample implanted by H⁺ ions exhibits two additional positron components with lifetimes of 182 and 204 ps. These components come from positrons trapped at new defects created by hydrogen loading. From comparison with theoretical ab-initio theoretical modeling these defects were identified as vacancies surrounded by two and one hydrogen atom. Presence of hydrogen attached to vacancies was confirmed also by CDB investigations. The concentration of hydrogen-induced defects was calculated from the shortening of positron length in positron back-diffusion VEPAS experiment.

Proving the Contact Rules for Phase Regions: Implications to Phase Diagrams of Metal-Hydrogen Systems

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The Palatnik-Landau contact rule for phase regions [1] is the most powerful theorem regarding the topology of phase diagrams of multicomponent systems and of lower-dimensional sections of such diagrams. Particularly, the cross rule [1] and the Rhines rule [2] can be considered as its consequences. At the same time, the Palatnik-Landau rule is rarely lectured at technical colleges and it is seldom used for the analysis of phase diagrams. In our opinion, this is because the proving of this rule in [1] is too lengthy and self-contradictory and the domain of applicability of the rule is indicated incorrectly.

This paper presents a short and rather straightforward proving of the Palatnik-Landau rule and rigorously specifies the types of phase equilibria obeying this rule and also the cross rule and Rhines rule. The types of equilibria thus specified are different from those assumed earlier, and the rules are re-formulated accordingly.

A specific feature of phase diagrams of the metal-hydrogen systems is that at temperatures high enough to establish thermodynamical equilibrium between hydrogen in the metal and in the surrounding gas, this equilibrium strongly depends on the gas pressure. As a result, projections of phase diagrams onto the temperature-concentration plane are often used along with the isobaric sections. The above contact rules are shown to be applicable to such projections, too, in the case of binary Me-H systems, in which the hydrogen content of the metal always increases with increasing gas pressure (this is a typical case).

The above rules, however, are inapplicable for the joints of three boundary lines, which are common elements of two-dimensional phase diagrams and two-dimensional sections of diagrams of a higher dimension. A rule that determines the position of boundary lines with respect to one another in the vicinity of a triple point has earlier been proven for the T-P diagrams of one-component systems only [3]. A new method of proving this rule [4] allowed us to advance its improved formulation. The formulation is independent on the choice of the coordinate axes used to construct the diagram, and the rule becomes applicable to the analysis of two-dimensional sections of phase diagrams of heterogeneous systems with any given number of components. The present paper additionally demonstrates that this rule is also valid in the important case of T-P phase diagrams of binary Me-H systems with the H₂ gas taken in excess.

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Structure and properties of hydrides of γ -U alloys.

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Uranium metal exists in 3 allotropic phases. Orthorhombic α -U stable at room temperature reacts with H₂ at low pressures, forming fine pyrophoric powder of β -UH₃. Its ferromagnetism was one of the first indications that U can form magnetic moments in solid state. Another form, α -UH₃, can be partly present if hydrogenated slowly at low T . Its magnetic properties could not be well established due to the admixture of β -UH₃. *bcc* Uranium exists as the high-temperature phase (γ -U), but can be prepared by quenching of Mo-or Zr-doped U. In the course of the study of superconductivity of such alloys we found that the γ -U alloys do not react with H₂ at 1 bar.

Testing the H absorption at room T and high pressures we found that U-Mo alloys start absorbing at about 5 bar H₂ and the kinetics becomes faster at higher pressures. The obtained hydrides, denoted as UH₃Mo _{x} , is brittle, but does not have a powder form. XRD indicating amorphous structure can be modeled as β -UH₃ structure with grain size around 1 nm. The finding is the increase of the Curie temperature T_C from 165 K in β -UH₃ to 200 K in UH₃Mo_{0.18} is contrasting with generally observed suppression of the $5f$ magnetism in disordered systems.

The atomic radius of Zr is comparable with that of U; we therefore expect occupation of U sites. Indeed, the hydrides formed at high H₂ pressures are crystalline. They form the α -UH₃ structure (the *bcc* U lattice filled with H), which could be thus prepared as a pure phase. $T_C = 170$ -175 K tends to decrease with decreasing x in UH₃Zr _{x} . The almost identical T_C values for α - and β -UH₃ explain why intrinsic ferromagnetism could have been attributed to β -UH₃ admixture.

The results prove that the γ -U alloys should be less sensitive than pure U metal to degradation by H, critical in applications. In the same time it suggests a technique how to produce U-Mo alloys in a powder form (for nuclear fuel pellets), by hydrogenation, milling and H desorption, which is completed between 450-500 °C.

Hydride Initiation Experiments using Spherical Uranium Powders

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The initiation of the reaction of uranium with H₂, a pitting reaction to form UH₃, has long been of interest due to its unpredictability, which is related to the purity of the metal and the hydrogen gas, the nature of the uranium oxide film, and mechanical properties of the uranium. A microscopic UH₃ “blister” forms underneath the oxide film in the vicinity of defects that eventually burst to initiate a pit that undermines the oxide film.[1] Using spherical uranium powder, this hydriding was initiated, as defined by an H₂ pressure decrease, at low pressures (130 Pa) and ambient temperature (19°C) using inert aging followed by ultra-high vacuum (UHV) aging conditions and H₂ purified by filtration through a UH₃ bed. The initiation time was decreased, but never eliminated, by baking the powder under UHV conditions, and these powders yielded predictable initiation times at ambient temperature as a function of the temperature at which they were baked. A pre-hydriding vacuum bake shortened the initiation time, but never reduced it to zero[2]. Compared to a typical U corrosion coupon, this powder has a high specific surface area without corners, back-sides, or metallurgical work. The uranium is cast metal, well annealed due to slow cooling from the melt during the UO₂ reduction process, and the spherical U particles are coated with a coherent oxide film resulting from water exposure during a leaching process to free the powder from its slag. The spherical particles are approximately the size of a UH₃ blister when it breaks, and are too small to have large inclusions to contribute as initiation sites, therefore initiation sites should be limited to defects in the oxide film such as grain boundaries. Scanning electron microscopy (SEM) has shown this powder to be reasonably spherical, with a normal distribution of diameters between 5 μm and 25 μm with 4% of the particles in the 25 μm to 50 μm that appear to be fused smaller particles. The surface of these particles was highly textured. Focused ion beam (FIB) dissection of these particles showed an oxide film that was variable in thickness from 30 nm to 300 nm, fitting the normal range for coherent films on uranium metal. This paper will report on experiments that use this powder to isolate the role of the uranium oxide film in the initiation of the hydriding of uranium.

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The influence of vacuum annealing on the uranium-hydrogen reaction and the progression from nucleation to growth mechanisms

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The constant pressure hydriding kinetics of uranium have been measured previously as a function of temperature for as-polished and vacuum annealed samples [1]. Enhanced hydrogen reactivity was observed for vacuum annealed samples between 65 °C and 120 °C. Earlier work suggests vacuum annealing enhances hydriding kinetics by altering by the microstructure of the bulk metal [2,3]. However, more recent work suggests the enhanced reactivity to be the result of surface modifications elevating the nucleation rate of the hydride phase [1].

This work presents an Arrhenius analysis that demonstrates the progression from nucleation to growth mechanisms. The apparent activation energies (E_a) for nucleation and growth were estimated to be ca 64 kJ mol⁻¹ and 36 kJ mol⁻¹ respectively. The mechanistic transition is evident during reaction for both as-polished and vacuum annealed samples (Figure 1). The transition to growth processes occurs sooner with vacuum annealed samples than as-polished samples an observation consistent with enhanced hydrogen reactivity resulting from elevated nucleation kinetics.

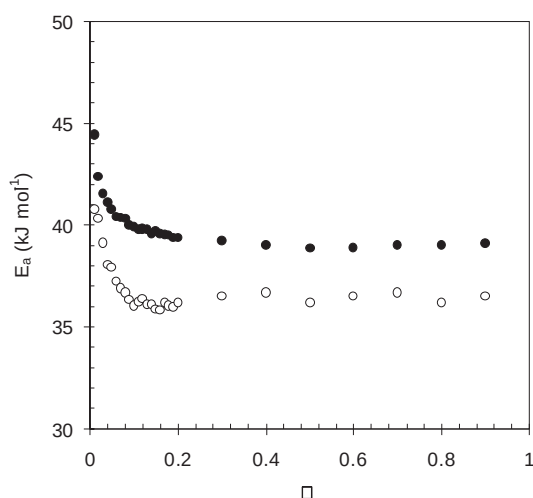


Figure 1. The variation in apparent activation energy as a function of reaction fraction (α) for as-polished (●) and annealed samples (○)

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Engineering Technologies for Fluid Chemical Hydrogen Storage System

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Fluid forms of chemical hydrogen storage materials require a gas/liquid separation between the evolved H_2 gas and the fluid phase that contains the reacted chemical hydrogen storage material. The United Technologies Research Center (UTRC) evaluated the performance of a particular gas/liquid separator (GLS) design over a wide range of temperature, pressure and mass flow rate with a silicone oil as surrogate for the fluid chemical hydrogen storage material and nitrogen gas as surrogate for hydrogen gas. The temperature was shown to have a large effect on the efficiency of the gas/liquid separator, prompting the need to cool down the two-phase mixture before separation. The experimental results show a critical gas flow rate above which the efficiency of the separation drops below 99.99%, as depicted in Figure 1. An optical high-pressure side glass assembly was installed downstream of the GLS in order to measure the droplet size distribution of the liquid that carried over with a laser droplet size analyzer. The difference in droplet size between the results of a Computational Fluid Dynamics (CFD) model and the experimental results was explained by the formation of a liquid film inside the vortex finder of the gas/liquid separator. The results from this project within the Hydrogen Storage Engineering Center of Excellence (HSECoE) contributed to the development of a H_2 storage system for light-duty vehicles that shall meet all 20 U.S. Department of Energy targets simultaneously [1].

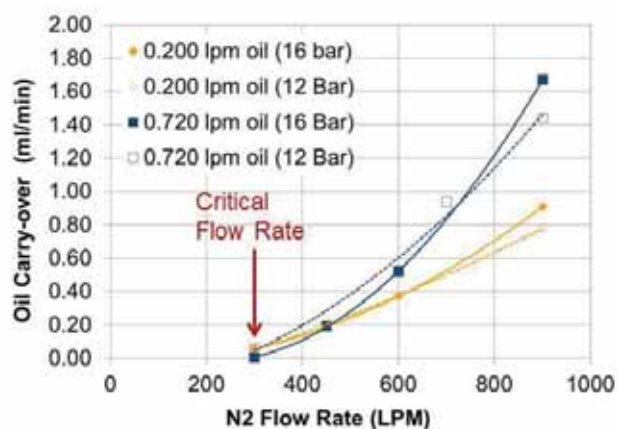


Figure 1. Critical flow rate of high-performance gas/liquid separator at 70°C.

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Reverse Engineering the Chemistry for High Capacity Chemical Hydrogen Storage Solutions

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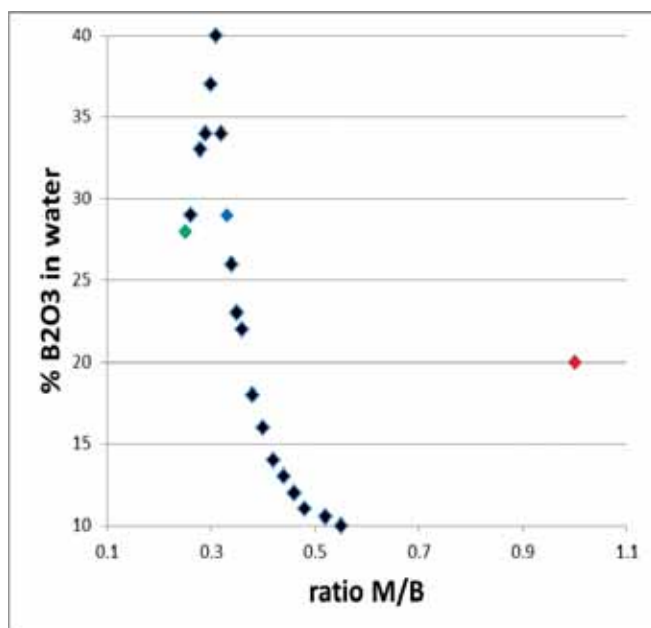
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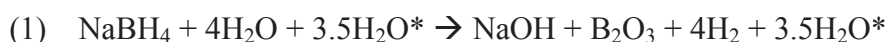
Aqueous solutions of sodium borohydride (SBH) have long been used as liquid phase hydrogen storage carriers for both vehicular and non-vehicular fuel cell applications. One of the limiting factors to practical implementation is the lower solubility of the hydrogen depleted product, sodium metaborate (SMB) limiting the available hydrogen, ca. 4.5 wt% while maintaining a single liquid phase. In this presentation we describe a reverse engineering strategy to increase the load capacity of an aqueous borohydride hydrogen storage material by designing the borohydride fuel carrier based upon the limiting solubility properties of the hydrogen-depleted products.

Figure 1 (data from US Borax library) shows that the solubility of the borate salts, measured as dissolved boron oxides, as a function of the metal to boron ratio (M/B). With a knowledge of which hydrolysis products are more soluble it should be possible to increase the carrying capacity of a liquid borohydride fuel. The goal is to use a borohydride that will yield soluble hydrolysis products. In the figure below we are directed to a borohydride that has a M/B ratio of ca. 0.31 for the maximum solubility. On the other hand, hydrolysis of the octahydrotriborates, (OHB), i.e., $M^{+n}(B_3H_8)_n^{-}$, the



magnesium salt, with M/B ca. 0.167 (♦) and the Na salt, with M/B ca. 0.333 (♦) will lead to the formation of borates that are expected to be more soluble than the borates formed from hydrolysis of SBH, with M/B = 1 (♦). The explanation for the increased solubility is most likely due to the formation of a diverse mixture of borate species, i.e., $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ and $B_5O_6(OH)_4^-$. The polyborate solution maintains a highly supersaturated state for a prolonged time because the local concentration of any one borate anion is relatively low, and precipitation of a mixed polyborate species does not occur. Equations 1 and 2 show the mass balanced

equations with the extra water (H_2O^*) required to maintain a liquid phase solution. Eq 1, SBH provides a net of 4.6 wt% hydrogen while Eq 2, OHB provides a net of 6.5 wt% hydrogen – an increase in performance over SBH while maintaining a single liquid phase.



Ionic Liquid Borohydride - A Liquid Phase Chemical Hydrogen Storage Material

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Aqueous sodium borohydride (NaBH_4) solutions are well known and represent a prospective liquid phase hydrogen carrier. Due to several adverse characteristics of sodium borohydride solutions, e.g. the unsatisfactory stability of the solution, aqueous solutions are not favourable for long term hydrogen storage. Hence in 2007 the U.S. Department of Energy (DOE) recommended a no-go decision for sodium borohydride for on-board automotive hydrogen storage [1]. Nevertheless offer liquid phase chemical hydrides some advantageous qualities compared to solid hydrides or other hydrogen storage technologies. A replacement of the sodium cation with an ionic liquid cation leads to an increased stability of the hydride and to a higher gravimetric hydrogen storage capacity due to an increased solubility of the BH_4^- and the BO_2^- anions [2, 3]. Heterogeneous metal catalysts can be used for the release of hydrogen at room temperature and ambient or elevated pressures. The improvement of the catalyst performance and the long term stability of the catalyst is in development.

The regeneration of the discharged sodium metaborate (BO_2^-) is essential to create a sustainable hydrogen storage material. Concerning the regeneration pure ionic liquid borohydrides offer some beneficial properties compared to aqueous sodium borohydride solutions, for example a larger electrochemical window compared to water. Ongoing research will show if the electrochemical reduction of sodium metaborate in an anhydrous system is realizable. Alternatives to the electrochemical reduction include an ion exchange of ionic liquid metaborate with sodium borohydride, or other recycling approaches originally developed for sodium borohydride.

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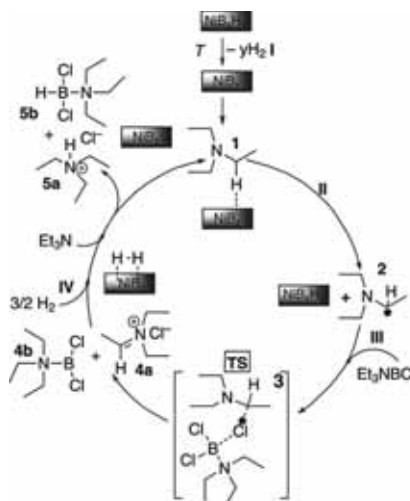
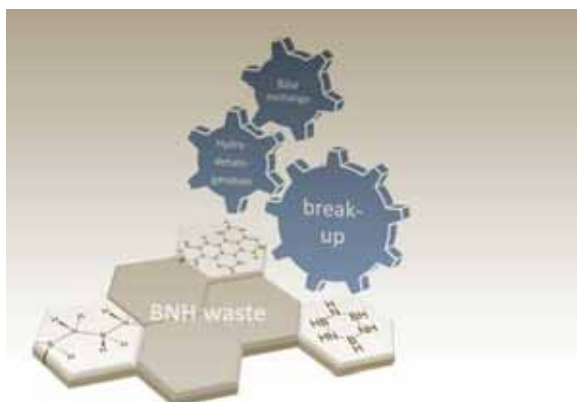
Hydrogen Rich Nickel Boride as Catalyst for the Recycling of Spent Ammonia Borane

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As a useful by-product from the development of a recycling procedure of spent Ammonia borane (AB), with AB being widely regarded as a potential hydrogen source or storage material, a general procedure to convert BN and BNH-polymers via the generation of BCl_3 and its catalytic hydrodechlorination back to hydrogen rich BN compounds was developed [1]. The closed procedure, i.e. a procedure without the formation of waste products, with the perspective of wide applicability to the efficient recycling of chlorinated compounds to non-chlorinated base chemicals utilizing NiB_3H_x catalysts will be presented. In the scheme introduced, amines are employed to make the desired reaction thermodynamically favorable. NiB_3H_x serves as a hydrogenation catalyst resistant to halide anion and amine poisoning. Of many catalysts tested, in solution grown nickelboride nanoparticles showed the best performance. The NiB_3H_x catalysts were characterized via XPS, XRPD, TEM, TPD, and BET measurements. Mechanistic studies with the best performing catalyst were conducted leading to a basic understanding of the underlying reaction mechanism [2].



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Control of Dehydrogenation/Rehydrogenation Reaction of Metal Borohydride-based Composites(Invited)

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Light metal borohydrides such as LiBH_4 , $\text{Mg}(\text{BH}_4)_2$, and $\text{Ca}(\text{BH}_4)_2$ have high hydrogen capacity (9.6 – 14.9 wt.% H_2), but dehydrogenation temperatures are rather high (above 573 K). The sluggish rehydrogenation reaction even at relatively high temperatures and under high hydrogen pressure is another major problem to be solved for practical applications. There have been numerous attempts to solve these problems and they include use of catalytic additives, cation and/or anion exchange, destabilization by mixing with metal hydrides or complex hydrides, size reduction via nano-confinement, and combination of these for further improvement.

Here we present an effective and practical solution by combining destabilization and size confinement effects for further improvement in both the dehydrogenation and rehydrogenation reactions. The eutectic composition between LiBH_4 and $\text{Ca}(\text{BH}_4)_2$, which has a melting point around 470K is infiltrated into chemically inert mesoporous carbon cages with narrow pore size distributions between 3 and 10 nm. It has been confirmed that both the dehydrogenation temperature and the rehydrogenation reaction rate could be significantly enhanced. In addition, both in-situ and ex-situ NMR spectroscopy have been extensively carried out to understand how the composite could infiltrate into mesopores at temperatures even well below the eutectic melting temperature.

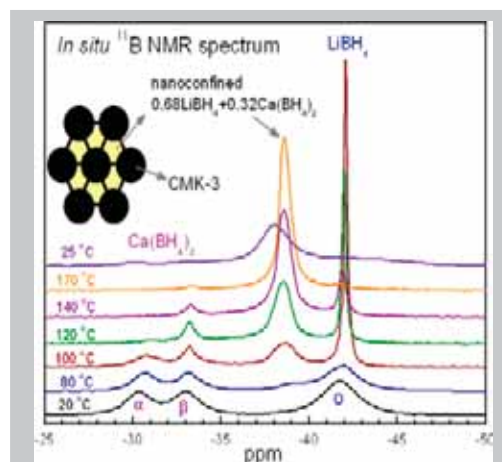


Figure 1. In-situ NMR spectra of $\text{LiBH}_4+\text{Ca}(\text{BH}_4)_2$ with CMK-3.

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New method of synthesis of dead-mass free mixed-cation borohydride materials for hydrogen storage applications

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'Screening by mechanochemistry and diffraction' is a popular scheme for investigation of novel metal borohydride materials [1,2]. Such mechanochemical approach, although fast and efficient, shows also serious drawbacks; the most preminent ones are difficulties with synthesis scalling-up and with purification of the product.

Recently, we have developed a method of synthesis of mixed-cation borohydrides: $M^{(3)}_y[M^{(2)}(BH_4)_z]$, where $M^{(3)}$ and $M^{(2)}$ are metal cations [3,4]. This method overcomes the problems of typical mechanochemical synthetic pathway, leading to "dead mass" free products, also those unachievable with the use of mechanochemistry.

Our approach, *Fig. 1*, is based on solvent-mediated metathetic reaction of the salt containing weakly-coordinating anion, $M^{(3)}[An]$, and a borohydride containing large organic cation, $[Cat]_y[M^{(2)}(BH_4)_z]$ (reaction III). The precursors in this reaction are commercially available (the salts of weakly-coordinating anions), or can be easily prepared via solvent-mediated or mechanochemical reactions, and subsequently purified by solvent extraction (borohydrides containing organic cations), according to the processes I and II (*Figure 1*).

In this contribution we will present the details of the new method as exemplified by numerous hydrogen-rich complex transition metal borohydrides (*e.g.* Zn, Sc, Y) [5].

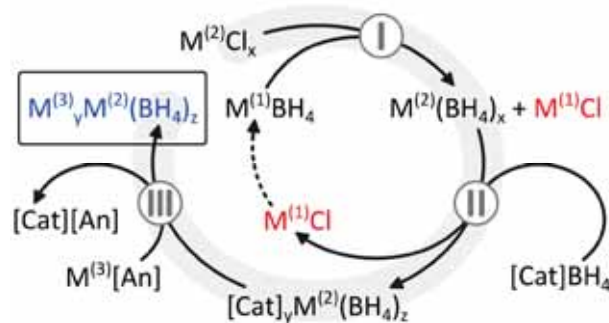


Figure 1. Synthesis of mixed-metal borohydrides, $M^{(3)}_y[M^{(2)}(BH_4)_z]$, $z = x + y$. For mixed-cation borohydrides prepared this way: $M^{(1)} = Li$, $M^{(2)} = Zn, Sc, Y, (...)$, $M^{(3)} = Li - Cs$, $[Cat] = [Bu_4N], [Ph_4N]$, $[An] = [Al\{OC(CF_3)_3\}_4]$ or $[B\{3,5-(CF_3)_2C_6H_3\}_4]$.

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Quantitative spectra-structure relation for borohydrides

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Among the different potential hydrogen storage materials, borohydrides have been largely investigated (see [1] and references therein) because of their high gravimetric and volumetric hydrogen content. In the analysis of borohydrides, vibrational spectroscopy plays an important role since it gives information on the local structure of the BH_4^- ion inside the solid[2], since in several solids the symmetry of the borohydride ion is distorted from the ideal tetrahedral symmetry. Here the GF method, developed by Wilson[3], is used to determine the local symmetry of BH_4^- in solid borohydrides starting from their vibrational spectra. Within this approach, the frequencies were calculated by solving the following secular equation:

$$|GF - I\lambda| = 0$$

where F contains the force constants, G is related with the geometry of the system, I is the identity matrix and λ contains the information about the vibrational frequencies. In contrast to literature approaches where the F matrix is parametrized using a specific type of force field, the initial F matrix is obtained by a DFT calculation on an isolated BH_4^- ion.

Two different cases of deformations of BH_4^- are studied. In the first one, the BH_4^- ion under chemical pressure (in different cubic alkali halides) is considered; in this case, BH_4^- keeps the T_d symmetry, while the bond lengths change according to the pressure.

In the second case, the effects of small angular variations on the vibrational spectra of borohydrides will be taken into account. In particular, starting from the splitting of the bands corresponding to the deformation modes, the angular deformations will be estimated. The practical example of LiBH_4 will be illustrated.

This work is supported by the Swiss National Science Foundation.

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Spectroscopic and Structural Characterization of γ -Mg(BH₄)₂ Thermal Decomposition: Vacuum vs. Hydrogen Atmosphere

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Among the complex metal hydrides, Mg(BH₄)₂ is particularly interesting for both its high H₂ densities (14.9 wt%), favourable thermodynamics, and partial reversibility [1]. Among the different phases, gamma phase shows a permanent porosity (area ~1500 m²/g [2]), expected to strongly facilitate the H₂ abs/desorption kinetics. Although the high number of studies aimed at shading light on the thermal decomposition of Mg(BH₄)₂ [1,2], at present an univocal description of the process with the temperature does not exist. This is mainly due to the lack of specific studies aimed at characterizing possible reaction intermediates. Moreover, decomposition studies have been usually obtained by using heating rates too fast to allow the system to reach the equilibrium conditions. In fact, a preliminary TGA study we performed in vacuum indicates that at $T < 250^\circ\text{C}$, over 10 h are necessary to reach the equilibrium (Figure 1A). Aim of this work is to identify the features characteristics of the decomposition intermediates in equilibrium conditions and the differences in the dehydrogenation process in vacuum and H₂. Furthermore, the importance of the different gas environment (static and dynamic vacuum, H₂ or inert gas flow) has not been properly addressed for γ -Mg(BH₄)₂. For this reason we performed an extensive thermal (microgravimetry), spectroscopic (Far-IR, ATR-IR, UV-Vis-NIR) and XRD study on samples obtained after 10 h isotherms at increasing T (25, 150, 190, 205, 255, 305°C, see Figure 1.B) in dynamic vacuum and H₂ atmosphere (< 500 mbar). This work is performed in the frame of FP7 BOR4STORE project (grant n. 303428).

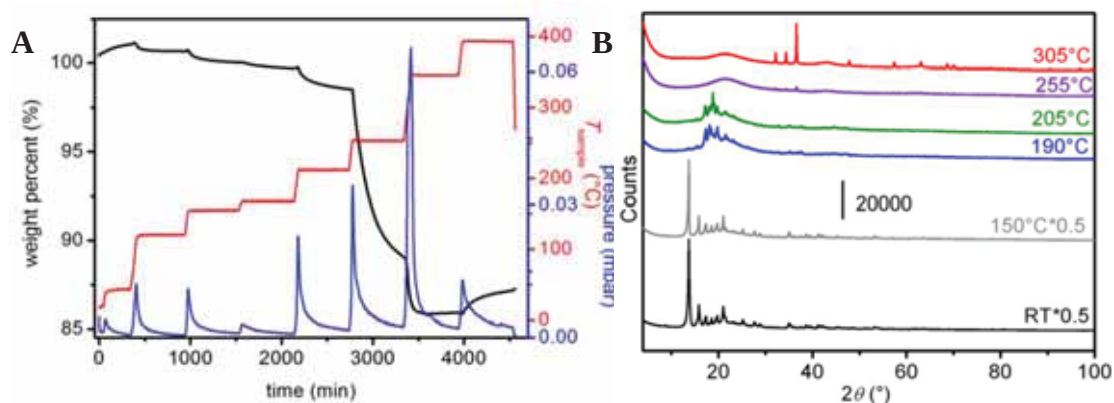


Figure 1. γ -Mg(BH₄)₂ A) TGA curve in vacuum and B) XRD patterns obtained on samples subjected to thermal treatments of 10 h at increasing T in dynamic vacuum.

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Hydride Initiation Experiments using Spherical Uranium Powders

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The initiation of the reaction of uranium with H_2 , a pitting reaction to form UH_3 , has long been of interest due to its unpredictability, which is related to the purity of the metal and the hydrogen gas, the nature of the uranium oxide film, and mechanical properties of the uranium. A microscopic UH_3 “blister” forms underneath the oxide film in the vicinity of defects that eventually burst to initiate a pit that undermines the oxide film.[1] Using spherical uranium powder, this hydriding was initiated, as defined by an H_2 pressure decrease, at low pressures (130 Pa) and ambient temperature (19°C) using inert aging followed by ultra-high vacuum (UHV) aging conditions and H_2 purified by filtration through a UH_3 bed. The initiation time was decreased, but never eliminated, by baking the powder under UHV conditions, and these powders yielded predictable initiation times at ambient temperature as a function of the temperature at which they were baked. A pre-hydriding vacuum bake shortened the initiation time, but never reduced it to zero[2]. Compared to a typical U corrosion coupon, this powder has a high specific surface area without corners, back-sides, or metallurgical work. The uranium is cast metal, well annealed due to slow cooling from the melt during the UO_2 reduction process, and the spherical U particles are coated with a coherent oxide film resulting from water exposure during a leaching process to free the powder from its slag. The spherical particles are approximately the size of a UH_3 blister when it breaks, and are too small to have large inclusions to contribute as initiation sites, therefore initiation sites should be limited to defects in the oxide film such as grain boundaries. Scanning electron microscopy (SEM) has shown this powder to be reasonably spherical, with a normal distribution of diameters between 5 μm and 25 μm with 4% of the particles in the 25 μm to 50 μm that appear to be fused smaller particles. The surface of these particles was highly textured. Focused ion beam (FIB) dissection of these particles showed an oxide film that was variable in thickness from 30 nm to 300 nm, fitting the normal range for coherent films on uranium metal. This paper will report on experiments that use this powder to isolate the role of the uranium oxide film in the initiation of the hydriding of uranium.

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Borohydrides: Stabilizing Light Metal Frameworks

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The metal borohydride systems are of interest due to their potential as hydrogen storage materials, solid state electrolytes in batteries and as novel hydridic frameworks. Crystal structures range from packed predominantly ionic compounds characteristic of e.g. the alkali-metal borohydrides, to 3-dimensional frameworks as well as nano-porous frameworks found amongst the alkaline-earth metal borohydrides. In between there exists a multitude of structures based on different building principles, mostly containing complex anions centered on the more electronegative metal, that are usually counterbalanced by alkali cations. Directional bonding between the alkaline-earth metal cation and the BH_4^- linker has been suggested to be at the origin of more open topologies of the alkaline-earth metal borohydrides. The question whether structural end-members of the more covalent group may form compounds with more ionic members has been only recently addressed in borohydrides [1].

In this presentation we will show on the example of the K-Li-Mg- BH_4 system that binary eutectic melting borohydride systems such as LiBH_4 - $\text{Mg}(\text{BH}_4)_2$, highly interesting from a gravimetric point of view, but not forming stable charge-balanced bimetallic compounds may be stabilised as a substructure by larger counter-cations in trimetallic systems. We will also show the unprecedented flexibility of the Li^+ cation and BH_4^- linker in the Li-Cs- BH_4 system to build various topologies ranging from single chains up to frameworks with 3 types of coordination mode, and connectivity rarely observed among the oxides such as tetrahedral edge sharing (Fig. 1) [2].

Various experimental methods such as *in-situ* synchrotron X-ray and neutron powder diffraction were combined with *ab initio* calculations in the solid state and topological analysis to unravel and explain structural details of increasing complexity. We will also discuss the first application of *in-situ* ball milling to complex hydride systems and show how its high time resolution (5 s) can reveal reaction pathways during mechano-chemical synthesis that are hardly predictable from the post-milled analysis.

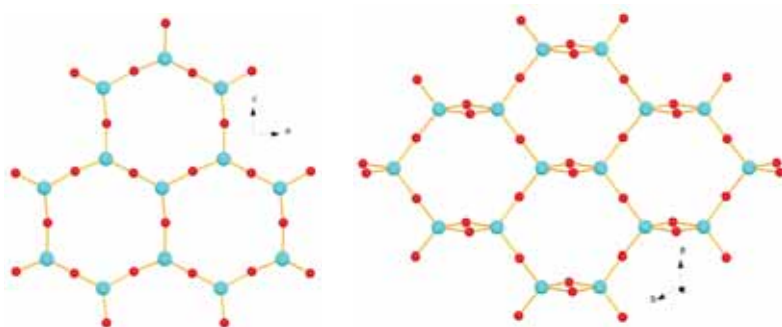


Figure 1. Two versions of a honeycomb sheet built from Li^+ cation and BH_4^- linker as observed in Li-Cs- BH_4 system. Li blue, B red, H omitted for clarity.

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Crystal Structures and Decomposition Properties of Hydrogen-Rich $\text{Al}(\text{BH}_4)_3 \cdot \text{NH}_3\text{BH}_3$ Complex

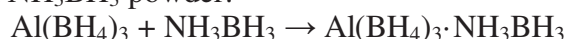
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During the recent years M-B-N-H systems of metal amidoboranes (MABs), ammine metal borohydrides (AMBs), and complexes with ammonia borane NH_3BH_3 (AB) are among the most attractive materials for potential solid-state hydrogen storage [1]. It is worth noting that overall good decomposition properties were reported for most of their Al-containing compounds and composites: $\text{Al}(\text{BH}_4)_3 \cdot n\text{NH}_3$ [2], $\text{Li}_2\text{Al}(\text{BH}_4)_5 \cdot 6\text{NH}_3$ [3], $\text{Li}_2\text{Al}(\text{BH}_4)_5(\text{NH}_3\text{BH}_3)_3 \cdot 6\text{NH}_3$ [4]. The stabilization of $\text{Al}(\text{BH}_4)_3$ hydrogen-rich molecule by formation of new complexes remains challenging for hydrogen storage and novel rocket fuel application as a green bipropellants [5]. Herein we report on the new complex of $\text{Al}(\text{BH}_4)_3 \cdot \text{NH}_3\text{BH}_3$ combining high hydrogen capacity and stabilization of starting aluminum borohydride.

White crystals of $\text{Al}(\text{BH}_4)_3 \cdot \text{NH}_3\text{BH}_3$ were obtained by addition reaction of freshly prepared $\text{Al}(\text{BH}_4)_3$ with NH_3BH_3 powder:



The X-ray single crystal structure determination reveals two polymorphs of the title compound. Both structures are monoclinic: α - $\text{Al}(\text{BH}_4)_3 \cdot \text{NH}_3\text{BH}_3$, space group Cc , $a = 10.8196(8)$, $b = 7.2809(4)$, $c = 11.3260(9)$ Å; $\beta = 107.69(1)^\circ$; β - $\text{Al}(\text{BH}_4)_3 \cdot \text{NH}_3\text{BH}_3$, space group $P2_1/c$, $a = 7.8639(3)$, $b = 6.8692(2)$, $c = 15.7293(11)$ Å, $\beta = 96.407(5)^\circ$ at room temperature. X-ray powder diffraction shows that both polymorphs can be obtained as a single phase. The two polymorphs have molecular structures where Al atom coordinates bidentantly 8 hydrogen atoms from three BH_4^- and one BH_3 groups. $\text{Al}(\text{BH}_4)_3 \cdot \text{NH}_3\text{BH}_3$ molecules are linked by weak bifurcated $\text{NH} \dots \text{HB}$ dihydrogen bonds. According to the variable-temperature *in-situ* powder X-ray diffraction and DSC, the title compound melts at ~ 50 °C. The further heating leads to the first decomposition step at 70 °C with a small mass loss of ~ 5 wt.% followed by a second step at 100 °C with a large mass loss of $\sim 25\%$. ^1H , ^{11}B and ^{27}Al NMR spectroscopy in deuterated toluene demonstrates that the $\text{Al}(\text{BH}_4)_3 \cdot \text{NH}_3\text{BH}_3$ complex is not stable in time at room temperature, yielding the same products in solution and on the first step of thermal decomposition (70 °C) of the solid. More detailed study is on the way aiming to understand the nature of the decomposition products and their reversibility.

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Towards Hydridic Nanoporous Frameworks: the First Imidazolate – Borohydride Compound Li_2ImBH_4 ($\text{Im}=[\text{C}_3\text{H}_3\text{N}_2]^-$)

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During the past decade, the field of complex hydride materials has encountered a huge development. First considered as a pseudo halide, the tetrahydroborate anion showed to have a more complex bonding scheme in many newly discovered structures [1], bonding to metals preferably via its edges. The discovery of a porous polymorph $\gamma\text{-Mg}(\text{BH}_4)_2$ forming a zeolite type framework was a good proof to the hypothesis of the BH_4 group acting as a directional ligand [2]. This new material is the first porous hydride compound reported and has interesting properties in the field of gas adsorption.

One possible strategy to extend the family of porous borohydrides is to use the borohydride ion together with an organic linker to form a hybrid material. Following this strategy, our aim is to synthesize alkali metal borohydride/imidazolate compounds. These are unlikely to be porous, but their formation will demonstrate the feasibility of this approach.

Previously unknown LiIm (synthesized for the first time in our lab, unpublished results) reacts with LiBH_4 forming Li_2ImBH_4 either by milling with small amounts of solvent (dimethyl sulfide or diethyl ether) or by heat treatment at 100°C . However, complete reaction has not been achieved yet. The highest conversion is around 75%. Solvent mediated reaction between BuLi , $\text{Me}_2\text{S}\cdot\text{BH}_3$ and ImH also yields the target compound together with unknown solid, indicating that liquid synthesis can also be a way to obtain such hybrid materials. Crystal structure was solved from synchrotron radiation powder diffraction data. Li_2ImBH_4 crystallizes in an orthorhombic unit cell with the *Imma* space group. The cell parameters are $a = 6.0005 \text{ \AA}$, $b = 14.9994 \text{ \AA}$ and $c = 6.4832 \text{ \AA}$. The imidazolate anion is coordinated to four lithium atoms, two per N, in an unusual manner, situated above and below the plane of the aromatic ring. The Li-N distance is $2.085 \text{ \AA}$. The BH_4 group coordinates to 4 Li in a square planar environment. The Li cation has two imidazolate and two BH_4 groups in a deformed tetrahedral coordination sphere. Neutron diffraction on a $^{11}\text{B}/^2\text{D}$ enriched sample will be performed to determine the orientation of the borohydride group.

This study shows that we obtained for the first time a hydrid hydride, combining complex hydride anion along with a classical anionic bridging ligand, such as imidazolate. The two synthetic approaches, in solid state and in solution, open a way to the series of potentially porous compounds, involving alkali and alkali earth metals.

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Mechanistic Studies of the Reversible Hydrogenation of Boranes to Borohydrides under Moderate Conditions - Invited

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Magnesium borohydride, $\text{Mg}(\text{BH}_4)_2$ is of interest as a potential hydrogen storage material, having among the highest hydrogen capacity and lowest enthalpy of dehydrogenation of the Group I and II borohydrides. The 11.2 wt% hydrogen that can be cycled through reversible dehydrogenation of $\text{Mg}(\text{BH}_4)_2$ to MgB_2 stands as the highest hydrogen storage capacity that has been experimentally demonstrated for any material that can be **directly** hydrogenated.[1] However, this cycling requires forcing conditions (dehydrogenation $>400^\circ\text{C}$; re-hydrogenation 400°C , 900 atm H_2). Studies conducted at more moderate conditions have revealed that the dehydrogenation of $\text{Mg}(\text{BH}_4)_2$ at lower temperature (200°C) results in the selective formation of $\text{Mg}(\text{B}_3\text{H}_8)_2$ and that rehydrogenation under moderate conditions result in the regeneration of $\text{Mg}(\text{BH}_4)_2$ without formation of $\text{MgB}_{12}\text{H}_{12}$. [2] In order to study the hydrogenation reaction in greater detail, we have prepared $\text{Mg}(\text{B}_3\text{H}_8)_2$ through an independent synthesis. We have found that hydrogenation of mixtures of the triborane and MgH_2 can be achieved at conditions as mild as 100°C and 40 atm H_2 . However, hydrogenation in the absence of MgH_2 or an alternative hydride source results in disproportionation to a mixture of $\text{MgB}_{12}\text{H}_{12}$, $\text{MgB}_{10}\text{H}_{10}$, $\text{Mg}(\text{BH}_4)_2$ and open cage polyboranes. We have also conducted DCS studies of the hydrogenation reactions. These studies have revealed that pronounced changes in the activation energy required to produce $[\text{BH}_4]^-$ occur upon replacing MgH_2 with other metal hydrides. We have also found that the hydrogenation reaction in the presence of NaH follows a different path involving two distinct exothermic steps. Our results confirm that the hydrogenation to $[\text{BH}_4]^-$ becomes increasingly favorable and selective as hydride stability decreases and indicate that $\text{MgB}_{12}\text{H}_{12}$ formation is prevented if the metal hydride intercepts intermediates at the reaction temperature. Finally, we have found that a modification of the reaction conditions that allows hydrogen cycling between $\text{Mg}(\text{BH}_4)_2$ and $\text{Mg}(\text{B}_{10}\text{H}_{10})$ thus increasing the hydrogen storage capacity from 2.7 to >7 wt %.

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Octahydrotriborates (B_3H_8^-): Synthesis and Hydrogen Storage---- invited

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Boranes (represented by NH_3BH_3) and borohydrides (represented by NaBH_4 and $\text{Mg}(\text{BH}_4)_2$) have been intensively studied for hydrogen storage because of their high hydrogen content.¹ Either pyrolysis or hydrolysis has been performed to extract the hydrogen from these compounds depending on many factors such as thermodynamics, kinetics, and spent fuel recovery. All these compounds have problems that prevent their practical use as hydrogen carriers. For example, pyrolysis of NH_3BH_3 produces undesirable volatiles, and its regeneration is very challenging. Hydrolysis of NaBH_4 needs a strong caustic additive to stabilize the solution, and the capacity is severely limited by the poor solubility of NaBH_4 and its hydrolytic product in water.

There is a great need to expand the search for new compounds. It is quite logical to examine compounds with a B-H bond, since such compounds have shown facile H_2 formation, as evidenced by many boranes and borohydrides. Researchers have looked at $\text{AlB}_4\text{H}_{11}$, $\text{NH}_3\text{B}_3\text{H}_7$, and NH_4BH_4 , which have high hydrogen content, but unfortunately, lack facile syntheses. Simple boranes such as B_2H_6 , B_3H_7 , and B_4H_{10} have high hydrogen content, but they are often highly volatile and flare up violently upon contact with air. The simplest anion, BH_4^- , has been intensively studied, we therefore turn our attention to another BH condensation up, octahydrotriborate (B_3H_8^-), which retains high hydrogen capacity.

We have successfully developed facile synthesis to several octahydrotriborates. In this talk, we will report recent developments in the synthesis of these compounds, including NaB_3H_8 , $\text{NH}_4\text{B}_3\text{H}_8$, $(\text{NH}_3)_2\text{BH}_2\text{B}_3\text{H}_8$, and $(\text{NH}_2)_4\text{CB}_3\text{H}_8$, as well as their thermal decomposition properties and hydrolytic performances. Their interesting hydrolytic performance and rather complicated decomposition performance, in contrast to borohydrides, are likely caused by the difference in structure between BH_4^- and B_3H_8^- (Figure 1).

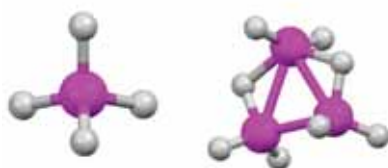


Figure 1. Schematic of BH_4^- (left) and B_3H_8^- (right). B: pink and H: light grey.

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A series of novel metal borohydride ammoniates

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Metal borohydride ammoniates, $M(BH_4)_m \cdot nNH_3$, have potential as hydrogen storage materials owing to their low temperature for hydrogen release and high hydrogen content. Here, we present synthesis of a range of novel solvent- and chloride-free metal borohydride ammoniates with tunable NH_3 content, i.e. tunable properties.

$Mn(BH_4)_2 \cdot nNH_3$ ($n = 1, 2, 3, 6$) and $Li_2Mn(BH_4)_4 \cdot 6NH_3$ have been prepared and the crystal structures for the four later are solved from synchrotron powder X-ray diffraction data. The coordination environment of Mn^{2+} changes from octahedral, to bipyrimidal to tetrahedral for $Mn(BH_4)_2 \cdot 6NH_3$, $Mn(BH_4)_2 \cdot 3NH_3$ and $Mn(BH_4)_2 \cdot 2NH_3$, respectively. Hydrogen release via dihydrogen elimination from the interaction between partly positive hydrogen, $H^{\delta+}$, from NH_3 and partly negative hydrogen, $H^{\delta-}$, from BH_4^- take place for $Mn(BH_4)_2 \cdot nNH_3$ ($n = 1, 2$), while NH_3 is released for $n > 2$.

The rare earth metal borohydrides, $Re(BH_4)_2$ ($Re = Y, Dy, Gd$) are known to be isostructural [1]. However, while Y and Gd form a series of metal borohydride ammoniates, i.e. $Y(BH_4)_3 \cdot nNH_3$ ($n = 7, 6, 5, 4$) and $Gd(BH_4)_3 \cdot nNH_3$ ($n = 6, 5, 4$), Dy only forms $Dy(BH_4)_3 \cdot 4NH_3$. Crystal structures have been solved for $Re(BH_4)_3 \cdot nNH_3$ ($n = 6, 5, 4$), while the crystal structure for $Y(BH_4)_3 \cdot 4NH_3$ is known [2].

Destabilization is observed for metal borohydrides with low electronegativity, while metal borohydrides with high electronegativity are stabilized by NH_3 , see Figure 1 [3].

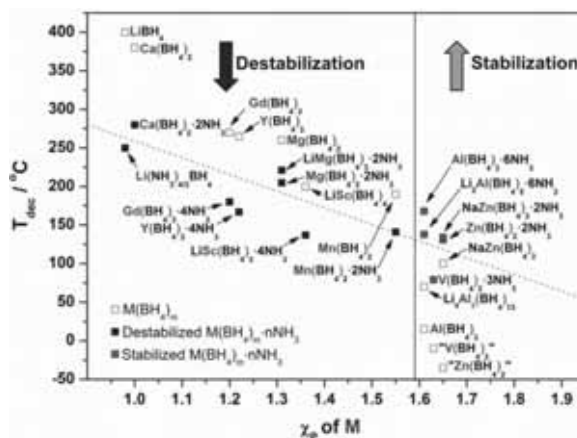


Figure 1 A correlation is discovered between decomposition temperatures, T_{dec} , for metal borohydride ammoniates and the electronegativity, χ_p , of the metal [3].

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Thermal decomposition of a $\text{NaZn}_2(\text{BH}_4)_5 + \text{MgH}_2$ composite

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Borohydride compounds have promising gravimetric hydrogen storage densities (up to 18 wt.%), however, they either have high decomposition temperatures with the release of hydrogen or low decomposition temperatures with the release of both hydrogen and diborane[1]. Previous studies into $\text{Zn}(\text{BH}_4)_2\text{-MgH}_2$ placed a layer of MgH_x ($x=0$ or 2) over the milling products of $\text{ZnCl}_2 + 2\text{NaBH}_4$ (molar ratio of MgH_2 to ' $\text{Zn}(\text{BH}_4)_2$ ' of around 15:1)[2]. This approach was shown to prevent the evolution of B_2H_6 .

In this work ZnCl_2 , 2NaBH_4 and $x\text{MgH}_2$ were ball-milled under Ar to form: $\text{NaZn}_2(\text{BH}_4)_2$, $\text{NaCl}_{0.9}(\text{BH}_4)_{0.1}$, MgH_2 and Na_2ZnCl_4 . Exothermic decomposition was observed between 80 and 125 °C with the evolution of H_2 and trace amounts of diborane totaling a mass loss of 8.5 wt.%. Upon heating to 200 °C, XRD reflections attributed to the decomposition products of $\text{NaZn}_2(\text{BH}_4)_2$ are observed along with $\text{Mg}(\text{BH}_4)_2$ and $\text{Na}(\text{B}_{12}\text{H}_{12})$ and a second unknown phase(s). Raman spectroscopy confirms the presence of $[\text{B}_{12}\text{H}_{12}]^{2-}$ [3] attributed to $\text{Na}_2\text{B}_{12}\text{H}_{12}$. A further two releases of H_2 were observed between 270 and 370 °C, with a mass loss of 1.5 wt.%, resulting from the decomposition of $\text{Mg}(\text{BH}_4)_2$. Substitution of NaBH_4 for NaBD_4 revealed that H_2 (from MgH_2) is only released between 80 and 110 °C, with all other gas evolution due to D_2 , indicating that B_2D_6 reacts with MgH_2 to form $\text{Mg}(\text{BD}_4)_2$.

Reversibility is unlikely due to the formation of zinc from $\text{NaZn}_2(\text{BH}_4)_5$ and the migration of boron to potentially form magnesium compounds. However, 8.5 wt.% hydrogen is evolved after heating to 125 °C, with only trace diborane.

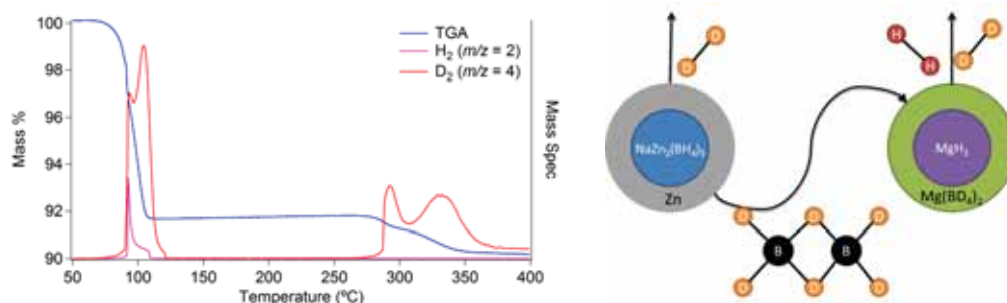


Figure 1a. TGA-MS plot for ball-milled (1 h) $4\text{NaBH}_4+2\text{ZnCl}+\text{MgH}_2$, heated at 2°Cmin^{-1} in flowing Ar (0.5 barg, 40 mlmin^{-1}) **1b.** reaction schematic of B_2D_2 released from $\text{NaZn}_2(\text{BH}_4)_5$ reacting with MgH_2 to release H_2 and D_2 with the formation of $\text{Mg}(\text{BH}_4)_2$

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Hydrogen storage in Ammine metal borohydrides (Invited)

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Owing to the high theoretical H content and low dehydrogenation temperature, ammine metal borohydrides (AMBs) have attracted extensive interests as one of most potential hydrogen storage materials. The traditional method of forming the ammine metal borohydrides is to react metal borohydrides with stoichiometric ammonia, such as $\text{LiBH}_4 \cdot \text{NH}_3$ [1], $\text{Al}(\text{BH}_4)_3 \cdot 6\text{NH}_3$ [2], $\text{Mg}(\text{BH}_4)_2 \cdot 2\text{NH}_3$ [3] and so forth. This method requires obtaining the metal borohydride starting substance, which clearly limits the formation of most of the ammine transition metal borohydrides due to the difficulties in obtaining these unstable transition metal borohydrides. To overcome this problem, a solid-phase ion exchange approach was developed to synthesize a series of new mono-/mixed-metallic AMBs by reacting LiBH_4 and $\text{MCl}_x \cdot n\text{NH}_3$ with various mole ratios, which provides a facile solution to accurately modifying the ratio of NH_3/BH_4 units towards a balanced number of dihydrogen groups, resulting in accelerated hydrogen evolution and depressed emission of ammonia. Meanwhile, by using the high-resolution synchrotron X-ray diffraction, we have successfully determined the structure of these new AMBs.

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Reactivity of the Different Magnesium Borohydride Polymorphs

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Magnesium borohydride is one of the very promising candidates for hydrogen storage. With its 14.9 wt% hydrogen content that can even store additional 3 wt% H₂ at low temperature under its porous form γ , Mg(BH₄)₂ attracts a particular interest in the research field [1]. Different additives or hydrogen content compounds were tested with Mg(BH₄)₂ to enhance its properties as upon temperature decomposition [2-4]. Recently nanoconfined eutectic LiBH₄-Mg(BH₄)₂, reported as amorphous, revealed a possibly different behavior upon decomposition such as the suppression of [B₁₂H₁₂]²⁻ species suggesting a possible reversibility of the process [4]. However, the multiple polymorphs of Mg(BH₄)₂ add a complexity to all these studies. For example, the compression of α -Mg(BH₄)₂ in a diamond anvil cell leads directly to the highly dense δ -Mg(BH₄)₂ phase whereas the compression of γ -Mg(BH₄)₂ passed by an amorphous state before its recrystallization into the δ -Mg(BH₄)₂. Moreover, different pathways upon temperature decomposition are observed depending on the starting polymorphs which is another proof that the reactivity and the behavior of the Mg(BH₄)₂ are strongly correlated with the starting polymorph [5].

The reactivity and the behavior of different polymorphs including the pressure-collapsed amorphous phase of Mg(BH₄)₂ were studied by X-ray diffraction under different conditions such as under compression and ball milling. The porous phase is the most reactive polymorph compared to the amorphous one and its crystalline quality is critical to enable reproducible synthesis of the derived compounds.

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Additives in magnesium borohydride: local structure and effect on reversibility

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Magnesium borohydride is a particularly interesting material for hydrogen storage due to its light weight and 14.9 wt% of hydrogen. Up to about 4 wt% have been found to desorb reversibly below 300°C and at a moderate pressure [1]. For rehydrogenation of the completely dehydrogenated material, however, much harsher conditions are needed [2]. In order to improve hydrogen sorption performance of $\text{Mg}(\text{BH}_4)_2$, a wide range of approaches are explored, including high energy reactive ball-milling, preparation of composite materials, dispersion in porous matrix, and addition of catalysts [3].

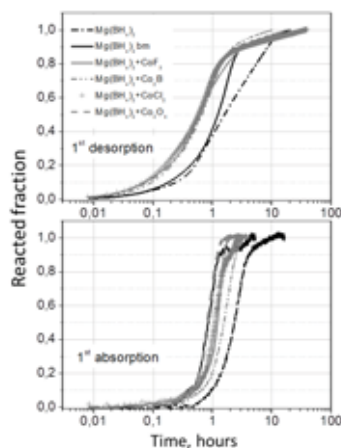


Figure 1. Desorption and absorption isotherms for $\text{Mg}(\text{BH}_4)_2$ as such, ball-milled (bm), and ball-milled with additives

the local state of metal atoms and the additives composition upon cycling.

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Study on the effects of repeated hydriding and dehydriding reactions on compacted ball milled Mg-based powders

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Widespread diffusion of hydrogen driven technologies is hindered by hydrogen storage step. Problems related to liquid and compressed hydrogen have not been overcome, in particular it is necessary to store hydrogen in a cheap and safe method.

Different types of materials have been studied for hydrogen storage. Even if some materials are able to store high quantities of hydrogen, the reversibility of the reaction of these materials with hydrogen is not always achievable. In the case of magnesium hydride (MgH₂) it is possible to store about 7.6 wt% of hydrogen and hydriding and dehydriding reactions are completely reversible. In order to make these kinetics faster, ball milling have been largely used. This process introduce defects in the microstructure and it causes a reduction of the particles and crystallite size which enhance hydrogen mobility. If a catalyst is added to the powders during ball milling it could be heterogeneously distributed in the particles of hydride enhancing nucleation of metallic or hydride phase [1].

The powders, in particular of hydrides, revealed to have low thermal conductivity and they tend to pack reducing the diffusivity of hydrogen. This drawback causes that, when powders are used in tanks (commonly with cylindrical shape), there are some volumes of powders where the reaction with hydrogen is not taking place. For these reasons the powders are compacted and materials with high thermal conductivity is used as a sort of binder [2].

In this work we compacted ball milled powders of MgH₂, niobia (Nb₂O₅) and expanded natural graphite (ENG) which has been used in order to increase the stability of the pellets and their thermal conductivity. The powders have been ball milled under argon in a SPEX 8000 grinder and they have been compacted at different pressures by an uniaxial press. The as-prepared pellets have been processed in a volumetric Sievert's type apparatus by repeated hydriding and dehydriding at 310°C and 8 and 1.2 bar respectively. The mechanical stability of the pellets revealed to be correlated to the compaction pressure while kinetics remained unaltered. The effect of the pressure on the distribution of ENG is reported. Surface and microstructural modification of the pellets due to cycling are discussed by the aim of Scanning Electron Microscopy and X-Ray diffraction.

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Tank Design Challenges and Optimization for Metal Hydride Based Hydrogen Storage

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Metal hydride based hydrogen storage is an interdisciplinary activity that benefits from the interaction of the fields of engineering and materials science. Thus, the challenges involved in the design of efficient and compact tanks can be best addressed. These challenges include management of the thermal energy involved in the hydrogen ab- and desorption, kinetics optimization (1), control strategy of the hydrogen sorption (2), as well as cost minimization of the total system, which includes not only a lean tank design but also the creation of cost-efficient storage material synthesis routes.

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Modelling around the design of a hydride hydrogen tank for heavy applications

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Hydrogen tanks based on metallic hydrides have shown efficient for storing hydrogen reversibly within reasonable temperature and pressure conditions (less than 30 bars and less than 70°C for instance). Even though car application remains unreachable with this technology, owing to the fact that the mass capacity of metallic hydrides is too low, some niche applications are making sense, like heavy vehicles as agricultural tractors or forklifts, or like maritime applications as submarines or boats.

The tanks developed for these kinds of applications have to be fast filled, with the smallest added volume and mass of the component system as regard to the hydride material volume and mass. Modelling is an efficient tool to optimize the design of the tank, and particularly the heat exchanger integrating the hydride powder material. In the past, many studies on modelling have been published in order to simulate the behaviour of an existing hydride tank. In this work, the modelling is done in order to dimension the geometry of the heat exchanger, and the methodology adopted for this is presented. The manufacture and test of the prototype is then shown, and it is checked that the simulation fits with the obtained measured performance of the manufactured hydride tank (2 kg of hydrogen stored in a TiFeMn hydride).

**Measure of the hydride breathing
while cyclically absorbing and desorbing hydrogen**

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When a hydride material absorbs hydrogen, the phase change occurring is accompanied by a volume change of the material. Very often, the material is of granular nature, and we finally end up with a powder material swelling and shrinking – which is referred to as the hydride breathing – in a close container.

Due to this breathing, and depending on the material apparent density and granulometry, severe mechanical stresses can appear and threatened the mechanical integrity of the container.

In the present work, an original method for measuring the stresses is presented. It combines the measure of a force transducer and a deformation field by image correlation.

Some experiments have been conducted on a metallic hydride type. They show that some configuration can lead to quite strong stresses. Particularly, the influence of the first absorption, namely the activation, is shown to be playing an important role concerning the maximum level of stress created.

High-Resolution In-Operando Neutron Radiography and Tomography of Hydride-Graphite Composites

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The design of hydride-based hydrogen storage systems is still challenging because of the complex interactions between kinetics, thermodynamics, heat and mass transfer and swelling/shrinkage of the hydride bed during (de-) hydrogenation. In-operando characterization of such systems is crucial to understand the tank behavior and to improve the performance. The most common methods to test hydride tank systems are pressure, local temperature as well as integral caloric and hydrogen mass flow measurements. However, these measurements are not suitable to determine the temporal-spatial resolution of the hydrogen density and of the structure of the hydrogen storage material.

In this contribution, we report on high-resolution neutron imaging of hydride-graphite composites (MHC) with up to 6.4 μm pixel size [1,2]. For the first time in-operando radiography during (de-) hydrogenation and tomography of stationary states will be shown for a composite of a AB_2 -type hydride and graphite. Such MHCs are advantageous due to their improved volumetric storage density and thermal properties [3]. This method allows real-time spatial resolution of the hydrogen density (reaction fronts) and of macro- and microscopic structural changes of the material during cycling.

During the first 45 cycles after the activation procedure, the MHC increase their total H_2 capacity. This capacity increase can be explained by locally hydrogenated clusters inside the MHCs which grow in size and/or number with increasing cycle number. These active clusters are randomly distributed over the MHCs. After activation and under fast (de-) hydrogenation conditions, reaction fronts were observed starting from the temperature-controlled tank wall. Throughout repeated cycling the MHC expand in volume, which is associated with the formation of radially orientated cracks in the upper part of the MHC (cf. Fig. 1). The implications of these finding of the placement of MHCs and the respective tank design are discussed.



Figure 1: High-resolution neutron radiography of cycled hydride-graphite-composites.

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Neutron studies of hydrogen adsorption in porous materials

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Adsorption of molecules in functionalized and high surface area microporous materials is of technological importance in a multitude of areas ranging from catalysis, drug delivery, chemical separations and energy storage to personal care products. Over the past several years we have focused our research efforts on understanding the properties of metal-organic frameworks (MOFs) for storage and separations of industrially important small molecules including hydrogen. The properties of metal-organic frameworks can be tuned to optimize electrostatic interactions by exposing open metal cation sites, such as in $M_2(\text{dobdc})$ (dobdc^{4-} = 2,5-dioxido-1,4-benzenedicarboxylate, $M=\text{Mg, Mn, Co, Fe, Ni, Zn, Cu}$) or $M_3\text{BTT}_2$ (BTT =1,3,5-benzene-tristetrazole, $M = \text{Mn, Cu, Fe}$). We will explore the details of materials that favor these interactions, through laboratory-based measurements through neutron diffraction, neutron inelastic scattering and diffusional behavior of hydrogen determined by quasi-elastic scattering.

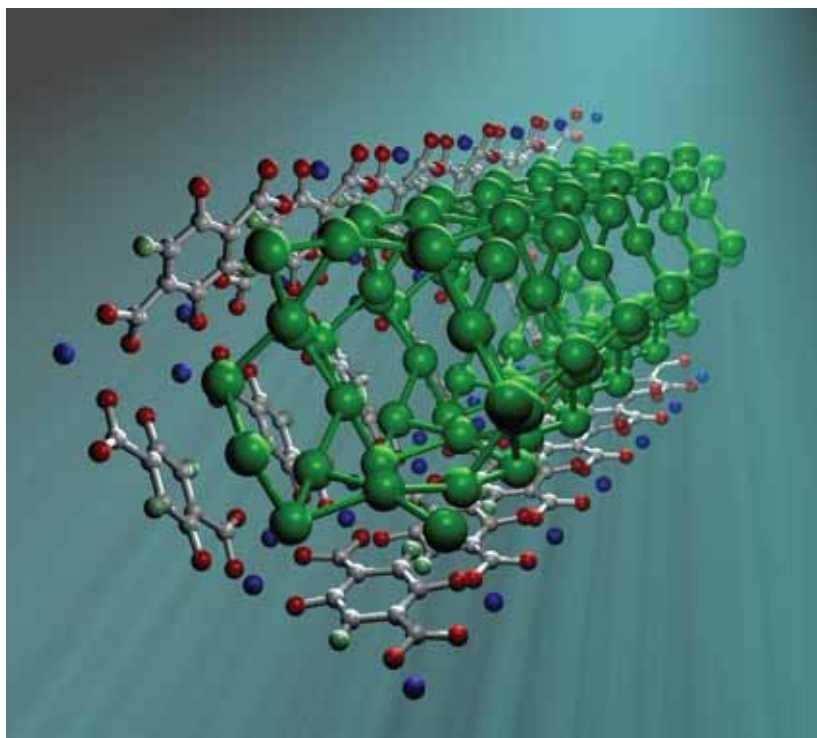


Figure detailing the close packing of hydrogen (green) adsorbed in the pore of a metal-organic framework.

High throughput Inelastic Neutron Scattering, from fiction to reality

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INS is a technique that is ideally suited to study hydrogen-containing materials due to the high cross section of hydrogen¹; it is also the case that INS spectra are straightforward to model². INS has been historically applied to the studies of metal hydrides since the mid 50s and it has been very successful in answering a number of questions in the field^{3,4}.

In this paper I will introduce the VISION spectrometer at the SNS in ORNL. Located at the Spallation Neutron Source (SNS) Oak Ridge National Laboratory in Tennessee, USA, the VISION spectrometer is the world's only high throughput, high resolution broadband INS spectrometer. With access to energy transfer range from -3 meV to 1000 meV a resolution $\Delta\omega/\omega \sim 1.5\%$ above 2 meV, the resolution at the elastic line is 150 μeV FWHM. One of the main barriers to the use of INS was long time required for data collection and large samples. Thanks to the optimization in the design, the use of the most advanced neutron optics available at the present moment and the brightest spallation neutron source in the world, VISION has already measured INS spectra, of publication quality in 200 sec or less⁵.

At the moment we are in the process of procuring a newly designed sample changer that will allow the exploitation of the high throughput capability and we will establish a mail-in program during fall 2014.

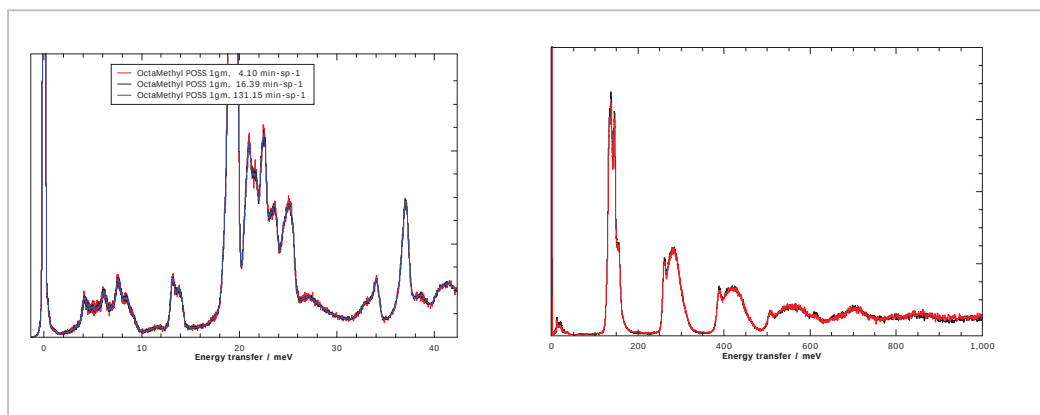


Figure 1. Left panel: the INS of Octamethyl-POSS Nanoparticles collected 4 mins (black) 16 mins blue 120 mins (blue). Right panel: The INS of ZrH_2 .

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Mechanochemical synthesis of hydrides followed *in situ* by X-ray diffraction

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Mechanochemistry is considered as “green” alternative to traditional wet chemistry synthetic methods, because it does not require the use of a solvent, which often causes a risk for the environment. It is a widespread way of synthesizing materials in various fields: from compact alloys to porous metal-organic frameworks (MOFs) and purely organic compounds [1-3]. Despite being a very attractive technique, the intermediate steps of the chemical reactions occurring over the milling process remain badly understood [1,2]. The combination of ball-mill synthesis with X-ray powder diffraction (XRPD) monitoring provides series of diffraction patterns collected at different times of the reaction with the time resolution of few seconds. These data help revealing the reaction pathways in the synthesis of various materials, allowing for the identification of possible intermediates. A very recent methodological development, published in 2013 [4,5], allows this real-time study of mechanochemical transformations without interruption of the milling process by means of *in situ* diffraction.

We used and tested the system for the synthesis and characterization of novel hydrides, with the setup available at the high energy beamline ID15 of the ESRF. Many aspects of the milling were tested, such centering of the X-ray beam, milling frequency, solvent assisted grinding. Remarkably, the current setup employing plastic milling jars is suitable to study reaction where gases are released. The XRPD data collected at the ID15 allow to identify known crystalline phases and to follow the phase transition, but they are not of a sufficient resolution for *ab initio* structure solution of novel phases. A different milling jars and lower energies should allow for data suitable for structure solution. We will present the methodology and will show the first results obtained on hydride systems.

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Diffraction Profile Broadening Owing To Vacancies In LaNi_5 : Simulations And In-Situ Neutron Diffraction

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Hysteresis theories are sometimes based on dislocations being the cause of hysteresis. However, Buckley et al [1] showed that after annealing a hydrogen cycled LaNi_5 sample at 200°C , most of the hysteresis present in the initial cycle was restored, as well as the hydrogen capacity of the initial cycle. The hydrogen capacity and pressure hysteresis are greater on the initial cycle. This temperature (200°C) is below the temperature at which dislocations are known to anneal [2]. Sakaki et al [3] used positron annihilation spectroscopy to show that there was a high vacancy density in hydrogen cycled LaNi_5 , which annealed at lower temperatures to dislocations. Therefore better understanding of vacancies in hydrogen cycled LaNi_5 is needed.

Krivoglaz et al [4] states that vacancies are first class defects, which do not cause a broadening of diffraction peak profiles, only a small shift in lattice parameter. However, computer simulations were performed on a simulated particle, which show that high vacancy densities do cause a broadening of the diffraction peak. An *in-situ* neutron diffraction experiment on LaNi_5 was carried out using the High Resolution Powder diffractometer for Thermal neutrons (HRPT) at the Paul Scherrer Institut (PSI), Switzerland. Annealing LaNi_5 under vacuum *in-situ* showed that as low as 200°C there was a decrease in diffraction peak breadth (figure 1). Since this is well below the annealing temperature for dislocations, this may be owing to annealing of vacancies. Therefore in this sample, vacancies are behaving as second class defects.

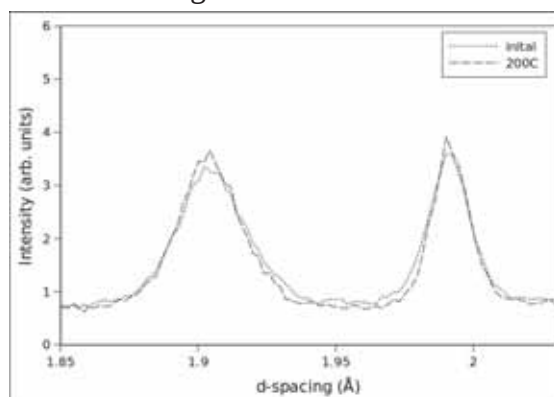


Figure 1. Shows the style to be used for graphs.

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Tailoring the hydrogen de-sorption thermodynamics of VH_2 by various alloying additives

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Abstract

Vanadium and its alloys could be a candidate materials for on board hydrogen storage application because of their high gravimetric hydrogen storage capacity (~ 3.8 mass %) which is even higher than AB_5 , AB_2 and AB intermetallics. Hydrogen de-sorption from VH_2 is a two step process: (1) $\text{VH}_2(\gamma)_{(s)} \leftrightarrow \frac{1}{2} \text{V}_2\text{H}(\beta)_{(s)} + \frac{1}{2} \text{H}_2$ and (2) $\text{V}_2\text{H}(\beta)_{(s)} \leftrightarrow 2\text{V}_{(s)} + \frac{1}{2} \text{H}_2(g)$. The hydrogen de-sorption from the first step takes place at an ambient temperature and pressure conditions. However, hydrogen de-sorption from the second step requires high temperature ($> 470\text{K}$). As a consequent only half of the total hydrogen storage capacity of vanadium hydride is available on subsequent ab-de-sorption cycle.

The cyclic hydrogen storage capacity of VH_2 could be enhanced by tailoring the thermodynamics and kinetics of hydrogen desorption reaction by alloying components. In the present investigation, the changes in equilibrium plateau pressure of first step of the hydrogen sorption reaction and changes in thermodynamics of second step of the hydrogen sorption reaction with respect to the alloying elements such as Ti, Zr, Nb, Mo and Cr have been studied.

The results showed that the plateau pressure of first step reaction is a function of atomic size, electronegativity and work function of the alloying components. However, the thermodynamics of second step of the hydrogen desorption process changes systematically with the alloying components. In few cases, the desorption peak of V_2H was completely disappeared. This could be due to either modification of thermodynamics or change in hydrogen de-sorption kinetics.

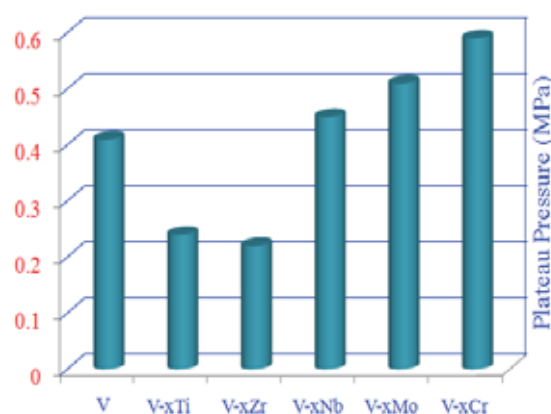


Fig 1 Variation of Plateau pressure of VH_2 phase with respect to alloying elements at 318K: x stands for 5M.

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Effect of Solid Solution Hardening by Interstitial Elements on Hydrogenation Properties of Vanadium Based BCC Alloys

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Cyclic durability is one of the most important properties for hydrogen storage materials. Although vanadium based bcc alloys have higher hydrogen weight density, the reduction of hydrogen storage capacity during cycling becomes significant with decreasing vanadium content. Our previous work showed that the cyclic durability is degraded by the accumulation of lattice defects in $V_{1-x}Ti_x$ and $Mg_{2-x}Pr_xNi_4$.^{1,2} In addition, when alloy hardness increased, the stress generated upon hydrogenation was mainly released by pulverization and the formation of dislocations was suppressed.² The durability is probably improved by increasing the formation energy of lattice defects. It is known that the addition of interstitial elements increases hardness, which is called solid solution hardening. In this study, the effect of solid solution hardening on hydrogen storage properties of pure vanadium and V-Ti-Cr alloys was investigated.

V and V-Ti-Cr alloys with and without nitrogen and carbon were synthesized by arc melting under Ar atmosphere. The alloys were annealed at 1673 K for 1-2 days in vacuum. *P-C* isotherms and cyclic properties were measured up to 100 cycles. XRD data were measured and were analyzed by the Rietveld method. The mechanical properties were measured using a dynamic ultra-micro-hardness tester. In order to evaluate the stabilities of possible hydrides, first-principles calculations were performed using VASP.

In V-N, the width of hysteresis and the elasticity decreased with increasing N content up to 0.2wt% and then increased. This suggests that addition of N affects the elasticity and the hysteresis is influenced by the elasticity. A new plateau was observed on *P-C* isotherms in V containing more than 0.6wt% of N. These alloys showed phase transformation different from pure V: a BCT phase with $c/a=1.1$ transformed to another BCT phase with $c/a=1.25$ followed by formation of an FCC phase. This suggests that the BCT hydride with $c/a=1.25$ was stabilized by the existence of interstitial elements. The ab-initio calculation showed that hydrogen fully occupies all O_z sites in BCT with $c/a=1.25$ while it regularly occupies part of O_z site in BCT with $c/a=1.1$.

In V-Ti-Cr-N, the cyclic durability and mechanical properties were evaluated. The relation between durability and mechanical properties will be presented.

This work was supported by Photon and Quantum Basic Research Coordinated Development Program from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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Niche Applications of Metal Hydrides and Related Thermal Management Issues

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Metal Hydrides (MH) have the ability to reversibly absorb and desorb large amounts of hydrogen in a wide range of temperatures and hydrogen pressures. They are characterised by their unique properties, including extremely high volume density of H atoms incorporated in the metal matrix, wide ‘‘tuneability’’ of thermodynamic performances, fast kinetics of hydrogenation / dehydrogenation, etc. MH technology possessing these features is a typical application-driven niche area able to provide very efficient solutions for hydrogen handling in a particular end-use application, by the tuning of component and phase composition of the parent MH material, system layout and operation parameters. MH offer several advantages over traditional hydrogen storage and processing systems, such as compactness, safety, possibilities of hydrogen supply at a pre-defined pressure, absence of moving parts, long operation lifetime, efficient and technologically flexible energy conversion between low-grade heat and the energy of pressurised H₂. These systems have found a number of promising applications including hydrogen storage and supply, hydrogen compression, heat management (storage, pumping, transforming and upgrade), etc.

The hydride formation / hydrogen absorption is an exothermic reaction, and the generated heat has to be effectively removed in order to achieve the desired H₂ charge rate. Accordingly, the endothermic hydride decomposition / H₂ desorption needs efficient supply of the heat to provide the necessary rates of H₂ discharge. Because of the importance of heat transfer which was identified as a main limiting factor for the H₂ charge / discharge dynamics in a MH reactor, many works have been focused on the design of innovative compact reactors – heat exchangers to address the heat transfer limitations in the MH systems. It was observed that the mere increase of external heat convection coefficient beyond a certain value does no longer affect much the charge / discharge time of the MH systems, and more attention has to be paid to the decrease of characteristic heat transfer distance and the increase of the effective thermal conductivity in the MH bed. A number of heat exchanger designs have been proposed to address these internal heat transfer enhancements. The heat transfer intensification can definitely improve dynamic performances of the MH containers but, at the same time, it may result in the increase of its overall weight thus lowering hydrogen storage capacity of the system and increasing the losses for transient heating / cooling. So optimal design of the MH container is essential, and it is different for various end-use applications.

The present work highlights an overview of recent developments and thermal management issues related to the MH systems for hydrogen storage, hydrogen compression and heat management. Special attention is paid to aligning the system features with the requirements of a specific application. The considered system features include MH material, MH bed on its basis in MH container, as well as layout of the integrated system.

Numerical Study on a Two - Stage Metal Hydride Hydrogen Compression System

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Hydrogen is one of the most promising energy carriers for the future energy needs. It can be stored with various ways: as adsorbed gas in the interatomic species of metal hydrides, as compressed gas in high pressure vessels and in liquid form [1]. Hydrogen compression based on the reversible hydrogen absorption/desorption ability of metal hydrides has been investigated as a reliable process to compress hydrogen at high pressure without contamination and with low energy costs. One of the challenges is to develop a multistage metal hydride hydrogen compressor (MHHC) system that allows a combination of different metal hydrides to increase the final compression ratio while managing the mass transfer and heat management of the system [2]. Therefore modelling potential compression scenarios is essential.

In the current work, a simulation study of a two-stage MHHC was performed. The numerical study utilised a COMSOL multiphysics multimedia package for finite method solution of differential equations, while the energy, mass and momentum conservation differential equations were solved simultaneously. The selected alloys used in the current study were an AB₅ LaNi₅-type for the first stage of compression and an AB₂ Ti-V-Nb-Mn-type for the second stage of compression. The results extracted from the simulation study were validated with experimental results in order to ensure that the current model describes in detail the compression system. Figure 1 shows the pressure distribution within the tanks during the compression cycle. The initial supply pressure is 10 bar, representing the pressure that an electrolyser can deliver, and after the end of the compression cycle, high pressures achieved depending on the temperature that the desorption takes place. For desorption at 150 °C a final pressure of 410 bar achieved yielding a pressure ratio 41:1.

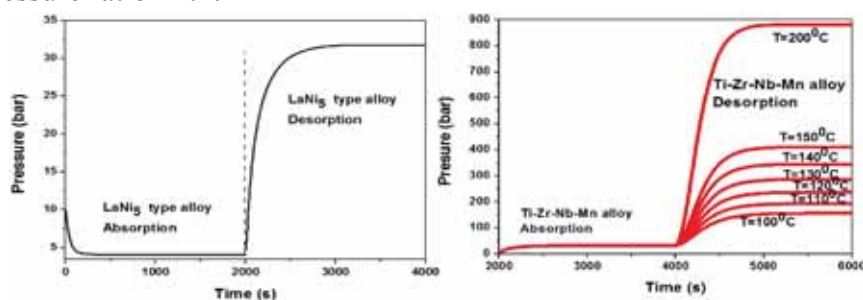


Figure 1. Pressure evolution within the tanks during compression cycle

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Hydrogen Storage Properties of Transition Metals Decorated Li Fullerides.

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Carbon based materials, such as fullerides and graphene derivatives, are fascinating systems for solid state H₂ storage. Theoretical studies have shown that some metal-decorated fullerides, namely Na₈C₆₀ and Li₁₂C₆₀, may absorb up to 9.5 and 13.5 wt% H₂ respectively.

Recent experimental works proved that alkali metal intercalated compounds (Li₆C₆₀ and Na₁₀C₆₀) are able even to reversibly absorb up to 5 wt% and 3.5 wt% H₂, through the formation of a hydrogenated phase of C₆₀ (called “fullerane”) at temperatures higher than 250 °C.

Muon spin relaxation studies, performed on Li₆C₆₀ and Na₁₀C₆₀ samples, evidenced that hydrogenation of charged C₆₀ molecules is even more efficient at cryogenic temperatures, suggesting that the high T needed for the hydrogen uptake by these materials is required to obtain the metal cluster assisted H₂ molecule dissociation. The insertion of a transition metal, able to promote such a dissociation, could therefore decrease the thermal energy required for the process and drive the material uptake properties to higher stored values.

In this work we describe the new synthesis and the improved H₂ sorption behavior (kinetic and thermodynamic features) of Li–fullerides doped with different amounts of Pd, Pt and Ni, evaluated by coupled manometric – calorimetric analyses.

X-Ray powder diffraction studies, scanning and transmission electron microscopies, Raman and MuSR spectroscopies are used to describe the hydrogenation mechanism of the compounds and to hypothesize the catalytic action mechanism of the transition metals.

In-situ TEM Observation on Hydrogenation of Mg-Ni Films Deposited by Magnetron Sputtering

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Metal hydrides which absorb/desorb hydrogen under ambient condition are one of the most promising candidates for hydrogen tanks in fuel cell vehicles. In these materials, hydrogen occupies interstitial sites. So they can store and transport hydrogen compactly and safely. When the metal hydride is formed, lattice defects such as vacancy, dislocation and stacking fault are introduced into the metal or alloy due to large volume expansion. In LaNi₅-based intermetallics, misfit dislocations along a-planes and c-planes of the hexagonal unit cell are observed after hydrogenation[1,2]. Regarding Ti-V based BCC alloys, twin boundaries and stacking faults are formed parallel to (111) in FCC hydrides to accommodate anisotropic expansion along the c-axis[3]. These lattice defects have a great effect on hydrogenation/dehydrogenation properties such as absorption pressure, kinetics and cycle ability. Formation of lattice defects are suggested to relate to microstructure evolution during hydrogenation/dehydrogenation. This study aims to elucidate the hydrogenation mechanism for storage materials with various crystal structures from the microscopic point of view, in order to improve the hydrogenation/dehydrogenation properties.

Mg-Ni films deposited by magnetron sputtering show optical switching property; they change from a metallic reflective state to a transparent state during hydrogenation [4,5]. Hydrogenation/dehydrogenation kinetics and light transmittance of the Mg-Ni film depend on the Mg/Ni ratio. In our previous study, it has been found that the Mg₆Ni film consists of Mg₂Ni nanocrystals and Mg-rich amorphous matrix. In contrast, Mg is revealed to crystallize in the Mg₁₀Ni film. Recently, we have succeeded in the high-resolution TEM observation on hydrogenation of Mg₆Ni films using environmental TEM with aberration corrected. As a result, it is found that MgH₂ crystallization occurs following Mg₂NiH₄. This suggests that Mg₂Ni has a catalytic effect on hydrogenation of Mg. In the future, the relation between the hydrogenation mechanism and Mg/Ni ratio of the films will be revealed. This study was partially supported by a grant-in-aid for Scientific Research (24560853) from the Japan Society for the Promotion of Science, Japan.

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In-situ STM and XRD studies on the Coherency state of Hydride Precipitation and Growth in Nb Thin Films

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In nano-sized metal-hydrogen systems, especially in the thin film below the critical film thickness [1], the hydride precipitation and sample hydrogenation mechanisms are expected to be controlled by the stress, notably by the stress distribution and the coherency state at the interface between the film and the substrate as well as between the hydride precipitates and the surrounding host-matrix [1].

In the present study we experimentally address the effect of coherency at the hydride/host-matrix interface upon phase transformation in Nb-H thin films.

In-situ hydrogen gas loading Scanning Tunneling Microscopy (in-situ STM, [1]) has been applied to show that even for very thin films of tens nm thickness phase transformation takes place at RT. The hydride precipitates distribution and their mean size is found to change depending on the film thickness, for similar pressures applied: For 40 nm films the number of nuclei is relatively small and lateral growth is found to be large, the local hydride expansion is high (Fig.1). For 25 nm films the density of nuclei is very high, but the absolute morphology change is much smaller in comparison to 40 nm films, the local hydride expansion is small (see Fig.2). The hydrides maintain their original cylindrical shape.

In-situ hydrogen gas loading X-Ray diffraction measurements (in-situ XRD) show that there appears a general change in the X-ray peaks when the film thickness is decreased. This change can be related to a different state of coherency at the hydride/host-matrix interface during the phase transformation. For the coherent phase transformation a strong peak shift and peak broadening appears. No separated new hydride related peak position is detectable, as it is the case of thicker films. Our interpretation stays in good accordance with previews results [1,2].

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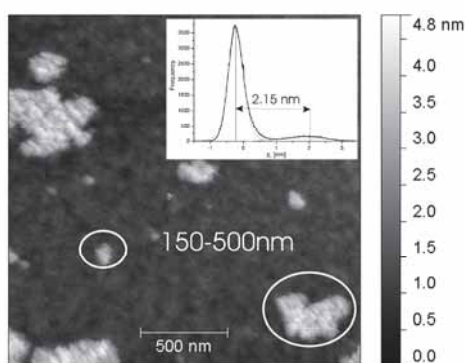


Figure 1. STM-surface image of 40 nm thick Nb after loading experiment (image size $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$, $p_{\text{H}}=1 \cdot 10^{-6}\text{ mbar}$). The height histogram (inset) has two separated peaks: big one corresponding to the α -phase regions (dark) and small one - related to the hydride phase formation (bright).

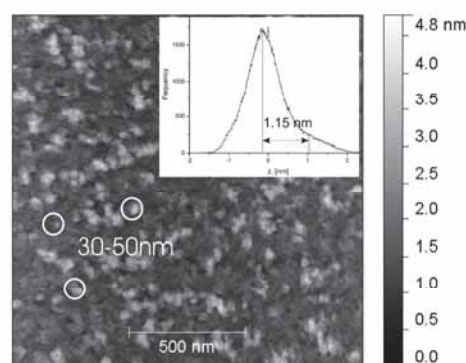


Figure 2. STM-surface image of 25 nm thick Nb after loading experiment (image size $1.5\text{ }\mu\text{m} \times 1.5\text{ }\mu\text{m}$, $p_{\text{H}}=1 \cdot 10^{-6}\text{ mbar}$). The height histogram (inset) has one main peak corresponding to the α -phase regions (dark) and a shoulder related to the hydride phase peak (bright).

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Closing the Pressure Gap in X-Ray Photoemission Spectrometry for the Study of Hydride-Forming Compounds

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From the oldest, state-of-the-art metal hydrides to the most recent, so-called complex and organic hydrides currently investigated in the scientific community, information relative to the chemical bonds involved and/or to the electronic configuration of the valence states is of great interest, especially regarding the surfaces of these materials. XPS is a powerful tool in this respect, providing insightful information about the elements present on a given surface, including their respective chemical state and concentrations across a few up to a few tens of atomic layers. However, the short mean free path of electrons with energies below 1500 eV in a gas at ambient pressure does not allow XPS analyses to be performed in realistic experimental conditions from the applications point of view. So does the required vacuum level for X-ray anodes and channeltrons [1]. These problems can be overcome by performing so-called “environmental”, “ambient-pressure” or “high-pressure” XPS [2]. Nonetheless, these techniques suffer from drawbacks, i.e. reduction of the energy resolution and sample freedom of movement, high cost and accessibility of the facilities due to the fact that most of them have been developed for operation at synchrotron light sources.

In this work, a new experimental approach is proposed in order to study materials exposed to high hydrogen pressures by means of XPS while keeping the analysis chamber at least in high vacuum, thereby ignoring the usual drawbacks relative to differential pumping. A new type of sample holder has been designed in this respect, consisting of a metallic membrane fed on one side with a high hydrogen pressure, and exposed on the other side to the X-ray beam at UHV compatible pressures. It is shown that, by choosing alloys exhibiting low dissociation barriers, appropriate hydrogen absorption enthalpies and fast hydrogen diffusion kinetics, monoatomic hydrogen can rapidly be generated and transferred through the bulk of the membrane to the surface exposed to vacuum. Moreover, adjusting the membrane temperature and the hydrogen partial pressure on the membrane feed side allows selecting the rate-limiting mechanism at the membrane low pressure side. Therefore, the hydrogen flow and concentration on the analyzed surface can both be controlled. By capping the membrane with any hydride-forming material, one is then able to study hydrides by means of XPS with realistic hydrogen concentrations. This new experimental concept will be illustrated here for two membrane compositions, i.e. pure Pd and Pd_{0.7}Ag_{0.3}.

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Nuclear Magnetic Resonance Studies of Atomic Motion in Borohydride-Based Materials (invited)

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While the volumetric and gravimetric hydrogen densities in light-metal borohydrides are quite high, their stability with respect to thermal decomposition and poor reversibility of hydrogen desorption/absorption remain the major obstacles on the way to their practical use as hydrogen-storage materials. In order to overcome these drawbacks, many new borohydride-based systems with mixed cations and anions have been synthesized over the last 5 years. Some of these systems were also shown to exhibit high ionic conductivity and, therefore, can be considered as prospective superionic conductors. Elucidation of complex structures and dynamics in these materials may give a key to improving their hydrogen-storage and electrochemical properties. This work presents a review of the dynamical properties of new borohydrides and related systems. It is based mainly on recent experimental results obtained by the nuclear magnetic resonance (NMR) group at the Institute of Metal Physics (Ekaterinburg). NMR appears to be especially effective technique for studies of atomic motion in this class of materials. In contrast to the case of transition-metal hydrides, the measured nuclear spin-lattice relaxation rates for borohydrides usually do not contain any significant contributions not related to atomic motion (such as the conduction-electron contribution in metallic systems). In favorable cases, this allows us to trace the atomic jump rates in borohydrides over the dynamic range of eight orders of magnitude ($10^4 - 10^{12} \text{ s}^{-1}$) [1]. Another important feature of these studies is that different nuclei (^1H , ^{11}B , ^7Li , ^{23}Na ,...) can serve as NMR probes of atomic motion, complementing each other. It should also be noted that NMR measurements in borohydrides are not affected by inherent limitations of the neutron scattering related to the presence of highly-absorbing ^{10}B isotope. Two basic types of atomic motion are known to exist in borohydride-based systems: the reorientational motion of complex anions (BH_4 , $\text{B}_{12}\text{H}_{12}$) and the translational diffusion of metal cations or complex anions. Both these types of motion will be addressed in our work. We shall discuss our results for bimetallic borohydrides, borohydride-amides, bimetallic borohydride-chlorides, $\text{B}_{12}\text{H}_{12}$ -based compounds and solid solutions of chalcogen anions in borohydrides. The motional parameters derived from our NMR measurements will be compared to those obtained by other techniques, such as quasielastic neutron scattering. We shall also address the relation between the reorientational motion of complex anions and the translational motion of metal cations [2,3].

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Probing Hydroborate Polyanion Reorientations via Quasielastic Neutron Scattering

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Hydroborate-based ionic compounds have garnered much interest within the metal-hydrogen research community in recent years, due to their promise as hydrogen-storage materials involving the tetrahydroborate (BH_4^-) anion, their presence as dehydrogenation by-products involving the overly stable decahydro-*clos*o-decaborate ($\text{B}_{10}\text{H}_{10}^{2-}$) and dodecahydro-*clos*o-dodecaborate ($\text{B}_{12}\text{H}_{12}^{2-}$) anions, and their potential as fast ion conductors involving all three of the aforementioned polyanions. Compared to their relatively low translational mobility within their ionic surroundings, these hydroborate anions typically undergo rapid reorientational motions, whose rates and mechanisms depend on their geometries, local environments, and rotational-potential landscapes. The very large neutron scattering cross section for hydrogen makes the neutron a particularly sensitive probe of the reorientational dynamics of these polyanions. In this talk, we summarize our recent quasielastic neutron scattering (QENS) results for BH_4^- , $\text{B}_{10}\text{H}_{10}^{2-}$, and $\text{B}_{12}\text{H}_{12}^{2-}$ (and $\text{B}_{12}\text{D}_{12}^{2-}$) anions in a variety of structural environments. For example, QENS clearly reveals the different $\text{B}_{12}\text{H}_{12}^{2-}$ reorientational behaviors within the low-temperature ordered monoclinic and high-temperature disordered cubic phases of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ [1], a compound that becomes a Na^+ superionic conductor in the latter phase [2,3]. The emergence of high reorientational mobility of the $\text{B}_{12}\text{H}_{12}^{2-}$ anion in this high-temperature phase may play a factor in the dramatic increase observed in cation mobility.

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Quasielastic neutron scattering on $\text{Mg}(\text{BH}_4)_2$

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Among the complex hydrides, magnesium borohydride is attractive due to a quite good thermodynamic stability and high hydrogen storage capacity (14.9 wt %), with a decomposition temperature of 613 K. We investigated two phases of $\text{Mg}(\text{BH}_4)_2$: the first one (α) is an hexagonal phase $P6_122$, stable till 490K. Upon heating this transforms irreversibly to a orthorhombic phase (β), with a $Fddd$ space group.

Quasielastic neutron scattering has been performed on the α and β phases of $\text{Mg}(\text{BH}_4)_2$ at the cold neutron time-of-flight spectrometer TOFTOF at FRM II, Munich. The incident wavelegth was choosen 2.5 Å, leading to a energy resolution of 500 μeV , and a momentum transfer Q in the range of 0.5–4 Å⁻¹. These settings enable us to observe hydrogen dynamics in the time scale of 10⁻¹² s, likely rotations or jump-diffusion motions. Spectra were recordered in the range of temperature from 11 to 500 K.

At low temperatures ($T < 200$ K), inelastic contributions have been observed in both phases, centered around 2.5 meV for the β -phase and around 4.3 and 8 meV for the α -phase. At higher temperatures a quasielastic contribution starts rising. The α -phase shows a more complex inelastic feature that persists till the phase transition at 490 K, while the quasielastic contribution is one order of magnitude smaller in intensity compared to the β -phase.

The quasielastic signal has been evaluated and used to determine the hydrogen motion in the scanned range of temperature.

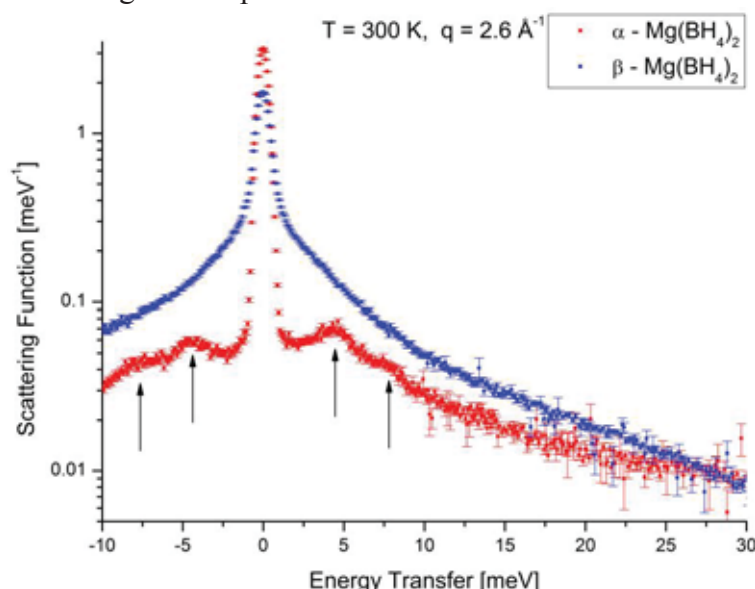


Figure 1: Quasielastic spectra recordered at 300 K for both α and β phases.

Probing Molecular Dynamics of Metal Borohydrides on the Surface of Mesoporous Scaffolds by Multinuclear High Resolution Solid State NMR

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The size effect on the molecular dynamics of nano-confined metal borohydride molecules have been thoroughly explored by use of *in situ* variable temperature (VT) magic angle spinning (MAS) NMR and some spin-lattice relaxation measurements. Understanding of surface interactions between borohydride molecules and the surfaces of porous supports have gained growing attention since a method of nano-confinement could provide with a unique engineering tool for improving reaction chemistries in general or for hydrogen storage application as in this particular case [1-3]. While various carbon based meso- or nanoporous scaffolds have been preferably utilized for confining metal borohydrides, their highly electrical surface property often interferes with spectroscopic probing. Here we have employed silica based mesoporous materials, such as MCM-41 and SBA-15, with pore sizes ranging between 2.5 nm and 10.7 nm for confinement of LiBH₄ or a mixed borohydride system, LiBH₄-Ca(BH₄)₂, LiBH₄-Mg(BH₄)₂, to gain insight on nano-confined borohydrides in various pore sizes. In this process, we have examined various confining methods such as wet infiltration and melt infiltration, as well as physically mixed and thermally induced infiltration to compare the size effects on infiltration process. We also observe the molecular dynamics changes as the pore filling was monitored. The role of cations in the molecular dynamics of confined borohydrides will be also discussed.

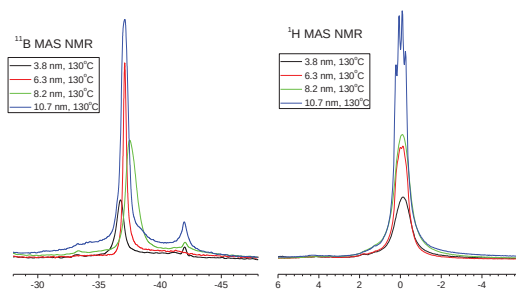


Figure 1. ¹H and ¹¹B MAS NMR at 130 °C of LiBH₄-Ca(BH₄)₂ confined in various pore sizes of SBA-15

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Hydrogen diffusion and interaction with microstructure of the Dual-phase stainless steels

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The challenge to combine high mechanical strength and excellent resistance to stress corrosion cracking in chloride solutions, as well as in the presence of hydrogen sulphide, has motivated the development of new steels for offshore applications. In order to increase the mechanical resistance the Cr and Ni content has been increased transforming these materials into stainless steels.

Two types of steel with these characteristics are largely used, such as: dual-phase stainless steel, which has ferrite-martensite microstructure and superduplex stainless steel with ferrite-austenite. Depending on the severity applications, these steels might suffer hydrogen embrittlement provoking accident with serious consequences involving significant losses and high costs. In this context, the aim of this work is to study the hydrogen diffusivity and solubility in these stainless steels as well as the interaction of this element with the microstructure.

Two hydrogen permeation procedures were used in the current study: an electrochemical hydrogen permeation test and a hydrogen-gas permeation test. In the first one the temperature range was limited to 80°C because of the aqueous electrolyte. In the hydrogen gas permeation test the temperature ranged between 150-300°C.

Samples of superduplex stainless steels were obtained from different processes such as: cold rolled, forging and HIP (hot isostatic pressing). These samples were investigated in the hydrogen gas permeation test. It has been observed that the microstructure plays an important role in the hydrogen permeation and trap. It is due to the influence of defects and interspace of austenite grains distribution.

The Dual-phase supermartensitic steel was investigated under different conditions of hydrogen fugacity for increasing the cathodic generation. It was observed a double sigmoidal shape in the hydrogen permeation curves for this microstructure. This is due to the hydrogen diffusing through ferrite and martensite structure separately.

The hydrogen diffusivity in the superduplex steel at room temperature is low ($5 \times 10^{-15} \text{ m}^2 \cdot \text{s}^{-1}$). At 250°C the hydrogen diffusivity increased to $2 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$. Long term tests were performed to analyze the possibility of hydrogen diffusion through austenite phase. With respect to the ferrite-martensite steel the hydrogen diffusivity is higher and occurs clearly in two steps that are related to each phase presented in the microstructure. In order to better understand the hydrogen diffusivity in double phase alloys, we developed an original hydrogen permeation test to distinguish the behavior of the resultant curves.

Effects of Hydrogen and Helium on Swelling in Electron-irradiated Pure Iron

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Reduced-activation ferritic/martensitic steels are candidate materials for the first wall of a fusion reactor, because of the excellent resistance to radiation damage, but it has been reported about model ferritic steel that void swelling is promoted by the synergistic effect of hydrogen and helium. From this result, a nuclear fusion reactor constructional material is expected that void-swelling is promoted by the synergistic effect of hydrogen, which arises by nuclear transmutation or a fusion reaction, and a helium. However, the effect of hydrogen and helium for void formation and the growth mechanism are not clear. It is well-known that helium has a strong interaction with vacancy [1]. It has been confirmed the enhancement of the cavity nucleation in Fe when helium exists in matrix [2]. In this study, in order to investigate the detail of the synergy effect for swelling behavior, hydrogen and helium are pre-injected to pure iron and then electron irradiation was performed by using a High Voltage Electron Microscope operated at 1250 kV. No voids were observed in the pure-iron without pre-injection after electron irradiation. In the pure iron doped with 1000 appmHe, the electron irradiation resulted in the formation of the cavities with high number density. In addition, the presence of helium produced the small cavities of 1-3nm diameter. On the other hand, formation of large cavities of 5-20nm diameter and disappearance of cavities after several dpa were observed in the pure iron doped with 2000appmH, meaning that hydrogen would enhance the growth of cavity in the early phase of irradiation. The synergistic effects of H^+ and He^+ for swelling was reported in the Fe-9Cr and Fe-12Cr alloys irradiated to 50 dpa at 783 K [3], which indicated that swelling was increasing by the effect of H^+ when H^+ and He^+ coexist. It suggests that the helium could assist the nucleation of cavity and hydrogen does the growth, which leading to a large swelling.

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Multiscale multiphysics atomistic-meso-continuum critical dislocation method for hydrogen embrittlement

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Hydrogen embrittlement of polycrystalline metallic material such as nickel and nickel alloys in aerospace rocket launcher combustion chamber calls for efforts to develop multiscale atomic method (AM) -meso critical dislocation (MCD)-macro continuum (MC) method to understand the role of hydrogen plays in multiphysics problem. The authors propose a coupled atomistic-mesoscale-continuum critical dislocation (CAMCD) model based on the input obtained from critical dislocation site meso scale microstructural model and atomistic simulations. Initially the individual microstructural phase properties of materials are determined from atomistic simulations by the precise relationship between mechanical stresses, strains and the diffusion of hydrogen. Then the effective properties of materials are calculated using finite element microstructural homogenization simulations with the help of heterogeneous intergranular and intragranular polycrystalline microstructural Representative Volume Element (RVE) model[1], followed by the implementation of subroutine developed using FORTRAN compiled programming language for trap model coupled with the continuum component model using Python script language. The microstructures RVE models are developed based on the real microstructural morphology and crystallographic microtexture data collected from experimental characterization of textured polycrystalline material. The critical dislocation sites of meso scale model are coupled with macro scale model using cut boundary by employing submodelling technique. The space coupled model initially solves the mechanical problem which is coupled sequentially with the chemical problem, in the form of mass transport analysis employing stress assisted hydrogen diffusion, using the finite element method. Fick's diffusion law is extended in finite element code by including the pressure gradient factor and trap parameters to drive the mass diffusion by means of hydrostatic stresses and trap model. The motivation of this testing investigation is to evaluate the CAMCD model and the benefits of experimental, submodel, homogenization technique to bridge the gap between atomistic, microstructural and continuum space scale for the hydrogen embrittlement problem.

Keywords

Hydrogen embrittlement; CAMCD model; atomistic simulation; FE microstructural model; nickel and nickel based super alloys; aerospace components;

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Hydrogen-induced defects and multiplication of dislocations in Palladium

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Pd can absorb relatively large amount of hydrogen and can be easily charged with hydrogen at room temperature. This makes Pd-H a good model system for investigation of hydrogen interaction with lattice defects. In the present work positron annihilation spectroscopy (PAS) was employed for investigation of hydrogen-induced defects in Pd. Well annealed Pd samples were electrochemically charged with hydrogen and the development of defects during hydrogen loading and unloading cycles was investigated. At low concentrations (α -phase, $x_H < 0.017$ H/Pd) hydrogen loading introduced vacancies. Hydrogen segregating at vacancies lowers remarkably the vacancy formation energy and causes significant enhancement of the equilibrium vacancy concentration. When hydrogen concentration exceeds 0.017 H/Pd particles of the α' -phase are formed. Stress induced by growing α' -phase particles leads to plastic deformation which generates dislocations in the sample. Moreover, additional vacancies are introduced into the sample during this stage by crossing dislocations.

Vickers hardness (HV) testing revealed that absorbed hydrogen causes hardening of the sample. In the α -phase region $HV \sim x_H^{1/2}$ which indicates solid solution hardening caused by dissolved hydrogen. At higher hydrogen concentrations when α' -phase precipitates are formed the slope of HV dependence is changed and further hardening is caused predominantly by dislocations. Decomposition of α' -phase particles during unloading causes further increase of dislocation density leading to remarkable hardening. Hence, loading-unloading cycling continuously generates dislocations in the Pd sample and makes the sample harder and harder.

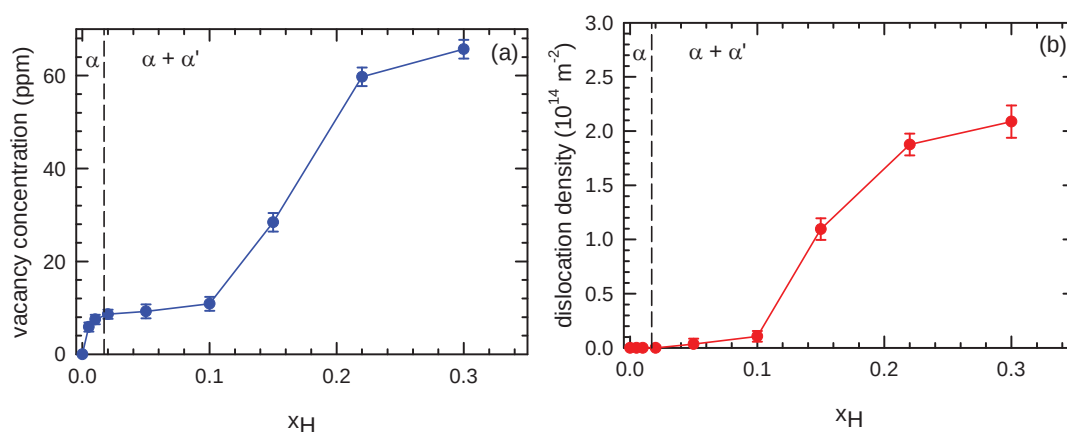


Figure 1. The concentration of vacancies (a) and the density of dislocations (b) determined by PAS as a function of hydrogen concentration in Pd. Dashed line at $x_H = 0.017$ H/Pd shows position of the boundary between the α -phase region and the two-phase field ($\alpha + \alpha'$ phase).

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Computational study of helium bubble release from titanium tritide surface under different temperatures

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Titanium is an essential hydrogen storage material through forming titanium hydride. In this way, the hydrogen storage density is much larger than liquid form of hydrogen. Except for hydrogen, titanium can also absorb isotopes of hydrogen to form titanium deuteride and tritide. As is known, tritium is naturally radioactive and would decay into 3-helium. Helium atoms in titanium tritide would migrate and accumulate to form bubbles, which could degrade the structural and mechanical properties of material. Therefore, it is significative to research the behavior of helium in titanium tritide.

In this paper, molecular dynamics simulation has been performed to investigate the escaping process of helium atoms from a helium filled bubble near the titanium tritide surface. When the depth of helium bubble is small enough, nearly all helium atoms will release from bulk material surface instantaneously through the channel connecting helium bubble and material surface after a short time relaxation. Oppositely, the bubble embedded deeply in titanium tritide will not fracture even through a long time at room temperature. This means that there is a helium-bubble-free-zone, also called denuded zone, where helium bubbles can not be stable. And then, we studied the effects of temperature on process of helium atoms release. The simulation results show that the size of denuded zone becomes larger with the temperature increasing. In another word, the helium bubble embedded more deeply in material can also rupture due to the high temperature.

Helium 3 Retention In Tritium Storage Materials

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In nuclear industry, tritium is generally stored in the form of tritides with low equilibrium pressure to ensure the required safety. Due to its high ability to easily absorb and desorb tritium and to retain helium 3 generated by radioactive decay, palladium is commonly used for tritium storage. However, when a critical helium 3 concentration is reached in the palladium ($(\text{He}/\text{Pd})_c = 0.33$), the helium 3 is released at a rate equal to, or higher than, its generation rate. Mastering and modeling helium 3 retention mechanisms is of crucial importance to design storage devices.

Experiments based on thermal desorption of palladium samples aged with tritium bring a new highlight on the helium 3 retention mechanisms. Palladium samples, with helium to palladium ratio from 0.05 to 0.28, have been characterized by this method. Three desorption peaks have been identified and attributed to three different helium 3 sites in the material. For Pd with $\text{He}/\text{Pd} < 0.05$, only one desorption peak at high temperature (660°C) is observed. A second helium site appears when He/Pd reaches 0.05 with a lower desorption temperature (400°C). Up to $\text{He}/\text{Pd} = 0.22$, the filling of both sites looks quite linear. The desorption temperature of the first site decreases, suggesting that its environment changes, whereas the second site one is stable. The third site, with a desorption temperature of 260°C, starts to be filled when the first site seems to be saturated ($\text{He}/\text{Pd} = 0.22$).

This new interpretation of the thermal desorption results on aged palladium samples leads to significant progress in helium 3 retention understanding. Nevertheless, this work has to be extended with older palladium samples in order to bring more information on the accelerated desorption phenomena which occurs when the critical He/Pd is reached.

Quasi-elastic neutron scattering studies of the hydrogen / deuterium diffusion process in palladium powder

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We report QENS measurements on micron scale palladium powder containing either hydrogen or deuterium (PdH(D)x) taken on OSIRIS at the ISIS neutron source at the Rutherford Appleton Laboratory. Measurements were made at multiple temperatures for both PdHx and PdDx with the solid composition kept stable through control of gas pressure with reference to existing isothermal measurements and monitored using the instrument's diffraction detector bank.

Measurements were made in specially designed stainless steel cans at pressures up to 41 bar and temperatures between 160°C and 225°C. The indirect geometry spectrometer was configured using the 002 reflection of the graphite analyser and the frequency was set to 25 Hz giving an energy range of -0.7 to +0.8 meV.

Although diffusion of hydrogen in palladium was one of the first measurements reported using QENS, the present results are novel in several respects. The experiments were performed on a commercially available micron scale powder at high resolution and count rate. The collected data shows two components with different broadening corresponding to two different residence times. One component shows a clear Q dependent broadening and corresponds to long range diffusion via octahedral – octahedral jumps in the palladium lattice. The second component shows a shorter Q-independent residence.

Equivalent measurements have been made with hydrogen and deuterium, yielding differing jump rates (and hence diffusion coefficients) for each as a function of temperature. These results show the well known anomalous behaviour of the isotope dependence in that the diffusion for deuterium is the larger at lower temperatures due to the lower barrier height whereas that for hydrogen dominates at higher temperatures due to the higher vibration frequency.

Hydrogen Isotope Separation in Nanoporous Framework Materials, Part 2 Experiment (Invited)

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Separating gaseous mixtures that consist of very similar particles (such as mixture of light gas isotopes) is one of the challenges in modern separation technology. Especially D₂/H₂ separation is a difficult task since its size, shape and thermodynamic properties share each other. Recently, quantum sieving [1] in confined space has received increased attention as an efficient method for hydrogen isotope separation. Despite many theoretical calculation [2], however, it has been difficult to identify a feasible microporous material up to now. Among various porous materials, the novel class of microporous framework materials (COFs, ZIFs and MOFs) is considered as the most promising approach for isotope sieving due to ultra-high porosity and uniform pore size which can be tailored in these materials.

In this talk, the feasibility of the microporous frameworks as isotope sieves is outlined through the experimental results obtained by low-pressure high-resolution isotherms and cryogenic thermal desorption spectroscopy (TDS) directly on isotope mixtures. Firstly, different porous frameworks have been investigated to establish a fundamental correlation between selectivity and pore diameter at optimized operating conditions [3]. The experiments indicate clearly that the optimum pore diameter for quantum sieving lies between 3.0 Å and 3.4 Å which can be an important guideline for designing and developing feasible microporous frameworks for isotope separation.

Afterwards, two strategies for satisfying industrial requirements are introduced. Firstly, the operating pressure is increased by introducing cryogenically flexible pore aperture in Py incorporated COFs [4]. Secondly, the operating temperature is increased by utilizing the different chemical affinity of isotopes on strong adsorption sites [5]. Finally, deuterium separation from a diluted isotope mixture is experimentally demonstrated by applying a temperature swing process.

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Hydrogen isotope separation in metal-organic frameworks: insights from theory

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It is well-known that metal organic frameworks (MOFs) are interesting hydrogen storage materials due to their large surface area and partially due to strong adsorption sites. Due to the rather weak interaction between hydrogen and the framework and the low weight of hydrogen, quantum effects are very important for these systems. As hydrogen and deuterium have a very large mass ratio, their quantum effects, i.e. their zero-point energies, can differ substantially if adsorbed at particular sites in some framework materials.

In this presentation we will discuss two hydrogen separation mechanisms: In the first one [1], we observe a gating effect in a particular MOF – MFU-4l – in order to preferentially allow D₂ to penetrate into and through the framework. In the second one [2], observed in CPO-27 and MFU-4l, we use the zero point energy difference to preferentially adsorb D₂ over H₂. A temperature swing process, working at high temperatures (~100K), is proposed to separate deuterium from hydrogen flue gas (Figure 1). Finally, we discuss tuning of our materials in order to enhance the hydrogen isotope separation.

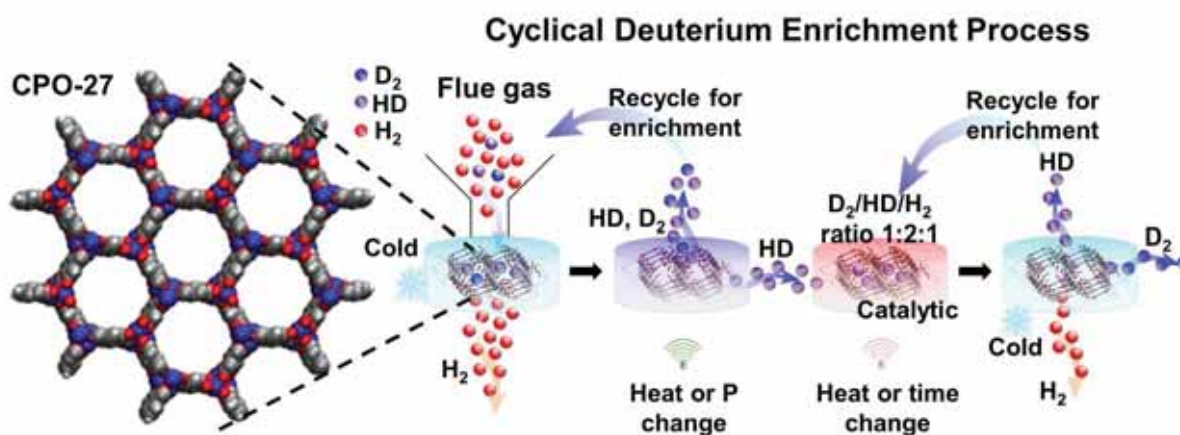


Figure 1. Temperature swing process to separate D₂ from hydrogen flue gas.

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Reversible Isotope Exchange Reactions in $\text{Ca}(\text{BH}_4)_2$

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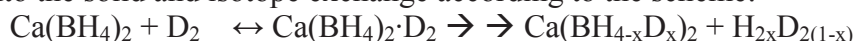
Borohydrides are actively considered as potential hydrogen storage materials. In this context, the fundamental understanding of the mechanism of breaking and forming the boron–hydrogen bond is very important. Isotope exchange reactions allow in principle to isolate some parts of this reaction without having to consider the chemical and structural changes associated with thermal decomposition reactions. We have studied in the past [1] the reaction between $\text{Mg}(\text{BH}_4)_2$ and $\text{D}_2(\text{gas})$ at 40 bar and found an activation energy of 50 kJ/mol.

New experiments were performed on $\text{Ca}(\text{BH}_4)_2$ and $\text{Ca}(\text{BD}_4)_2$ as a function of temperature and pressure. The temperature ranged from 140 °C to 200 °C, and the D_2 (H_2) pressure from 1 to 35 bar.

The experiments show that it is possible to entirely convert $\text{Ca}(\text{BH}_4)_2$ to $\text{Ca}(\text{BD}_4)_2$ and also that this reaction is reversible.

The activation energy estimated from first order kinetics of the forward reaction ($\text{Ca}(\text{BH}_4)_2 \rightarrow \text{Ca}(\text{BD}_4)_2$) was found to be 82.1 ± 2.7 kJ/mol ($P = 35$ bar), and the one for the backward reaction ($\text{Ca}(\text{BD}_4)_2 \rightarrow \text{Ca}(\text{BH}_4)_2$) was found to be 98.5 ± 8.3 kJ/mol ($P = 35$ bar).

Pressure dependent studies show that the reaction rate increases with increasing pressure up to 35 bars. This behavior is consistent with a first adsorption step prior to diffusion into the solid and isotope exchange according to the scheme:



Further, the reaction of BH_4^- with deuterium radicals was studied theoretically using DFT calculations, yielding activation energy about 97 kJ/mol. This value is comparable to the experimental values and suggests that deuterium (hydrogen) radicals may indeed be involved in the isotope exchange reaction.

This work is supported by the Swiss National Science Foundation.

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Isotope effect on magnetic and structural properties of $Y_{1-y}Gd_yFe_2(H_zD_{1-z})_{4.2}$ compounds

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YFe₂ Laves phase can absorb up to 5 H(D) atom/f.u., forming YFe₂H(D)_x hydrides with various crystal structures depending of the H(D) content [1]. These structures are derived from the cubic C15 structure of YFe₂ with a symmetry lowering related to H(D) atoms ordering in preferential interstitial sites. Upon heating, an order-disorder transition towards a cubic structure is observed at T_{O-D} [1]. For x=4.2, this structural transition occurs in two steps: from monoclinic to rhombohedral and then rhombohedral to cubic structure between 320 and 350K [2, 3]. An other original behaviour has been observed in YFe₂D_{4.2} which present a transition from a ferromagnetic (F) towards an antiferromagnetic (AF) structure at T_{F-AF}= 84K. This transition is isotope sensitive since T_{F-AF} increases of 47 K upon H for D substitution [4]. It is rather surprising, as generally, the H for D substitution has no influence on the magnetic properties of metal hydrides. This isotope behaviour has been explained by a larger cell volume of YFe₂H_{4.2} compared to that of YFe₂D_{4.2}. T_{F-AF} can be also reduced by the application of an external pressure, or tuned by the substitution of Y by another rare-earth element (R= Gd, Tb, Er) [5, 6].

A systematic study of the $Y_{1-y}Gd_yFe_2(H_zD_{1-z})_{4.2}$ compounds, has been undertaken to follow the influence of both Gd and (H,D) substitution on the F-AF magnetic transition. However, this study has shown that not only the F-AF magnetic transition but also the O-D transition was sensitive to the isotope effect. A change of the nature of the intermediate phase (orthorhombic/ rhombohedral) as well as a strong hysteresis effect between heating and cooling was observed in the hydrogen rich compounds (z > 0.5).

Spin polarized band structure calculations have been therefore performed in order to compare the stability of the YFe₂H_x hydrides in the different crystal structures (cubic, monoclinic and orthorhombic) for 3.5 < x ≤ 5 and understand the role of the H content as well as the cell volume variation on the relative stability of these phases.

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Core-shell hydride nanoarchitectures: Design and hydrogen behaviour

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The properties of nanomaterials are known to be size depend. Such size depend effects could offer powerful means to finally control both the thermodynamic and kinetic properties of hydride materials at the molecular level [1] and thus enable the practical design of hydrogen storage materials from these effects. However, investigations through such an approach require new strategies to both synthesise and stabilise nanoparticles of highly reactive hydride materials and the understanding to control the key parameters that will allow reversibility with high storage capacity. The use of porous host structures offers such a route, however the storage capacity usually remains limited by the intrinsic difficulty of entirely fill the porosity.

Herein, the potential of a new core-shell confinement approach and recent progress we have made through this nanosizing method will be discussed [2]. Since, complex hydrides still undergo phase transitions including melting at the nanoscale, this core-shell approach has proven to be an very effective strategy to stabilise and simultaneously catalyse the reversible storage of hydrogen with hydrides including borohydrides and alanates (Figure 1). It also provides us with new means to stabilise against oxidation highly reactive nanoparticles of elements such as lithium.

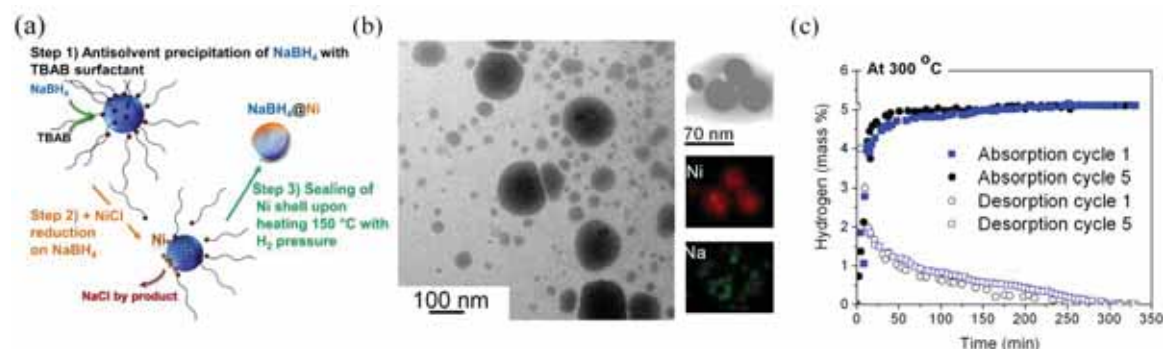


Figure 1. (a) Approach for the synthesis of core-shell borohydrides and (b) TEM and associated elemental mapping of $\text{NBH}_4@\text{Ni}$, and (c) corresponding hydrogen cycling.

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Hydrogen Pipe Diffusion in Palladium: First Principles, Kinetic Monte Carlo, and Experiments (Invited)

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Palladium has a high hydrogen solubility and diffusivity. Hydrogen occupies octahedral sites and in dislocation cores, which act as nanoscale H traps—forming Cottrell atmospheres that are metal-hydride-like at low temperatures. Previous work has measured the formation of a Cottrell atmosphere in situ with inelastic neutron scattering, and ab initio density-functional theory modeled the formation of the atmosphere and low temperature nanoscale hydrides. New computational studies of hydrogen at a dislocation core in palladium predicts changes in kinetics for diffusion above and beyond the changes due to elastic strain. We use this data for kinetic Monte Carlo studies of hydrogen pipe diffusion at different temperatures, and compare with new quasielastic neutron scattering measurements to identify hydrogen pipe diffusion in palladium.

Hydrogen absorption properties of $\text{Pd}_{0.75}\text{M}_{0.25}$ solid solution alloy

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Pd alloys, which show hydrogen (H) absorption capability, have attracted much attention in various fields of chemistry and physics. Recently, bimetallic Pd-based nano particle alloys have been studied and the enhancement/decrease of H absorption capacity were observed [1]. In this study, we theoretically investigated the H absorption of Pd alloys by using density functional theory (DFT) and discussed the effect of alloying elements.

We analyzed H absorption energy with zero point energy correction and density of states (DOS) of the $\text{Pd}_{0.75}\text{M}_{0.25}$ ($\text{M} = \text{Rh}, \text{Pd}, \text{Ag}, \text{Ir}, \text{Pt}, \text{Au}$) alloys. The models consist of three Pd and one M atoms in fcc cubic cell. Projector augmented wave (PAW) method were employed. Perdew-Burke-Ernzerhof (PBE) with generalized gradient approximation (GGA) is used for exchange-correlation functional. All calculations are performed by VASP.

In Fig. 1, H absorption energy of two distinct octahedral sites (Pd_6 and Pd_4M_2) with different number of H ($n = 1$ to 4) are shown. Open circles show the results when only Pd_4M_2 sites are occupied; filled squares are the results for occupied Pd_6 site. We can see the different trend between Pd-Ir and Au alloys. For $\text{Pd}_{0.75}\text{Ir}_{0.25}$, Pd_4M_2 sites are preferable and the energy decreases with increasing n ; for $\text{Pd}_{0.75}\text{Au}_{0.25}$, Pd_4M_2 sites are unfavorable and the energy increases with increasing n . We will discuss this site dependence of the H absorption through the analysis of the DOS.

Acknowledgement

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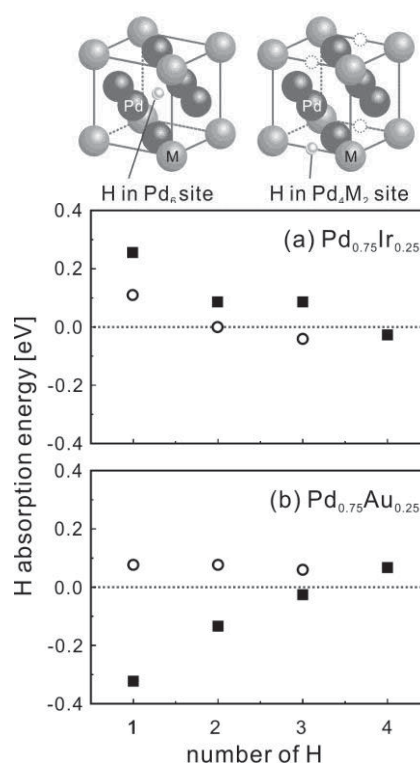


Figure 1. H absorption sites and H absorption energy of $\text{Pd}_{0.75}\text{Ir}_{0.25}$ and $\text{Pd}_{0.75}\text{Au}_{0.25}$ for $n = 1$ to 4.

Superior effect of Ni-substitution on the hydrogenation kinetics of $\text{Mg}_6\text{Pd}_{1-x}\text{TM}_x$ (TM = Ag, Cu, Ni) pseudo-binary compounds

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In this investigation, the H-sorption kinetics of Mg_6Pd and $\text{Mg}_6\text{Pd}_{1-x}\text{TM}_x$ (TM = Ag, Cu, Ni) pseudo-binary compounds at the TM solubility limit have been studied by isothermal hydrogen absorption, thermal desorption spectroscopy and *in-situ* neutron diffraction. Isothermal absorption curves have been obtained at 623 K under 2 MPa of hydrogen pressure. Among all studied compounds, the fastest absorption kinetics takes place for the Ni-substituted one. The fit of the absorption curves to established model equations for solid-gas reaction shows that hydrogenation is controlled by diffusion. Thermal desorption studies also reveal that the Ni-substituted compound exhibits the fastest kinetics. The desorption peak temperature is 90 K below that of MgH_2/Mg system and is characterised by a low activation energy of 60 kJ/molH₂. To better understand these results, neutron diffraction experiments during *in situ* thermal desorption of deuterated Mg_6Pd and $\text{Mg}_6\text{Pd}_{0.25}\text{Ni}_{0.75}$ compounds were carried out at the D1B diffractometer at Institut Laue Langevin, Grenoble, France. These experiments demonstrate a synergetic effect between MgH_2 and Mg_2NiH_4 hydrides as responsible for the remarkable kinetics of the Ni-containing compound.

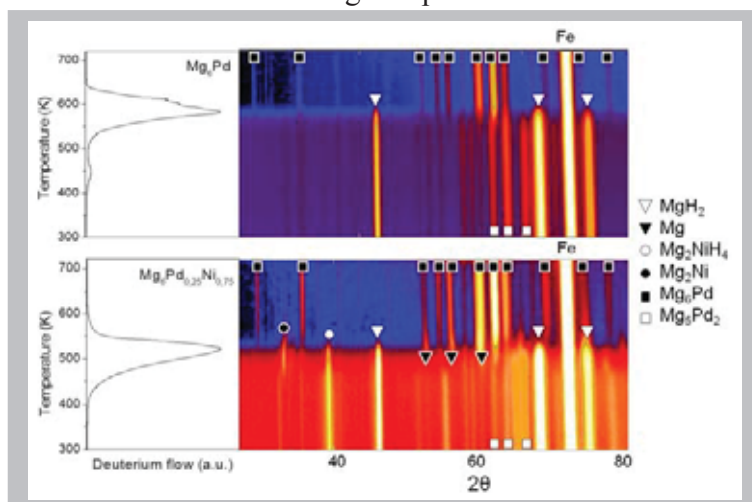


Figure 1. Thermal desorption curves and corresponding 2D projections of neutron diffraction patterns obtained during *in situ* thermal desorption of deuterated Mg_6Pd (top) and $\text{Mg}_6\text{Pd}_{0.25}\text{Ni}_{0.75}$ (bottom) pseudo-binaries.

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Hydrogen Storage: From academia to the market

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Cella Energy is a small UK/US company aiming to commercialise hydrogen storage technology based on chemical hydrides.

Historically much of the focus for hydrogen storage has been on vehicular transport, certainly all of the US DOE targets were predicated on this being the first market. Although these applications are exciting the market is very price sensitive and conservative, and a business plan based on it alone, is unlikely to be credible.

Most new technologies need to seek out early adopters; those willing to pay a premium. For example: Cella has been developing technologies for applications such as small electric Unmanned Aerial Vehicles. This sector is set to expand rapidly in civilian markets; most users have a desperate need for a high specific-energy power source and are many are willing to pay a premium for it.

In this talk I will discuss Cella's technology and how it can be implemented in a number of different markets and at different scales, and how its advantages and disadvantages map onto a credible road-map for commercialisation. I will also give a flavour of the journey that the company has made from its start as academic spin out, to where it is today, four years on.

Metal Hydride Heat Storage Prototype for Concentrating Solar Thermal Power

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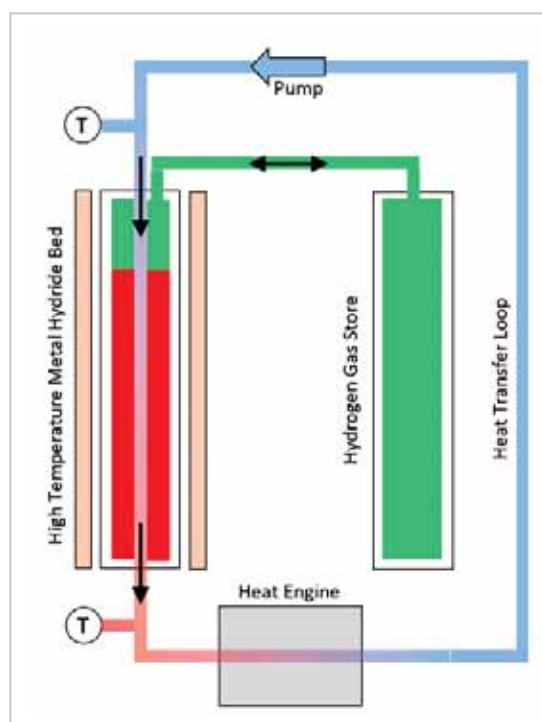
Concentrating solar thermal power (CSP) plants can store solar energy as heat, which is used to generate electricity after sunset. The dominant heat storage material used at current CSP plants is a eutectic mixture of molten nitrate salts. Metal hydrides can also be used to store thermal energy through reversible hydrogen absorption/desorption cycles, which are exothermic and endothermic [1, 2]. Metal hydrides are 10 – 30 times more energy dense than molten salt, meaning that less material is required to store heat and significant cost savings could be made in second-generation CSP plants.

We have developed a working prototype of a metal hydride based thermal energy storage system (see Figure). This prototype is designed to undergo ‘day/night’ cycles so that metal hydrides (currently up to 50 g) can be tested and investigated for their suitability in CSP plants. Heat is applied to the metal hydride in the *day* cycle, resulting in decomposition and hydrogen release. During the *night* cycle hydrogen is absorbed back into the metal hydride, providing heat. The heat energy is continuously extracted during both the *day* and *night* cycles by a heat transfer fluid that is pumped through the hydride bed. The temperature difference between the heat transfer fluid entering and exiting the bed allows for heat energy to be calculated.

The prototype system will be discussed in detail including some of the design issues and scientific considerations.

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Material Development for Metal Hydride Thermal Energy Storage Systems for Future Concentrating Solar Power Plants

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The Department of Energy's (DOE) Solar Energy Technology Office introduced its SunShot Initiative in February 2011 to help make solar energy more affordable and make solar energy plants competitive with today's fossil fuel plants. To achieve its goal, all future Concentrating Solar Power (CSP) plants will need to have significant thermal energy storage (TES) capacity with the ultimate 2020 SunShot CSP Target estimating a need for 14 hours TES capacity [1].

Because of their very high thermal capacity (approximately 15-20 times that of current molten salt systems), metal hydride TES systems, currently, are being revisited for this application. The Savannah River National Laboratory (SRNL) and Curtin University (CU) are collaborating on a DOE SunShot project to evaluate the use of metal hydrides for CSP TES systems. As part of this collaboration, a preliminary techno-economic analysis was performed [2] that identified three pairs of metal hydride materials that have good potential to meet the DOE SunShot targets. However, while the material pairs were found to meet many of the targets none of the pairs were able to meet all of DOE targets. A joint materials development program was initiated by SRNL and CU to examine material improvements and modifications to the proposed metal hydrides to improve their performance and lower their cost for TES applications.

In this paper, the preliminary experimental results on the modifications of several high and low temperature metal hydride materials will be presented. In addition, a discussion on how these improvements may affect the performance and cost targets of a CSP TES system will also be described.

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Metal Hydride Hydrogen and Heat Storage Systems as enabling Technology for Spacecraft Applications

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Abstract: Next generation telecommunication satellites will demand increasingly more power of 30 kW or more within the next 10 years. Battery technology that can sustain 30 kW for an eclipse lengths of up to 72 minutes will represent a major impact on the total mass of the satellite, even with new Li-ion battery technologies. Regenerative fuel cell systems (RFCS) were identified years ago as a possible alternative to rechargeable batteries. Nevertheless, one major drawback has been identified by several independent system studies, namely the need to dissipate large amounts of heat from the fuel cell during Eclipse. This in turn requires massive thermal hardware (mainly large radiators) that can contribute up to 50% of the system mass. FOTEC has suggested the use of metal hydrides as combined hydrogen and heat storage system to overcome this issue and is currently designing a technology demonstrator within an ongoing project funded by the European Space Agency (ESA).

Furthermore, FOTEC is one of the main research partner for EOS GmbH, developing new processes for laser sintering technologies (3D metal printing). Thus, a laser sintering facility is available at the FOTEC Laboratories. Such manufacturing techniques allow for new, innovative heat exchanger solutions that have not been possible before due to limitations in the manufacturing process. Such highly advanced heat exchanger solutions have been introduced in the optimization of the spacecraft metal hydride tank geometry, opening yet another area of improvements in tank design with respect to the state of the art.

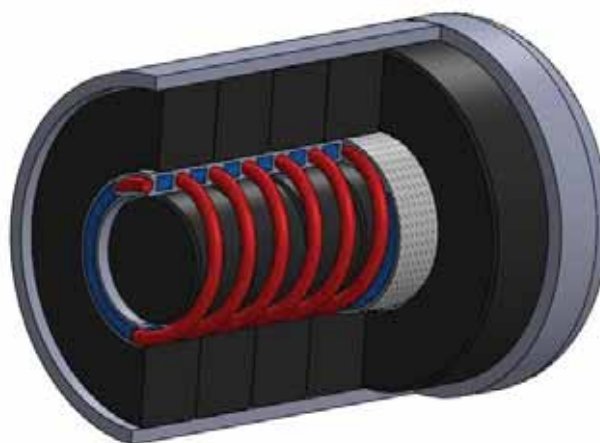


Figure 10 - Generic design of a spacecraft MH hydrogen and heat storage system using advanced laser sintering manufacturing methods

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In Pursue of Light Intermetallic Hydrides

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The search for a “magic” intermetallic compound, absorbing reversibly and easily copious quantities of hydrogen, has been pursued since the discovery of the first intermetallic hydrides, forty-fifty years ago. Obviously, such intermetallic compounds should contain light metal elements. The hydrogenation behavior of Al-containing intermetallics will be reviewed with a special attention given to their elastic properties. Recent attempts to find pseudobinary intermetallic hydrides, containing other light metals, e.g. Li, Ca, will be also presented. These attempts are conducted by considering the complex interplay between the various factors which regulate the hydrogen absorption in intermetallic compounds.

Expanding Complex Aluminum Hydrides Towards Heavier Group I and II Family Members (Invited)

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After the pioneering discovery of Bogdanović and Schwickardi that NaAlH_4 , a complex aluminum hydride, can be reversibly hydrogenated if a catalyst is added, these class of materials was intensively investigated as potential solid hydrogen storage compounds [1]. Starting with the light metal elements of the alkali and alkaline earth groups, their synthesis, crystal structures, dehydrogenation pathways and thermodynamic properties were subject to numerous publications. Even though the thermodynamic characteristics of most of the light metal complex aluminum hydrides are at present not promising for a commercial use, the detailed knowledge of their intrinsic properties will contribute to a deeper understanding of these interesting materials. This, on the other hand, may help to conceive why some of the compounds can be reversibly hydrogenated whereas others cannot. In order to extend the knowledgebase for such materials, we have prepared a series of new complex aluminum hydrides containing elements of group I and II with higher atomic numbers. The new compounds include $\text{Sr}(\text{AlH}_4)_2$ and the isostructural $\text{Eu}(\text{AlH}_4)_2$ and their dehydrogenation products as well as RbAlH_4 and CsAlH_4 and their intermediates. Special attention was paid to the crystal structures of the new compounds and to their decomposition products to gain more information about the structure-property relationship of complex aluminum hydrides. In situ diffraction studies combined with thermal analysis and thermolysis and rehydrogenation experiments provide a comprehensive set of information on the family of complex aluminum hydrides.

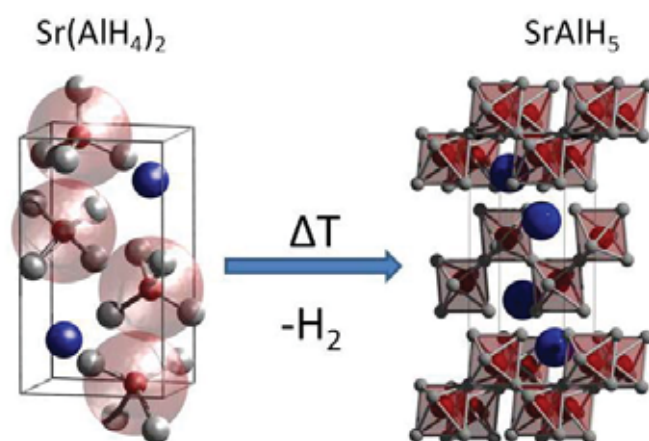


Figure 1. Crystal structures of $\text{Sr}(\text{AlH}_4)_2$ and SrAlH_5 [2]

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Experimental and numerical modelling studies of the kinetics of hydrogen evolution from zirconium hydride

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Zirconium hydride, because of high atom content of hydrogen, $7.0 \times 10^{22} \text{ atoms/cm}^3$, is regarded as a promising potential material for hydrogen storage. Moreover, it is potentially one of the most ideal moderators in nuclear reactors because of its high neutron scattering cross-section, low neutron absorption cross-section and negative temperature coefficient of reactivity. However, hydrogen would lose from zirconium hydride and thus reduce the H/Zr ratio at the reactor working temperature, which is the major performance constraint for these reactors. Although many studies on the thermal, mechanical and electrical properties of zirconium hydride have been reported, limited information is available on hydrogen desorption kinetic process. Therefore, it is extraordinarily important to understand the hydrogen desorption kinetics of zirconium hydride for the development of its application fields.

In this work, decomposition of zirconium hydride powders was investigated by a coupled thermogravimetry (TG) and thermal desorption spectroscopy (TDS) technique (IGA, Hiden Analytical). The structural changes were identified by the XRD experiments. It was found that phase transforming was the rate limiting step and corresponded to the observed desorption peaks. To identify the origin of each desorption peak, we have elaborated a novel mathematical model, which takes into account recombination of hydrogen on the surface, the diffusion of hydrogen and phase transformation steps. The simulated TDS results agreed satisfactorily with the experimental data and showed clearly a four-step process. The desorption kinetic parameters such as activation energy and pre-exponential factor for each step were estimated with the help of numerical fitting. The numerical modelling method could be applied to other metal-hydrogen system with the given thermodynamic parameters.

Hydrogen Accumulates in and UH_3 Precipitates at Carbides in Uranium Supersaturated in H and C.

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The spatial distribution of UC is easily seen by microscopy, but the distribution of UH_3 is not known, but has been proposed to occur at carbides [1]. A 30 keV caesium ion beam of a CSD Cameca NanoSIMS 50 sputtering 9 squares (1600 to $12600 \mu\text{m}^2$) to depths between 1 and $9 \mu\text{m}$ produced the elemental distributions of H^- , C^- , and O^- in figure 1. Images $\alpha 1$ and $\alpha 2$ reveal a perfect one-to-one correspondence between carbon and hydrogen. Images $\beta 1$ and $\beta 2$ ($\sim 10 \mu\text{m}$ carbide) show that some hydrogen accumulates inside carbides, but has the highest concentration at their perimeters. In small carbides ($\sim 2 \mu\text{m}$ size, image γ) H and C have about equal concentration throughout. Image δ summarizes the H/C^- ratio results: 0.038 ± 0.053 in large, and 1.87 ± 2.09 in small inclusions. The ternary (UCH) phase diagram is unknown, but likely has high H content phases (analogous to (LaCH) [2] and (YCH) [3]). The high H/C^- ratio at perimeters of large UCs and in small UCs indicates UH_3 precipitation (stable only at low temperatures). UH_3 dissociates H_2 and is thus a catalyst for hydride initiation at H-exposed U surfaces; the observed frequency of hydride initiation at UC boundaries, and its dramatic decrease after electro-etching U and thereby eliminating UH_3 around UC inclusions [4] is consistent with our results.

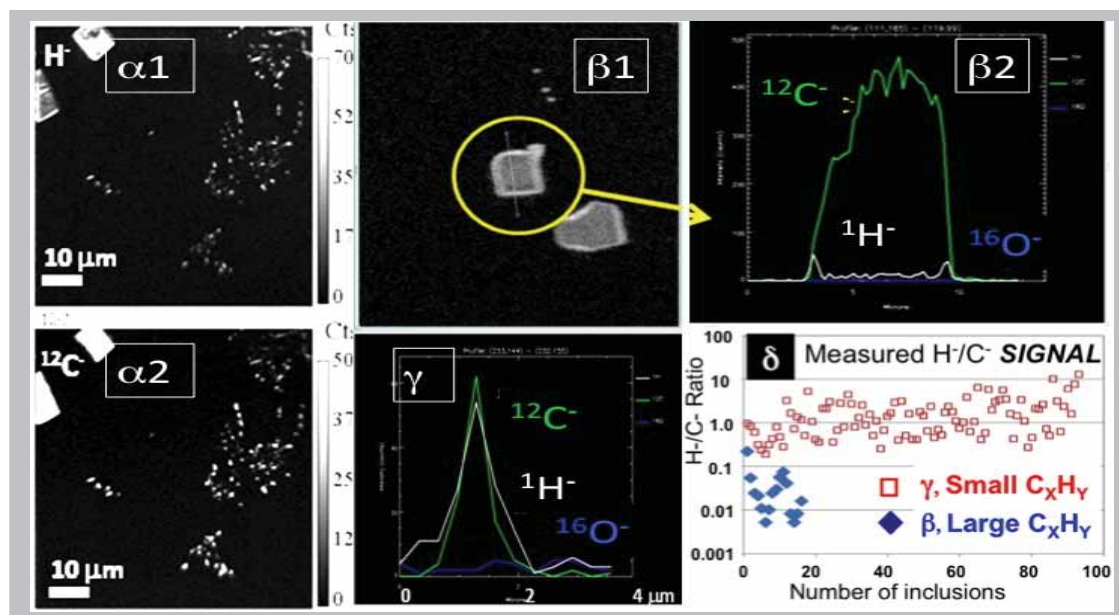


Figure 1. Hydrogen and oxygen distribution in and around uranium carbide inclusions.

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Interactions of C₆₀ with Metal Hydride Systems

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Abstract:

Extensive theoretical and experimental studies have demonstrated that nanocomposites prepared from hydrides and carbonaceous nanostructures (graphene, CNT's, C₆₀, etc.) are unique materials that can store hydrogen reversibly under milder conditions than the pure hydrides themselves. Initial work by our group has demonstrated that the intimate mixing of carbon nanostructures with complex metal hydrides (NaAlH₄, LiBH₄, and LiAlH₄) enhances the desorption/absorption of hydrogen in these materials and forms novel nanocomposites. Fullerene (C₆₀) consistently outperformed other carbonaceous nanomaterials examined. In order to identify the role of C₆₀ in these nanocomposites, a systematic spectroscopic and thermo-gravimetric analysis was performed. It was determined that the active hydrogen storage material is M_x-C₆₀-H_y and suggested that simple metal hydrides (i.e. LiH) can be used to prepare the nanocomposites. For example, it was determined that a nanocomposite prepared using a 6:1 mole ratio of LiH and C₆₀ produced a material that can reversibly store 5 wt % H₂ via a chemisorption mechanism and that the hydrogen was bound on the fullerene cage in the form of C-H bonds. Other composites were also examined using LiBH₄ and C₆₀ resulting in a composite made of C₆₀H_y and LiBH₄. This composite was found to be reversible, including the LiBH₄ fraction of the composite. The mobility of Li and H ions in LiBH₄/C₆₀ composites were found to be enhanced due to the presence of C₆₀. The enhancement in lithium ion mobility of the annealed material is comparable to that previously observed for LiX (X=halide) addition to LiBH₄. Further studies of these materials have demonstrated that they could potentially serve as components of new and novel energy storage and conversion devices.

Structure Determination of Metal-C₆₀ Nano-composites - invited

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Recent investigations demonstrated an improved desorption/absorption of hydrogen when mixing complex metal hydrides, NaAlH₄, LiAlH₄ and LiBH₄, with carbon nanostructures [1]. Fullerene (C₆₀) proved to be the best choice among the various carbonaceous nanomaterials examined. After systematic evaluation of the data, the studies suggested that metal hydrides, i.e. LiH and NaH, can be used to synthesize intercalated fullerenes capable of reversibly storing hydrogen as M_x-C₆₀-H_y (M = Li, Na) [2-4]. It was determined that the weight percent of hydrogen stored in the material is intimately linked to the stoichiometric ratio of M:C₆₀. For instance, a 6:1 molar ratio of LiH and C₆₀ can reversibly store 5 wt% hydrogen with an onset temperature of 270 °C.

During multiple hydrogen desorption/absorption cycles the fragmentation of the M_x-C₆₀-H_y cage of fullerene can be very complex and advanced tools, such as the neutron scattering instruments of the JEEP II research reactor at Institute for Energy Technology, can shed light on fundamental relations between the structural characteristics and the performances of our materials.

In order to follow the phase transformations and change in the sample's morphology after treatment under various conditions we performed both small-angle neutron scattering (SANS) and powder neutron diffraction (PND) on samples of Li_x-C₆₀-D_y and Na_x-C₆₀-D_y. From the powder X-ray and neutron diffraction data on Li_x-C₆₀-D_y and Na_x-C₆₀-D_y, we could verify that reversible phase transitions occur during absorption/desorption. For instance, in the case of Li_x-C₆₀-D_y, during deuterium absorption the Li atoms de-intercalate from the Li₆C₆₀ phase and form LiD. During desorption LiD disappears, suggesting a reversible reaction. Furthermore, the data show the importance on the chosen temperature in determining the type of phase formed during absorption in the case of Na_x-C₆₀-D_y.

From SANS performed on M_x-C₆₀-D_y after the first absorption/desorption cycle it is clear that the "as prepared" sample undergoes nanostructural changes upon treatment, but the morphology remains similar after further cycles.

The identification of the exact structure and morphology of the different phases formed during hydrogenation/dehydrogenation on both Li_x-C₆₀-D_y and Na_x-C₆₀-D_y could potentially serve to clarify the performances of these materials as components in new energy storage and conversion devices.

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Investigation of the hydrogen distribution inside a storage tank by *in situ* Neutron Radiography of a hydrogen storage tank

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Due to the sensitivity of neutrons towards hydrogen, Neutron Radiography (NR) is the ideal technique for *in situ* investigations in order to directly observe the hydrogenation behaviour of metal hydride powder beds and pellets inside a storage tank under operating conditions.

First-time *in situ* NR measurements of a hydrogen storage tank filled with sodium alanate using fission neutrons were successfully performed at the instrument NECTAR at FRM II. In the course of these measurements, a new evaluation method was developed allowing for a quantitative investigation of the hydrogen distribution inside the storage tank. The results confirm previous studies performed at GeNF/FRG-1 [1,2] and reveal an interesting correlation between the material packing density and the reaction kinetics. Further measurements were performed at NEUTRA/ PSI and at NIF/NIST using thermal neutrons to allow for a more detailed investigation with an enhanced contrast and time resolution. With the aid of these results, the production of metal hydride powder compacts for and the design of storage tanks can be optimized with respect to efficiency, capacity, kinetics and safety.

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Cycle Stability of Gas Atomised Alloy Electrodes

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The cycle stability of negative electrodes based on AB₅-type alloys is the most valuable parameter determining their use in Ni-MH batteries. The stability of electrodes depends on the alloy bulk and surface composition, e.g. corrosion or passivation in the electrolyte, and the lattice expansion upon hydriding, which leads to mechanical stress in the alloy. There are several ways to improving the cycle stability, among them the alloy fabrication technology can influence the electrochemical characteristics, storage characteristics and especially the cycle stability of the MH electrodes.

High pressure gas atomisation (HPGA) is a synthesis method, which allows to produce spherical intermetallic alloy powders in the micrometer size range and a high cooling rate up to 10⁶K/s. The particle surface possesses enhanced corrosion resistance, i.e. leading to an increased cycle stability [1]. The HPGA technology can produce a large quantity of alloy (1g – 10 kg/h) therefore, gas atomisation results directly in small particles and simplifies the standard long route for manufacturing the AB₅ type materials for battery electrodes [1, 2].

The influence of the composition and special structure obtained by HPGA on the electrochemical characteristics and cycle life of gas atomised LaNi_{4.5}Al_{0.5}, LaNi_{2.5}Co_{2.4}Al_{0.1}, (La+Mm)Ni_{3.5}Co_{0.7}Al_{0.35}Mn_{0.4}Zr_{0.05}, MmNi_{4.3}Al_{0.2}Mn_{0.5} alloy electrodes have been investigated. All samples exhibit the hexagonal CaCu₅-type structure. The lattice expansion upon hydriding for all alloys is by ~7% less than for LaNi₅. The particles of the gas atomized alloy without Co have a spherical shape, whereas the Co-containing alloys are irregularly shaped, e.g. the shape of particles is dependent on the alloy composition. The cycle life curves for the alloy electrodes without Co have similar behavior and show a fast activation (2-3 cycles to reach max. capacity), but also fast degradation (130-180 cycles for 50% of maximum discharge capacity). LaNi_{2.5}Co_{2.4}Al_{0.1} and (La+Mm)Ni_{3.5}Co_{0.7}Al_{0.35}Mn_{0.4}Zr_{0.05} alloy electrodes activate after 5-7 cycles and show a very stable discharge behavior (more than 400 cycles). The Co-containing alloy electrodes mostly loose the cycle stability because of mechanical decrepitation, whereas the alloys without Co suffer from selective dissolution of aluminum. This is confirmed by means of SEM, WDX and ICP-OES data. According to this data, the most easily dissoluble element from the alloys is aluminum.

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Shaped Chromium-based Metal-Organic Frameworks (Cr-MOFs) for Hydrogen Storage Applications

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Abstract

Materials-based solutions continue to attract increasing attention as viable options for hydrogen storage applications [1]. Chromium-based MOFs are widely regarded as promising materials for hydrogen storage due to their high surface areas, porosities, functionality and structural resistance toward atmospheric moisture [2]. However, their practical use is hindered by the low packing densities since they are normally obtained as fine powders.

In this work, Cr-MOFs were synthesized in large amounts, combined with a binder and shaped using a granulator. The materials were then evaluated as packed adsorbent for hydrogen storage applications. The shaped Cr-MOF materials have relatively higher packing densities, better thermal conductivities and higher volumetric hydrogen sorption capacities than the powder material. These improved properties and the ease of handling the material make shaped Cr-MOFs particularly suitable for practical hydrogen storage applications.

Keywords: Cr-based MOF, packing density, shaped powder, hydrogen storage

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Catalyzed Hydrogen Storage Reaction of $2\text{LiH}+\text{MgB}_2$

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LiBH_4 is considered as a candidate for hydrogen storage because it can offer a high capacity of 18.4 wt%. Among LiBH_4 based composite hydrides, $2\text{LiBH}_4+\text{MgH}_2$ exhibits promising properties such as reduced thermodynamic stability, improved reversibility and good reaction kinetics. In this study, we report our catalyst developments for the hydrogen storage reaction of $2\text{LiH}+\text{MgB}_2$, which is converted reversibly to $2\text{LiBH}_4+\text{MgH}_2$. Additions of lanthanum and zirconium based compounds were found to be very effective in catalyzing the composite hydrides. The catalyzed composites demonstrated significantly enhanced hydrogenation and dehydrogenation kinetics. Moreover, their cycling stability was greatly improved. Further analytical investigations revealed that both the composition and nanostructure of catalyzing species are crucial for the effects.

Investigation of dehydrogenation processes of ammonia borane and metal hydride composites

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AB-MH (Ammonia Borane-Metal Hydride) composites, such as AB-LiH [1], AB-NaH [1] and AB-MgH₂ [2], have been extensively studied up to now. However, systematic investigation on these composites has not been explored.

We have synthesized various kinds of AB-MH (M = K, Na, Li, Ca, Mg, Al) composites by ball-milling and investigated their dehydrogenation properties [3]. The prepared composites were heated to 200 °C and the amount of by-product gases were estimated by using TG-MS results. There was a good correlation between the amount of by-product gases (NH₃ and B₂H₆) and Pauling electronegativity of M, χ_p , as shown in Fig. 1. The amount of NH₃ was decreased as χ_p increased. On the other hand, the amount of B₂H₆ was decreased as χ_p decreased. These results suggest that combining both AlH₃ and NaH (LiH) with AB can suppress all the by-product gas emissions. On the basis of above results, we synthesized AB-MAIH₄ (M = Na, Li) composites because MAIH₄ (M = Na, Li) is the compound consisting of MH (M = Na, Li) and AlH₃. As shown in Fig. 2, both composites did not desorb NH₃, B₂H₆ and B₃H₆N₃ at all within the accuracy of our apparatus. Three exothermic peaks were observed in DTA profiles. About 4-5 wt% H₂ was desorbed below 260 °C. From XRD analysis, the formation of mixed-metal amidoborane phase was suggested. Detailed reaction processes will be discussed by comparison with the results of composites prepared by hand-milling.

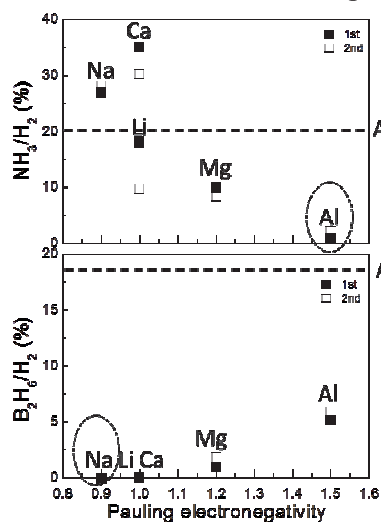


Fig. 1 The amount of NH₃ and B₂H₆ desorbed from AB-MH composites.

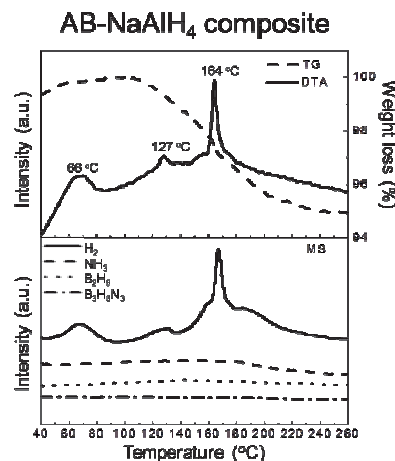


Fig. 2 TG-DTA-MS results of AB-NaAlH₄ composite. The heating rate was 5 °C min⁻¹.

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Hydrogen storage properties and microstructural evolution of the mixtures $\text{MgH}_2\text{-Li}_3\text{N}$ with different ratios

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The Li-Mg-N-H system has attracted great attentions due to its high capacity, reversibility and moderate operating conditions [1-3]. LiMgN , with a theory hydrogen capacity of 8.2 wt%, is one of the promising hydrogen storage materials. In our previous work [4], LiMgN-2LiH was obtained by ball milling of MgH_2 and Li_3N at the molar ratio of 1:1. The ball-milled $\text{MgH}_2\text{-Li}_3\text{N}$ (1:1) mixture has a capacity about 3.2 wt% under a pressure of 10 MPa with an onset absorption temperature at 130 °C. In this work, different molar ratios of $\text{MgH}_2\text{-xLi}_3\text{N}$ ($x=0.5, 1, 2$) mixtures were prepared by ball milling in order to obtain high amount of LiMgN . It revealed that the higher content of Li_3N is effective for the formation of LiMgN . XRD patterns showed that the phase constitutes are changed with molar ratios of MgH_2 and Li_3N . Mg_3N_2 , MgH_2 and LiH phases were obtained in the $\text{MgH}_2\text{-0.5Li}_3\text{N}$ mixture, seen Fig.1, but, LiMgN and LiH phases were detected in the $\text{MgH}_2\text{-(1, 2)Li}_3\text{N}$ mixtures. The hydrogen storage properties of the as-prepared $\text{MgH}_2\text{-xLi}_3\text{N}$ ($x=0.5, 1, 2$) mixtures were studied by a Sieverts'-type apparatus. Powder XRD, FTIR and SEM measurements were used to identify the phases structure and microstructural characterizations of the products during the hydrogenation/dehydrogenation process. The reaction mechanisms during the hydrogenation/dehydrogenation process are discussed.

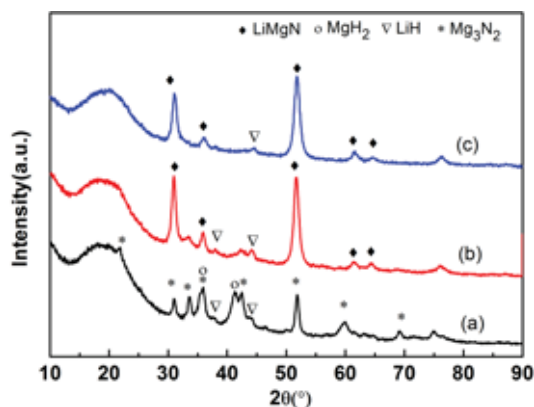


Figure 1. XRD patterns of the ball-milled $\text{MgH}_2\text{-xLi}_3\text{N}$ mixtures with different molar ratios: (a) $x=0.5$; (b) $x=1$; (c) $x=2$. The amorphous-like broad peak ($14\text{-}26^\circ$) is from the Scotch tape that was used to cover the powders.

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Thermodynamics of ammine complex of Metal Halide and Borohydride

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Ammonia (NH₃) is promising hydrogen carrier because of its high gravimetric density of 17.8 wt.%. Moreover, by compression of more than 0.85 MPa at room temperature, a high volumetric density can be realized due to the liquifaction. However, this liquified pressure is slightly high for practical use. In order to decrease this pressure effectively, some halides or complex hydrides are focused on because large amount of NH₃ as molecule in solid phase can be absorbed to form ammine complex. The volumetric densities of ammine complex are almost comparable with that of liquid NH₃. By using the NH₃ absorbing materials, NH₃ can be stored effectively and safely because of its low absorbing pressure.

In this work, we have systematically investigated the NH₃ absorption and desorption properties of various kinds of metal halides and borohydrides by volumetric technique, which is so-called pressure-composition (PC)-isothermal measurement. The NH₃ pressure from 0.001 to 0.8 MPa can be measured by using this PC-isothermal apparatus. By the systematical research, the correlation between plateau pressure due to ammine complex formation and electronegativity of cation or anion in metal halides or borohydrides is discussed to obtain the guideline for designing the NH₃ storage materials on a safe practical use.

Figure 1 shows PC-isotherm for LiCl at 293 K. The plateau pressure corresponding to the ammine complex formation was observed at 0.178 MPa, and 4 mol of NH₃ were absorbed as the equilibrium state.

By systematic investigation of thermodynamic properties for various kinds of halides or complex hydrides, it was clarified that the materials with larger difference of electronegativity between cation and anion revealed the higher equilibrium pressure.

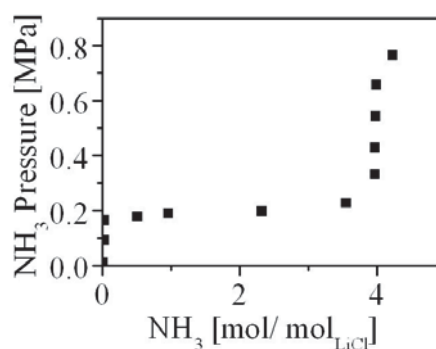


Figure 1. PC-isothermal measurement of LiCl.

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Hydrogen Storage Properties of Transition Metals Decorated Li Fullerenes.

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Carbon based materials, such as fullerides and graphene derivatives, are fascinating systems for solid state H₂ storage. Theoretical studies have shown that some metal-decorated fullerides, namely Na₈C₆₀ and Li₁₂C₆₀, may absorb up to 9.5 and 13.5 wt% H₂ respectively.

Recent experimental works proved that alkali metal intercalated compounds (Li₆C₆₀ and Na₁₀C₆₀) are able even to reversibly absorb up to 5 wt% and 3.5 wt% H₂, through the formation of a hydrogenated phase of C₆₀ (called “fullerane”) at temperatures higher than 250 °C.

Muon spin relaxation studies, performed on Li₆C₆₀ and Na₁₀C₆₀ samples, evidenced that hydrogenation of charged C₆₀ molecules is even more efficient at cryogenic temperatures, suggesting that the high T needed for the hydrogen uptake by these materials is required to obtain the metal cluster assisted H₂ molecule dissociation. The insertion of a transition metal, able to promote such a dissociation, could therefore decrease the thermal energy required for the process and drive the material uptake properties to higher stored values.

In this work we describe the new synthesis and the improved H₂ sorption behavior (kinetic and thermodynamic features) of Li–fullerides doped with different amounts of Pd, Pt and Ni, evaluated by coupled manometric – calorimetric analyses.

X-Ray powder diffraction studies, scanning and transmission electron microscopies, Raman and MuSR spectroscopies are used to describe the hydrogenation mechanism of the compounds and to hypothesize the catalytic action mechanism of the transition metals.

Direct Hydrogenation of Li-Mg Alloy by High-energy Reactive Milling

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Ternary Mg-based hydrides A-Mg-H (A = alkali metals) have received attention as possible hydrogen storage media, due to their relatively high H₂ content (e.g. NaMgH₃ exhibits a nearly reversible 6.0 wt% H₂ capacity) [1]. Furthermore, the interest in some perovskite-type AMgH₃ compounds is not restricted to hydrogen storage, but also potentially for use in future electronic devices [2].

With interest in a high H₂ capacity and possible favourable electrochemical properties, previous theoretical studies suggested that Li-Mg-H ternary hydrides were most likely to be trigonal LiMgH₃ (8.8 wt% H₂), and/or orthorhombic Li₂MgH₄ (9.5 wt% H₂) [3]. However, attempts to synthesise new Li-Mg-H compounds either by ball-milling mixtures of LiH and MgH₂ powders, or by hydrogenation of Mg-rich Mg-Li alloy at 40 bar H₂ and 200-400 °C, were not successful [4].

Ilika used a unique ultra-high vacuum high-throughput physical vapour deposition (HT-PVD) to synthesize a wide range of Li-Mg-H thin films and then screen their hydrogen storage properties [5]. It was demonstrated that a sample with a composition of Li_{0.76}Mg_{0.24} could store 10.6 wt% H₂ which was reversible under mild conditions.

In this work, high-energy reactive milling of a Li-Mg alloy was carried out in 100 bar H₂, to attempt to directly insert H atoms into the sites of the ordered Li-Mg alloy phase. After milling, the majority of the Li-Mg phase was hydrogenated to form LiH and MgH₂ phases; XRD refinement suggests that the MgH₂ contains a small concentration of Li. In addition, TGA/TPD shows a small release of H₂ at around 425 °C, which might suggest the formation of a minor Li-Mg-H phase. Although this dehydrogenation temperature is too high for mobile hydrogen storage, it may have properties that are of interest for other applications such as heat storage and electrodes in lithium batteries. The structural and thermodynamic properties of the mixed-hydrides composite during heating will be discussed.

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Producing Hydrogen from Ammonia Using Sodium Amide

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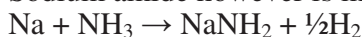
Ammonia offers attractive properties for use as an energy vector: it has a hydrogen content of 17.8 wt %, there are no carbon dioxide emissions associated with its endpoint usage, it is produced on the hundred million tonne scale each year already, it is liquid at 10 bar and ambient temperatures, it is not highly flammable like hydrogen, petrol and LPG. Ammonia can be envisaged as a hydrogen store in the hydrogen energy cycle, where it is decomposed into its constituent hydrogen and nitrogen parts and the hydrogen used in a fuel cell with oxygen to release energy with water as a byproduct.

A significant problem with this ammonia/hydrogen cycle is that the kinetics of ammonia decomposition are slow and require precious metal catalysts (ruthenium is the best known catalyst).

In this talk, I will present the results of work recently carried out at the ISIS neutron source at the Rutherford Appleton Laboratory. We used sodium amide as a catalyst to decompose ammonia into nitrogen and hydrogen with similar/better kinetics to the state-of-the-art ruthenium (see figure 1). Sodium amide has been studied previously with regard to its hydrogen storage potential since it decomposes to give nitrogen and hydrogen via the following:



Sodium amide however is manufactured according to the following reaction:



Therefore flowing ammonia over sodium (or sodium amide) means the above equations are combined to give the decomposition of ammonia:

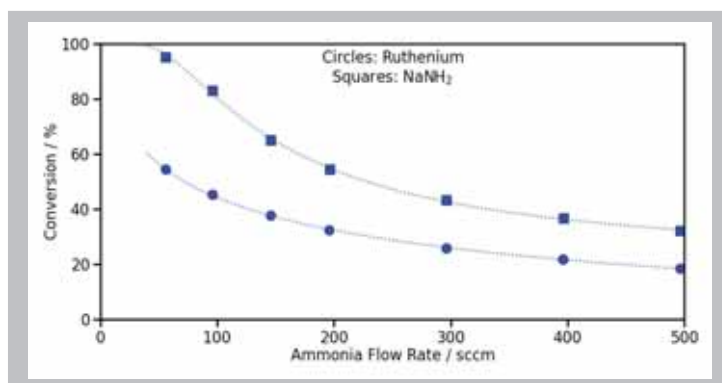
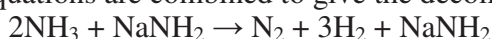


Figure 1: Sodium amide catalyst compared to ruthenium for various flow rates at 500 °C.

At current efficiencies we would need approximately 1 kg of sodium amide to provide enough catalyst to fuel a car with ammonia (35 kW hydrogen fuel cell).

A Class of Superior Ammonia Storage Materials Based on Solid Solution Barium Strontium Chloride Salts

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Metal halide ammines are very attractive materials for ammonia absorption and storage¹. Applications include thermochemical heat pumps², ammonia separation³, and ammonia storage⁴ for fuel cells⁵ and selective catalytic reduction (SCR) of nitrogen oxides from combustion processes⁶. Especially, for ammonia storage applications, the practically accessible or usable gravimetric and volumetric storage densities are of critical importance as is the release temperature (here defined as the temperature at which the ammonia begins to desorb at 1 bar). Many pure metal halide ammines have been characterized in terms of gravimetric ammonia density and release temperature. Volumetric ammonia density, though at least as important, has only been reported for a few salts⁸. The reason for using metal halide ammines for ammonia storage is the inherent safety associated with a solid that cannot leak out of a container. However, if the release temperature is less than ambient, all ammonia will escape (although much slower than liquid ammonia) from a leaking container. On the other hand, if the release temperature is too high, it is difficult to release the ammonia. A release temperature below 100 °C is highly desirable for multiple reasons: engineering materials are cheap and readily available, many of the storage applications within SCR or fuel cells are water cooled with waste heat below 100 °C and the energy and time needed to reach the release temperature is limited. Thus, ammonia storage materials, which combine high storage capacity with release temperatures between 20-100 °C, are particularly valuable. Here, the usable ammonia capacity is defined as the amount of ammonia released at 1 bar in this temperature range.

We synthesized, with spray drying and characterized, with *in situ* thermogravimetry and structural characterization, a range of new stable strontium - barium chloride solid solutions, predicted by ab-initio computations, with superior ammonia storage densities. By tuning the barium/strontium ratio, different crystallographic phases and compositions can be obtained with different ammonia ab- and desorption properties. In particular we show, that in the molar range of 35-50% barium and 65-50% strontium, stable materials can be produced with a practically usable ammonia density (both volumetric and gravimetric) that is higher than any of the pure metal halides, and with a practically usable volumetric ammonia density of 99% of liquid ammonia.

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Comparative Studies of Sticking Efficiencies in Gas Adsorptions Analysis on Selected Metal Organic Frameworks

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Materials are being sought that will be capable of adsorbing large amounts of gas for practical applications. It has been well established that MOFs with high surface areas are good adsorbents for various gases [1]. It has also been established that high surface area MOFs generally adsorb more gas than those with low surface areas. However, in some cases the amount of gas adsorption on a MOF is greater than that which would be expected based on surface area alone. It is believed that the sticking efficiency of a gas on the surface is an important factor that must be considered when comparing gas adsorption on MOFs. Therefore the concept of sticking factor was introduced as a way to compare the sticking efficiency of various gases on different MOFs [2].

In this study, the gas adsorptions of three gases on five different MOFs were studied and compared. The gases chosen were hydrogen, methane, and carbon dioxide. The MOFs were Zn-BDC, Zn-NDC, Zn-Mim, Cu-BTC, and Fe-BTC. These MOFs were selected because three of them (Zn-BDC, Zn-NDC, Zn-Mim) contain the same zinc metal but different linkers. Therefore it should be possible to determine the effect of linker on the sticking factor. Two others (Cu-BTC, and Fe-BTC) contain the same linker but different metals. It was found that in the three MOFs containing a common metal but different linkers, the Zn-NDC had the highest sticking efficiency. Since the linker in this MOF is 2,6-naphthalenedicarboxylic, it was concluded that it is the most effective linker. In the two MOFs with the same linker but different metals the Cu-BTC had a greater sticking efficiency than Fe-BTC. Therefore it was concluded that copper was a more effective metal for adsorption than iron. It should be noted that all of the zinc-containing MOFs had higher sticking efficiencies than copper or iron. This indicates that zinc may be a more effective metal than iron or copper but additional experiments containing MOF with these three metals and a common linker must be done to confirm this.

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Hydrogen Adsorption Characteristics of Magnesium Combustion Derived Graphene at 77 and 293 K

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Bulk graphene was prepared by combusting magnesium in a CO_2 atmosphere, producing moderately large quantities of material with a different morphology and a more ordered carbon lattice than reduced graphene oxide and other bulk graphene synthetic methodologies. Approximately 200 mg of graphene in powder form was used for each sorption measurement and the graphene samples were heated to 523 K for at least 12 hours under vacuum to remove any oxygen or water. The volume of the graphene sample was determined via ultra-high purity (99.999%) helium pycnometry performed at 523 K. A quite low surface area of 235.5 m^2/g was determined and X-ray photoelectron spectroscopy showed *ca* 9 at.% of magnesium and its oxides which do not contribute to hydrogen adsorption.

The hydrogen sorption measurements were performed on a custom built Sieverts apparatus. Results for the hydrogen sorption measurements at 77 K and 293 K are shown in Figure 1. For a cryogenic temperature of 77 K the adsorption at 65 bar was found to be 0.85 wt.% with a desorption showing a slight hysteresis. For the equivalent pressure of 65 bar but at a room temperature of 293 K the adsorption was found to be approximately 0.2 wt.%, significantly lower than at 77 K. This significant adsorption decrease with increasing temperature is consistent with low binding energies associated with physisorption of molecular hydrogen to the carbon surface. For 293 K, the adsorption isotherm was performed through to 340 bar with a maximum storage capacity of 0.9 wt.%.

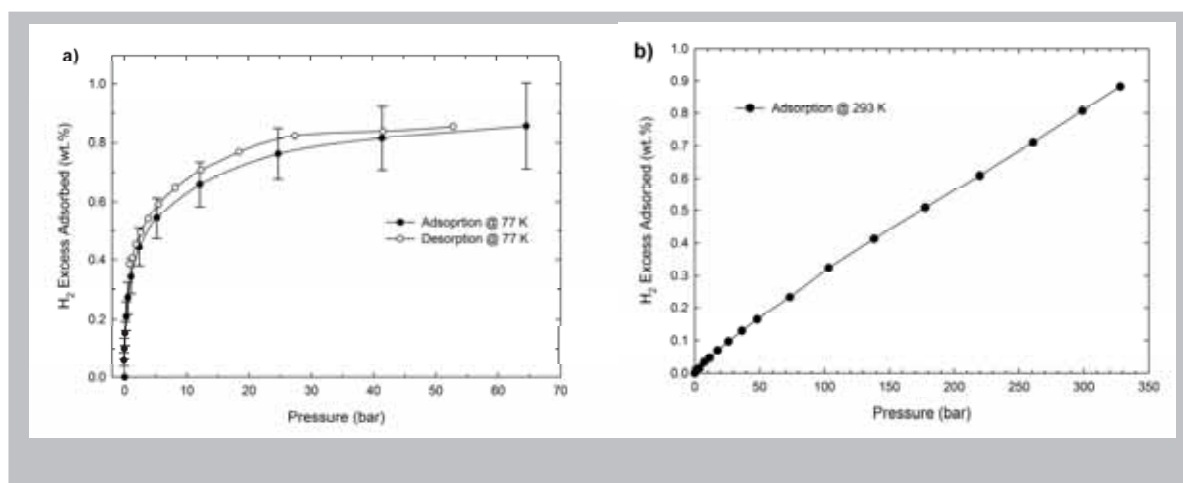


Figure 1. a) Hydrogen adsorption/desorption isotherm of graphene at 77K to 65 bar
b) Hydrogen adsorption isotherm of graphene at 293K to 340 bar

Hydrogen-storage Properties of Pd Nanocrystals covered with Metal-organic Framework

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Research into the reaction of metals with hydrogen is very important for the development of potential applications, such as effective catalysts for hydrogenation or advanced materials for hydrogen storage and purification. Many investigations into hydrogen storage using bulk metals or alloys have been carried out over the past half-century. Recently, metal nanoparticles have been investigated as hydrogen-storage materials. On the other hand, metal-organic framework (MOF), which are assembled from metal ions and organic bridging ligands, have received much attention because of their many attractive applications in catalysis, selective gas adsorption, chemical separations, drug delivery, and proton conductivity. In addition, MOFs have played a significant role in the field of hydrogen adsorption in recent years. Here, we present remarkably enhanced capacity and speed of hydrogen storage in Pd nanocrystals covered MOF, HKUST-1 (copper(II) 1,3,5-benzenetricarboxylate). The Pd nanocrystals covered with the MOF have twice the storage capacity of the bare Pd nanocrystals. The significantly enhanced hydrogen storage capacity was confirmed by hydrogen pressure composition isotherms and solid-state deuterium nuclear magnetic resonance measurements. The speed of hydrogen absorption in the Pd nanocrystals is also enhanced by the MOF coating.

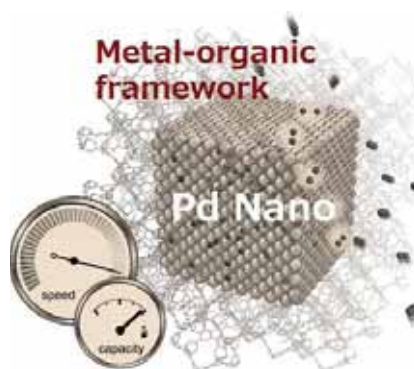


Fig. Hydrogen storage in Pd nanocrystals covered MOF

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Neutron Diffraction of Hydrogen Adsorption in Metal-Organic Frameworks at High Pressures

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Metal-organic frameworks (MOFs) have received significant attention as adsorbent materials for on-board hydrogen storage. As the interaction of H₂ molecules with these materials is fairly weak (5-15 kJ/mol), storage at elevated pressures is likely required to reach volumetric uptake targets for many applications. While low-coverage adsorption sites for H₂ in several MOFs have been determined using neutron diffraction methods,¹⁻³ very little experimental data exists on the structure of adsorbed H₂ at higher pressures. We have carried out neutron diffraction experiments in which H₂ is loaded in several MOFs at pressures of 10-100 bar and data is refined using both Rietveld and maximum entropy methods. Density plots obtained from these experiments (Figure 1) are a first step towards the elucidation of the organization of H₂ molecules inside the pores of a MOF.

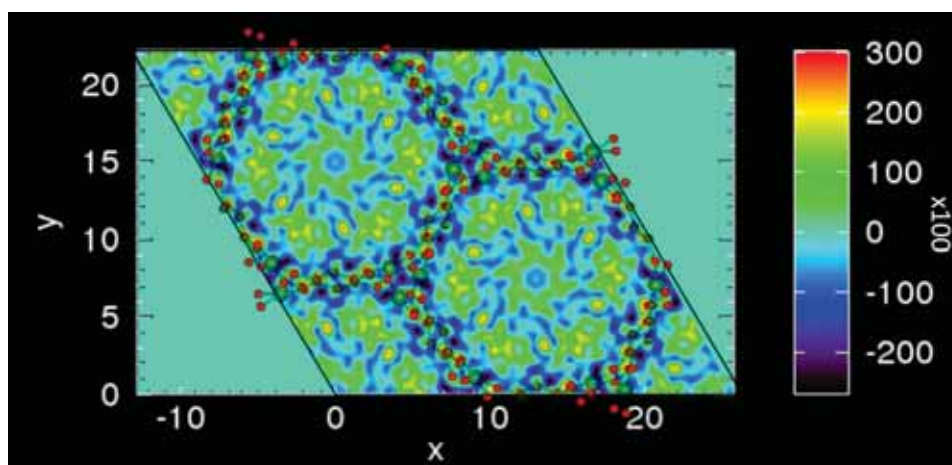


Figure 1. Fourier difference plot derived from refinement of neutron diffraction data of Zn₂(dobdc) loaded with 90 bar D₂ measured at 77 K.

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Morphological Studies on the Formation of TiO₂ Nanotubes Arrays: Improvements in the Photocatalytic Response for Hydrogen Production

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In times where the search for new viable routes of renewable energy production is the focus of the technological research, devices which may present the possibility of energy production from photoprocesses should be considered. Hydrogen production via photocatalytic water splitting has been extensively studied in recent years, being that any factor that may play a role on the efficiency of the photocatalytic cells used for this application is of capital importance. Among the many semiconductor materials used in photocatalysis, the titanium dioxide (TiO₂) is far the most studied due to its better activity for light induced processes. One of material engineering challenges behind the production of anodized nanotubular TiO₂ photoanodes is the understanding that the different process parameters have over the tubular structure produced. Among these effects may be pointed the presence of a disordered oxide structures or “nanograss” which occurs due to the chemical etching and eventual dissolution of the nanotube tops leading to a decrease on the photocurrent response necessary to a satisfactory performance of the hydrogen production device. In this work, it was employed a experiment design based on orthogonal arrays via Taguchi method in order to evaluate the effect of parameters such as the substrate chemical pre-treatment, water content, HN₄F concentration and applied potential. In this way, the samples went through an anodization process in a 1:3 etileneglycol and glycerol base electrolyte with variable parameter values accordingly to the proper orthogonal array. The morphological study was based on scanning electron microscopy (SEM) images of the anodized samples, and X-Ray diffraction (DRX) analysis evaluated the crystalline structure after the heat treatment, aiming to understand the influence of the variations not only on the morphology, but also on the crystallite structure of the TiO₂ nanotubes. The results showed that the Taguchi method of experimental design could be a powerful tool when applied on the study of systems with a small number of variants, having been satisfactory in the case of this work with respect to the understanding of the outcome of specific parameters variation and thus on the control of the nanotubular structure obtained. Special attention was given to the nanograss formation, being that the images obtained point the strict relation between its formation and the studied parameters.

Hydrogen Storage on Defective Graphene Foam

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Graphene is a monolayer of graphite. It has an extremely high surface-area-to-weight ratio, is strong, cheap, chemically inert, and environmentally benign. As such it may be an ideal substrate for hydrogen storage. The theoretical maximum surface area of graphene is $2630 \text{ m}^2/\text{g}$. However, commercially available graphene powders tend to have surface areas limited to around $600 \text{ m}^2/\text{g}$. This is due to restacking of the individual graphene sheets such that the surfaces stick back together very easily. In order to solve this problem some kind of three dimensional graphene architecture is desirable.

We synthesize defective graphene foam by simple combustion of sodium ethoxide, followed by heat treatment in various gases. This can be produced in gram-scale batches, with surface areas as large as $1700 \text{ m}^2/\text{g}$. The structure is highly porous with micron-scale hollow spheroidal cells encapsulated by graphitic walls approximately 2 nm in thickness. Pore size distribution was measured by nitrogen adsorption and a high proportion of small $< 5 \text{ nm}$ pores are observed.

Hydrogen sorption isotherms were measured at 77K at up to 1 MPa on a sample with $1200 \text{ m}^2/\text{g}$ surface area. The hydrogen sorption capacity was measured as $2.1 \text{ wt}\%$, compared with $1.2 \text{ wt}\%$ for commercially obtained graphene, largely as a result of the improved surface area. In more recent results with $1600 \text{ m}^2/\text{g}$ graphene foam we have reached $2.6 \text{ wt}\%$ hydrogen sorption capacity.

We also measured samples at room temperature and recorded a hydrogen sorption capacity of $1.6 \text{ wt}\%$ at 1 MPa .

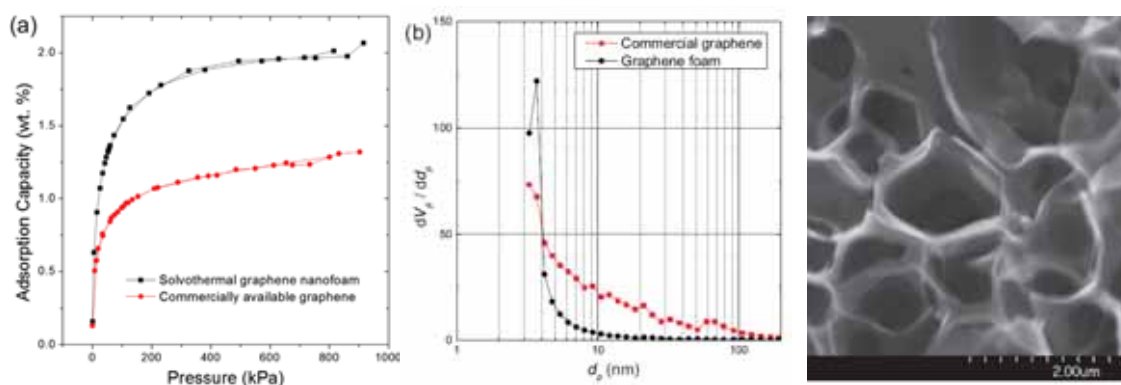


Figure 1. (a) Hydrogen sorption capacity of graphene foam versus a commercially available graphene powder. (b) Pore size distribution. (c) Electron micrograph.

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Hydrogen Storage Properties of Pd-doped Thermally Oxidised Single Wall Carbon Nanohorns

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The difficulties associated with the solid storage of hydrogen remain a major drawback for its widespread use as energy carrier. Single wall carbon nanohorns (SWCNHs) are considered promising materials for gas adsorption/storage applications [1,2], especially after tube opening and/or hole forming, a process that can increase the rather low specific surface area of the as-grown SWCNHs [3]. On the other hand, doping of carbon materials with transition metals has been reported to improve their H₂ storage capacity at ambient temperature, through metal-carbon synergistic effects [4]. In this work, SWCNHs were subjected to controlled heat treatment under air, while avoiding significant burn-off [3,5,6]. Both pristine and air-oxidised SWCNH samples were subsequently decorated with Pd nanoparticles. The doped and undoped samples were thoroughly characterized and their H₂ sorption performance was examined at 298 K up to 20 bar.

The pristine SWCNHs sample was produced by AC powered arc discharge in air [7,8]. Hole-opening was achieved by thermal oxidation at 550 °C for 5 min under flowing Ar/air (90/10) mixture. The deposition of Pd nanoparticles (~ 10 wt %) on both the pristine and the air-oxidised SWCNH samples was carried out by using Pd(NO₃)₂·2H₂O (40 % Pd) as metal precursor [4]. Based on N₂ adsorption measurements at 77K and IR spectroscopy it was found that oxidation increases significantly the specific surface area of the pristine sample, while the surface chemistry remains practically unaffected. Room temperature high-pressure hydrogen sorption measurements of the undoped samples (pristine and oxidized) revealed Henry-type behaviour and a rather low hydrogen storage capacity, which was however significantly enhanced upon metal-doping. The uptake of the doped samples could not be explained by simply adding the contributions from the Pd hydride formation and the sorption on the carbon support. This fact may constitute an indication of synergistic effects, for instance spillover triggered sorption and/or enhanced Kubas-type interactions with Pd nanoparticles.

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The Effect of Pd Loading on the Hydrogen Storage Capacity of Templated Porous Carbon Structures Grown in MCM-41

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As hydrogen is an environmental friendly alternative to fossil fuel sources, there is an increasing demand in its production. However, the difficulties in the hydrogen storage stand as the main bottleneck for the potential use of hydrogen. Therefore, materials which have large surface area, porous structure, and high affinity of hydrogen are needed to support hydrogen storage technologies. Carbon based materials are good candidates for hydrogen storage as they can accept and release hydrogen easily. MCM-41 which is a silica based material with ordered structure, high surface area, and large pore size can be used as template for the synthesis of porous carbon structures. It is known that loading transition metals in the carbon structures can enhance their hydrogen storage capacities. For this reason in this study, the effect of Pd loading on the hydrogen storage capacity of templated porous carbon structures was investigated. Microwave heating method which is both energy and time efficient was used for MCM-41 synthesis. After microwave heating the MCM-41 was filter washed and calcined, and then it was mixed with furfuryl alcohol. The templated porous carbon material was synthesized by heating the mixture up to 1000 °C. The morphology and structure of the MCM-41 template and the porous carbon material were characterized by scanning electron microscope, FTIR spectroscopy and X-ray diffraction analysis. Surface area, pore size and adsorption capacity were measured by Brunauer-Emmett-Teller (BET) method and the hydrogen uptake was determined by intelligent gravimetric analyzer (IGA) at room temperature up to 10 bar pressure.

Keywords: Hydrogen Storage, MCM-41, Templated Porous Carbon, Pd

abstract not submitted

Hydrogen Interaction with MOF-5 using Dispersion Corrected DFT for a Correct Interpretation of Rotational Inelastic Neutron Spectra

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H₂ adsorption in MOF-5 has been studied by density functional theory (DFT) simulation with the addition of a semi-empirical dispersion correction (DFT-D) to deal with the dispersive forces. Important zero-point energy corrections have also been calculated, yielding effective binding energies between 37 and 83 meV / H₂ (3.5 – 8.0 kJ / mol) in good agreement with MP2 level calculations [1] and previous dispersion corrected DFT results [2]. The rotational potential for a hydrogen molecule in each binding site has been evaluated through mapping the adiabatic surfaces. The rotational Schrodinger equation is solved directly to obtain the spectra of rotational states. Transition energies of the hindered rotational states have been calculated between 10 and 25 meV for the J(1←0) rotational transitions. The model is verified by comparing with neutron scattering spectra [3]. The inclusion of the dispersion correction with DFT-D is shown to significantly improve the H₂ framework interaction.

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Distributed “Hybrid” MH–CGH₂ System for Hydrogen Storage and its Supply to LT PEMFC Power Modules

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Slow charge/discharge of MH hydrogen storage units limited by heat transfer is a serious problem for the MH hydrogen storage and supply systems for LT PEMFC applications. Special engineering solutions are required to address this issue. The most efficient way is in the use of “hybrid” hydrogen storage where a Metal Hydride (MH) material possessing low hydride thermal stability is disposed in high pressure composite cylinder thus combining both Compressed Gas (CGH₂) and MH hydrogen storage advantages [1]. However, the implementation of such innovative approach requires addressing a number of engineering challenges which are often very expensive.

This presentation describes the layout and operating performances of a prototype distributed “hybrid” hydrogen storage and supply system for Low Temperature (LT) PEMFC applications ([2]; Figure 1) which uses individual MH (1) and CGH₂ (2) tanks with common gas manifold comprising a pressure reducer (3) and a refuelling valve (4). The heat exchanger (5) of the liquid heated-cooled MH tank (1) is a part of a circulation loop which includes air-liquid heat exchanger (6) with a fan (7), an expansion tank (8) with a circulation pump (9), as well as a heat exchanger (10) thermally coupled with the elements of the FC system (11) generating heat during its operation. The solution allows (i) an increase of hydrogen storage capacity of the whole system and the reduction of H₂ charge pressure, as compared to CGH₂ cylinders alone; (ii) shorter charging times in the refuelling mode and smoother peaks of H₂ consumption during its supply to the FC stack; and (iii) the use of standard parts with simple layout and low cost, (adding flexibility in the layout and placement of the components of the hydrogen storage and supply system).

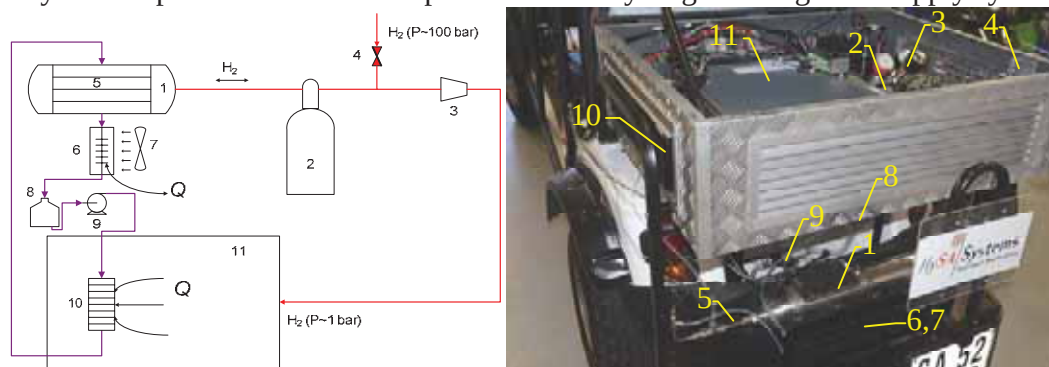


Figure 1. System layout (left) and example of its integration in a light FC vehicle (right).

Acknowledgements

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The Integrated Metal Hydride System for the Application of Fuel Cell

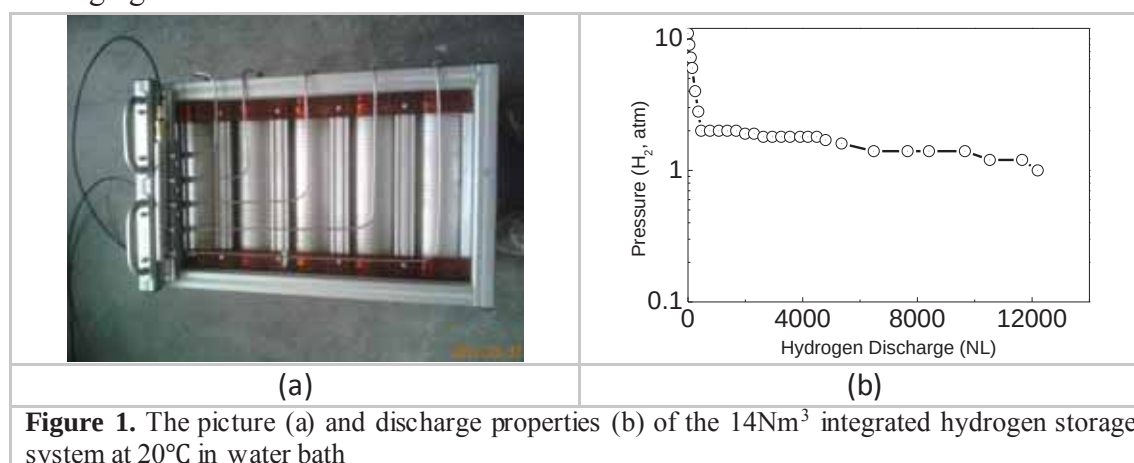
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The cost of per kilowatt (kW) for high volume production of transportation fuel cells moved closer to DOE's target of \$30 per kW. As a result, the development of fuel cells calls for suitable hydrogen storage system for commercialize application.

Our study focus on the research of rare-earth based metal hydrides, which has both high capacity and low production cost, prepared by rapid quenching method in medium frequency induction furnace. (La, Mg)Ni_x (x=3.25, 3.5, 3.75) alloys was prepared and optimized heat treatment process was adopt to improve the discharge capacity, plateau and efficiency. The maximum discharge capacity of the alloy reach 1.71wt% with flat and broad plateau pressure at c.a.2 atm after heat-treatment. The cost of producing such alloy is only 72.3% of the conventional AB₅ alloys. The influence of the heat transfer from internal to external part of the hydrogen storage canister was studied. A honeycomb like aluminium cell structure with high thermal conductivity coating was designed to speed up the double way radiating rate between the material and the environment. The discharge capacity of the hydrogen storage canister (ST2800L) filled with the alloy is 2578.04NL with an efficiency of c.a. 92.07% at 30°C in water bath. The system gravimetric density is around 1.2wt%, corresponding to volumetric density of c.a. 50.65 kgH₂/m³. The discharge properties of 14Nm³ integrated hydrogen storage system composed by 5 ST2800L canisters is tested at 20°C in water bath. The whole system discharges 12196.42NL of hydrogen with an efficiency of 87.12%. Such a system can sustained work as energy source for 1.5kW Fuel-cell for over 8 hours. A 42Nm³ integrated system was also built to provide over 10 hours hydrogen energy for 3kW fuel cell. The whole system discharge 35.2Nm³ of hydrogen at a rate of 30L/min. the discharging rate can reach 83.8%.



Surface Modification of Mg Materials based on Ultra Violet Imprint Lithography for Faster Kinetics in H₂ De- and Absorption

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Magnesium is a very promising material for hydrogen storage, due to its effective storage capacity of up to 7.6 wt% for H₂ [1]. One disadvantage of this storage technology for commercial application are the poor kinetics in de- and absorption, limited by the bulk diffusion coefficient of H₂ in Mg/MgH₂.

In this work, we want to improve these kinetics by surface modification based on ultra violet imprint lithography. A big advantage of UV imprint lithography is the cost efficient fabrication of large area micro- and nano-patterned surfaces [2]. Structuring of the Mg material lead to surface enlargement and thus to an increase of the H₂ dissociation rate. To achieve this goal we established a process where micro-structured stamps, fabricated by UV imprint lithography, are pressed into the Mg material by compression molding. With this mechanical deformation process the pattern from the stamp is transferred into the substrate. Two different materials are investigated for this structuring process, Mg ribbon (Figure 1a) and MgH₂ powder (Figure 1b). With the former described compression molding process the MgH₂ powder became a solid material with a structured surface.

For prevention against oxidation of the surface, the structured material can be coated with an UV curable imprint resist.

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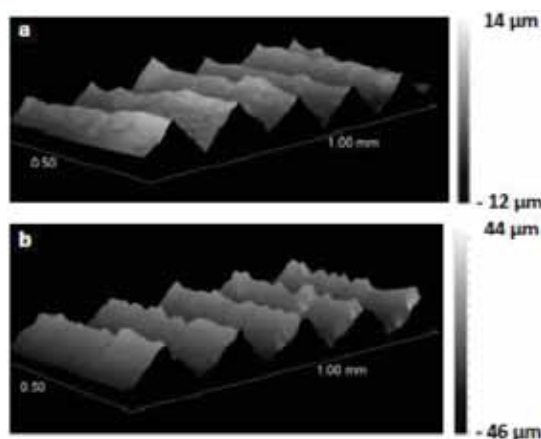


Figure 1. Profilometer images of structured surfaces by compression molding.

a) prism-shaped structured Mg ribbon (applied pressure 20 MPa)

b) prism-shaped structured MgH₂ powder (25 MPa)

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Optimization of Cooling Fins for Metal-Hydrogen Storage Tanks

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Metal hydrides are one of the most promising candidates for hydrogen storage systems, however heat transfer has always been a significant challenge owing to their poor thermal properties. Many research works have been done so far to enhance heat transfer in metal-hydride tanks. Most of the recent works have used the internal heat exchanger by tubes equipped by transverse fins to improve heat transfer throughout metal-hydride beds [1, 2]. To construct a realistic metal-hydrogen tank it is necessary to determine the geometrical features of the cooling system, such as thickness, spacing, radius and material of fins that need to be optimized. Garrison et al. [3] optimized fin geometries based on maximizing gravimetric capacity of the hydrogen using Nelder-Mead methods of built-in matlab routines. A drawback of this is that no constraint has been applied so the obtained geometries are impractical in some cases. Nyamsi et al. [4] studied the relationship of fin dimensional parameters and their effectiveness.

However, efficiency, which is an important parameter to evaluate the performance of fins, was not taken into account. This work presents the optimal dimensions of fins taking into consideration both fin effectiveness and efficiency to reach the highest performance of the metal-hydride tank. In addition, a template is introduced to model annular fins in symmetrical, metal-hydride reactors in order to find the optimum design for fins in a cooling system. In this study, mathematical modeling and analytical solutions are presented for fin design parameters in the metal-hydride tank. The impact of the effective factors on the performance of the fins has been investigated and optimized using MATLAB in a constant volume fraction. The results show a decrease in fin thickness and increase in radius both cause increase in the effectiveness of the fin and a drop in the efficiency. Since economical aspects are of paramount importance for industries and the value of the fin efficiency indicates how cost-effective the fin is, it is necessary to optimize the geometrical parameters to achieve a balance between effectiveness and efficiency in particular for designing large scale applications.

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Performance Analysis of Metal Hydride Based Hydrogen Storage Tanks with Various Heat Exchange Options

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Metal-hydrides (MH) can provide an efficient way of on-board hydrogen storage for fuel cell utility vehicles where the H storage weight capacity is not a critical issue, but safety and compactness are of a paramount importance. Hydrogen absorption / desorption processes in MH are accompanied by significant heat effects, so as the H₂ charge / discharge performances of the MH hydrogen storage and supply systems will be essentially determined by the processes of heat exchange between cooling / heating fluid and MH bed.

A 3D numerical model has been developed for the predicting hydrogen uptake and release performances of cylindrical MH reactors filled with AB₅- or AB₂-type hydrogen storage materials. The considered options of heat exchange between the MH and the heat transfer fluid (HTF) for the cooling and heating included (i) shell and tube and (ii) helical coil internal heat exchangers (HE) in the powdered MH bed, as well as (iii) external cooling / heating of the tubular MH reactor comprising the MH powder and transversal fins. The modelling was focused on the calculation of hydrogen flow rates at different H₂ pressures (see example in Figure 1) that is very important for practical applications.

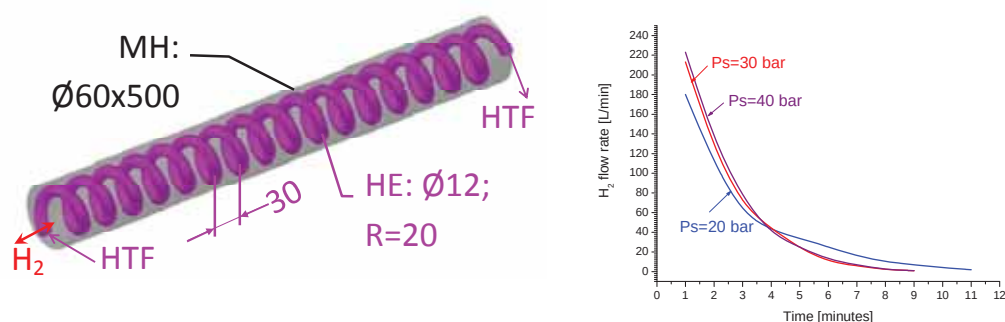


Figure 1. Left: Schematic representation of cylindrical reactor (3.75 kg of MmNi_{4.5}Al_{0.5}, dimensions in mm) with helical coil internal heat exchanger; Right: Calculated H₂ absorption flow rates

Acknowledgements

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Metal hydride Tank Designs for in situ Neutron Radiography (NR) and Tomography (NCT) Experiments

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For the optimization of hydrogen storage tanks based on metal hydrides regarding capacity and kinetics as well as heat exchange behavior, a precise knowledge of the processes inside the metal hydride bed during sorption is necessary. Neutron imaging is an ideal technique to visualize the hydrogen distribution inside a storage tank [1,2,3]. However, to use this method in the most efficient way, a special tank design is required concerning the choice of materials and tank geometry to allow for an optimal resolution and contrast. We developed several designs, tailored for use with different metal hydride materials, but as well in line with scaled-up pilot tank designs like e.g. StorHy [4].

We will present tank properties and different tank designs for metal hydride powder and compacts. In detail, we will give an overview about our sealing technologies and tank hull materials.

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Characterization of a thermally optimized hydride container

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Hydrogen storage in hydride containers is a complex process that can be addressed under different perspectives. Many efforts have been done so far to understand sorption phenomena of bulk hydride inside containers given that temperature and concentration profiles play an important role in addition to point-mass properties.

In a previous article we defined a thermal optimization procedure for LaNi_5 containers, based on a mathematical method and supported by experimental outcomes. The fraction of high conductivity material within the container, e.g.: internal fin or metal foam, was evaluated in order to obtain the maximum hydrogen absorption for fixed time and conditions.

With this optimization procedure we designed and built a prototype of 200 NL capacity filled with $\text{MmNi}_{4.7}\text{Al}_{0.3}$ alloy. From preliminary results we confirm fast sorption reaction, both in absorption and desorption, and discuss about performance and possible applications.

Metal hydrides for optimal hydrogen storage system of fuel cell electrical vehicles

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In the perspective of coupling hydride tank and fuel cell systems, the choice of the hydride is significant for both the sizing of the hydrogen tank and the thermal and electrical energy of the overall system (a hydride hydrogen tank coupled to the fuel cell generator). A state of the art concerning the coupling between hydride storage and various types of fuel cells (low and high temperature) is proposed in this study. The paper will underline the technology of solid hydrogen storage (metal-hydrides), with the objective to bring out hydrides which are answering better, in regard with several criteria as storage capacity, temperature and pressure of hydrogenation and dehydrogenation, kinetics, cost, ease of activation, cyclic stability and other parameters. The results of this synthesis will give ways to help the choices of hydride type in the case of coupling with fuel cell system technologies.

Keywords : hydrogen tank, hydrogen, hydride storage, fuel cell, fuel cell electrical vehicles (FCEV)

Development of hybrid hydrogen tank

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Hydrogen attracts attention as clean energy of the next generation. In order to put a hydrogen energy system to practical use, the technical development of safe and efficient storage/transportation media is one of the most important subjects. On board hydrogen tank which is under development can be classified into following two types; 1) high pressure hydrogen tank, 2) metal hydride storage tank. However, metal hydride storage tank does not meet the requirement for on board storage of hydrogen in weight densities. Many fuel cell vehicles adopt a high pressure hydrogen tank (35MPa, 70MPa), but have a problem to volumetric storage density now. Hybrid hydrogen tank has been developed to store hydrogen for fuel-cell vehicle (FCV) [1,2]. “Hybrid hydrogen tank” is superior to a high pressure container of 70MPa in volumetric storage density. This research is the development of a “hybrid hydrogen tank” which is a combination of type 3 high pressure hydrogen tank and metal hydride. In this presentation, the development status of recent “hybrid hydrogen tank” will be introduced.

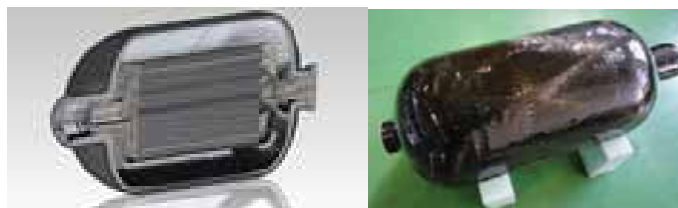


Figure.1 Hybrid hydrogen tank

Acknowledgment

This development projects were supported by New Energy and Industrial Technology Development Organization (NEDO). This research has been conducted as a part of the “Development for Safe Utilization and Infrastructure of Hydrogen Research and Development of Vehicle Components” and “Development of Technologies for Hydrogen Production, Delivery and Storage Systems” [3,4].

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Transient modeling and simulation of hydrogen supply from a metal hydride tank

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In this study, a three dimensional (3-D), transient state model of a metal hydride (LaNi₅) based hydrogen storage tank is presented. The hydrogen absorption and desorption dynamic characteristics are dependent on the local pressure and temperature distribution in the tank. This in turn is related to the dimension and geometry of the tank along with the microstructure of the storage material. The model is further used to predict the hydrogen storage and evolution of a hydride tank with novel design for improved performance.

Static and Dynamic Performance Tests on Room Temperature Hydride Tank

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This experimental work deals with the feasibility of a vehicular hydrogen tank system, using a commercial interstitial metal hydride as storage material. The tank was designed to feed a fuel cell in a light prototype vehicle and the material, Hydralloy C5 by GfE, was expected to be able to absorb and desorb hydrogen in a range of pressure suitable for that. A systematic analysis of the material in laboratory scale is useful to make an extrapolation of the thermodynamic and reaction kinetics data. The development of the tank was done according to the requirements of the prototype vehicle propulsion system.

The task for static tests (measurements with automatic flow control and constant settings) is to evaluate whether the requirements for desorption are met by this tank set-up. Moreover the settings for the most convenient reloading of the tank were experimented.

The following step was the design and the application of dynamic tests, where the requirements were still met and the hydrogen flow, provided by the tank, was fluctuating following a hypothetical on-road test. It was possible to underline the thermal issues of high-demanding performances and to propose a solution for that. Different cycles were performed on the tank to find the ideal setting for high average and peak flow in a realistic experiment.

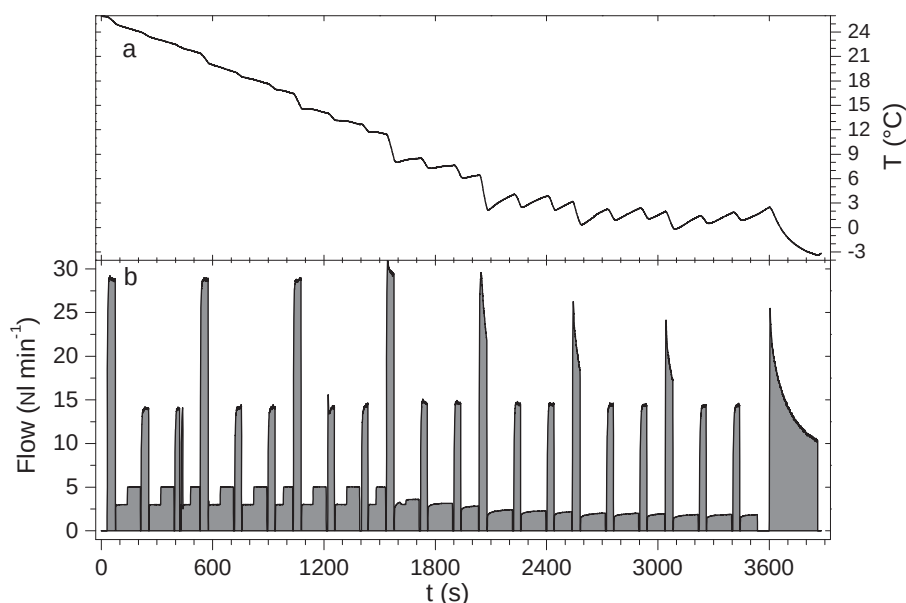


Figure 1. Dynamic test cycle: average temperature of the tank (a) and hydrogen flow (b).

High Capacity Hydrogen Storage Alloy Negative Electrodes for Use in Nickel-Metal Hydride Batteries

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A vanadium-based hydrogen storage alloy hydride, $\text{TiV}_{1.4}\text{H}_{4.6}$, has high theoretical gravimetric hydrogen storage capacity of 1036 mAh g^{-1} , and therefore is a potential candidate as negative electrode active material for Ni-MH batteries. In our previous study, we found that the $\text{TiV}_{0.9}\text{Ni}_{0.5}$ electrode had the highest discharge capacity (390 mAh g^{-1}) among $\text{TiV}_{1.4-x}\text{Ni}_x$ ($0 \leq x \leq 1$) electrodes [1] and the $\text{TiV}_{2.1}\text{Ni}_{0.3}$ alloy, which was the primary phase of $\text{TiV}_{0.9}\text{Ni}_{0.5}$, had a much higher discharge capacity (540 mAh g^{-1}) than the original alloy [2]. Some surface modifications of the $\text{TiV}_{2.1}\text{Ni}_{0.3}$ alloy contributed to the increase in discharge capacity [3,4]. However, its poor charge-discharge cycle durability was scarcely improved because the dissolution of the V constituent in the 6 M KOH electrolyte solution could not be inhibited. Recently, we demonstrated that bulk modification such as partial substitution of V with Cr was effective for suppressing the deterioration of the $\text{TiV}_{2.1}\text{Ni}_{0.3}$ alloy [5]. In this study we examined electrochemical properties of $\text{TiV}_{2.1-x}\text{Cr}_x\text{Ni}_{0.3}$ ($x=0.4-1.0$) alloys.

The $\text{TiV}_{2.1-x}\text{Cr}_x\text{Ni}_{0.3}$ ($x = 0.4-1.0$) alloy ingots were prepared by arc-melting a mixture of Ti, V, Cr and Ni powders under an Ar atmosphere. Each alloy ingot was pulverized with high pressure hydrogen. Alloy negative electrodes used in this work were prepared according to our previously published procedure [5]. The electrolyte solution was 6 M KOH, and the positive and reference electrodes were a $\text{NiOOH}/\text{Ni}(\text{OH})_2$ and Hg/HgO electrodes, respectively. In typical charge-discharge cycle tests, the negative electrode was charged at 100 mA g^{-1} for 8 h and discharged at 50 mA g^{-1} to the cut-off potential of -0.75 V versus Hg/HgO . After each charging, the circuit was kept open for 10 min. All electrochemical measurements were carried out at 303 K.

All $\text{TiV}_{2.1-x}\text{Cr}_x\text{Ni}_{0.3}$ ($x=0.4-1.0$) alloys were composed of two phases like the $\text{TiV}_{2.1}\text{Ni}_{0.3}$ alloy, but the content of each phase changed with Cr content. The V and Cr contents in the primary phase was higher than that in the secondary phase, whereas the Ti and Ni contents were lower in the primary phase. The alloy electrode with $x=0.4$ exhibited the maximum discharge capacity of ca. 440 mAh g^{-1} at the second cycle, and its cycle stability was greatly improved compared to the $\text{TiV}_{2.1}\text{Ni}_{0.3}$ alloy electrode. Over $x=0.4$, the maximum discharge capacity was decreased and the cycle number for initial activation was increased with an increase in Cr content. High-rate dischargeability of the alloy electrode with $x=0.4$ was the best, and it was lower for the alloy electrodes with higher Cr contents.

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Electrochemical Properties of $\text{Ti}_{49}\text{Zr}_{26}\text{Ni}_{25-x}\text{Pd}_x$ Quasicrystals Produced by Mechanical Alloying.

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Ti-Zr-Ni icosahedral (i) quasicrystals have unique structures that possess a large number of tetrahedral interstitial sites [1]. They are worth studying from view point of not only engineering but also science. In our previous study, the maximum discharge capacity of the $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ i-phase electrode measured was 23.9 mAh/g at a current density of 15 mA/g, although the theoretical charge capacity estimated from its chemical composition and the maximum H/M (1.9) was 795mAh/g, suggesting that some hydrogen atoms (protons) seemed to remain in the structure even after discharge process because of strong chemical affinity with surrounding metallic atoms such as Ti and Zr. We have also investigated the effect of substitution of Ti or Zr for Ni, and Ti for Zr on the hydrogen storage characteristics, and the maximum discharge capacity achieved was about 130mAh/g from a $\text{Ti}_{49}\text{Zr}_{26}\text{Ni}_{25}$ i-phase electrode [2].

In this study, we investigated the effect of substitution of Pd for Ni on the discharge performance of the i-phase ($\text{Ti}_{49}\text{Zr}_{26}\text{Ni}_{25-x}\text{Pd}_x$) electrodes produced by mechanical alloying by a three-electrode cell at room temperature. All the powders after MA were amorphous, but a subsequent annealing caused the formation of the i-phase with Ti_2Ni type crystal phase as a minor phase. The quasilattice constant increased with increasing amount of Pd substituted. The maximum discharge capacity and the stability for hydrogen cycling were improved after substitution of Pd for Ni.

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Electrochemical charge-discharge properties of MgH_2 via LiBH_4 solid electrolyte

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Niobium oxide (Nb_2O_5) known as the best catalyst for hydrogen absorption shows also good catalytic effect for the reversible reactions of MgH_2 as anode material of all-solid-state lithium ion battery (LIB) with sulfide-based electrolyte [1]. However, the coulombic efficiency for the MgH_2 anode is still low, and therefore further improvement is required. As one of the reasons for such a low coulombic efficiency, high resistance layer could be formed in electrode-electrolyte interface because electrochemical potentials of lithium ions should be largely different between hydride-based electrode and sulfide-based electrolyte [2]. In this study, we investigate the electrochemical properties of MgH_2 anode, which is catalyzed by Nb_2O_5 , and, we especially focus on LiBH_4 [3] as a hydride-based electrolyte for this all-solid-state LIB. It is expected that hydride-based materials should play a significant role in construction of interface to realize the better electrochemical properties.

Fig.1 shows the charge-discharge curves corresponding to this combination. The plateaus of Li insertion/extraction reactions were observed at around 0.5 V for both cycles and the Li insertion capacities corresponding to cycle 1 and 2 were approximately 1670 and 1780 mAh/g, respectively. The coulombic efficiencies of initial and second cycles were 107% and 89%, respectively, indicating higher values than that corresponding to sulfide-based electrolyte (the initial coulombic efficiency : 32%). After the initial cycle, the $\text{Mg}(\text{BH}_4)_2$ phase were confirmed in X-ray diffraction profile, suggesting that following side reaction occurred,

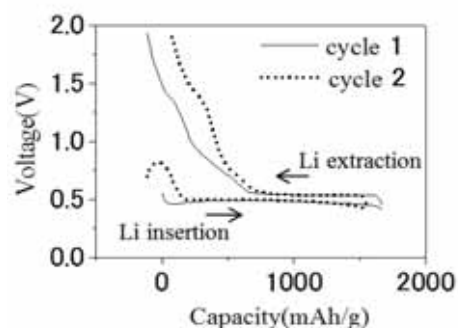
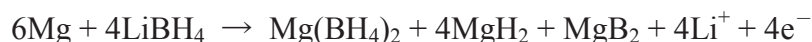


Fig.1 Charge-discharge curves of MgH_2 / LiBH_4 / Li cell at a current density of 0.11 mA/cm^2 at 130°C



Although a part of electrolyte could act as an electrode, which leads to the excess coulombic efficiency of the initial cycle, high cycle properties was able to be realized by using LiBH_4 as electrolyte.

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Phase-Structural and Electrochemical Properties of the $R_2Mg(Ni,Co)_9$ -Based Electrode Materials for Ni-MH Batteries

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Beside the classical AB_2 or AB_5 compounds, which are being used in commercial Ni-MH batteries, the ternary AB_{3-4} (A – rare earth or alkaline metals, B – transition metals, magnesium and aluminium) phases and alloys have also evaluated for possible application as negative electrode materials for Ni-MH batteries [1]. Much attention has been concentrated on the alloys close to the R_2MgM_9 composition. It was found that these materials possess high hydrogen storage capacity, high discharge capacity and low production cost compared to other alloys. However, the poor cyclic stability (degradation during the cyclic process) is the main problem, which hinders its practical application. Several methods were adopted to improve the cyclic stability of such alloys. Metal substitution, mechanical milling and various preparation techniques are some of them [2]. In present work, we investigated the influence of different preparation methods and compositions of R_2MgM_9 alloys on the phase-structural and electrochemical properties.

The R_2MgM_9 ($R=Y, La, Ce, Nd, Tb$; $M=Ni, Co, Mn$) samples were prepared from the metal powders by sintering/annealing at 800°C. Selected alloys were hydrogenated. XRD data were obtained using Dron-3M diffractometer (CuK α radiation). MH electrodes were prepared by two different methods: a) mixing of the powdered alloys with carbonyl Ni (1:1 weight ratio) and pressing into a pellet b) mixing of the powdered alloys with carbon and polymerization of the PTFE. After that they were sandwiched between two Ni foams with fixed conductor. Some additional details are described in [3].

The $PuNi_3$ -type phases were the main products of the prepared alloys. Upon hydrogenation the structure of the parent compounds was preserved. Hydrides usually demonstrated slightly higher discharge capacity comparing with those of the parent compounds. Milling process decreases discharge capacity for R_2MgM_9 alloys. For example, C_{max} were found as 245 and 342 mAh/g for milled and powdered La_2MgNi_9 , respectively. Increasing amount of the binder (Ni) in the electrodes leads to slightly increase discharge capacity and activation time. Additional heat treatment of the milled alloys increases discharge capacity too. Cyclic stability can be improved by addition the catalytic (TiZr) $_2$ Ni based phases with the concentration up to 20 wt.% to the initial La_2MgNi_9 alloys. Electrodes prepared by the polymerization of the PTFE show lower discharge capacity. For example, C_{max} for La_2MgNi_8Mn/Ni and $La_2MgNi_8Mn/C/PTFE$ are equal to 338 and 275 mAh/g, respectively. It should be noted that obtained discharge capacity for R_2MgCo_9 alloys ($R=Y, Ce, Tb$) show significantly small values.

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Porous carbon as anode and cathode catalyst supports for direct borohydride fuel cell

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This work explores the use of porous carbon as the anode and cathode catalyst support to improve performance of the direct borohydride fuel cell. Carbon aerogel (CA) and macroporous carbon (MPC) supported Pt catalysts are synthesized by template method, as shown in Figure 1. The pores in porous carbon materials of anode catch hydrogen bubbles to regulate the contact of anolyte to catalytic sites, leading to depression of hydrogen evolution during BH_4^- electrooxidation. However, hydrogen bubbles in pores deteriorate charge carrier transport simultaneously, leading to increase in anode polarization. CA supported Pt catalyst shows improved coulombic efficiency of BH_4^- electrooxidation but lower performance than MPC supported Pt catalyst. MPC has suitable pore distribution to improve coulombic efficiency of BH_4^- electrooxidation without decrease in the anode performance.

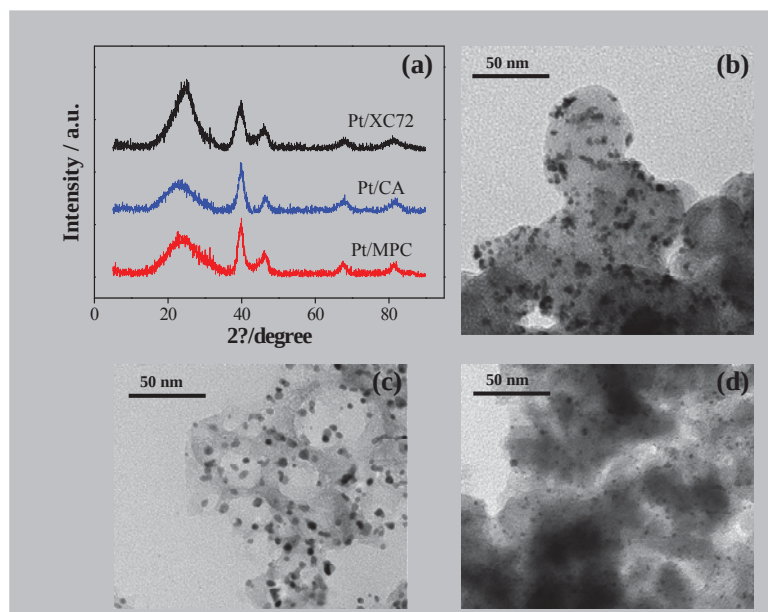


Figure 1 (a) X-ray diffraction patterns of synthesized carbon materials, and SEM images of XC72 (b), macroporous carbon (c) and carbon aerogel (d).

The pores of carbon materials in MPC provide larger reaction area to decrease the cathode polarization. However, the small pores in CA results increase mass transportation resistance, leading to an increase in polarization to decrease cell performance.

Characterisation Of Corrosion Products Of (La, Mg)₂Ni₇-Type Hydrogen Storage Alloys For Nickel-Metal Hydride Batteries And Influence Of Magnesium

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To improve the performances of Nickel-Metal Hydride batteries, understanding of the corrosion processes that take place in the electrode material is an important step. This is particularly true for the new Mg-containing materials based on the (La,Mg)₂Ni₇ system.

The calendar corrosion of such alloys in 8.7M KOH medium was investigated from 6 hours to 16 weeks of soaking. Structural and elemental characterisation techniques (X-ray diffraction, Raman micro-spectroscopy, scanning and analytical transmission electron microscopy; Figure) have been combined to identify the corrosion products developed at the surface of those systems. Surprisingly, we demonstrate [1] that Ni and Mg combine into a pseudo-binary hydroxide phase Mg_{1-x}Ni_x(OH)₂ whereas La corrodes into La(OH)₃ hollow needles. Those results are compared to previous work on LaNi₅-based materials [2].

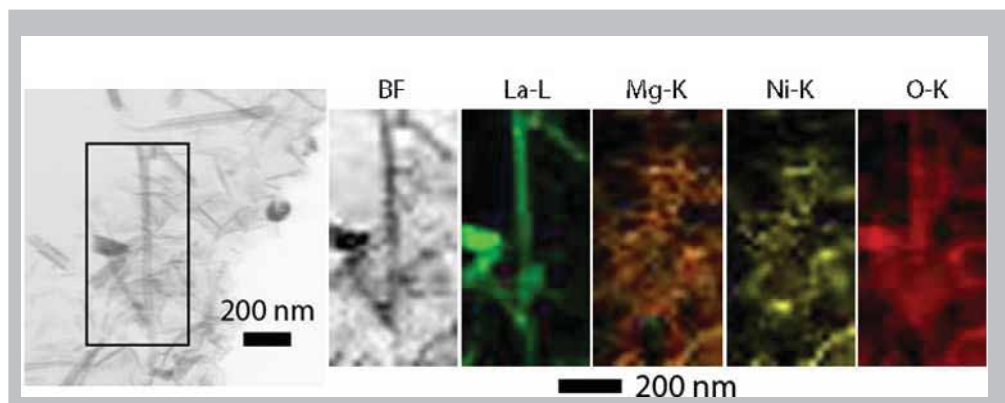


Figure : EDX-STEM mapping for the compound La_{1.5}Mg_{0.5}Ni₇ corroded 8 weeks in KOH.

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Development of CaNi_5 Compounds for Metal Hydride Batteries

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NiMH batteries have superior properties which are long cycle life, low maintenance, high power, light weight, good thermal performance and configurable design. Hydrogen storage alloys play a dominant role in power service life of a NiMH battery and determining the electrochemical properties of the battery. LaNi_5 , belonging to the CaCu_5 crystal structure type, satisfy many of the properties. The most important property of LaNi_5 is fast hydrogen kinetics. In this manner, CaNi_5 gets more importance rather than LaNi_5 due to its low cost, higher hydrogen storage capacity, good kinetic properties and much more discharge capacity. Nevertheless, the main restriction of usage CaNi_5 is lower cycle life.

The aim of the study is to obtain a more stable structure providing higher cycle life by the addition of different alloying elements. In this study, the effect of sixteen alloying elements (Mn, Sm, Sn, Al, Y, Cu, Si, Zn, Cr, Mg, Fe, Dy, V, Ti, Hf and Er) on cycle life was investigated. Sm, Y, Dy, Ti, Hf and Er were added for replacement of Ca and Mn, Sn, Al, Cu, Si, Zn, Cr, Mg, Fe and V were added for replacement of Ni. Alloys were produced by vacuum casting and heat treating followed by ball milling. The cells assembled, using the produced active materials as anode, which were cycled for charging and discharging. As a result, replacement of Ca with Hf, Ti, Dy and Er, and replacement of Ni with Si and Mn were observed to show better durability rather than pure CaNi_5 .

Keywords: Ni-MH batteries, hydrogen storage materials, CaNi_5

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Effects of Surface Oxidation on Hydrogen Permeability of Nb-TiNi Two-phase Alloy

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The Nb-TiNi alloys, consisted of both bcc-(Nb, Ti) solid solution and B2-TiNi intermetallic compound, show equivalent hydrogen permeability to that of pure Pd without hydrogen embrittlement [1]. Therefore, these alloys are promising candidates for non-Pd hydrogen separation and purification alloy membrane. In order for dissociation of hydrogen molecules to atom and avoidance of oxidation, Pd is coated on the surface of Nb-TiNi alloys. However, their hydrogen permeation performance is gradually degraded at high temperature for long period, which is caused from diffusion of Pd into the alloys. It is strongly desired for practical hydrogen permeation alloys to avoid interdiffusion of Pd and alloy elements.

In the present study, the surface of the Nb₄₀Ti₃₀Ni₃₀ alloy is oxidized by heat treatment in air. The surface color changes visually after heat treatment, and the Nb₂O₃ phase is detected by XRD analysis in some samples. The Nb₂O₃ and other oxides are formed on the surface of the alloy. Then Pd is coated on the oxidized surface of the sample. Initial hydrogen permeability of the oxidized sample is lower than that of non-oxidized one. That is, hydrogen diffusion is suppressed by the oxide layer. On the contrary, degradation rate becomes also smaller and hydrogen permeability of the oxidized alloy is higher than that of non-oxidized alloy after 50 hours. Therefore, the oxide layer acts as a diffusion barrier between Pd and alloy elements.

Acknowledgement

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Synthesis and Evaluations of hydrogen permeability on TCN-Ni composite membranes by sol-gel process

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For the purpose of hydrogen separation from syngas as a pressure driven that contain impurities at high temperatures, membrane separation methods are well known in today's industry. In particular, ceramic membrane has high permeation rate of hydrogen and chemical stability. In this research, $\text{Ti}_2\text{Cr}_4\text{Nb}_4\text{O}_2$ (TCN) were successfully prepared by using the sol-gel process. Niobium oxide is attractive catalyst in hydrogenation behavior [1]. Chromium oxide is thermally stable at high temperatures and not susceptible to oxidation [2]. Titanium oxide possess low tortuosity, thus provide a high hydrogen flux [3]. Therefore, TCN is expected to have a good influence on hydrogen permeation. A precursor sol was prepared from titanium ethoxide, chromium nitrate, niobium ethoxide. After gelation, the gel was heated at 973K, and yellow powders, which consisted mainly of TCN, are obtained. Also, some Nb_2O_5 peaks are confirmed (Fig.1). To compensate disadvantage of the ceramic membrane such as the embrittlement, the TCN oxide with 10 wt.% Ni metal powder as a composite membrane was prepared by hot-press sintering (HPS) method with a high-energy milling process. The obtained membranes were characterized by XRD, TG/DSC, BET, SEM and EDS. finally, we evaluated hydrogen permeability by Sievert's type hydrogen permeation membrane equipment.

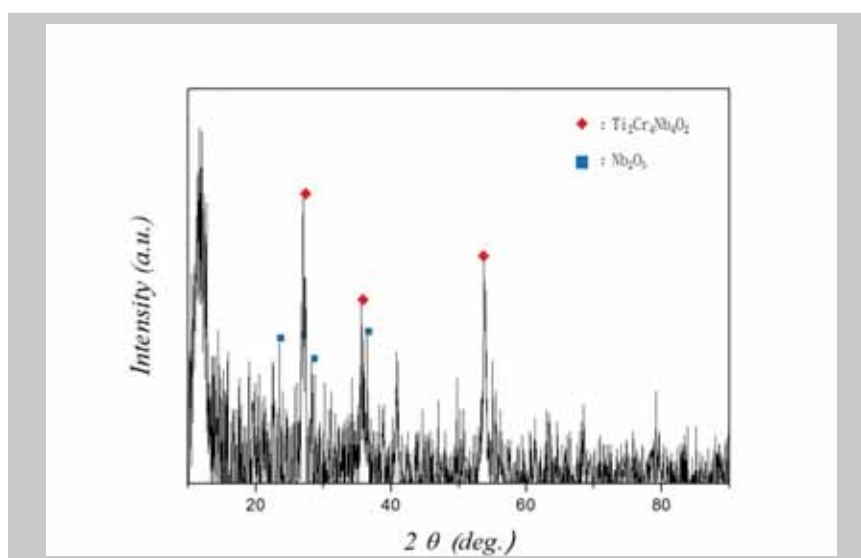


Figure 1. XRD patterns of TCN powders calcined at 973K for 5h.

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Relationship between Microstructure and Hydrogen Permeability in Nb-TiNi Alloys

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The Nb-TiNi alloys, consisted of the B2-TiNi and bcc-(Nb, Ti) phases, are one of the most promising candidates for non-Pd hydrogen permeation alloy. They have equivalent hydrogen permeability to that of Pd alloys with good resistance to hydrogen embrittlement ^[1]. Their microstructure changes drastically depending on the alloy compositions and annealing conditions ^[2, 3], which affects their hydrogen permeability and resistance to hydrogen embrittlement. Therefore, it is quite important to understand the relationship between microstructure and hydrogen permeation performance for practical applications. In the present study, microstructure and hydrogen permeability of the as-cast and annealed Nb-TiNi alloys are investigated, and their relationship is discussed using a mixing rule.

The as-cast Nb₁₉Ti₄₀Ni₄₁ alloy has a fully lamellar type eutectic structure consisted of the (Nb, Ti) and TiNi phases. The primary (Nb, Ti) and TiNi phases appear when Nb composition is higher and lower than 19 mol%, respectively. Their hydrogen permeability increases and decreases with increasing the volume fraction of the (Nb, Ti) and TiNi phases. According to the mixing rule, their hydrogen permeability can be expressed as that of the model alloy in which the granular primary phase is surrounded by the eutectic structure.

Upon annealing, the eutectic structure disappears and is replaced by a granular (Nb, Ti) phase embedded in a TiNi matrix, and their hydrogen permeability is decreased after annealing. Hydrogen permeability of the annealed Nb-TiNi alloys are controlled by the TiNi phase, because the (Nb, Ti) phase (high permeability) is perfectly surrounded by the TiNi phase (low permeability)

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Zr-Based Amorphous Hydrogen Separation Membranes Fabricated by Magnetron Sputtering

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Amorphous membranes are under development because of their resistance to hydrogen embrittlement, improved mechanical properties, resistance to corrosion and most importantly lower intrinsic cost. However, their thermal stability and hydrogen permeability need to be improved in order to be a viable alternative to Pd-based crystalline alloy membranes [1,2].

The Closed Field Unbalanced Magnetron Sputter Ion Plating (CFUBMSIP) technique enables rapid production of uniform films of almost any composition, while enabling the control of film size, thickness and uniformity. In this study, thin-film amorphous $\text{Zr}_{54}\text{Cu}_{46}$, $\text{Zr}_{36}\text{Ni}_{64}$ and $\text{Zr}_{30}\text{Cu}_{60}\text{Y}_{10}$ membranes were fabricated by CFUBMSIP onto glass substrates. Crystallisation temperatures as well as activation energies for nucleation and growth of $\text{Zr}_{54}\text{Cu}_{46}$, $\text{Zr}_{36}\text{Ni}_{64}$ films were investigated by DSC, and are in good agreement with reported values [3,4] for amorphous membranes fabricated by other techniques such as melt spinning. Thus, thermal stability seems to be mainly determined by the alloys composition rather than fabrication method. Surface segregation was observed in all samples after heat treatments at 500 °C under vacuum or hydrogen atmosphere. In addition, the evolution of phases under hydrogen was investigated by *in-situ* XRD analyses. The addition of yttrium to zirconium-copper sample was found to be effective for stabilisation of the amorphous structure either under vacuum or hydrogen, leading to segregation/crystallisation occurring at a temperature almost 150 °C higher than for the zirconium-copper sample.

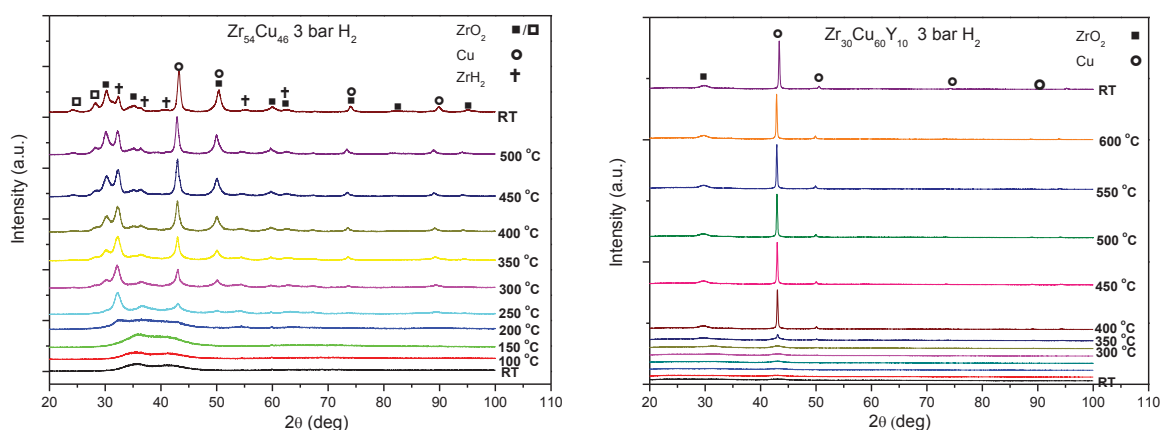


Figure 1. *In-situ* XRD patterns for $\text{Zr}_{54}\text{Cu}_{46}$ and $\text{Zr}_{30}\text{Cu}_{60}\text{Y}_{10}$ versus temperature.

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Alloying effects on hydrogen permeability of V without Pd overlayer

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Non Pd-based alloys with group 5 metals, (V, Nb and Ta), are promising material for hydrogen separation membranes, because of their lower cost and higher hydrogen permeability than currently used Pd-based alloys. For such non Pd-based alloy membranes, the Pd coating on the surface is considered to be necessary to obtain practical hydrogen flux through them [1].

However, we have recently found that a bare V membrane without Pd overlayer exhibits excellent hydrogen permeability [2]. The hydrogen flux through pure V membrane with a thick 100 μm sample was as high as 45 $\text{cc}/\text{cm}^2/\text{min}$ at 823K, which is about 5 times higher hydrogen permeability than currently used Pd-Ag alloy membrane.

In this study, the alloying effects of Cr, Mo and W on the hydrogen permeability of V membrane without Pd overlayer have been investigated. The correlation between the hydrogen flux and the inverse of the membrane thickness is shown in Fig.1. Excellent hydrogen permeability is observed for all the alloys even without Pd overlayer. The hydrogen flux changes depending on the alloy composition and they are classified roughly into three groups.

These results are analyzed in view of the following new diffusion equation proposed by Suzuki *et al.* [3],

$$J = \frac{RTB}{2L} \int_{c_2}^{c_1} c \frac{d \ln(P/P^0)}{dc} dc = \frac{RTB}{2L} f_{PCT} \cdot (1)$$

It is found that the mobility, B , for hydrogen diffusion is nearly constant, but the PCT factor, f_{PCT} , changes depending on the alloy composition. The PCT factor is classified into three groups in good agreement with the results of the hydrogen permeability shown in Fig.1.

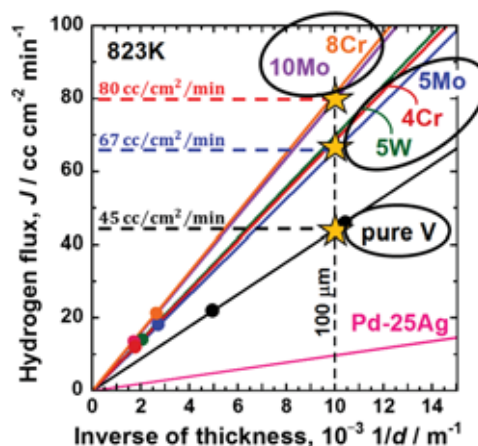


Fig.1. Correlation between hydrogen flux and membrane thickness.

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Combinatorial Thin Film Membranes for Hydrogen Separation

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Hydrogen separation membranes allow filtration of hydrogen from mixed gases. Such mixtures may be produced via steam reforming of natural gas/coal/lignite or through gasification of municipal wastes. Hydrogen separated in this way may be used in fuel cells to generate electricity or may be fed directly to the natural gas grid. It is likely that the current network of natural gas will soon be transformed into a “gas” grid where hydrogen would be an essential ingredient. All these require the use of efficient separation membranes, which when made possible would lead to an easy availability of hydrogen as is currently the case for natural gas. Thus the separation membranes has a much wider scope than normally anticipated and therefore there would be a need for separation membranes that are more efficient and in particular of low cost.

In the current work a method is described which can be used to identify material compositions in a ternary alloy system that would be suitable as separation membranes. The method allows the production of multiple material compositions in the form of thin film membranes. This was achieved using a purpose built sputter deposition unit incorporating a 6 inch diameter substrate holder. The system incorporates three sputter targets arranged in triangular fashion positioned vertically and axially to yield a uniform film thickness over an extended area in the substrate. The substrate holder was in the form of a magazine comprising a total of 21 disc shape substrates each 19 mm in diameter arranged in triangular form aligned with the sputter targets underneath. This allows the deposition of 21 thin film membranes in a single experiment each with a different composition. The membranes may then be screened using permeability testing, or alternatively a preliminary evaluation could be made with resistivity measurement. The method was applied to Ag-Pd-Ti alloy system where the membranes covered a considerable portion of the ternary phase diagram. This choice was made since it is known that Ag-Pd is the well-known binary system for hydrogen separation. Results using resistivity measurement allow mapping of ternary compositions which have a potential as hydrogen separation membranes.

Keywords: Hydrogen separation membrane, thin film membrane, combinatorial, resistivity measurement

Effects of Thin Film Pd Deposition on the Hydrogen Permeability of rolled Pd₆₀Cu₄₀ Membranes

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Palladium-based dense alloy membranes, such as Pd-Ag and Pd-Cu, are used for H₂ purification applications due to their high catalytic activity for H₂ dissociation, high H₂ permeability and mechanical robustness [1]. The Pd-Cu alloy system is of particular interest as the lower Pd content may lower the cost, and it exhibits better resistance to H₂S poisoning compared to Pd-Ag alloys [2,3].

A Pd thin film with a thickness of approximately 100 nm was deposited onto one side of a 40 µm thick as-received rolled Pd₆₀Cu₄₀ (nominal wt. %) foil using magnetron sputtering in order to study its effects on the hydrogen permeability.

Two as-received rolled Pd₆₀Cu₄₀ membranes were used in this work. Sample 1 had been cycled three times from 50 to 450 °C giving a maximum permeability of $1.93 \times 10^{-8} \text{ mol s}^{-1} \text{ m}^{-1} \text{ Pa}^{-0.5}$. Sample 2 was heated to 650 °C, reaching a permeability of $3.27 \times 10^{-9} \text{ mol s}^{-1} \text{ m}^{-1} \text{ Pa}^{-0.5}$ due to the phase transition from bcc to fcc.

Two further rolled Pd₆₀Cu₄₀ membranes (Samples 3 and 4) were sputtered with 100 nm Pd films, and their hydrogen permeabilities measured under the same conditions as for Sample 1. The Pd film was on the feed-side of Sample 3, giving a permeability of $1.78 \times 10^{-8} \text{ mol s}^{-1} \text{ m}^{-1} \text{ Pa}^{-0.5}$. While the Pd was on the permeate-side of Sample 4 resulting in a permeability of $1.49 \times 10^{-8} \text{ mol s}^{-1} \text{ m}^{-1} \text{ Pa}^{-0.5}$. The presence of a Pd-rich Pd-Cu fcc layer on the sputtered surfaces of Samples 3 and 4 may be responsible for the reduction in permeability. It was observed that interdiffusion occurred at the Pd film surfaces between 300 and 550 °C under 4.45 bar of both flowing helium and hydrogen.

The difference in hydrogen permeability will be explained in terms of localised phases formation as a function of conditions.

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APPLICATION OF METAL HYDRIDES AS BLOWING AGENTS FOR METAL FOAM MANUFACTURING

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Metal foams are rather perspective materials possessing a unique combination of properties: low-density, low heat conductivity, good sound absorption and sufficient mechanical strength [1]. It causes wide application of such materials in automotive industry, building, noise insulation systems, and also using as electrodes, filters, catalyst carriers and so on. One way to produce metal foam consists in addition of blowing agents, actively releasing of gaseous products at this temperature, in molten metal, due to which foaming of the melt is achieved. The subsequent cooling and solidification of the foam leads to formation of metal with porous structure.

In processes of manufacture of most widespread aluminum foams the titanium hydride powder as a blowing agent is most often used [2,3]. Modern technologies of manufacturing of products from aluminum foams exclude a stage of sample mechanical processing that considerably reduces the end-product cost. It is produced by the addition of the titanium hydride powder into the melted aluminum alloy by any methods, and by further mixing and quickly cooling of mixture, making it impossible to proceed an active foaming. After that necessary quantity of this semiproduct is inserted into the mould of the needed part and then is heated and further quickly cooled up for the formation of metal foam [4]. In addition carrying out of the specified technological operations of aluminum foam manufacturing has a problem of the fast decomposition of titanium hydride, while for homogeneous mixing of melted aluminum with the titanium hydride powder some time period is needed.

In the present work possible versions of suppression of adverse blowing agent decomposition process at the temperature similar to aluminum melting point, by the preliminary processing of the titanium hydride powder [5], as well as by increasing of external pressures on the system during foaming, are considered. In addition the method of production of a semi-finished product for manufacturing products from metal foams is developed [6].

This work was supported by the International Science and Technology Centre (Project ISTC No.2272).

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Effect of Hydrogen on the Structural and Phase State and Deformation Behavior of the Ultrafine-Grained Zr-1Nb Alloy

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Grain refinement to submicron size (grain size is less than 1 μm) is an efficient way to improve the strength properties of metal polycrystals at low homologous temperatures. In this study the effect of hydrogen on the ultrafine-grained structure forming, deformation behavior and mechanical properties of a Zr-1Nb alloy was investigated.

It has been established that the ultrafine-grained heterophase structure with predominantly large angle grain boundaries and an average grain size of grain-subgrain structure elements of 0.4 μm is formed at a Zr-1Nb alloy by pressing with the change of the deformation axis at room temperature and intermediate annealing at a temperature of 823 K for 1 hour. Similar ultrafine-grained structure at the Zr-1Nb-0.22H (hereinafter, the hydrogen concentration is indicated in mass %) alloy is obtained by quenching from the ($\alpha + \beta$) region and a single uniaxial compression by 70–75 % at 873 K.

Formation of the ultrafine-grained structure in the Zr-1Nb and Zr-1Nb-0.22H alloys by both methods described above leads to a significant (by 2–3 times) increase in the values of its ultimate strength and yield strength in comparison with the original fine-grained state. In addition to that the strength characteristics of the ultrafine-grained Zr-1Nb-0.22H alloy are slightly higher than the characteristics of Zr-1Nb alloy obtained by pressing with the change of the deformation axis.

Hydrogen presence in the solid solution at the ultrafine-grained Zr-1Nb-0.22H alloy is shown to prevent the development of plastic deformation localization on the meso- and macrolevels in the tensile process at room temperature and increase the effect of strain hardening and deformation of uniform elongation. At elevated temperatures, hydrogen presence in the ultrafine-grained Zr-1Nb-0.22 alloy reduces the resistance to deformation localization at the macrolevel and value of deformation to failure in tensile tests.

Influence of surface structure on hydrogen interaction with Zr-1Nb alloy

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Concentrated energy fluxes, in particular, pulsed electron beams are a promising method for surface modification. At such exposure, the conditions for the formation of metastable, amorphous, nano- and submicrocrystalline structures in the surface layer are created. The presence of such structures in the surface layers of zirconium alloys can have a significant influence on the interaction of hydrogen with materials. In this work, the modified structural-phase state in the surface layer ($\sim 10 \mu\text{m}$) of the Zr-1Nb alloy has been formed with the help of high-current pulsed electron beam. Surface treatment was carried out with the following electron beam parameters: energy density of $(10\text{--}25) \text{ J}/\text{cm}^2$ and quantity of impulses of $(1\text{--}4)$. Hydrogen sorption behaviour of Zr-1Nb alloy has been studied depending on structure characteristics and temperature. Temperature of hydrogen saturation was varied from $350 \text{ }^\circ\text{C}$ to $550 \text{ }^\circ\text{C}$. The structure changes of modified zirconium alloy after hydrogen saturation has been studied.

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Application of Acoustic Emission Method for Investigation of Hydrogen Embrittlement Mechanism in the Low-Carbon Steel

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The mechanism of hydrogen embrittlement (HE) of metals is still under discussion. Since the first notice on HE of steels, a number of mechanisms has been suggested to explain the nature of this phenomena. At the time being the only two mechanisms are considered variable: 1) the decohesion model and 2) hydrogen-enhanced localized plasticity (HELP) mechanism. The first one relays on the hypothesis on the hydrogen-induce lower lattice cohesion force giving rise to brittle cleavage-like fracture along the crystallographic planes [1]. The HELP theory is based on experimental observations of increased local dislocations mobility at presence of hydrogen [2]. In this case cleavage-like fracture is explained by localisation of plastic deformation along some atomic planes. making use of the outstanding sensitivity of the acoustic emission (AE) technique to fracture and deformation processes, we apply this technique aiming at clarifying the actual HE mechanism. The simplest distinction between these modes of damage can be made based on the waveform differences: the low-temperature cleavage cracking is accompanied by the transient AE pulses of high amplitude and a short rise time, whereas plastic deformation by dislocation slip generates noise-like continuous AE [3]. Thus, the AE method is ideally suited for recognition of one of HE mechanisms.

The smooth specimens of the commercial low-carbon steel S235JR were used for the uniaxial tensile tests at the different strain rates ranging from 10^{-4} to 10^{-1} s⁻¹. All specimens were annealed at 950 °C during 30 min in the vacuum. Specimens were electrochemically hydrogen charged to different hydrogen concentrations. AE acquisition during tensile tests was performed using a broadband piezoelectric sensor. The RMS voltage and a number of parameters obtained from the continuously recorded at 5 MHz AE streams were computed and analysed.

The considerable reduction of ductility of the hydrogen charged specimens was observed with the increase in hydrogen concentration as well as with the decrease in the strain rate. In the both cases, the ductility reduction was accompanied by the increase in the area fraction of the cleavage-like patterns on the specimens fracture surfaces. The negative strain rate dependence indicated that the HE phenomenon, which was associated with mobile hydrogen, originated in deformation-related mechanisms during plastic straining. Importantly is that the only continuous noise-like AE was observed near the yielding point during all tests; no any signs of burst type AE were detected. Thus, the cleavage-like patterns which were found on the fracture surfaces cannot be associated with conventional cleavage, which is typically observed at low temperatures, and thus the HE phenomenon cannot be simply explained by the decohesion mechanism.

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PdAu Alloy Nanoparticles for Nanoplasmonic Hydrogen Sensing

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The notion of hydrogen economy has catalyzed the development of various fields, like the use of metal-hydride systems as signal transducers in optical hydrogen sensors^[1]. For this application PdAu alloys are attractive because of their very narrow hysteresis upon hydrogen sorption. Moreover, and of particular interest here, both Au and Pd when confined in a nanoparticle exhibit so-called localized surface plasmon resonance (LSPR), i.e. collective excitations of the conduction electrons upon irradiation with near-visible light^[2]. Pure Pd nanoparticles have thus successfully been used for plasmonic optical hydrogen sensors^[1].

In this work, we present a means to fabricate plasmonic PdAu alloy nanoparticles for hysteresis-free plasmonic hydrogen sensing with superior response time. For this purpose, quasi-random arrays of PdAu alloy nanoparticles were fabricated using Hole-mask Colloidal Lithography^[3] and alternating deposition of layers of Pd and Au, followed by annealing at 500°C to promote alloying. The spectral position of the LSPR of the PdAu alloy nanoparticles was used as readout for real-time optical hydrogen detection.

We found that varying the Au content in the alloy lowers the width of the hysteresis (Figure 1). Moreover, the sorption kinetics in the PdAu alloy are found to be faster than in pure Pd nanoparticles. While this obviously is beneficial for the sensing application due to faster response time, the finding also suggests different rate limiting steps compared to pure Pd nanoparticles.

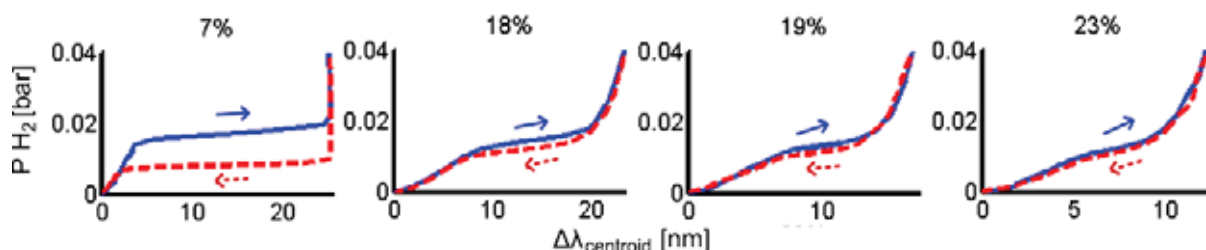


Figure 1. The decreasing width of hysteresis in hydrogen uptake/release as an effect of increasing Au content (at%) in PdAu nanoparticles.

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Development of Hydrogen Storage Alloys for a Soft Actuator Device in Medical Rehabilitation

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An actuator is a type of devices for creating motion by an energy source. There are various kinds of actuators such as electric motors and pneumatic actuator. However, most of them do not meet requirements for medical rehabilitation devices; silent, cushioning action and compact. One of authors has developed a new actuator using hydrogen storage alloys which is called a metal hydride (MH) actuator.¹ Because of high hydrogen density in volume, the MH actuator is compact. Since hydrogen gas released from a hydride is used to create motion, the MH actuator shows cushioning action and silent motion.

The requirements for hydrogen storage alloys of the MH actuators are cyclic durability, small hysteresis and flat plateau on the Pressure-Composition (*P-C*) isotherms, and to be easily activated. (Ti, Zr)Mn₂ based alloys are candidate materials in aspects that equilibrium pressure can be widely tuned by changing Zr/Ti ratio and for some compositions show excellent durability even though they had larger hysteresis and sloping plateau.² In this paper, therefore, the effect of substitution elements on hysteresis and flatness of plateau was investigated in Zr_xTi_{1-x}Mn_{0.8}V_{0.2}Ni_{1.0} to develop (Ti, Zr)X₂ alloys suitable for the MH actuators in rehabilitation devices.

Zr_xTi_{1-x}Mn_{0.8}V_{0.2}Ni_{1.0-y}X_y (X=Fe,Cu,Al,Ni) were synthesized by arc melting under Ar atmosphere. The annealing was done at 1273 K for 24 h in Ar atmosphere. *P-C* isotherms and cyclic properties were measured. XRD data were collected and analyzed by the Rietveld method. The MH actuator for test and demonstration was established as shown in fig.1. Performance of the MH actuator was evaluated with weight blocks (20,40,60 kg).

The equilibrium pressure of the alloy was tuned for the requirement of the MH actuator by changing the Zr/Ti ratio. Al substitution reduced hysteresis although Fe and Cu substitution did not. The effects of Al and Fe substitution indicates that ferrovandium can be used for these alloys to reduce not only the material cost but also the hysteresis. Zr_{0.5}Ti_{0.5}Mn_{0.8}V_{0.2}Ni_{0.9}Al_{0.1} developed in this study showed no significant reduction of hydrogen capacity or no change in the shape of *P-C* isotherms even after 1000 cycles. Temperature-swinging reaction kinetics measurement showed that 80% of absorption and desorption reactions were completed within two and seven minutes, respectively. It was demonstrated that 60 kg of weight blocks were lifted up at 353K by the actuator containing around 10 g of Zr_{0.5}Ti_{0.5}Mn_{0.8}V_{0.2}Ni_{0.9}Al_{0.1}.

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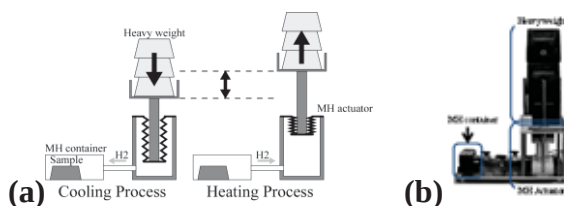


Fig.1 A MH actuator; (a) a schematic image and (b) a photo

Development of a Hand-Size Soft Actuator Utilizing Hydrogen Storage Alloy

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We have developed a hand-size soft actuator utilizing hydrogen storage alloy by applying bellows made of thin film as an end effector.

An actuator used for a part of a human-machine interaction system in medical field, such as a rehabilitation system, should be safe, compact, and silent¹. To realize an actuator which meets these needs, we have developed metal hydride (MH) actuators utilizing the properties of a hydrogen storage alloy, which can reversibly absorb and release a large amount of hydrogen gas^{2,3}. The MH actuator consists of a bellows and a container of the hydrogen storage alloy sealed with Peltier devices (MH module) as a source of bellows motion (Figure 1). The MH actuator derives mechanical power from the internal pressure changes, due to thermal control of the state of metal hydride i.e. heating for increasing pressure by releasing hydrogen from the hydride, and cooling for decreasing pressure by absorption of hydrogen. This operating principle allows the MH actuator to implement silent operation and shock-absorbing function like a cushion. In this study, a 50 mm size soft bellows made of 0.1 mm-thick laminated aluminum film was developed and utilized as the end effector of the MH actuator (Figure 2). By controlling temperature of the MH module between 288 K to 313 K, the MH actuator achieved cyclic movement of expansion and contraction.

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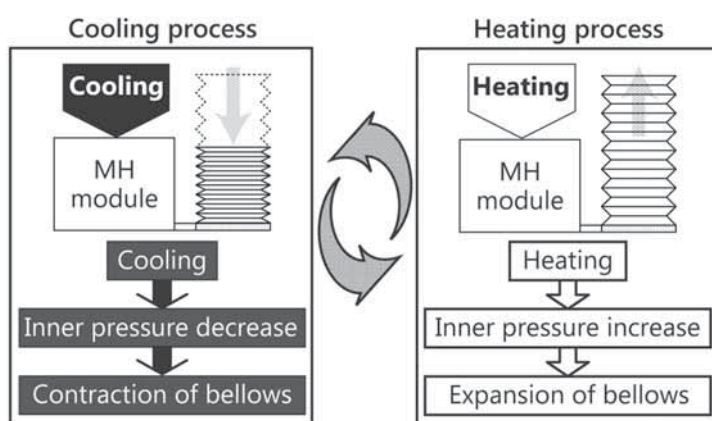


Figure 1. Operating principle of the MH actuator.

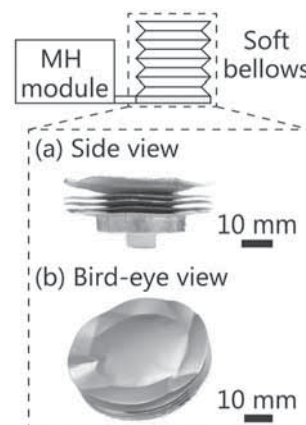


Figure 2. Soft bellows.

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Sensing of hydrogen in gas phase using ferromagnetic Pd-Co alloy

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Palladium alloys could be applied to the sensors of hydrogen in gas phase, because physical and chemical properties of palladium alloys depend on the amount of hydrogen absorption. In the conventional hydrogen sensing device, the electrical resistance of detecting elements is often measured to detect hydrogen gas. The electrical contacts with Pd alloy in a sensing device cause less the reliability of the device by an expansion and a contraction of the Pd alloy with hydrogen absorption and desorption. On the other hands, the magnetic susceptibility measurements of Pd alloys are attractive for the application of hydrogen sensing device, because magnetic properties can be measured without the any electrical contact with the detecting elements. Pd-Co alloy at the cobalt concentration above 8at% showed ferromagnetic behavior at room temperature, and its magnetic susceptibility decreased with hydrogen uptake [1]. Especially, the magnetic susceptibility at hydrogen dissolving phase, generally named as alpha phase, was proportional to hydrogen concentration in bulk. Therefore, Pd-Co alloy is suitable to be applied to hydrogen detecting device through magnetic susceptibility. In this study, we demonstrate that the hydrogen concentration in gas phase can be determined by the measurement of the magnetic susceptibility of Pd-Co alloy.

Pd-Co powder with an diameter under 100 μm and Pd-Co film with a thickness of 0.9 μm on PET substrate were prepared. Its cobalt concentrations were adjusted to about 10at%. The hand-made gas flowing system was used in this study. The ratio between nitrogen and hydrogen gases was controlled by mass flow controllers. The mixture gas was fed to the quartz pipe including Pd-Co at a flowing speed of 100 sccm, and the pressure of the quartz pipe inside was maintained to ambient pressure. The magnetic susceptibility of Pd-Co was measured continuously by induced method.

The magnetic susceptibility of Pd-Co powder under a flow of nitrogen was adjusted to be a background value. When 9vol% of hydrogen in nitrogen was fed, the susceptibility decreased and reached to a constant value after 500 sec. After the mixture gas was changed to nitrogen only, the susceptibility went back the background value. This behavior results from the effect of absorbing and desorbing hydrogen in Pd-Co powder. In addition, the difference between the background and the constant values increased with increasing hydrogen concentration from 0.2% to 9% in nitrogen, revealing that the magnetic susceptibility of Pd-Co alloy can be applied to the index of hydrogen concentration in gas phase. To apply this method to hydrogen sensing device, it is necessary to shorten the reaction time. It was expected that the reaction time depended on the diffusion of hydrogen in Pd-Co. Therefore, the magnetic susceptibility measurement of Pd-Co film under the same condition was performed. The susceptibility of the film in the flow of mixture gas showed the same behavior as that of the powder sample, and the reaction time of the film became shorter than that of the powder sample.

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Hydrogen Production, Storage and Purification using the Steam Iron Process

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Low temperature fuel cells are one of the most promising technologies for emission free power generation. In order to achieve a successful market introduction of this technology a comprehensive hydrogen infrastructure based on renewable resources has to be established. The decentralised conversion of bio-based fuels such as biogas, ethanol or solid biomass to a hydrogen rich synthesis gas (syngas) is one step towards this hydrogen infrastructure. In order to fulfil the requirements in hydrogen quality for low temperature fuel cells complex purification steps are necessary. Due to the fact that pressure swing adsorption is not suitable for decentralised applications and membrane based hydrogen purification is not technologically mature an additional process for syngas cleaning was developed. The steam iron process is one technology that enables the decentralised purification of syngas as well as the secure and loss-free storage of hydrogen.

In this two-step process a syngas is used to reduce magnetite to iron (1) which is then re-oxidised using steam (2).



Since the oxidation reaction is performed independent of the reduction reaction the process enables hydrogen storage. As long as the contact with air is avoided no undesired oxidation takes place and therefore no hydrogen losses occur. In the development of this process two major challenges have to be mastered:

The formation of solid carbon by the Boudouard-reaction (3) has to be avoided by optimising the reduction conditions. Otherwise at the consecutive oxidation reaction the formation of carbon monoxide (4) reduces the purity of the produced hydrogen.



For the economic feasibility of the process the iron/iron-oxide has to undergo thousands of reduction-oxidation cycles without losses in reactivity. As pure iron tends to deactivation owing to sintering processes its stability has to be increased. Therefore stable oxides such as alumina oxide (Al_2O_3) are added.

Investigation of Long Term Cycle Stability – First Results of metal hydride composites

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Reversible reactions of solid powders and hydrogen can be used for hydrogen storage as well as for thermal applications like heat storages or heat conversion systems. For all applications, one of the fundamental prerequisites is the cycle stability of the reaction material and - if required - its bulk structure.

At the Institute of Technical Thermodynamics at the German Aerospace Center a test bench to investigate the cycle stability of reversible gas/solid-reactions has been developed and brought into operation (Figure 1, left). The main feature is the possibility to investigate larger quantities of the materials and therefore to investigate also complete structures, e.g. matrixes for heat transfer enhancement.

Until now Hydralloy C5 pellets have been cycled more than 1000 times. The bench can be operated automatically, provide temperature levels between 50 and 400°C and a pressure up to 100 bar.

The temperature is controlled by a thermostatic bath and allows monitoring any shift in the heat transfer during cycling. The pressure can be increased or decreased quickly so highly dynamic tests can be run. The measurement of temperature and pressure is carried out online at different positions and the overall conversion is measured by an included Sievert's apparatus. In cooperation with the Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM we have recently investigated different compositions of hydralloy C5 and graphite as well as four different pellets of metal hydride with different diameter at the same time. Figure 1, right shows the temperature (T), pressure (p) and pressure difference caused by absorption (DSD) for two cycles of one of these pellets as an example.

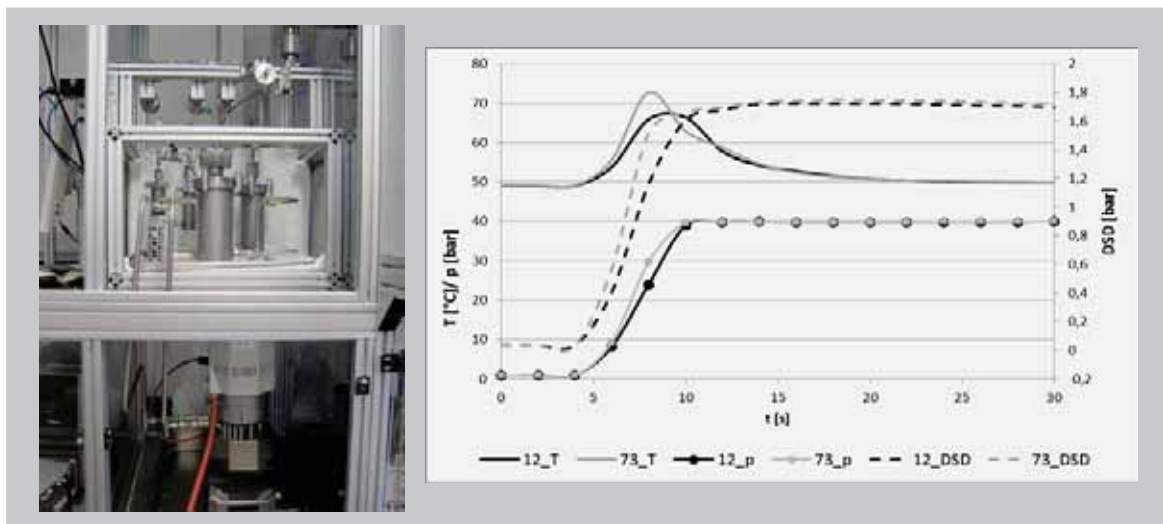


Figure 1. Picture of testbench (left).
Example of absorption of a hydralloy C5 pellet in test bench (right)

Investigating the effect of severe plastic deformation on the hydrogenation properties of TiFe for stationary applications

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TiFe exhibits remarkable hydrogenation properties which allow it to be one of the interesting hydrogen storage materials for stationary applications. It can absorb and desorb hydrogen reversibly with 2 H/f.u. capacity (2 wt%) under the ambient conditions. However, TiFe suffers from the severe surface oxidation which does not allow the hydrogen absorption without a sophisticated activation process.

Previous studies in our group showed that TiFe is fully activated after the severe plastic deformation (SPD) with high pressure torsion (HPT) process [1, 2]. The nano structured TiFe becomes active after the HPT process and is not deactivated even after storage for several days under the air.

In this study the effect of other SPD techniques have been investigated on the hydrogenation properties of TiFe. The main aim of this study is to develop a SPD technique to scale up the production of TiFe for stationary applications. The proposed techniques are cold rolling and ball milling. In this study TiFe was mechanically deformed by Mechanically Grinding (MG) starting from TiFe powder. The Mechanically Alloyed (MA) TiFe is also obtained from milling TiH₂ and Fe powder followed by heat treatment at 873 K. The mechanically deformed TiFe, showed the interesting activation properties even after exposure of milled powder to the air. The hydrogenation capacity reaches to 1.5 wt% at the first hydrogenation cycle. The microstructural characterization of the milled powder showed the formation of nanoscale particles in the range of 10 to 100 nm. According to these results the processing using severe plastic deformation (SPD) could be a solution to activate TiFe.

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***Ab-initio* Molecular Dynamics Simulations with Fractional Atomic Occupation Numbers**

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Molecular dynamics simulations have been widely used to investigate the thermodynamical properties of materials at finite temperatures, in which the number of atoms containing a simulation cell is usually kept at fixed. For hydrogen storage alloys, however, since the hydrogen content as well as the structure of an alloy depend on the chemical environment (temperature and pressure of gaseous hydrogen), it is convenient to keep the chemical potential μ rather than the number of atoms. To this end, I introduce a fictitious fractional occupation number for each hydrogen atom in density functional calculations. The total energy is expressed by a similar manner to the virtual crystal approximation[1]. The total-energy derivative with respect to the occupation number can be calculated analytically, which is closely related to the chemical potential μ . Combining this with the conventional *ab-initio* molecular dynamics simulations, the plateau range in the pressure-composition isotherm can be effectively predicted.

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Interaction of V-M (M-Cu, Co and W) alloys with hydrogen under high pressure.

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Hydrides of metals and alloys to be used as materials for safe and compact storage of hydrogen. Vanadium dihydride content a high mass percent of hydrogen, but hydrogenation conditions and low pressure of decomposition to limit it for practical applications. For to extract hydrogen from vanadium hydrides under more soft conditions is used alloying of vanadium by different metals.

At present work was studied the interaction of V-Cu, V-Co and V-W alloys with hydrogen at pressure up to 2500 bars. Isotherms of absorption and desorption at different temperatures were measured and thermodynamic parameters of reaction were calculated. Alloying of V by Cu, Co and W leads to increasing of equilibrium pressure and decreasing of the maximum amount of hydrogen. X-ray of $V_{0.94}Co_{0.06}$ and $V_{0.9}W_{0.1}$ high-pressure hydrides showed formation of phase with fcc lattice corresponding to vanadium dihydride.

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Interaction of $V_{1-x}Mn_x$ ($x=0.1-0.3$) alloys with hydrogen under high pressure.

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It is known that vanadium and vanadium alloys after interaction with hydrogen to form phases with high amount of hydrogen. These hydrides are promising materials for storage and transportation of hydrogen. Amount of hydrogen and thermal stability these hydrides depends of the proportion of components in alloy.

At present work was studied interaction of $V_{1-x}Mn_x$ ($x=0.1-0.3$) alloys with hydrogen at high pressure (up to 2500 bars). Were measured isotherms of absorption and desorption at different temperatures and calculated thermodynamic parameters of reaction. Vanadium alloying by Mn leads to decreasing of the hydride phases stability. X-ray analyses of hydride phases formed at low and high pressures was carried out.

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Calorimetric study of hydrogen interaction with $\text{Sm}_2\text{Fe}_{17}$

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$\text{Sm}_2\text{Fe}_{17}\text{N}_3$ which as comparison with $\text{Nd}_2\text{Fe}_{14}\text{B}$ possesses a higher Curie temperature and a more anisotropy field is a perspective material for production of resin-bonded magnets. In the several works it has been shown that preliminary hydrogenation of $\text{Sm}_2\text{Fe}_{17}$ permitted to carry out nitride hardening more completely at more soft conditions. However the hydrogenation process itself was not studied enough at present. There are only a few works in which it was reported about the thermodynamic properties of the $\text{Sm}_2\text{Fe}_{17} - \text{H}_2$ system. For example, in the works [1, 2] the partial molar enthalpies of the reaction of hydrogen absorption (ΔH_{abs}) by $\text{Sm}_2\text{Fe}_{17}$ were calculated from the van't Hoff plots based on the measured P-C-T relations (P – equilibrium hydrogen pressure, T – experiment temperature, $C = \text{H} / \text{Sm}_2\text{Fe}_{17}$). There are no data about the study of hydrogen interaction with $\text{Sm}_2\text{Fe}_{17}$ by means of the calorimetric method which permits us to measure thermodynamic values directly.

In the present work the $\text{Sm}_2\text{Fe}_{17} - \text{H}_2$ system was studied by the calorimetric method using of the differential heat-conduction calorimeter Tian-Calvet type connected with a conventional Sieverts-type apparatus for gas dosed feeding. The apparatus scheme and the experimental technique were described elsewhere [3]. The $\text{Sm}_2\text{Fe}_{17}$ sample was prepared by induction melting of the constituent elements under a pure argon atmosphere and annealing in the vacuum resistance furnace at 1100°C during 40 hours. X-ray analysis (diffractometer Rigaku Ultima IV, Cu K α radiation, a graphitic monochromator) as well as a roentgen fluorescent analysis on spectrometer Rigaku Primus II and X-ray spectrography microanalysis with a scanning electron microscope JEOL JSM-6610 LV shown that after heat treatment the sample under investigation contained 95% $\text{Sm}_2\text{Fe}_{17}$, 4% SmFe_3 and less than 1% $\alpha\text{-Fe}$.

The calorimetric measurements of the $\text{Sm}_2\text{Fe}_{17} - \text{H}_2$ system were carried out at 200 and 250°C. The P – C and $\Delta H - C$ dependences were obtained for the process of hydrogen desorption from $\text{Sm}_2\text{Fe}_{17}$ hydride. In the P – C isotherms there are no any plateau as it was shown in the works [1, 2]. At the same time in the plots of the $\Delta H - C$ dependences there are the plateau regions where the enthalpy values remain constant or near constant. Thus at 200 °C on the region of hydrogen concentration $1.88 < C < 3.35$ the values of ΔH_{des} change negligibly (from 72 to 65 kJ/molH₂). Then with rising of the hydrogen concentration in the metallic matrix the enthalpy values decrease sharply in modulus to ~ 20 kJ/molH₂ at $C = 4.2$. At 250°C in the plot of the $\Delta H - C$ dependence there is region ($0.9 < C < 2.7$) where the enthalpy values remain constant ($\Delta H_{\text{des}} = 74.3 \pm 0.9$ kJ/molH₂).

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Hydrogen-Induced Superabundant Vacancies in Electrodeposited Fe-C Alloy Films

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The susceptibility of steels to hydrogen embrittlement increases with increase of carbon contents. In order to elucidate the mechanism of hydrogen embrittlement, analysis of the interaction between vacancy-hydrogen (Vac-H) and vacancy-carbon-hydrogen (Vac-C-H) clusters is advanced. We have succeeded by electrodeposition to obtain Fe-C alloy films containing C and H to fairly high concentrations [1], and examined the hydrogen behavior in the annealing process utilizing XRD, TEM and TDS methods. The atomistic structure of Vac-H and Vac-C-H clusters in Fe-C alloy films is discussed, based on these experiments.

Fe-C alloy films were electrodeposited on a Cu plate coated with amorphous Ni-P layer or a SUS304 plate, from the solution of FeSO₄ with varying amounts of ascorbic acid as a source of carbon. The deposition was carried out at 298 K at a constant current density of 500 A m⁻².

The hydrogen content of Fe-C alloy films in atomic ratio, $x_H = \text{H/Fe-C}$, increased nearly in proportion to the carbon content x_C up to 6.8 at% C, as shown in Fig. 1. Figure 2 shows the lattice parameter of Fe-C films as a function of x_C . The lattice contraction of about 0.1% was observed in the Fe films, whereas the lattice expansion increasing with carbon contents was observed in Fe-C alloy films. No precipitation of iron carbide was observed. Both the lattice contraction of Fe films and the lattice expansion of Fe-C alloy films was decreased as H was desorbed during heat treatments. Some inferences were made of the atomistic structure of Vac-H and Vac-C-H clusters in light of the recent Monte Carlo simulation on the SAV formation process in Fe [2].

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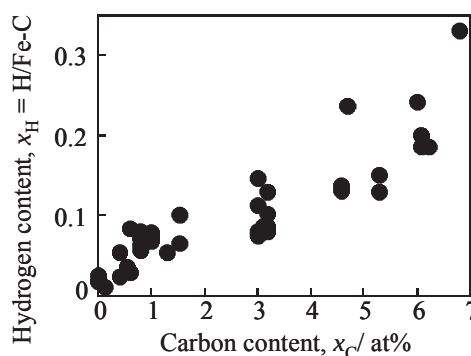


Fig. 1 Relation between carbon content x_C and hydrogen content x_H in electrodeposited Fe-C alloy films.

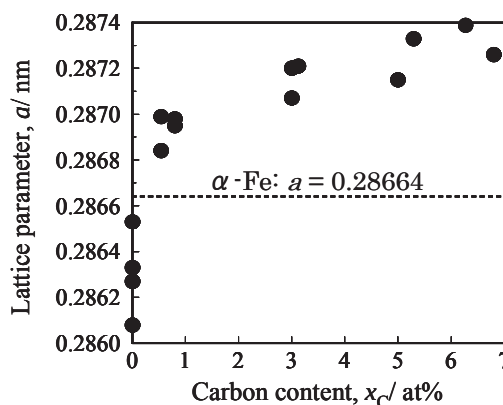


Fig. 2 Lattice parameter of Fe-C alloy films as a function of carbon content x_C .

Hydrogenation-induced Microstructure Changes in Titanium

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The paper reports recent research on investigation of defects in hydrogen-saturated titanium performed at Department of General Physics, National Research Tomsk Polytechnic University [1,2]. Microstructure changes of commercially pure titanium in a wide range of hydrogen concentration from 0.8 to 32.0 at.% were studied by means of positron lifetime spectroscopy (PLS) and Doppler broadening spectroscopy (DBS). New experimental data about the evolution of the positron annihilation parameters τ_f , τ_d and their corresponding intensities I_f , I_d , as well as the relative changes in the parameters S/S_0 , W/W_0 depending on the hydrogen concentration in commercially pure titanium after hydrogenation in gaseous atmosphere at temperature of 873 K was obtained. Based on the experimentally obtained results supported by scientific literature review the relationship between fluctuations of positron annihilation characteristics and microstructural changes in titanium was established.

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Synthesis, Crystal Structure and Dehydrogenation Reaction on a Mixed Alkali and Alkaline-earth Metal Alanate $\text{LiCa}(\text{AlH}_4)_3$

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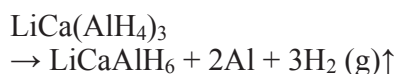
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Since discovery of reversible hydrogen storage properties on Ti doped NaAlH_4 [1], Al based complex hydrides (so-called alanates) have been extensively studied [2]. Due to fundamental understandings of material properties (e.g. thermodynamical stabilities, crystal structures and so on) on the alanates, researchers have attempted to synthesize various kinds of alanates [3]. Although they are generally composed of a metal cation M^{n+} (n : valence of a metal M) and a complex anion $[\text{AlH}_4]^-$, $\text{LiMg}(\text{AlH}_4)_3$ is of interests in terms of a mixed alkali and alkaline-earth metal cations. Recently Liu et al. reported a novel mixed alkali and alkaline-earth metal alanate, $\text{LiCa}(\text{AlH}_4)_3$, synthesized from 3LiAlH_4 and CaCl_2 [4]. The dehydrogenation reaction has still not been properly understood because of the poor crystalline products.

In order to clarify the reaction, we directly prepared $\text{LiCa}(\text{AlH}_4)_3$ with better crystallinity by mechanochemical milling of LiH , CaH_2 and AlH_3 in molar ratio of 1:1:3 under hydrogen gas at 0.3 MPa. The products were characterized by X-ray diffraction, Raman spectroscopy, thermogravimetry combined with first-principles calculations.

From the present study, $\text{LiCa}(\text{AlH}_4)_3$ with a hexagonal unit cell ($a = 8.9278 \text{ \AA}$ and $c = 5.8947 \text{ \AA}$) was dehydrided into LiCaAlH_6 with a tetragonal unit cell ($a = 6.59347 \text{ \AA}$ and $c = 16.79651 \text{ \AA}$) below 150°C with 4.2 wt.% of H_2 release (Figure 1). This indicated that the dehydrogenation reaction was



Focused on both crystal structures of $\text{LiCa}(\text{AlH}_4)_3$ and LiCaAlH_6 , they commonly showed that Ca^{2+} and complex anions ($[\text{AlH}_4]^-$ or $[\text{AlH}_6]^{3-}$) were located in between Li^+ layers.

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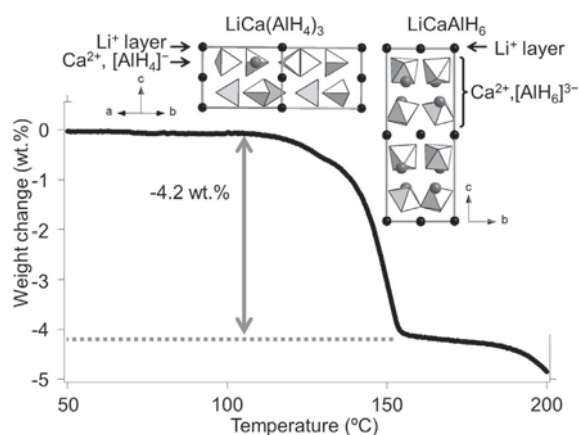


Figure 1 TG curve of $\text{LiCa}(\text{AlH}_4)_3$. Insets show crystal structures of $\text{LiCa}(\text{AlH}_4)_3$ and LiCaAlH_6 . Black and gray circles and tetrahedra and octahedra indicate Li^+ , Ca^{2+} , $[\text{AlH}_4]^-$ and $[\text{AlH}_6]^{3-}$, respectively.

Fluorite MgD_2 in a MgD_2 - TiD_2 Composite

In deuterium magic-angle spinning NMR, the amplitudes of the spinning sidebands (SSBs) reflect the strength of the electric field gradients (EFG) acting at the sites of the D atoms. In the standard rutile crystal structure of MgD_2 (or MgH_2), the D atoms are surrounded by 3 Mg atoms in the same plane, leading to a large EFG and large amplitude SSBs. We have heat treated a composite of MgD_2 - TiD_2 (80-20) at 400 C. Upon return to room temperature, the D resonances of the MgD_2 and TiD_2 components are clearly separated by the large metallic (Knight) shift of the TiD_2 . Unlike spectra obtained on material before the heat treatment, the heat treated material has very small SSBs associated with the MgD_2 component. The implication is that the crystal structure of the magnesium deuteride has transformed to a structure with small EFG, implying local cubic or tetrahedral symmetry, such as the fluorite structure.

Improving the connection between neutron scattering and computational modeling

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We will present a summary of the current developments on the integration of materials modeling and simulation into the data analysis of neutron scattering data obtained from beamlines at the Spallation Neutron Source (SNS). This will include using modeling both as an aide in the offline analysis of experimental data but also how we can link streaming data with leadership class computational resources to provide near real-time from modeling and simulations in order to optimize the information obtained from individual experiments. We will present an overview of the architecture of the systems and software that have been deployed together with relevant scientific use cases.

Mantid Data Reduction and Visualization

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The large amount of data collected at the Spallation Neutron Source has brought forward new opportunities for science, but also present challenges for data reduction and visualization. A joint collaboration between ISIS and ORNL, Mantid[1.] is a data reduction, visualization, and analysis framework for neutron and muon experiments. Most instruments at ORNL two neutron sources (SNS and HFIR) are already using Mantid as part of their data processing. This framework allows user implemented workflows, which include customized algorithms and visualization tools. Users have multiple options of interacting with the program, from graphical user interfaces (GUI), to Python scripts, including the ability to generate a script based on an initial use of the GUI. One of the main features of this framework is the possibility to use event data. Event data allows using novel techniques, such as asynchronous parameter scans, including continuous angle or temperature, and pump probed experiments. Mantid also provides advanced visualization for 4-dimensional views of inelastic neutron scattering as a function of energy transfer and three dimensional momentum transfer, and/or other parameters, such as temperature, pressure or magnetic field.

References:

1. <http://www.mantidproject.org>

Kinetics and Thermodynamics of Hydrogen Sorption as Studied by Hyphenated Calorimetric and Volumetric Techniques

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The management of large amounts of heat released during the formation of a metal hydride is critical for practical applications. It is thus necessary to quantify and validate hydriding enthalpies in situ during a sorption measurement. This is made possible with coupled calorimetric and volumetric techniques.

In the Sievert's volumetric method, a sample at known pressure and volume is connected to a reservoir of known volume and pressure through an isolation valve. Opening the isolation valve allows a new equilibrium to be established. Absorbed amounts are determined by a difference between the actual equilibrium pressure versus calculated pressure. In the PCTPro, a fully automated Sievert's instrument, the sample reservoir can be a pressure resistant calorimetric cell, placed in a temperature controlled calorimeter. This way, the heat of sorption can be directly measured.

It is illustrated by an experiment where the calorimetric cell contained 880mg of Pd and was kept isothermally at 170°C during the whole process (Figure 1). Gas injections with DeltaP of 1bar in a reservoir volume of 5.78mL were programmed. Each peak corresponds to the injection of one gas dose. The heat evolved increases when the beta phase starts being produced. The average differential heat of sorption in the alpha phase is found equal to 23.2kJ/mol, which corresponds literature values [1].

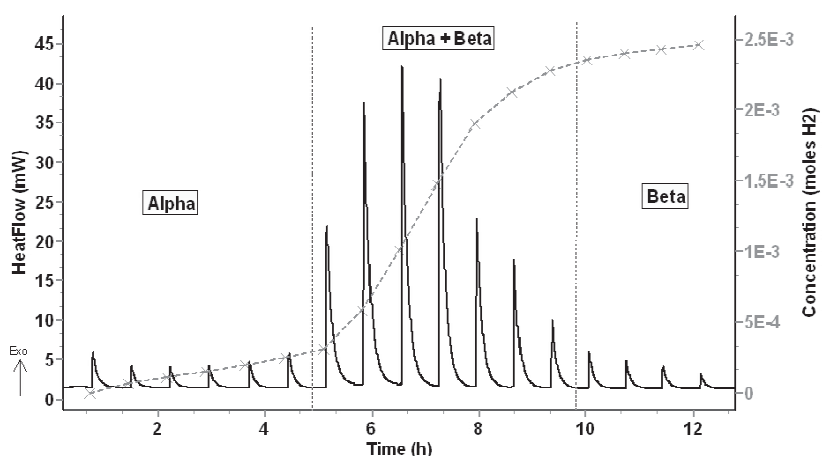


Figure 1. Simultaneous Heatflow as measured by a C80 calorimeter and Hydrogen concentration as measured by a PCTPro device.

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Tailoring the Properties of Metal Hydrates through Superlattice Growth.

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From the perspective of using hydrogen as fuel, manipulating the properties of metal hydrides is crucial for making an effective hydrogen carrier. Vanadium constitutes as an exceptional candidate when it comes to researching for efficient storage media for hydrogen, addressing a problem which is holding back its potential for application. In combination with other metals, such as Iron, Chromium, Molybdenum etc., superlattices can be grown successfully and interesting characteristics can be taken into account.

Superlattices are artificial single crystals, of two or more components. Their crystallinity makes their study quite interesting because they make perfect samples for scattering experiments. Altering attributes, such as interface to volume ratio and internal strain, the thermodynamics of the Hydrogen-Metal system exhibit interesting deviations from a simple thin film. Internal strain states can dictate phase transitions within the metal matrix and they can be easily controlled by different kinds of components and the ratio between them, due to the fact that the mismatch, because of the difference in lattice parameters, is responsible for the strain. The interface to volume ratio can give rise to finite size effects, while internal strain can be made to remain the same, allowing those effects to be the only parameter under investigation. Furthermore, in the case of superlattices it is observed that the quality of the matrix is not degraded with loading and unloading the samples with hydrogen. This is a quality of the superlattices that can play a role in future applications.

In this work the above aspects of metal hydrogenation are addressed through extensive studies done with X-rays (and neutron) scattering. Since the superlattices provide information on three different length scales, the effect of hydrogenation on such samples is easily observable and can be measured with respect to different characteristics of the superlattice, from the atomic plane distance (position of the $\sim 61^\circ$ peak corresponding to $\sim 0.2\text{nm}$), to the chemical repeat distance (satellite peaks positioned at $\sim 54^\circ$, $\sim 69^\circ$, $\sim 78^\circ$ corresponding to $\sim 3\text{-}5\text{nm}$) and finally to the total thickness regime (Laue oscillations corresponding to $\sim 50\text{nm}$). All these characteristics construct a unique and detailed scattering pattern as shown in figure 1 that is altered with hydrogenation and can be quantified properly.

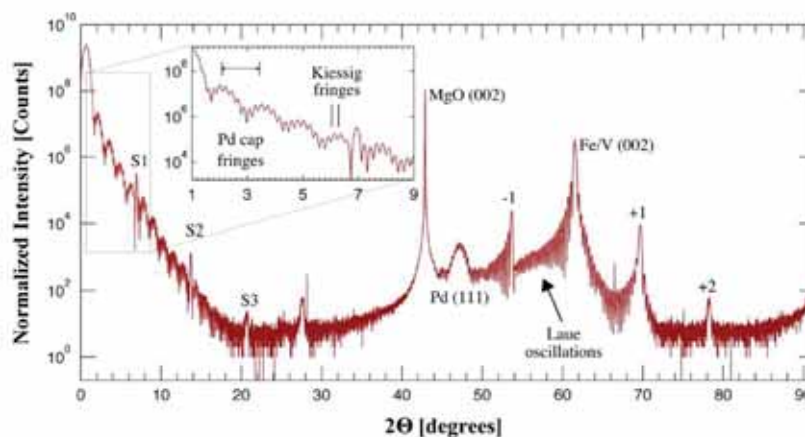


Figure 1: Illustration of the accessible length scales of a superlattice through scattering.[1]

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In-situ Diffraction Measurements of Hydrogen Storage Materials by High-Intensity Neutron Total Diffractometer, NOVA

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A high-intensity neutron total diffractometer, NOVA, at Japan Proton Accelerator Research Complex (J-PARC) realizes new opportunity to explore structures of hydrogen storage materials [1]. Crystalline structure as well as amorphous and liquid structure was investigated by NOVA for AlD₃ [2], LaD_x [3] and LiAl(ND₂)₄ [4]. Also, time-transient measurement during hydrogen absorption and desorption process under hydrogen/deuterium gas atmosphere (max 10 MPa) is feasible on NOVA, using a tight cell made from single crystal sapphire. The diffraction profiles of powder samples in the tight cell are obtained by removing the Bragg peaks of the single crystal sapphire. Absorption was carried out by submitting Pd powder to a deuterium pressure of 2 MPa at 393 K and letting it absorb with its own kinetics in quasi-equilibrium conditions. The time-divided neutron diffraction profiles during the deuterium absorption reaction revealed that the phase continuously transforms from metal Pd through α -PdD_x to β -PdD_{~0.7} in a few seconds.

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A Study on Hydrogen Absorption and Desorption Kinetics of Hydrogen Storage Alloys at Temperatures from 77K to 298K.

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The hydrogen storage alloys are attracting high attention as the effective absorber of hydrogen boil off gas from liquid hydrogen gas. In this case, the alloys should have high reactivity with hydrogen gas even at low temperatures. However, actual data for hydrogen absorption and desorption at temperatures below 298 K is not well known. In this study, we examined the hydrogen reactivity of hydrogen storage alloys at temperatures from 77K to 298K.

Effects of CsOH Pretreatments on the Hydrogen Absorption Kinetics of a Mm-Ni Based Hydrogen Storage Alloy

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This study reports the effects of cesium pretreatments on the initial rate of hydrogen absorption by a mischmetal (Mm) based hydrogen storage alloy ($\text{MmNi}_{3.48}\text{Co}_{0.73}\text{Mn}_{0.45}\text{Al}_{0.34}$ (Mm= $\text{La}_{0.35}\text{Ce}_{0.65}$)) in electrochemical process. For the enhancement of electrochemical hydrogen absorption rate, the cesium pretreatment was found effective. Surface analyses of the alloy samples by ESCA revealed that this treatment is responsible for the promotion of the dissociation rate of H_2O molecules in electrochemical process, and according enhancement of hydrogen absorption rate. This paper demonstrates an effective surface treatment of cesium pretreatments, which reduced the work function of the alloy surface by cesium.

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Catalysis of Thermally Stable Nickel Nanoparticles for Ammonia Decomposition

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NH₃ is a promising material as H₂ carrier because it has high gravimetric and volumetric H₂ density, which are 17.8 mass% and 108 g/L (in liquid NH₃), respectively [1]. Although Ru is the most active catalyst for NH₃ decomposition, the development of catalysts of base metals is industrially important [2]. Ni also have catalysis for NH₃ decomposition, but its activity is much lower than Ru [2]. Therefore, catalysis of Ni must be improved for practical use. It is reported that reducing the size of catalysts to smaller than 5 nm significantly improve their activities. However, the nanoparticles sinter and form large particles at high temperature, resulting in deactivation [3]. We previously proposed synthesis method of stable Ni nano-particle, which kept the nanosize even at high temperature such as 400 °C [4]. In this work, the catalysis and stability for the NH₃ decomposition are investigated.

Ni nanoparticles, which were named "CH_{zeolite}", were synthesized by adsorption and decomposition of an organometallic compound of Ni, Ni(C₅H₅)₂, in pores of zeolite [4]. As reference, Ni particles were also synthesized on zeolite and alumina by a conventional incipient wetness impregnation process with NiCl₂ solution and were named "IMP_{zeolite}" and "IMP_{Al₂O₃}", respectively. NH₃ decomposition reaction was carried out in a closed reactor at 500 °C for 24 h. The reaction was repeated 5 times to investigate the catalytic stability of CH_{zeolite}.

CH_{zeolite} showed much higher conversion ratio than IMP_{zeolite} and IMP_{Al₂O₃}. Furthermore CH_{zeolite} showed no significant deactivation during the repeat tests. It is noticed that TEM images (Figure 1) of catalysts after the reaction demonstrated that Ni nanoparticles of CH_{zeolite} kept the nanosize, smaller than 5 nm, even after the repeated reactions, whereas Ni particles synthesized by impregnation method formed larger particles. In conclusion, both the high dispersion level and thermal stability of the nanoparticles significantly improved the catalysis of Ni.

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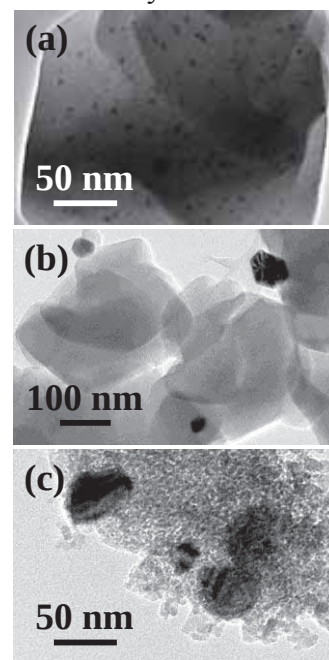


Figure 1. TEM images of (a) CH_{zeolite} after durability test, (b) IMP_{zeolite}, and (c) IMP_{Al₂O₃} after reaction at 500 °C for 24 h.

The desorption of hydrogen from uranium hydride

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Uranium is regularly used as a hydrogen storage material [1]; for this reason understanding its activation towards hydrogen, the desorption kinetics and associated thermodynamics is essential. In this work the number of hydriding-dehydriding cycles required to achieve consistent hydrogen absorption characteristics was corroborated [2] and the desorption kinetics of uranium hydride in a closed system was investigated. Consistent hydrogen absorption characteristics were achieved after five hydriding-dehydriding cycles at 200 °C and a value for the apparent activation energy of bulk hydrogen desorption was calculated to be 14.1 kJ mol⁻¹.

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Observation of Dynamic Structure during Hydrogenation Reaction for Pd Nanoparticles by using Real-Time-Resolved X-ray Absorption Fine Structure Spectroscopy

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Palladium nanoparticles show different hydrogen absorption and desorption properties from those of bulk Pd, which is typically observed in an ambiguous α - β transition. We have developed the real-time-resolved X-ray absorption fine structure (XAFS) spectroscopy observation system with the dispersive optics in order to understand the dynamic structural change of the Pd nanoparticles during hydrogen absorption and desorption reactions. It was succeeded to obtain the spectra of 5 ms exposure time in the real-time-resolved mode and determine the reaction time below 10 ms [1]. Here, we show the dynamic structure of the Pd nanoparticles during hydrogenation reaction. This reveals the reaction model between hydrogen gases and the Pd nanoparticles.

XAFS spectra were observed at BL14B1 and BL28B2 of SPRING-8 by dispersive mode. The local structural transformation of Pd nanoparticles on Al_2O_3 during hydrogen absorption reaction was investigated with the real-time-resolved mode.

Figure 1 shows the changes of the interatomic distance and the Debye-Waller factor of the Pd nanoparticles of Al_2O_3 during the hydrogenation reaction. XAFS spectra were monitored with real-time-resolved mode at 50 Hz. Sudden increase of the interatomic distance shows the Pd nanoparticles was transformed to the β phase in 0.5 s. The positive peak of the Debye-Waller factor is only observed during the interatomic distance increases, which indicates that both the long and short interatomic distances exist at the middle stage of the reaction. This may not be consistent with the result that the limiting-rate process of the reaction is the surface dissociative adsorption of the hydrogen molecule, not the penetration of the hydrogen atoms inside of the Pd nanoparticles [1]. We want to state that the hydrogen atoms move very quickly with making the distortion of Pd local bonds at the middle stage of the hydrogenation reaction.

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO) under “Advanced Fundamental Research Project on Hydrogen Storage Materials (Hydro-Star)”.

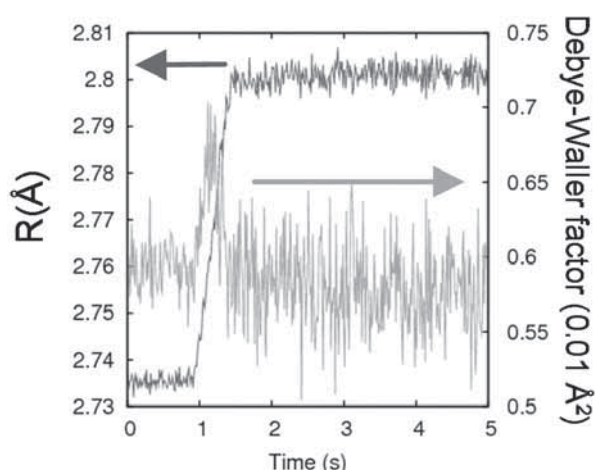


Figure 1. Interatomic distance and Debye-Waller factor changes by the hydrogenation reaction for the Pd nanoparticles.

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The Hydriding Kinetics of Cerium and Morphology of the Reaction Sites

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Many metals undergo reaction with hydrogen to produce discrete metal-hydride sites on the surface; an example is cerium [1]. During use or extended storage potential environments can be generated leading to the formation of the hydride phase. The formation of hydride phases has safety implications such as the potential to adversely change mechanical properties [2] and to cause unintended thermal excursions, pressurisations and/or breaches of containment [3-5]

In this study the morphology and growth kinetics of discrete reaction sites formed under 100 mbar of hydrogen between 30 to 100 °C was investigated using a combination of in-situ imaging and post reaction optical and electron microscopy. Values for the reaction site growth velocities in the lateral (V_l) and penetrative directions (V_p) as a function of temperature were determined. Reaction sites were found to have grown with oblate hemispherical morphology as a result of anisotropic growth kinetics, with values of $V_l > V_p$. Arrhenius analysis indicated V_l and V_p have equivalent apparent activation energies of ca 40 kJ mol⁻¹ suggesting mechanistic equivalence.

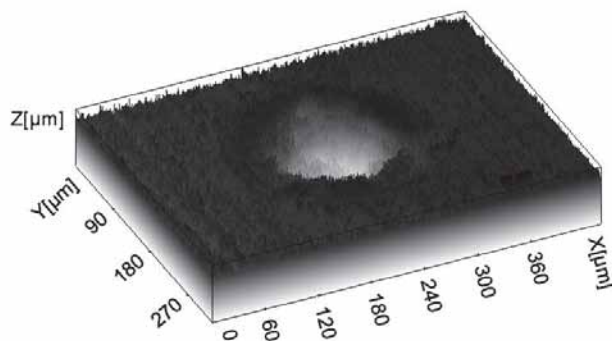


Figure 1. Iso axial projection of a typical crater formed by the growth of a cerium hydride reaction site obtained from post reaction extended focus microscopy

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Nuclear Magnetic Resonance Study of Atomic Motion in New Bimetallic Perovskite-Type Borohydrides $\text{RbCa}(\text{BH}_4)_3$ and $\text{CsCa}(\text{BH}_4)_3$

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Borohydrides are considered as promising materials for hydrogen storage due to their exceptional volumetric and gravimetric hydrogen densities. Apart from the practical relevance, these compounds are of considerable interest as model systems for studying the correlation between atomic dynamics and crystal structure. In this work, we report the results of the first nuclear magnetic resonance study of atomic jump motion in novel bimetallic perovskite-type borohydrides $\text{CsCa}(\text{BH}_4)_3$ and $\text{RbCa}(\text{BH}_4)_3$. Measurements of the ^1H and ^{11}B NMR spectra and spin-lattice relaxation rates were performed over wide ranges of temperature (84 – 580 K) and resonance frequency (14 – 90 MHz).

In the studied temperature range, the proton spin-lattice relaxation rates R_1^{H} measured at three resonance frequencies for $\text{CsCa}(\text{BH}_4)_3$ and $\text{RbCa}(\text{BH}_4)_3$ exhibit a frequency-dependent peak near 320 K and 290 K, respectively. Such a peak is expected to occur at the temperature at which the reorientational jump rate becomes nearly equal to the resonance frequency. The reorientational motion responsible for this peak is characterized by the activation energy of 0.50 eV for $\text{CsCa}(\text{BH}_4)_3$ and 0.52 eV for $\text{RbCa}(\text{BH}_4)_3$. It is found, that for both systems some additional motional processes contribute to the low-temperature data; this leads to the presence of an additional smeared peak at low temperatures. Generally, the behavior of $R_1^{\text{H}}(T)$ for $\text{CsCa}(\text{BH}_4)_3$ at $T < 380$ K and for $\text{RbCa}(\text{BH}_4)_3$ at $T < 340$ K resembles that for $\alpha\text{-Y}(\text{BH}_4)_3$ [1], where the linear coordination of a BH_4 tetrahedron by two metal atoms is believed to lead to coexistence of several inequivalent types of reorientations [2].

The reappearance of the frequency dependence of R_1^{H} accompanied by the increase in R_1^{H} with the increasing temperature has been found for $\text{CsCa}(\text{BH}_4)_3$ at $T > 500$ K and for $\text{RbCa}(\text{BH}_4)_3$ at $T > 400$ K. Such a behavior indicates the onset of an additional motional process corresponding to translational diffusion of intact BH_4 groups. This is supported by the temperature dependence of the ^1H and ^{11}B NMR line widths which drop to very small values (~ 1 kHz) at high temperatures.

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Ab initio simulation of hydrogen mobility in hcp, bcc, fcc magnesium lattice

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MgH₂ has attracted a lot of attention as a reversible hydrogen storage material because Mg is abundant on the Earth, inexpensive, and has a high hydrogen capacity of 7.6 mass%. However, any practical applications are limited by the slow kinetics and high temperature of reactions with hydrogen. Nevertheless, it was found that a limited dissociation rate of hydrogen on the metal surface may be improved by additions of transition metals catalyst (TM). But up to now the role of the interface border between Mg and TM remains unclear.

In our previous work [1] using DFT calculation we have studied the microstructure of the Mg/Nb interface. It was found that Nb additives stabilize the Mg bcc structure near the interface border. Also we have studied hydrogen induced transition in Mg [2]. It was found that at low hydrogen concentrations all the three hcp, bcc and fcc structures of MgH_x can exist. The rutile structure of MgH_x (β-phase) becomes stable only at high hydrogen concentration ($x \approx 2$). Our DFT studies have shown that hydrogen atoms tend to be randomly distributed over the interstitial sites in the bcc-MgH_x structure, whereas into other lattices (hcp, fcc and rutile) hydrogen atoms prefer to occupy neighboring interstitial sites, forming a kind of clusters.

In this contribution we report on the results of DFT calculations of hydrogen mobility in various (hcp, bcc, fcc) structures of magnesium. For each structure we have determined the activation energies for hydrogen migration pathways. Then taking into account ZPE correction we have made an estimation of the hydrogen diffusion coefficient.

It has been found that bcc-Mg structure exhibits the highest diffusion rate and the lowest activation barriers. Keeping in mind that in bcc-Mg hydrogen atoms do not form any clusters, it seems the bcc phase of magnesium is a good promoter of hydrogen. From this point of view the catalytic effect of transition metal additives, such as Nb, that do not form any bulk alloy with Mg, can be explained by the following way: the presence of Nb layers or particles helps to stabilize the bcc structure of Mg, in which the hydrogen diffusion is faster due to (i) the lower activation energy and (ii) the homogeneous distribution of hydrogen atoms over tetrahedral interstitial sites.

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Effect of Grain Boundaries on Hydrogen Diffusion in Ultrafine-Grained Palladium

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There is controversy whether the grain boundary in metallic materials acts as a trapping site or a fast diffusion path for hydrogen diffusion. It is generally difficult to produce bulk ultrafine-grained materials but in this study, a process of high-pressure torsion (HPT) [1] was used for grain refinement of pure palladium. Hydrogen behavior is then investigated by electrochemical permeation test for the HPT-processed disks including cold-rolled disks for comparison.

Palladium (99.9% purity) disks were prepared for electrochemical permeation tests after annealing, cold-rolling and HPT-processing. Microstructure information including grain boundary characters and dislocation densities was obtained by electron back-scatter diffraction (EBSD) analysis and X-ray diffraction (XRD) analysis. Diffusion coefficients were determined from break-through time, t_b , of permeation curves obtained by permeation tests consisting of absorption step and desorption step.

EBSD and XRD analyses reveal that the rolled disk has a high density of dislocations, whereas the HPT-processed disk has not only a higher dislocation density but also many random boundaries. Difference in permeation curve among the three types of disks can be seen in Fig. 1. Insets are enlargement of the initial stage of the permeation tests to elucidate the difference in t_b . In the adoption step, t_b is longer in the cold-rolled disk and the HPT-processed disk than that in the annealed disk. This arises because dislocations act as trapping sites. In the desorption step, however, the effect of the trapping sites hardly appears and t_b in the HPT-processed disk is higher than that in the annealed disk because grain boundaries act as a fast diffusion path.

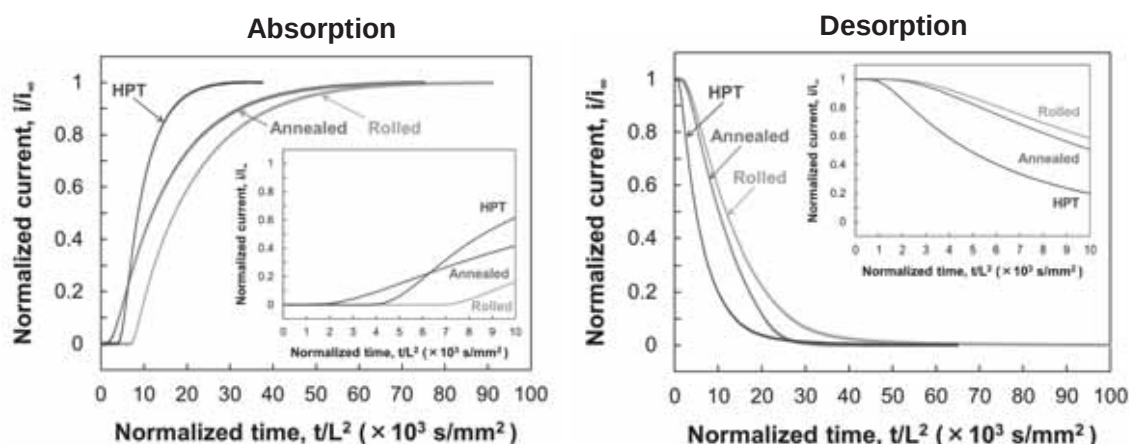


Fig. 1 Permeation curves with charging current density of 5 A/m² and test temperature of 20°C. Insets are enlargement of initial stage of charging.

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Structural Analysis of Possible Lithium Migration Paths in Borohydrides

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Borohydrides have been attracting significant interests as potential solid electrolytes since the discovery of fast Li-ionic conduction in hexagonal LiBH_4 [1]. In general, borohydrides exhibit rich crystal chemistry (ionic crystals and frameworks containing mixed cations and mixed anions) which can be linked analogically to oxide family. This allows extensive possibilities of synthesizing new compounds in search for novel fast ion conductors with improved properties. Therefore, the understanding of the ionic migration path is important to screen ionic conduction through a wide range of new borohydride structures.

Studies of voids and channels as Li-ion migration paths in Li-containing borohydrides with different compositions will be the focus of this presentation. TOPOS software is employed to analyze geometrically the possible conduction space by using Voronoi-Dirichlet Polyhedra (VDP) method. Previously, this method has been systematically applied for oxide compounds [2]. In addition, migration paths can also be modelled as the path of lowest electron density [3] calculated by Hirshfeld surface analysis tool available in Crystal Explorer software. One example of the compounds studied, the high temperature LiBH_4 with hexagonal structure can be shown to possess 3D Li-ion conduction (Figure 1).

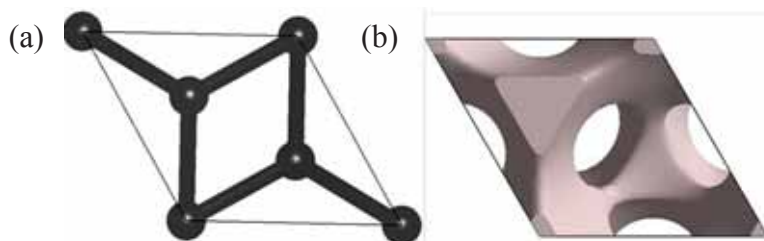


Figure 1. Possible Li^+ pathways in hexagonal LiBH_4 calculated from (a) VDP (b) Hirshfeld surface analysis

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Atomistic Simulation of Hydrogen Dynamics near Dislocations in Vanadium Hydrides

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Lattice defects are known to play important roles on the property of metallic material. They are inevitably generated during hydrogen sorption processes and possibly affect hydrogen storage property. Kim et al. [1] suggested by X-ray total scattering data that increasing structural disorder by cyclic hydrogen sorption is caused by dislocation pileup. It is desirable to understand how dislocation modifies hydrogen kinetics in metallic lattice and hydrogen storage property.

In this study, the author carried out classical molecular dynamics simulation of H atoms in vanadium hydrides including dislocation. Atomistic models were prepared based on α -, β - and γ -vanadium hydride single crystals. Dislocation models with 3D-periodicity were generated by DLstudio [2] by loading even numbers of positive and negative, edge or screw dislocations into single crystal. The number of atoms in the model varies from ca. 5 000 to 50 000 depending on assumed dislocation density and hydrogen concentration. Many-body and pairwise potentials were assumed for V-V, V-H and H-H interactions [3,4]. At the initial stage, hydrogen atoms were distributed homogeneously. After relaxation at low temperature, constant-*NPT* simulation up to 2 ns was carried out at 0.1 MPa and 100 to 600 K.

During the initial relaxation, hydrogen atoms aggregated in the vicinity of dislocation core. The number density of H at the dislocation core region was about five-times larger than in other region. Simulated self-diffusion coefficients of H in α -phase single crystal were in good agreement with experimental data [5]. In the dislocation region, self-diffusion coefficients of H were found to be about one-order lower than in single crystal. The Arrhenius plot shows that activation energy of H-diffusion near dislocation increases at high temperature. Dependencies on dislocation type (edge/screw) and hydride phase were also analyzed.

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Hydrogen Diffusion in $\text{La}_{1.5}\text{Nd}_{0.5}\text{MgNi}_9$ Alloy Electrodes of the Ni-MH Battery

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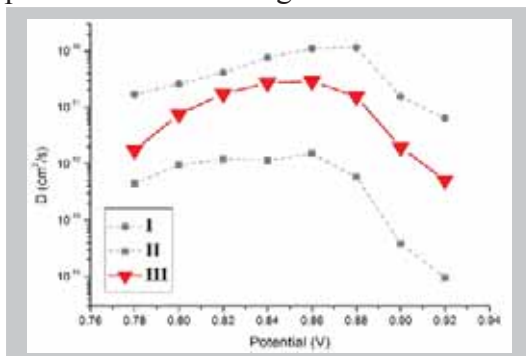
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Cost efficient La–Mg–Ni hydrogen storage alloys offer benefits of high drain discharge, good performance at subzero temperatures and increased cycle stability in the Ni-MH battery applications [1]. Battery performance at high discharge currents is very important. Its optimisation requires assessment of hydrogen diffusion in the MH electrode at various testing conditions.

The goal of present study was to evaluate hydrogen diffusion coefficient D in the modified by neodymium $\text{La}_{1.5}\text{Nd}_{0.5}\text{MgNi}_9$ alloy electrodes, as D is the parameter contributing to the discharge rate control. Initial alloy was synthesised by induction melting and was annealed at 960 °C. X-ray diffraction and SEM analyses showed formation of PuNi₃-type R_2MgNi_9 intermetallic as the main phase and $\text{R}_3\text{MgNi}_{14}$ and $\text{R}_4\text{MgNi}_{19}$ intermetallics as secondary phases. Earlier, during studies of hydrogen transport in the bulk AB₅ type MH alloys, a dependence of D from the electrode potential was roughly estimated [2-4]. It is well known from lithium intercalation research that the diffusion rate depends on the degree of intercalation (and by these means on the potential); to obtain this dependence, one should use chronoamperometry with low amplitude of a potential step.

We measured low amplitude (0.02V) chronoamperograms in an interval from -0.78V to -0.96V (Hg/HgO reference electrode) obtained in a three electrode open cell. D values were calculated using linear regions of the plots I vs. $t^{-1/2}$ (I for longer and II for shorter time intervals), and also from $1/It^{1/2}$ vs. $t^{-1/2}$ (III) according to the approach proposed earlier in [4]. To check Cottrellian behavior for certain time domains, the minima of $It^{1/2}$ vs. $\log t$ curves were considered according to [4]. Technique III was found to be the most accurate. All techniques confirm the existence of D maximum (Figure), which is observed at the initial stage of the discharge and corresponds to the beginning of the plateau at the discharge curves.



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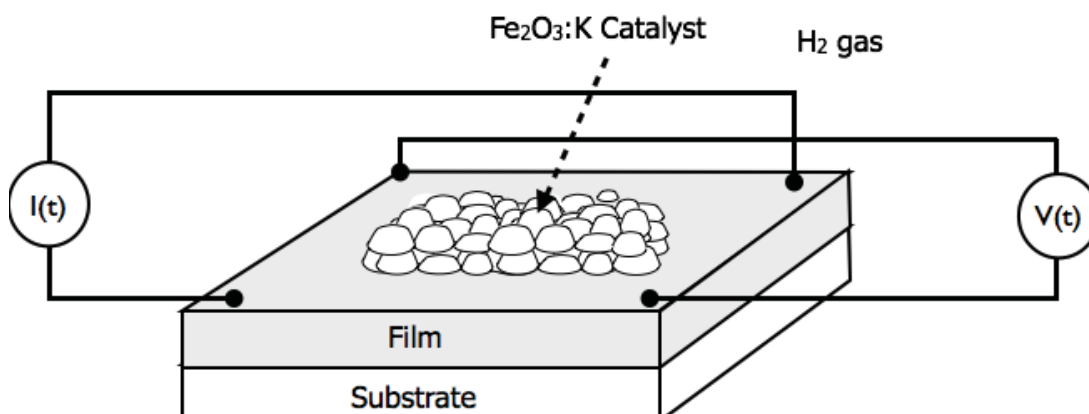
Figure. D values for $\text{La}_{1.5}\text{Nd}_{0.5}\text{MgNi}_9$ electrode calculated using techniques I - III.

Conductivity of H and D Rydberg matter condensed on ultrathin metal films.

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Rydberg matter of H and D is formed inside a standard industrial styrene catalytic material. The catalytic material consist of mixture Fe, K oxides that during industrial usage lose the K content. First measurements on the conductivity of Rydberg matter H and D phases will be reported and discussed. The Rydberg matter is condensed on top of surface of ultra thin Pt film grown on MgO substrate.



By placing shutter between the source and the surface and changing gas pressure and temperature in the experiment, thermodynamics and lifetime of Rydberg matter will be studied, Rydberg matter has shown some interesting properties still surprisingly waiting for experimental confirmation or recognition. Among these properties are ultra dense form [1] and low energy laser induced D fusion [2-3] that surpasses easily any other reported rate. The aim of this preliminary first work is to study this strange matter phase of H and D and take the first step in explore and confirm Leif Holmlid work.

1. Excitation levels in ultra-dense hydrogen $p(-1)$ and $d(-1)$ clusters: Structure of spin-based Rydberg Matter. Leif Holmlid.

International Journal of Mass Spectrometry 352 (2013) 1–8

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Review Of Scientific Instruments 82, 013503 (2011)

3. Laser-induced fusion in ultra-dense deuterium $D(-1)$: Optimizing MeV particle emission by carrier material selection. Leif Holmlid

Nuclear Instruments and Methods in Physics Research B 296 (2013) 66–71

Chemical Diffusion and Surface Exchange in Ln-Ba-Sr-Co-Fe Perovskite System in Hydrogen- and Oxygen-containing Atmospheres

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For processes, which are controlled by transport of ions, determination of chemical diffusion coefficient (D) and surface exchange coefficient (K) related to the reaction at the phase boundary is essential. Commonly, relaxation techniques are used, which are based on measurements of mass or electrical conductivity changes during immediate changes of the oxygen partial pressure [1, 2]. Theoretical basis for these methods relies on the solution combining first and second Fick's law and flux density at surface boundaries. Depending on the geometry (3D, disc-like, etc.), the respective solutions are different, however, for simultaneous determination of both coefficients $0.03 \leq l \cdot K/D \leq 30$ condition has to be satisfied [3]. This shows importance of dimensional parameter l , and makes such calculations possible only for the certain geometry and size of the samples.

In this work we present results concerning determination of chemical diffusion coefficient and surface exchange coefficient, measured by mass and electrical conductivity relaxation techniques, for materials from Ln-Ba-Sr-Co-Fe perovskite system (Ln - selected lanthanides). The measurements were performed at elevated temperatures (600-800 °C) in a wide range of oxygen partial pressures, including H₂-containing atmospheres. The calculations were done in a custom-made Matlab code. As predicted by the theory, it was found that geometry of the samples may limit possibility of simultaneous calculation of D and K.

Interestingly, the same theoretical basis for determination of D and K can be implemented also in the case of lithium transport in electrode materials for lithium batteries. In particular, it was found that the results of appropriately conducted Potentiostatic Intermittent Titration Technique (PITT) measurements allow for such the calculations [4]. Therefore, in addition the above results for Ln-Ba-Sr-Co-Fe system, we discuss applicability of the PITT-based relaxation method for determination of D and K during electrochemical hydrogenation of quasicrystal-based hydrogen storage materials.

Acknowledgements

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Nuclear magnetic resonance study of hydrogen diffusion in the transitional metal alloys lattice

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During the last decades Ti-V-Cr alloys have been extensively studied as promising materials for hydrogen storage [1]. Despite a comparatively low hydrogen storage capacity (up to 3.8 wt% for selected compositions) Ti-V-Cr alloys exhibit low hydrogen release temperature and rather high hydrogen sorption kinetics. From this perspective the information about hydrogen mobility in the metal lattice is of great importance, and nuclear magnetic resonance (NMR) is one of the most powerful tools to obtain it.

The onset of hydrogen diffusion has a clear effect on the NMR signal. Hydrogen diffusion coefficient (D) can be measured directly using NMR with limited information about other properties of the Me-H system. Furthermore, knowing the host metal structure one can identify the diffusion mechanisms. Moreover, we can obtain the activation energy of an atomic motion (E_a) from temperature dependencies of the diffusion coefficient.

Here we report on the results of our ^1H NMR study of the hydrogen self-diffusion coefficient in hydrides of Ti-V-Cr alloys with different compositions: $\text{TiV}_{0.8}\text{Cr}_{1.2}\text{H}_{5.29}$, $\text{Ti}_{0.33}\text{V}_{1.27}\text{Cr}_{1.4}\text{H}_{1.13}$ and $\text{Ti}_{0.5}\text{V}_{1.9}\text{Cr}_{0.6}\text{H}_{5.03}$. In the initial alloys the distribution of the Ti, V and Cr atoms over both sites of the bcc lattice is random. For $\text{TiV}_{0.8}\text{Cr}_{1.2}$ and $\text{Ti}_{0.5}\text{V}_{1.9}\text{Cr}_{0.6}$, which can uptake more hydrogen, hydrogenation induces a bcc-to-fcc structural phase transition. We have also studied alloys with the addition of a minor fraction of $\text{Zr}_7\text{Ni}_{10}$, as such materials exhibit a specific microstructure and display excellent sorption kinetics [2]. The hydrogen diffusion measurements have been performed employing the static field gradient nuclear magnetic resonance method (SFG NMR) [3] within the temperature range from 293 to 403 K. All hydrides exhibit rather slow hydrogen diffusion ($D = 1\div 3 \times 10^{-11} \text{ m}^2/\text{s}$) at room temperature. Such low values of the hydrogen diffusion coefficient are quite typical for transition metal hydrides with a high hydrogen concentration [4]. It was found that the activation energy increases in the series $\text{Ti}_{0.5}\text{V}_{1.9}\text{Cr}_{0.6}\text{H}_{5.03} < \text{TiV}_{0.8}\text{Cr}_{1.2}\text{H}_{5.29} < \text{Ti}_{0.33}\text{V}_{1.27}\text{Cr}_{1.4}\text{H}_{1.13}$. Finally, we have found that addition of $\text{Zr}_7\text{Ni}_{10}$ does not affect the hydrogen diffusion parameters.

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Study on the States of α -phase Palladium Hydride by *in situ* Solid-State ^1H NMR Measurement Under Controlled Hydrogen Gas Pressure

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Palladium (Pd) is well known as an effective catalyst for reactions related to hydrogen and a hydrogen absorbing metal. At low hydrogen gas pressure, hydrogen molecules dissociate into the atoms on Pd surface and the atoms permeate inside Pd lattice to form solid-solution phase (α phase; Pd+H). With increasing the pressure, the first-order phase transition from solid-solution (Pd+H) to hydride (β phase; Pd-H) takes place at plateau pressure. Due to the lack of the study on α phase, the states of hydrogen atoms dissolved in palladium lattice is still unclear. In this study, we have investigated the states of hydrogen dissolved in palladium lattice as α phase by *in situ* solid-state ^1H -NMR measurement under controlled hydrogen gas pressure.

In this study, Pd powder was used as bulk Pd sample for all measurements. From the hydrogen pressure–composition (PC) isotherm of Pd powder at 303 K, we confirmed that the plateau pressures, corresponding to the phase transition between α phase and β phase, are ca. 3 kPa and 1 kPa in absorption and desorption processes, respectively. From *in situ* powder X-ray diffraction under controlled hydrogen gas pressure, it was found that the Pd lattice was slightly expanded with the formation of α phase. Fig. 1 shows solid-state ^1H NMR spectra around plateau region. The absorption lines, originating from ^1H inside the Pd lattice, became sharp and shifted to lower magnetic field with increasing the pressure. These chemical shifts correspond to the phase transition from α phase to β phase. The detail of the NMR results will be discussed.

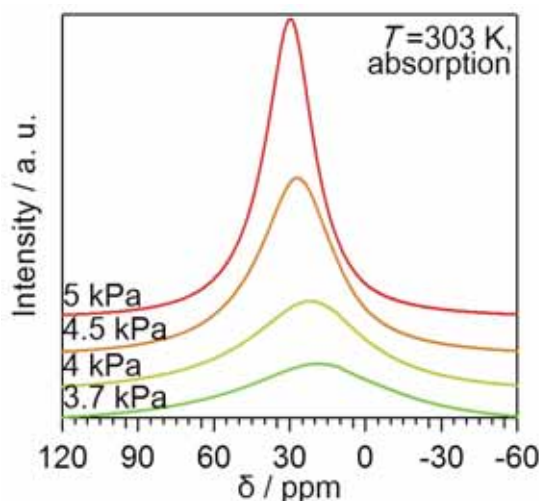


Fig.1 Solid-state ^1H NMR spectra under controlled hydrogen gas pressure

Analysis of hydrogen mobility in Nb-based alloy membrane in view of new description of hydrogen permeability based on hydrogen chemical potential

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Hydrogen permeable metal membranes are ones of the most important materials for hydrogen separation and purification technologies. For such metal membranes, the hydrogen diffusion is generally the rate limiting process of the total reaction of hydrogen permeation through them. Strictly speaking, the hydrogen diffusion is driven by the gradient of the hydrogen chemical potential, $d\mu/dx$, and the diffusion equation is expressed as follows,

$$J = -cB \frac{d\mu}{dx}, \quad (1)$$

where c is the hydrogen concentration and B is the mobility of the hydrogen atom. Assuming the following three conditions, (1) the hydrogen permeation reaction reaches to the steady state condition, (2) the equilibrium condition is established between gaseous hydrogen and dissolved hydrogen atom, (3) the mobility, B , is independent of the hydrogen concentration. Then, Eq (1) can be modified as follows [1],

$$J = \frac{RTB}{2L} \int_{c_2}^{c_1} c \frac{d \ln(P/P^0)}{dc} dc, \quad (2)$$

where R is gas constant, T is absolute temperature, L is the membrane thickness, c_1 and c_2 are the hydrogen concentration at the inlet and outlet sides of the membrane, P is hydrogen pressure and P^0 is the standard hydrogen pressure (101325Pa).

In this study, the mobility, B , for hydrogen diffusion during hydrogen permeation through Nb-based alloy membranes is analyzed in view of the new description of hydrogen permeability expressed by Eq (2). Figure 1 shows the Arrhenius plots of the mobility for hydrogen diffusion for pure niobium and Nb-based alloys. As shown in Fig. 1, there is liner relationship for each system. The activation energy for hydrogen diffusion is estimated from the slop of the each line shown in Fig.1. It is found that the addition of tungsten or molybdenum into niobium decreases the activation energy.

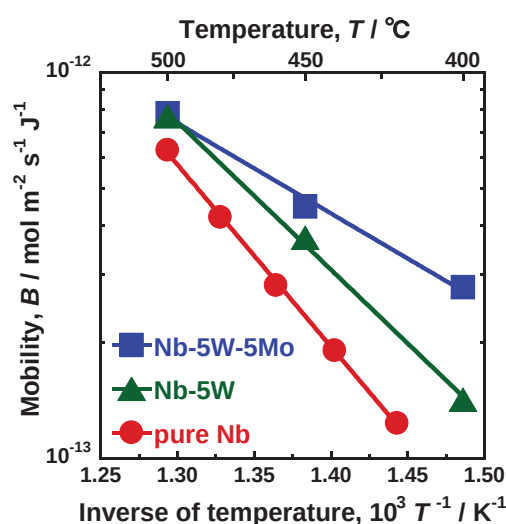


Fig. 1. Arrhenius plots of the mobility for hydrogen diffusion for pure niobium and Nb-based alloys.

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Diffusion of Hydrogen in Nano-confined Vanadium

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Diffusion of hydrogen is an important parameter for hydrogen purification and hydrogen storage in metal-hydrides. Hydrogen in nano-sized materials has attracted interest in recent years because of the fascinating changes in properties compared to bulk. When hydrogen is absorbed in a nano-sized vanadium thin film or Fe/V superlattice, the lattice is expanded along the direction perpendicular to the surface of the sample, thereby behaving differently from bulk vanadium. This is caused by the strain from the MgO substrate. In Fe/V superlattices, the strain state of the V is furthermore altered by the Fe layers. For instance, in a Fe/V superlattice built up from respectively 3 and 21 monolayers, hydrogen only exists in octahedral sites and not in tetrahedral sites. Control of the above characteristics create the possibility of changing the diffusion of hydrogen in nano-sized thin films or superlattices. Therefore, the chemical diffusion of hydrogen is measured in a 50 nm bcc vanadium film by an optical transmission method. The concentration dependence of hydrogen diffusion in the α and α' phases for a 50 nm vanadium thin film is being investigated. Furthermore, because of the epitaxial relation between V and the MgO substrate, hydrogen diffusion as a function of lattice direction may be measured, while an Fe/V superlattice enables an investigation of the effect of site-occupancy on diffusion.

We use magnetron sputtering to deposit the V films and Fe/V superlattices on MgO, with a Pd capping layer deposited on top. This protects the vanadium from oxidation and also catalyses the decomposition of molecular hydrogen into atomic hydrogen. Thereafter, Al₂O₃ is deposited on most of the Pd, leaving open a small window for hydrogen to enter the sample [1]. Then, the hydrogen will diffuse laterally in the vanadium film, a process that we detect through the change in optical transmission, as displayed in Figure 1.

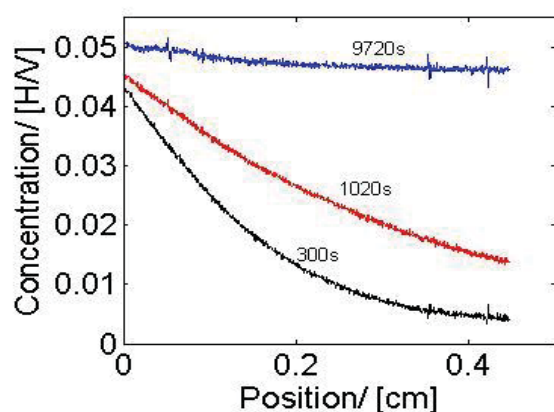


Figure 1. Hydrogen chemical diffusion profiles at several times in the [010] direction, recorded at 493K in a 50 nm V thin film as a function of position. The obtained diffusion coefficient is $D = 5(2) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [1].

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Hydrogen Atom Absorption in Pd(110) Surface

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The absorption of hydrogen in metal surfaces is a crucial process in hydrogen storage and permeation applications. Pd and Pd-based surfaces are popular materials for hydrogen technology related applications due to their capability to absorb large volumetric quantity of hydrogen [1]. In this present study, the absorption of H atom in Pd(110) was investigated by employing density functional theory based calculations. Being the least stable low-index surface of Pd, the (110) surface is known to reconstruct when dosed by large amount of H [2]. Although the presence of H in the subsurface of the reconstructed surface is observed experimentally [3], the absorption mechanism is not yet theoretically established.

In unreconstructed Pd(110), the absorption of H atom is accompanied by a large activation barrier suggesting the tendency of H-trapping in the surface and near-surface regions for low H concentration [4]. On the other hand, the absorption of initially adsorbed H atom in missing-row reconstructed Pd(110) is found to be non-activated and happens through the assistance of incoming H atom from vacuum [5]. It was also verified that neither the monoatomic absorption of H nor the assistance of initially adsorbed H atoms explains the experimentally observed subsurface population of H in Pd(110) for high H coverage. Aside from the non-activated absorption of H in the H-covered surface, the present results also revealed that the dissociation of H₂ is the rate-limiting process (Fig. 1) which completely reverses the behavior of H in a clean Pd(110) surface. The difference in the calculated activation barriers of H₂ approaching the ridge and trough sites of the missing-row surface is completely elucidated by investigating the electronic structure of the systems.

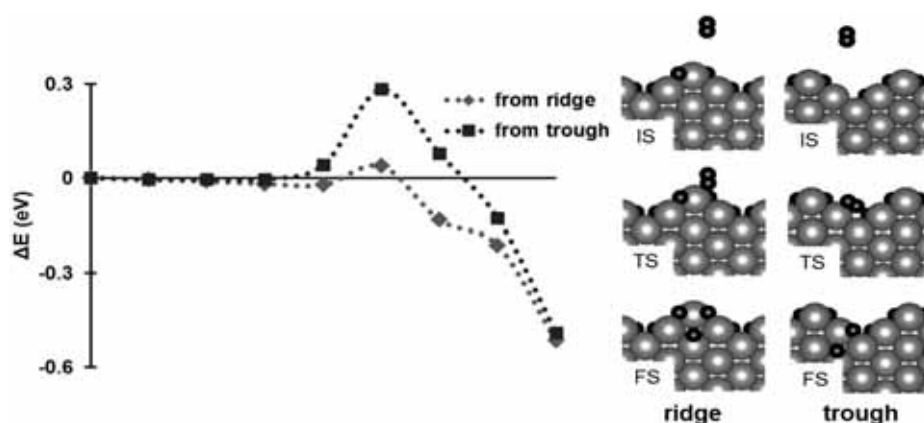


Figure 1. Reaction path of H₂ approaching the ridge and trough sites of Pd(110) (1×2) missing-row surface. (IS: initial state; TS: transition state; FS: final state)

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Theoretical and experimental synthesis of hydrogenated iron clusters over graphene

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Theoretical studies suggest that small gas-phase iron clusters are able to form chemical bonds with hydrogen [1]. However, the synthesis of iron hydride under ordinary conditions has been considered to be challenging as iron and hydrogen do not form chemical bonds. The synthesis of iron hydride is investigated from both theoretical and experimental approaches.

Density functional theory (DFT) calculation predicts that small gas-phase iron clusters are able to absorb large amounts of hydrogen shown in Figure 1 [1]. Surface screening was performed using DFT in order to find the optimal substrate for supporting hydrogenated iron clusters. Calculations revealed that a single layer graphene/Cu substrate is able to stabilize the hydrogenated iron clusters.

A single layer graphene is deposited on Cu substrate using the chemical vapor deposition. Iron clusters are deposited on graphene/Cu substrate using vacuum deposition. Scanning transmission electron microscopy shows that 1-3nm of iron clusters are observed on graphene/Cu substrates [2]. Hydrogenation was performed at 1atm of hydrogen pressure and under liquid nitrogen for 4 hours. Hydrogenated iron clusters on graphene/Cu was heated up to 400°C. Mass spectrometry indicated that hydrogen was released at 190°C [2]. Thus, the existence of iron hydride was experimentally confirmed.

Hydrogenated iron clusters were successfully synthesized experimentally according to theoretical predictions. The results show that iron hydride clusters are stabilized on the graphene substrate where the iron hydride clusters are stable under ordinary conditions.



Figure 1, Theoretically predicted structural model of Fe₁H₁₀ [1].

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Hydrogen production from hydrides : microwaves and hydrolysis methods

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Magnesium hydride could be considered as a good candidate for the hydrolysis reaction because it can be produced at a relatively low cost. However, this reaction is incomplete and very slow because of the formation of a magnesium hydroxide layer on the surface of MgH_2 particles. In order to overcome this problem, various treatments such as ball milling with or w/o additives, addition of acids, slated water, ultrasounds and increase of temperature, have been tried. Different characterization methods such as XRD, BET, particle size, SEM etc... have been used to explain the effects of the various treatments on the improvement of the kinetics and the yield of the MgH_2 hydrolysis reaction [1]. As an example, a fuel cell has been powered by this regulated hydrolysis reaction and the performance will be presented.

Also, to get a fast desorption of hydrogen, microwaves treatments [2] were also applied. Release of Hydrogen from binary MgH_2 - x wt % C mixtures (x = 0, 2, 5 and 10 wt % and C as carbon fibers (CFs), graphite (G) or diamond (D)) were studied. The relationship between the morphology of the powders, the particle size distribution, the MW power and time will be discussed. Carbon additives transfer the heat, generated from absorbed microwave irradiation, to the MgH_2 matrix which induces the hydrogen release. As an example, 90 % of conversion into Mg phases was obtained after only 10 sec for 5 h ball milled MgH_2 +10% CFs mixtures under 1500 W.

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Atom Probe Tomography (APT) Analysis of Deuterium-loaded V/Cr Thin Films

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It has been regognized recently that Atom Probe Tomography (APT) analysis is a promising technique to investigate the 3-dimensional distribution of hydrogen species in metals on the sub-nanometre scale [1]. In first investigations, the authors analyzed the impact of hetero-interfaces and defects on the deuterium (D) distribution in metallic thin films using conventional tomographic atom probe. Conventional APT offers a narrow field of view (FOV) of around 15 nm x 15 nm. Thus the volume of analysis is small.

In this study, we have employed a large FOV atom probe, called Local Electrode Atom Probe (LEAP) 4000X to investigate D distribution in V/Cr sandwiched films. The larger analysis volume provides information on a more global scale without losing spatial resolution. Sample films were prepared by Ar⁺ ion beam deposition by alternately depositing V and Cr on a Si microtip substrate. The films were capped by a Pd overlayer. Subsequently, the sample was deuterided at 50 Pa D₂. Results carried out at 20 K with laser pulsing revealed that D atoms were successfully detected in V layers, showing $c_D = 0.2$ D/Metal (Fig. 1). Additionally, a small modulation of the D concentration was found in different V layers. We discuss the influence of the laser pulse energy on this concentration modulation.

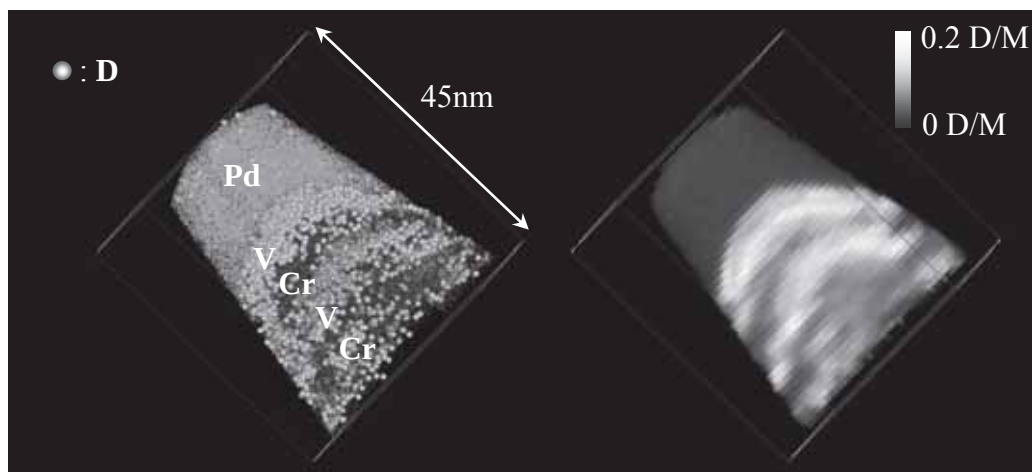


Figure 1. Left: Deuterium distribution in Pd/V/Cr films (volume: 37 nm x 37 nm x 45 nm). Right: Iso-concentration map of 0.2 D/Metal, showing D absorbed in V layers.

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Buckling of Mg films due to hydrogenation stress and its effect on sorption behaviour

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Thin film methods used to fabricate Mg based materials often show different behaviour to bulk and have led to improved fundamental understanding of hydrogen sorption behaviour at the nano scale. The effects of stress on hydrogen sorption behaviour, which is fundamentally related to the enthalpy dependence of volume expansion of the hydride phase, has been shown to increase absorption plateau pressures of MgH_2 [1]. The thermodynamic effect of substrate clamping has been demonstrated for PdH_x [2] and Mg_2NiH_4 [3] films, affecting the plateau pressure. In addition, the effects of various film preparation conditions have been shown to affect desorption temperature [4]. Stress effects allow for 'thermodynamic tuning' which could be useful for hydrogen storage as well as hydrogen sensors.

Using magnetron sputtering (*Teer Coatings, CFUBMSIP*) in a variety of experimental conditions, 800 nm Mg films were fabricated with a 40 nm Pd cap layer. XRD (*Bruker D8*) shows the preferential growth of Mg along the basal plane, but with a variation in diffracted intensity, probably related to grain size and misorientation. Samples were hydrided at 100 °C, 1 bar H_2 for 48 h. The resulting XRD patterns reveal different amounts of MgH_2 formation, suggesting that absorption behaviour is dependent on film microstructure produced using different sputter conditions. The film with the highest phase transformation exhibits buckling as a stress release mechanism, while those that do not hydride significantly appear to be well adhered to the substrate. The hydrogen content has previously been related to critical buckling stresses in NbH_x films [5].

Temperature programmed desorption measurements of the films reveals differences in peak desorption temperature. The buckled film exhibits the highest desorption temperature, probably due to elastic energy release from buckled regions. The films that remain clamped to the substrate desorb at lower temperatures, suggesting a thermodynamic shift due to stress build-up. Of the films that remained clamped, the sample that had hydrided to a greater extent desorbed at the lowest temperature; probably due to a higher stress build-up. Similar effects due to compressive stresses have been reported in Pd/Mg/Pd layers [6].

The results show that sputter conditions affect film microstructure, and that this affects the films ability to absorb hydrogen (under the hydrogenation conditions used). It would seem there is a maximum hydrogen uptake achievable before buckling becomes energetically favourable, and that if buckling can be avoided there is a thermodynamic effect due to hydrogenation stress. Work is in progress to quantify stress build-up within the films, as well as quantifying the hydrogen capacity.

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Effect of Particle Size on Dehydrogenation of MgH_2

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Mg is attractive as a hydrogen storage material because of its high gravimetric storage capacity, abundant resource and inexpensive material cost. Sluggish dehydrogenation rate as well as low equilibrium H_2 pressure at ambient temperatures, however, is the issue to be solved for practical application of MgH_2 . In the dehydrogenation of MgH_2 , incubation period, which is not observed in hydrogenation, appears. This implies that its dehydrogenation can be controlled by the mechanism which is different from that in hydrogenation. It can be expected that the clarification of the mechanism causing incubation period observed only in dehydrogenation can contribute to deeper understanding of Mg- H_2 system. In the present study, the effect of particle size on incubation period followed by dehydrogenation of MgH_2 was examined in order to obtain information which can contribute to the clarification of the mechanism.

Three MgH_2 samples with different particle sizes were prepared by using mechanical grinding. They are as purchased (Johnson Matthey, 98 % in purity), milled for 3.6 ks and milled for 36 ks, respectively. In order to minimize the influences of unreacted Mg (major impurity of as purchased MgH_2) and metastable phase as well as strain introduced by mechanical grinding on dehydrogenation properties, dehydrogenation followed by rehydrogenation was conducted once or more in advance for all the samples. Dehydrogenation properties were measured in the range from 653 to 693 K using conventional Sieverts' type instrument, where initial pressure was controlled so that initial driving force $\Delta_r G$ could be -2.3 kJ mol^{-1} , according to thermodynamic data [1].

There is the tendency that incubation time decreases with an increase in temperature, independent of samples. The incubation time and particle size decreases and increases in order of as purchased and the samples milled for 3.6 ks and 36 ks, respectively, which can indicate that incubation period decreases with an increase in specific surface area. The dehydrogenation behaviors at 693 K for the three samples were analyzed by using Kolmogorov-Johnson-Mehl-Avrami (KJMA) equation. The Avrami exponent n is approximately constant ($n \approx 2$) in the fairly wide range less than 0.5~0.7 of the fraction dehydrogenated, f , independent of sample. The result implies that the dimension for the growth direction of Mg grains is limited to 1~2 from very early stage of dehydrogenation due to the contact and impingement between grains or the preferred orientation of Mg grain growth.

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Minimally strained hydride nucleation on a strained Gd/W(110) surface

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Abstract

Gd islands grow on an annealed Gd(0001)/W(110) layer in the Kranski Krastanov mode. When hydrogen is adsorbed on strained Gd islands, we find that the GdH₂ nuclei are formed specifically close to the edges of the islands, 80% of them being located between $r/R=0.6$ and 0.9 , where r is the distance of the nucleus from the center of the island and R is its radius. This is in contrast to the usual case where the reaction is on the edge. We show by qualitative arguments and quantitative calculations that the density of the elastic energy is minimal in hydrides that are located near the island edge. Thus, the self elastic energy *in* the hydride nuclei is the factor determining the preferred location of the nucleation and not the global energy of the system. This is apparently not a kinetic effect but reflects the dominant factors for small nuclei. Additional conclusion of the analysis are that the epitaxial strain in Gd on W is tensile, larger than 0.04 and that the stresses are largely relaxed in islands with shape ratio $h/R > 0.1$. The uncertainty about the rate of relaxation prevents quantitative predictions of the preferred location of the hydride nuclei.

Nothing in our model depends on the specific hydride nucleation or any specific chemical reaction, so it is applicable to any nucleation product on a strained surface, the volume differs from that of the matrix in which it nucleates. These considerations apply to every gas-solid interaction, starting by nucleation on a strained surface.

In Situ XPS Investigation of a Platinum Catalyst Supported on Ceria Nanocubes under a Hydrogen Atmosphere

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A key factor in the catalytic activity of ceria-based catalysts is the redox property of ceria. The oxidation state of well-defined ceria nanocubes under gas environments was analyzed in situ by means of near-ambient pressure X-ray photoelectron spectroscopy using a synchrotron X-ray source. Here, the aim was to quantitatively determine the degree of cerium reduction in a nano-structured ceria-supported platinum catalyst as a function of gas environment. To obtain a non-destructive depth profile at near-ambient pressure, in situ surface analysis was performed by varying kinetic energies of photoelectrons and thus the probing depth. In the ceria nanocubes doped with platinum, there is facile formation of oxygen vacancies at the topmost layers of ceria, by assuming the exponential depth distribution, under the atmosphere of hydrogen at 1 mbar and 403 K. For the pristine ceria nanocubes, only a minor difference in the cerium oxidation state under the atmospheres of hydrogen respectively oxygen was observed as a function of probing depth. In the absence of platinum, hydrogen cannot dissociate and lead to reduction of ceria.

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Computational Study of Spectroscopic Properties of Different Borohydride Species

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Dehydrogenation of borohydrides is complex and pass through multistep processes¹. There are several possible intermediates formed during decomposition processes². Therefore the identification of intermediates is important. We studied B_xH_y , $H_xH_y^-$, $B_xH_y^{2-}$ for $x,y = 1-12$ species and predict the vibrational and NMR spectra using B3LYP/6-311++G** level. The combination of vibrational and NMR spectra can help to identify the species observed, as vibrational or NMR spectra alone could lead to different candidates. The calculated spectra were compared with experimental data.

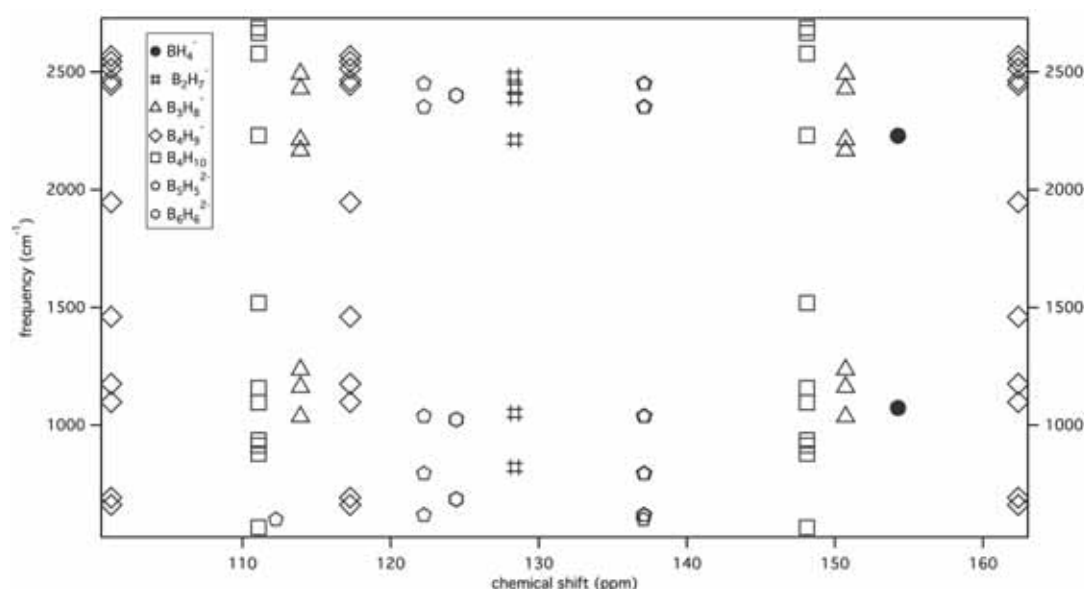


Figure 1. The combination of IR frequencies and chemical shift NMR for different borohydrides from B1-B6.

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Composition dependence of H storage capacity for Rh-Ag alloy

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Hydrogen (H) storage alloys have attracted much attention in various fields of chemistry and physics. Kusada *et al.* found that the $\text{Ag}_x\text{Rh}_{1-x}$ solid solution alloys can store H as well as the Pd metal, which is well known as an H storage material. [1]. They also observed that the H storage capacity is depending on the alloy composition and the capacity was in the order $x = 0.5 > \text{Rh-rich} > \text{Ag-rich}$ cases. In this study, we theoretically investigated the H storage of $\text{Ag}_x\text{Rh}_{1-x}$ alloys by using density functional theory (DFT) and discuss the composition dependence.

We mainly analyzed H storage energy and density of states (DOS) of the $\text{Ag}_x\text{Rh}_{1-x}$ alloy models that consist of eight Ag or Rh atoms in rhombohedral cell. A plane wave basis set and projector augmented wave (PAW) method were employed. Perdew-Burke-Ernzerhof (PBE) with generalized gradient approximation (GGA) is used for exchange-correlation functional. The energy cut-off is 400 eV and $13 \times 13 \times 13$ k-points were used. All calculations are performed by VASP.

In Fig. 1, total and partial DOSs for Rh and Ag in $\text{Ag}_{0.5}\text{Rh}_{0.5}$ alloy are shown in solid, broken and dotted lines, respectively. We found that the contribution of PDOS for Rh is larger than Ag around Fermi level. H storage energies for various sites in $\text{Ag}_{0.5}\text{Rh}_{0.5}$ alloy are shown in Table 1. Ag_nRh_m ($n + m = 6$) represents octahedral H storage sites. Negative value means attractive interaction between H and Ag_nRh_m site. We observed that $\text{Ag}_{0.5}\text{Rh}_{0.5}$ alloy has H storage capability as well as experimental result. In addition, we found that Rh-rich site (Ag_2Rh_4) is more favorable.

Acknowledgement

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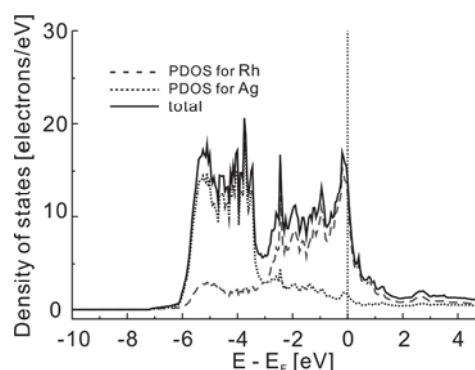


Figure 1. Total and partial DOSs for $\text{Ag}_{0.5}\text{Rh}_{0.5}$ alloy.

Table 1. H storage energy for various sites in $\text{Ag}_{0.5}\text{Rh}_{0.5}$ alloy.

Sites	Ag_2Rh_4	Ag_3Rh_3	Ag_4Rh_2
ΔE_{H} [eV]	-0.381	-0.096	0.080

Parametrization of the dielectric function of Pd thin films as function of film thickness, temperature and hydrogen absorption

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Palladium hydride is one of the most studied metal-hydrogen systems and it has been used in many applications. Recently Pd nanostructures have been proposed as part of a nanoantenna-enhanced gas sensor [1] which makes use of the dielectric function changes upon hydrogen absorption. In this work we present the parametrization of the Pd's dielectric function of thin films of thickness between 10 to 30 nm for different hydrogen concentrations and temperatures. The films were prepared by e-beam evaporation at 7×10^{-7} mbar base pressure and their electrical resistance and optical transmission (for wavelengths between 240 and 1050 nm) were measured as hydrogen pressure increased up to 920 mbar and for three different temperatures between 22 and 190 °C. The Pd films' dielectric function was determined by inverting the direct transmission measurements using a spectral projected gradient method. Hydrogen concentration was determined from the same optical measurements and taking into account the films' granular nature. The parametrization of our results has been made using the Brendel-Bornmann model [2,3] which incorporates the Drude contribution in terms of the plasma frequency, damping factor, and static dielectric constant, as well as the Lorentz terms involving resonance frequencies, lifetimes, oscillator strengths, and widths of the absorption resonances.

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Parametrization of the dielectric function of Pd thin films as function of film thickness, temperature and hydrogen absorption

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Formation of Mg_2Ni with Enhanced Kinetics: Using MgH_2 Instead of Mg as a Starting Material

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Magnesium (Mg) is one of most promising lightweight materials for solid-state reversible hydrogen storage. However, with a high gravimetric hydrogen density of 7.6 wt.% (MgH_2), application of pure Mg as a hydrogen storage material is plagued by the kinetic and thermodynamic barriers for sorption. An effective approach for altering properties of pure Mg is to form Mg-based compounds via alloying Mg with metal elements [1]. However, because of problems with a low melting point (650 °C) and the severe vaporization of Mg, a high-quality Mg-based compound is rather difficult to obtain by the conventional metal-melt method. For instance, when induction- or arc-melting is employed to prepare Mg_2Ni , the product obtained is usually a mixture of MgNi_2 , Mg and Mg_2Ni phases rather than a single Mg_2Ni phase. To improve the purity of the resulting material, hydriding combustion synthesis was developed. Shao et al. [2] obtained pure Mg_2Ni by first hydriding Mg and Ni nanoparticles under a 3–4 MPa hydrogen atmosphere to form Mg_2NiH_4 and then dehydriding the formed Mg_2NiH_4 where hydrogen is believed to play an important role in the process.

Recently, We have found that at a temperature over the decomposition point (375 °C) of MgH_2 , the formation of Mg_2Ni is greatly enhanced from the $2\text{MgH}_2+\text{Ni}$ system, as compared to the $2\text{Mg}+\text{Ni}$ system. In support of this finding, in-situ observation of X-ray absorption fine structure of the two systems indicates that Mg–Ni bonds form faster in the MgH_2+Ni system than in the $\text{Mg}+\text{Ni}$ system (see Figure 1). Furthermore, theoretical modeling also shows that Mg atoms are readily released from MgH_2 using much less energy and thus are more available to react with Ni once the dehydrogenation of MgH_2 occurs, as compared to normal Mg. One important thing behind the present work is that the H-induced effect may be positively applied to the synthesis of other Mg-based compounds that are difficult to be prepared by the methods of induction- or arc-melting.

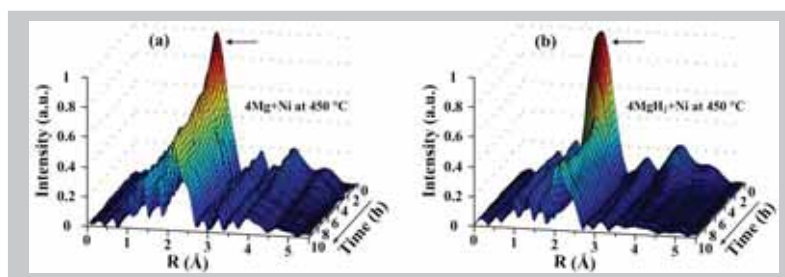


Figure 1. Time-resolved radial distribution functions in normalized Ni k^2 -weighted EXAFS Fourier transforms spectra for samples of (a) $4\text{Mg}+\text{Ni}$ and (b) $4\text{MgH}_2+\text{Ni}$ during the sintering process at 450 °C for 10 h.

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Multi-Slice Simulations for In-situ TEM Studies of Nanostructured Magnesium Hydride at Elevated Hydrogen Pressures of 1 bar

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Nanostructuring of many hydrides has been shown to reveal improved thermodynamic and kinetic properties, which are needed for both mobile or stationary applications of solid-state hydrogen storage materials. During structural characterization utilizing conventional TEM, however, hydrides such as MgH_2 degrade fast upon the irradiation with the imaging electron beam due to radiolysis in vacuum and as a consequence, the hydride phase cannot be studied at highest resolution. This problem can be overcome using a novel nanoreactor recently developed by H. Zandbergen (TU Delft) that allows for in-situ TEM studies at elevated hydrogen pressures (up to 4.5 bar) and temperatures (up to 500°C) [1]. A point resolution of $1.8 \text{ \AA}$ has already been demonstrated experimentally for Cu nanocrystals [2].

We have studied the feasibility of HRTEM investigations of light weight metals such as Mg and its hydride phase with the nanoreactor by means of multi-slice HRTEM contrast simulations. Such a setup allows to fundamentally study the dehydrogenation and hydrogenation reactions at the nanoscale under realistic working conditions. We analyze the dependence of both the spatial resolution and image contrast on parameters such as the defocus, metal/hydride thickness, hydrogen pressure and nanoreactor geometry to explore the possibilities and limitations of in-situ experiments with this reactor. Such simulations may be highly valuable to pre-evaluate future experiments.

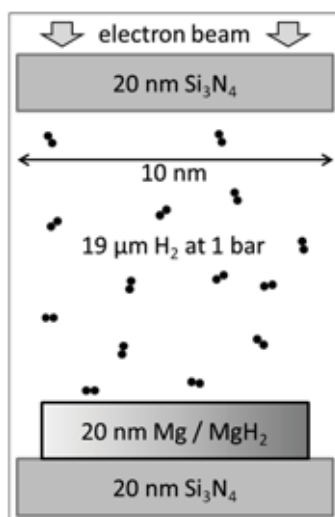


Figure 1. Schematic illustration of the simulated supercell representing the nanoreactor.

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The Effect of Uncertainties and Calibrations on Hydrogen Uptake Measurements

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Both the Sieverts and gravimetric techniques are common methods used to measure gas uptake in and on different materials. In particular, accurate hydrogen uptake measurements are an essential part of the characterisation of potential hydrogen storage materials.

Issues with regard to sources of error in both these techniques have been well covered in the literature [1, 2], however, recent round-robin exercises for hydrogen uptake both on carbon materials and in Mg have demonstrated the large variation in results from different laboratories for the same materials [3, 4].

More recently a full uncertainty analysis has been made for the Sieverts method [5] and the gravimetric technique [6]. These calculations enable the specification of error bars on isotherm plots (or PCT diagrams) of hydrogen uptake vs pressure and consequently the statement of uncertainty in the quoted result which is typically the maximum uptake at the maximum pressure achieved.

Another area of concern in the determination of accurate uptake measurements is the calibration of volumes as well as measurement instruments used in the experiments. This paper reviews recent developments in both uncertainty analysis and calibration techniques to summarise the best methods for determining both accurate and precise hydrogen uptake measurement values.

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Monitoring vacancies, nanopores and metal-to-insulator transitions in Mg-Ti films and Mg hydride nanoparticle layers using positrons

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Mg-Ti thin films are very interesting materials for the development of hydrogen sensors and hydrogen storage media. At Ti-concentrations beyond ~15 at%, a cubic (fluorite) $\text{Mg}_{1-y}\text{Ti}_y\text{H}_x$ metal hydride phase is formed which shows substantially faster hydrogen sorption kinetics than the common tetragonal (rutile) MgH_2 phase [1, 2]. Further, layers with Mg and MgH_x nanoparticles were generated by spark discharge generation [3, 4], showing a favorable low-temperature hydrogen sorption. We employed various sophisticated positron beam techniques to monitor the presence of vacancies and vacancy clusters as well as the changes in electronic structure upon hydrogenation.

In particular, positron lifetime studies with the pulsed low-energy positron system PLEPS revealed the presence of divacancies in the as-deposited and hydrogenated coherent Mg-Ti metal films [5], which are locally chemically segregated into Mg and Ti nanodomains [2, 5]. The divacancies may induce the fast hydrogen sorption kinetics in the cubic fluorite MgH_2 phase. Further, 3-5 μm thick films prepared by impacting either Mg or MgH_x nanoparticles with a primary particle size of ~10 nm on Si substrates were investigated. A clear positronium signal characteristic for the presence of nanopores was present in the positron lifetime spectra, which was used to obtain depth-resolved insight into the porous character of the films.

Finally, we obtained experimental evidence of the larger affinity of positrons for Mg compared to Ti in positron annihilation Doppler broadening studies on Pd/Ti/Mg/Ti multilayers. This difference in positron affinity enabled us to probe the effects of hydrogenation on *exclusively* the Mg domains present in the $\text{Mg}_{1-y}\text{Ti}_y$ films [2, 5] in 2D-ACAR studies using the intense positron beam POSH. The observed strong changes in electronic structure associated with the metal-to-insulator transition for both rutile and cubic phase MgH_2 are discussed. The extracted electron momentum densities and positron lifetimes are compared with ab-initio calculations.

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Synthesis of Hydrides by Interaction of Intermetallics with Ammonia

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In present study we developed a process of synthesis of the hydrides of intermetallic compounds with various stoichiometries, including AB, AB₂, AB₅, A₂B₁₇, by interaction of intermetallics with ammonia at temperatures 100–200°C and at pressures 0.6–0.8 MPa of NH₃, which was performed in presence of NH₄Cl as a promoter of the synthesis process.

The mechanism of NH₄Cl-promoted interaction of intermetallics with ammonia appears to be affected by the temperature of the process, particle size, thermal cycling history and time of the processing. Effect of NH₄Cl is related to its reversible decomposition-recombination $\text{NH}_4\text{Cl} \leftrightarrow \text{NH}_3 + \text{HCl}$, and consecutive interaction of the formed hydrochloric acid with the surface oxides. This facilitates interaction of the bulk intermetallics with ammonia and, also, with hydrogen formed during the ammonia splitting.

Synthesis process requires use of elevated temperatures between 150 and 250 °C and yielded ternary hydrides with compositions TiAlH_{1.5} (at 150°C [1]), Zr₂NiH_{4.7} (at 250°C [2]), Zr₃Al₂H_{1.1} (at 250°C [3]), and Ti₃AlH_{3.0} (150°C [1]). The synthesis products were comprehensively characterised using various techniques.

In some cases interaction resulted in the insertion of relatively small amounts of nitrogen into the hydride phases thus yielding formation of the mixed hydridonitrides. As example, interaction of TiAl with ammonia at 200°C yielded TiAlH_{1.9}N_{0.1}.

At interaction temperatures around 200°C, ferromagnetic alloys of the rare earth metals, which are utilised in the production of permanent magnets, including Sm–Co, Sm–Fe and Rare Earth–Fe–B, accommodate significant amounts of interstitial nitrogen. This leads to the marked improvement of the magnetic properties (increase of Curie temperature and coercivity).

Formation of the hydrides and hydridonitrides results in a significant decrepitation of the bulk alloys and a formation of the fine alloy powders. Thus, interaction with ammonia, similar to the absorption of pure hydrogen gas, may be utilised for the chemical decrepitation of the hydride-forming metals and multicomponent alloys.

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Delocalized Adsorption States of Hydrogen Isotopes on fcc-Fe(111) Surfaces

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Hydrogen is one of the most important elements in the damage process of materials. It has been reported that hydrogen can stabilize vacancies[1], which causes reduction of its ductility. In addition, hydrogen-assisted cracking[2] is also well-known problem in structural materials. From these points, the atomic- and electronic-scale understanding of hydrogen embrittlement process is necessary to develop new long-life materials. In order to understand hydrogen behaviors in commonly-used iron-based materials, we investigated the adsorption properties of hydrogen isotopes on fcc-Fe(111) surfaces with the aid of first principles calculations based on spin-polarized density functional theory. We also adopted the quantum mechanics calculations of hydrogen nuclei, because the importance of delocalization and zero-point energy of hydrogen nuclei has been reported in various papers. [3,4]

At first, we investigated the potential energy surfaces of hydrogen on fcc-Fe(111) surfaces. We can find that the most stable adsorption site is the *fcc-hollow* site from Fig. 1. We also investigated the hydrogen adsorption states on fcc-Fe(111) surfaces by calculating schrödinger equation for hydrogen nuclei. Calculated wave function of the ground state of H atom on fcc-Fe(111) surfaces is shown in Fig. 2. We found the delocalization of H atom in the ground state from Fig. 2. In addition, we clarified the non-negligible isotope effects in delocalization and zero-point energy of hydrogen isotopes. [5]

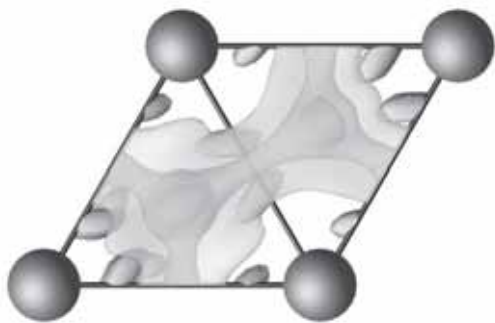


Fig. 1 Potential energy surfaces of hydrogen on fcc-Fe(111) surfaces. Grey balls indicate Fe atoms.



Fig. 2 Wave function of hydrogen on fcc-Fe(111) surfaces. Black balls indicate Fe atoms.

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^3He NMR measurements on palladium samples aged under tritiumM. Segard^{1*}, T. Charpentier², M. Moskura², S. Challet¹, A. Fabre¹¹ CEA / DAM, centre de Valduc, F-21120 Is-sur-Tille, France² CEA / DSM, centre de Saclay, F-91191 Gif-sur-Yvette, France

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Palladium is often used as catalyst in hydrogenated-gas-treatment technologies. In the case of tritium (hydrogen radioactive isotope) gas mixtures treatments, some problematic issues are encountered. Indeed, tritium decay into helium-3 is responsible for aging phenomena, which are largely due to the nucleation and the growth of ^3He nano-bubbles within the metal.

NMR experiments are used to measure ^3He pressure inside bubbles as a function of aging time since ^3He spin-lattice relaxation time is connected to its physical state in bubbles [1]. By changing the sample temperature, typically from RT to 150 K, measurements of relaxation times show an abrupt change when a fluid $\leftrightarrow$ solid transition of ^3He occurs. Using the state transition temperature and an appropriate He EOS, the mean bubble pressure calculation is compared with modeling predictions.

In this work, ^3He pressures estimated within bubbles range from 5 to 15 GPa on aged palladium samples with He/Pd ratio varying from 0.01 to 0.19.

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Stress Release during Cyclic Loading of Thin Palladium Films

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Palladium-hydrogen (Pd-H) system is used as a representative model system for hydrogen in metals. Palladium can absorb relatively high amount of hydrogen and can be loaded with hydrogen easily. Physical properties of Pd-H become radically different from those of a bulk material when one dimension is restrained, e.g. for a thin film fixed on substrate.

In this work we studied hydrogen absorption in thin Pd films with the thickness of 20 nm deposited on single crystalline Al_2O_3 substrate. Nanocrystalline films deposited at room temperature were compared with epitaxial films deposited at 800 °C.

Nanocrystalline and epitaxial Pd films were gradually hydrogenated from hydrogen gas atmosphere at the pressures from 10^{-2} mbar up to 900 mbar. Structural development of hydrogen loaded Pd films was examined by *in-situ* X-ray diffraction measurements using synchrotron radiation. Hydrogen loading cycles were followed by unloading and the whole loading-unloading sequence was then repeated.

Both nanocrystalline and epitaxial film exhibit compressive in-plane stress in the as-grown state caused by lattice mismatch between the films and the substrate. In the nanocrystalline film the compressive stress was relaxed after the first loading-unloading cycle. On the other hand, in the epitaxial film the in-plane stress remains after the loading-unloading sequence. The X-Ray diffraction pattern of the epitaxial film exhibits typical thickness fringes interference pattern visible in Fig 1. The thickness fringes side peaks around the (111) Bragg reflection were observed also after the completion of phase transition to α' -phase which suggests coherent phase transition from α - to α' -phase.

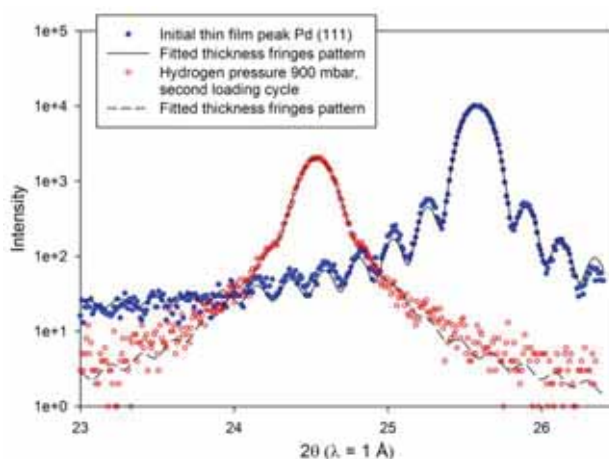


Figure 1. Synchrotron X-ray diffraction spectrum of (111) Bragg-peaks for the α - to the α' -phase

H/D exchange in micron powder Pd H/D measured using neutron diffraction

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Palladium is used within a modern experimental fusion reactor as separation medium for the purification of tritium. To aid the design and efficiency of separation devices hydrogen (protium) and deuterium can be used as analogues of the deuterium and tritium experienced in actual fusion reactors. Micron scale palladium powder is used to absorb the hydrogen (deuterium) as the surface is easily de-oxidized and the beta phase is relatively easily formed below 300K. Neutron diffraction is the only method available to identify the location of hydrogen (and its isotopes) in the lattice and also, due to the differing scattering amplitudes of the isotopes, to make a distinction between the different isotopic species. The observed isotopic separation factor – between the gas and solid phases – which arises from the difference in the quantum states of H and D in these phases – can be derived from the isotopic composition of the gas and the observed diffraction peak intensities. Using the high resolution, high intensity, neutron diffractometer, D20, at the ILL and the HIDEN HTP1 gas handling system, we can flow one isotope through the sample can and then change to the other isotope without changing the gas pressure. Thus, we have followed the exchange of one isotope (i.e. hydrogen) for another (i.e. deuterium) and have deduced the progress of the reaction via neutron diffraction. This analysis depends on the fact that, for the sodium chloride type crystal structure, the scattering amplitudes for Pd and for the (concentration-weighted) H(D) are added for reflections with all h,k,l even and subtracted for reflections with all h,k,l odd. The resulting diffraction intensities are very sensitive to the isotope exchange because the scattering amplitude for hydrogen is negative and that for deuterium is positive. In the experiment, we obtain the time dependence of the isotopic exchange in the Pd lattice and the isotope dependence of the lattice parameter with great accuracy. The technique has also been used to directly determine the isotherm for D absorption into the micron scale Pd powder by deriving the D concentration as a function of D₂ pressure. This isotherm, which has also been measured directly gravimetrically, reflects an isotherm approximately midway between the measured bulk material and that of nanoscale Pd/D.

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Kinetics of Hydrogen Isotope Exchange over Solid Storage Media

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The phenomenon of exchange, which occurs when one isotope of hydrogen (e.g. protium) is passed through a storage bed containing a different isotope (e.g. deuterium) and replaces the stored gas, has not been characterised in detail. A number of investigators have examined the exchange reaction, but poor understanding of the reaction mechanisms, in particular the rate-limiting step, still exists. The topic is of fundamental interest to gas separation and purification, fusion engineering and, in particular, isotope separation.

A unique gas flow apparatus has been commissioned and installed in the Department of Chemical Engineering, University of Bath, to investigate the effects of pressure, temperature and flowrate on the exchange process over packed-powder beds of β -phase palladium deuteride (hydride). A bespoke quadrupole mass spectrometer is used to analyse the isotopic gas composition leaving the bed in real-time, allowing direct monitoring of HD. Results from both exchange directions (D $\rightarrow$ H and H $\rightarrow$ D) over a wide temperature range involving varying input pressures are presented. HD production has been significantly less than observed by other investigators [1], indicating potential different reaction pathways than previously postulated.

The authors have developed models of the process in COMSOL Multiphysics and MATLAB in order to elucidate kinetics of the individual reaction steps (adsorption, dissociation, surface-bulk transfer, bulk diffusion, bulk-surface transfer, recombination, and desorption) involved in the exchange, and determine the rate-limiting step. Understanding the role of the surface is considered vital by the authors and this has been duly considered in the kinetic model. Kinetic rate constants for the individual steps have been estimated through fitting of experimental data obtained over a temperature range 208 – 373 K with input pressures from 1.5 – 20 bar(a). The project is supported by an EPSRC CASE Award studentship with Simon Owens as the PhD student supervised by Dr Timothy Mays.

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Low Temperature Raman Measurements of AlH_3 and AlD_3 Systems

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Pressure and temperature effect on Raman spectra of solids provide us with an important information concerning lattice dynamics of the materials under investigations. The intensity, shift and a half-width of the corresponding Raman modes with pressure and temperature could be accounted for the anharmonicity of the system.

In this contribution measurements of Raman scattering of aluminum hydride and deuteride in the temperature range from liquid helium to 300 K will be presented. Significant deviation from the linearity has been observed for the both main Raman modes of hydride and deuteride with temperature. Simultaneously increase in half-width of peaks has been noticed. The obtained results will be analyzed in terms of corresponding isobar and isothermal mode-Grüneisen parameters in relation to the anharmonicity of both systems. It is worthy to note that the strong anharmonicity is blamed for the suppression of superconductivity in AlH_3 under pressure.

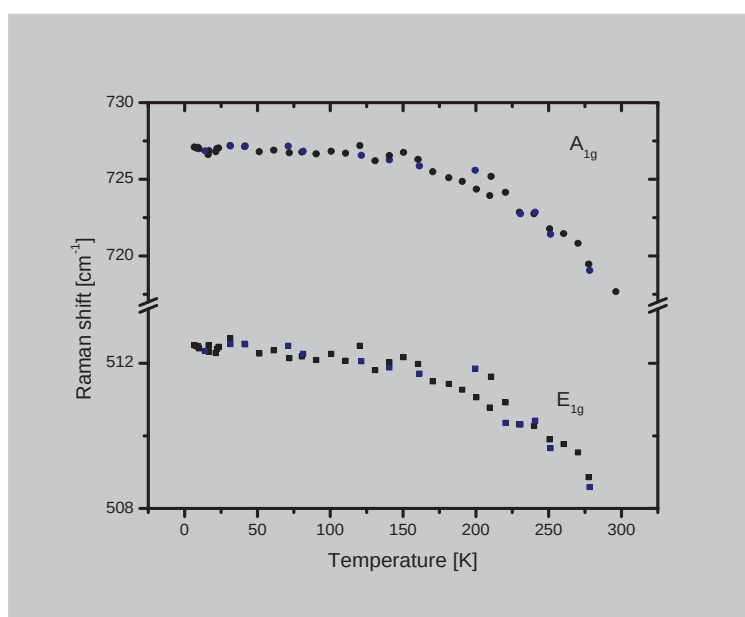


Figure 1. Temperature dependence of the Raman shift in aluminum hydride.

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Monte Carlo Simulations of Hydrogen Isotopes in Palladium

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A series of Monte-Carlo investigations on the Palladium Hydride system are presented. It is demonstrated that a simple long-range concentration dependant attractive force reproduces the form of the pressure composition isotherms well. Short range pairwise repulsive forces reproduce much of the hydrogen ordering seen within the lattice. A suitable scaling between the long and short range forces has been found which appears to reproduce both the isotherms and short-range ordering to a reasonable degree.

Programs have been written to generate virtual diffractograms in 1 d and 2d in order to observe ordering in the simulations and inform those performing experimental diffraction studies

Studies have been performed of the isotope dependence of adsorption rate and separation factor by accounting for the differing zero point energies of the three hydrogen isotopes.

Analysis of Hydrogen Isotope Mixed Gas at High Pressure Using Raman Spectroscopy

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Metal-hydrogen systems at high pressure have a certain interest for some research. Sometimes using metal hydrides obtained at high pressures may be useful [1]. Using of high pressure metal-hydride sources greatly simplifies experiments with hydrogen at high pressures [2,3]. The determination of the gas composition may be necessary for performing such works.

Raman spectroscopy is the most effective means for analyzing, monitoring and controlling gas mixture of hydrogen isotopes [4,5]. However, using of this method at high pressures is associated with certain difficulties.

This paper describes a remote fiber-optic Raman spectroscopy probe designed for investigation gases at pressure up to 400 MPa in real time, as well as the experimental data on the composition of gas mixtures obtained from the metal-hydride sources at pressures up to 200 MPa.

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Properties of ZrNi_5 hydride and deuteride synthesized under high deuterium pressure

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High hydrogen pressure method has been successfully used to synthesize new hydrides with interesting properties like RFe_2H_5 and RMn_2H_6 compounds [1,2]. It has also allowed to increase the hydrogen content in ZrM_2 Laves phases ($\text{M}=\text{Co}, \text{Fe}$) [3]. In this context, we have investigated the hydrogenation properties of ZrNi_5 which contrary to LaNi_5 display a very limited solubility of hydrogen at 10 MPa(H_2) [4]. ZrNi_5 was submitted to 1 GPa of hydrogen pressure at 373 K. Fast XRD measurements at room temperature have shown that ZrNi_5 was able to form a cubic hydride, which desorbs very rapidly forming a mixture of α and β phases [5]. In order to stabilize the phase and investigate its crystallographic properties, ZrNi_5D_y was submitted to high pressure, quenched into liquid nitrogen and transferred very fast into the He cryostat on the G4.1 spectrometer (LLB neutron center, Saclay, France). The neutron diffraction patterns were measured from 2 to 290 K. At 2 K, ZrNi_5D_y crystallizes in a monoclinic structure derived from the parent AuBe_5 cubic structure due to D order into a Zr_2Ni_3 interstitial site (Figure 1). Between 240 and 265 K, a progressive change from monoclinic toward cubic structure was observed. Deuterium desorption starts above 265 K and a β - α transformation is observed upon heating to 290 K. First principle calculations have been performed using DFT method in order to compare the stability of the phase in both monoclinic and cubic structures and to estimate the enthalpy of formation of ZrNi_5 hydride.

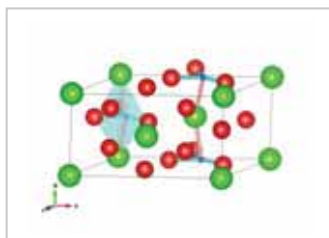


Figure 1. Structure of monoclinic $\text{ZrNi}_5\text{D}_{0.9}$ at 2 K (Zr in green, Ni in red, D in blue).

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Crystal Structure of the Gold Hydride

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Transition metals form hydrides usually with the close-packed atomic arrangements (face centered cubic or close-packed hexagonal) of metal atoms and an interstitial arrangement (tetrahedral and/or octahedral) of hydrogen in the metallic host lattice. In these hydrides the hydrogen atom usually brings ~ 0.5 electrons into the valence d -band of the host metal as was shown by measurements of the magnetic properties on the transition metal hydrides [1]. The gold hydride was synthesized using this method by annealing of a pure gold in the hydrogen atmosphere at ~ 50 kbar and $\sim 400^\circ\text{C}$ with the composition close to MeH. The conditions of AuH synthesis and suggested orthorhombic lattice are described in [2].

In this presentation the crystal structure of AuH is considered with the structural relationship to the nearest neighbor of Au in the Periodic Table – mercury. The position of gold in the Periodic Table is in the group IB just after transition metals. The electron energy levels for gold correspond to the completely filled $5d^{10}$ band and one electron is on the outer $6s$ level. The crystal structure of gold has a face-centered cubic cell as for majority of metals. Elements from the neighboring IIB group have different structures with deviations from the close-pickings. Thus, Hg forms at normal pressure a rhombohedral distorted fcc structure and at pressure above 3.4 GPa – tetragonal distorted bcc, which is retained at atmospheric pressure at low temperatures. Lattice parameters of Hg at 77K are $a = 3.995\text{ \AA}$ and $c = 2.825\text{ \AA}$, axial ratio $c/a = 0.707$, space group $I4/mmm$, two atoms in the unit cell, Pearson symbol $tI2$, atomic volume $22.54\text{ \AA}^3$ [3].

Following the assumption that hydrogen atom by entering in the metal host lattice brings his electron into the common electronic system of a metallic hydride, one should expect for the gold hydride AuH some similarity in the electronic and structural behavior with the neighboring two-valent metal – mercury. Analysis of the diffraction pattern for AuH revealed the possibility of indexing the group of strong diffraction peaks on the base of a tetragonal body-centered cell with lattice parameters $a = 3.933\text{ \AA}$ and $c = 2.782\text{ \AA}$, $c/a = 0.707$, atomic volume $21.5\text{ \AA}^3$ assuming two atoms in the unit cell. This structure is very similar to the mercury structure Hg - $tI2$. Detailed analysis of the AuH structure needs further considerations. The reasons of stability for this kind of structure are discussed within the nearly-free electron model with consideration of the Fermi sphere – Brillouin zone interactions [4].

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Hydrogenation of CsCl-type Al TM ($TM = \text{Fe, Co, Ni}$) alloys at high pressures and high temperatures

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We investigated hydrogenation of CsCl-type Ti-based alloys at high pressures and high temperatures (HPHT) and found that these alloys formed BCC hydrides after order-disorder phase transitions from CsCl to BCC structure [1]. In the present study, we have studied hydrogenation of CsCl-type Al TM ($TM = \text{Fe, Co, Ni}$) alloys to clarify whether the order-disorder phase transition generally occurs in CsCl-type alloys during hydrogenation at HPHT or not. More importantly, Al is a promising material in hydrogen-storage materials because of its abundance, lightweight and harmless nature. However, almost all Al-based alloys (≥ 50 at.% Al) including the Al TM alloys cannot absorb hydrogen near ambient conditions owing to surface oxide; few Al-based alloy hydrides have been synthesized [2]. The obtained results from the present study are, therefore, important for development of Al-based hydrogen-storage alloys.

The CsCl-type AlFe, AlCo and AlNi alloys were prepared by melting method. HPHT conditions were generated using a cubic-anvil high-pressure apparatus installed in beamline BL14B1 at SPring-8, Japan. The hydrogenation processes were monitored by *in situ* synchrotron radiation X-ray diffraction (SR-XRD) measurements. Details of the experimental apparatus and techniques are described elsewhere [3, 4]

Figure 1 shows the selected *in situ* SR-XRD profiles of the AlFe alloy kept in hydrogen fluid at 9 GPa and 650°C. The Bragg peaks of the CsCl structure 5 min after the alloy was heated to 650°C slightly shifted to low energy side, which indicated the lattice expansion of the sample. The lattice expansion was caused by a formation of solid solution with hydrogen (α_1). New Bragg peaks appeared 30 min after the sample was held at the conditions, which showed formation of a new phase (α_2). The new peaks was indexed by the CsCl structure; the new phase was a solid solution with high hydrogen content. This phase became a single phase after 530-min hydrogenation treatment. After that, no change of the XRD profile was observed. Thus, we found that an order-disorder phase transition did not occur in the CsCl-type AlFe alloy.

In this presentation, we will report the results of hydrogenation of AlCo and AlNi alloys at HPHT.

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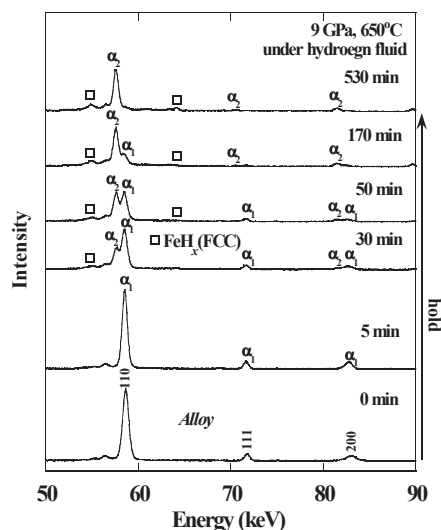


Figure 1 Selected *in situ* SR-XRD profiles of the AlFe alloy under hydrogen fluid.

Solubility of hydrogen in Zircaloy-4 nuclear fuel cladding

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A key issue with water cooled nuclear reactor fuel is hydrogen pickup by the zircaloy fuel pin cladding. This has many consequences regarding safety and economics of the fuel, particularly due to the low solubility of hydrogen in zirconium alloys (~60 ppm at 300°C)¹ and the resulting precipitation of a brittle hydride phase which appears as a needle-like precipitate². These hydrides are an issue during any reactivity initiated accident where a sudden increase in temperature and pressure within the fuel pin can rupture the cladding.

In the literature 2 very different models of the mechanism for DHC have been proposed. The precipitate first model (PFM) suggests that hydrogen in supersaturation within the zirconium matrix will precipitate out in the presence of a hydrostatic tensile stress at a flaw such as a crack tip. The precipitation of the hydride phase removes hydrogen from solution and sets up a hydrogen concentration gradient from the bulk (high concentration) to the crack tip (low concentration), causing flow of hydrogen to the crack tip meaning the hydride grows until a critical hydride size causes it to crack.

The opposing model is known as diffusion first model (DFM). DFM suggests that the introduction of a flaw producing a tensile hydrostatic stress field will reduce the chemical potential of hydrogen in this region. The chemical potential gradient set up between the crack tip and the bulk causes hydrogen to flow to the crack tip until it exceeds the solubility limit and causes the precipitation of a hydride. Provided the stress remains tensile and there is a much greater amount of hydrogen in the bulk than can be consumed, this process continues allowing hydrides to grow until they reach a critical size for fracture.

Previous studies have studied the behaviour of the system only under tensile stress. Here we study the behaviour of the system under compressive stress, allowing much higher stress to be applied to the system than previously achieved. We have performed a series of X-ray diffraction experiments on both pure and electrochemically hydrided zircaloy-4 under compression of up to 10 GPa pressure in a diamond anvil high-pressure cell, both in an inert atmosphere and in a hydrogen atmosphere. Using this technique, we estimate the solubility of hydrogen in zircaloy as a function of pressure by observing a lattice expansion of the zircaloy upon absorption of hydrogen, and also observe the precipitation of hydrogen out of solution on pressure decrease through the observation of separate X-ray diffraction peaks originating from a hydride phase.

Our results give strong support to the PFM model: that hydrostatic compressive stress increases hydrogen solubility in zircaloy and hydrostatic tensile stress decreases it.

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Preparation of cost-effective hydrogen storage materials for on board application

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Although V-based BCC-type alloy is one of the most suitable materials for hybrid tank system, a major disadvantage is the high cost of low oxygen V. The purpose of this research is to find ways to lower the cost of low oxygen V by combining thermite reaction and deoxidation by rare-earth (RE) metal.

Estimating the cost of V-based BCC-type alloy, it was $\$22.08 + \alpha$ /kg, here α is profit, as of January 2014 for the Ti12Cr23V64Fe1 alloy[1] using V through thermite reaction (hereafter this V will be referred as the “thermite V”), hence the cost will be largely reduced in comparison to using commercial low oxygen V.

Using V₂O₅ as a raw material, V metal is produced thorough thermite reaction. The purity of thermite V was 96.0%. A large portion of impurities were O (33741ppm) and Al (0.31 wt.%). As a deoxidation, the thermite V was melted with La metal, and this process led to 275 ppm of O content in the thermite V.

Ti12Cr23V64Fe1 alloy was obtained using the deoxidized thermite V. Hydrogen absorption/desorption property was evaluated (Figure 1). It was found that the amount of hydrogen absorption was similar to the alloy which was the same composition using the “commercial low oxygen V”. However, the equilibrium pressure was larger than the alloy using the commercial low oxygen V, and this reason seemed to be affected by the Al content as a solid solition in the alloy.

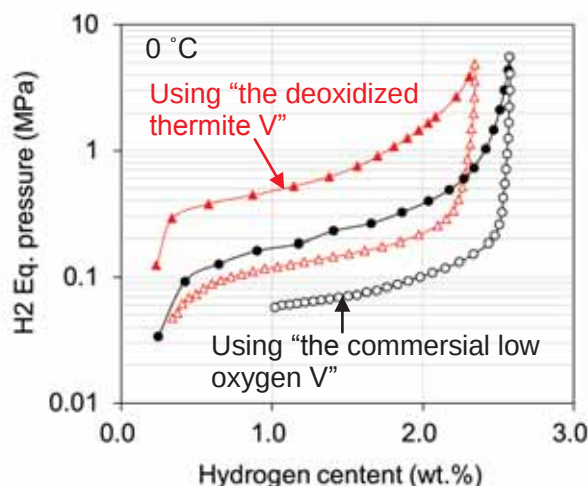


Figure 1. PCT isotherms for Ti12Cr23V64Fe alloys using the “commercial low oxygen V” (circle) and the “thermite V” (triangle) measured at 0 °C.

This work has been supported by the New Energy and Industrial Technology Development Organization (NEDO) under “Survey and study of hydrogen storage materials for fuel cell vehicles” and “Hydrogen Utilization Technology Development”.

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The Effect of Carbon Additives on the Hydrogen Uptake of Magnesium Hydride

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Hydrogen is a potential energy carrier with significant environmental advantages including extremely low pollution from combustion products and the capability of being generated using renewal energy sources such as solar and wind. However, safe and compact storage remains a problem, especially for mobile applications. Light metals such as lithium, magnesium, sodium are possible storage media as metal hydrides, but these are very stable and typically require high temperatures to extract the hydrogen. Carbon in the form of nano-structured carbon has been shown to destabilise the metal-hydride systems [1] and carbon nano-tubes have also been used to enhance hydrogen uptake in magnesium hydride [2]. Carbon in forms such as fullerene (bucky-balls) and graphene may provide also a possible path to de-stabilisation of these hydrides.

In this study, Magnesium Hydride was ball-milled initially for 20 h and then for varying times in a planetary ball-mill together with different amounts of the carbon material (C60 and other carbon forms). The mixture was then desorbed in a custom temperature programmed desorption apparatus to determine the desorption temperature onset and profile and then re-hydrided at 50 bar and 523 K. The results were then compared to the 20 h milled metal hydride (without carbon additive) as well as results from the same experiments with additives known to improve the kinetics of some metal hydrides substantially, oxides of titanium and niobium.

This paper reports the changes in desorption temperature onset/profile and absorption kinetics of the metal-carbon mixtures compared to hydrides without carbon as well as the hydrides with transition-metal oxide additives.

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Effects of Scaling in Metal Hydride Materials for Hydrogen Storage and Compression

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Recently most of the research activities in the field of metal hydride technologies are aimed to the improvement of hydrogen storage material characteristics (capacity, operation temperature, pressure, etc.). Much less attention is paid to the problems appearing during design of metal hydride energy systems. Most of common investigation techniques of hydrogen storage materials properties involve the testing of small-scale samples (less than 10 g) whereas pilot devices for hydrogen energy system must contain kilograms of storage material. Change of the alloy cell volume during hydrogen absorption or desorption leads to stresses of the alloy/hydride lattice. In the large-scale systems inside the bulk fill the reciprocal influence of particles inhibits the lattice relaxation. This process affects the thermodynamic characteristics of hydrogen absorption and desorption. The experimental data of present work allows to suppose that properties of LaNi₅-based storage materials depend on their scale and geometry.

Influence of impurities on the performance of a metal hydride

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The subject of the present work takes place in the field of hydrogen storage in intermetallic compound operating at room temperature. The study focuses on the influence of impurities on the performance of a metal hydride (Hydrogen capacity, kinetic, structure, ...). The compound selected belongs to the body centered cubic (BCC) family consisting of Titanium, Vanadium and Iron. Nomura and Akiba showed in 1995 that this kind of material is able to store reversibly more than 2 wt.% and can be used at ambient temperature and pressure [1].

Thanks to modelling, it appears that $\text{Ti}_{15}\text{V}_{71}\text{Fe}_{14}$ presents interesting absorption and desorption pressures at room temperature. All the properties of this alloy, elaborated on optimum conditions (5 fusions and annealing 5 days at 1000°C) are collected by X-ray diffraction, SEM, EPMA and hydriding on a PCT apparatus. It shows a reversible hydrogen capacity of 1.72 wt.% (2.5 wt.% at first absorption at 25°C and $P_{\text{max}} = 60\text{bar}$) and a good kinetic ($t_{90\%} = 1\text{hour}$).

A small amount of impurity (Al or Si) is added to the alloy (1 wt.% to 5 wt.%). Firstly, we studied the perturbation of the crystallographic structure by Rietveld analysis of X-ray diffraction. Furthermore, the different storage parameters were measured by hydriding and will be presented (absorption and desorption pressures, kinetics, maximum and reversible hydrogen capacity).

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Development of low-cost hydrogen storage materials – intrinsic effects of low-purity raw materials

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Intermetallic hydrides such as V-based body-centered solid solutions and AB₂-type alloys are considered for stationary and mobile hydrogen storage applications due to favorable thermodynamic and kinetic properties [1],[2]. However, high raw material costs yet limit their commercial applications. It is therefore desirable to reduce raw material costs. One strategy of cost reduction is to replace vanadium by a cheap ferrovanadium master alloy [3]. Another strategy is to use titanium sponge instead of Ti ingots [4]. Different ferrovanadium compositions are commercially available, which differ greatly in their respective compositions.

Microstructural effects of replacing V, Fe and Ti in a V-Fe-Cr-Ti BCC solid solution by various FeV master alloys will be investigated by means of XRD and SEM. Volumetric and high-pressure DSC measurements will be used to test their hydrogen storage properties. The microstructural changes occurring during hydrogen desorption are to be determined by *in-situ* SR-XRD.

V, Fe and Ti of a Ti-Zr-Mn-V-Fe-Al AB₂-type alloy will be replaced by FeV and Ti sponge. XRD and SEM will be used to investigate the microstructure. The hydrogen storage properties will be tested by means of volumetric measurements.

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The effect of internal hydrogen pressure on the energetics of hydrides

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Abstract

A simple model to compare the effect of interstitial hydrogen atoms in different structures on their stability will be discussed. Hydrogen is treated as electron gas expanding the metallic lattice. Several systems based on hexagonal metals will be compared. It indicates the way how parameters for hydrogen storage could be improved.

Experimental and Quantum Chemical Studies of Hydrogen Interaction with Nanostructured Composites and Clusters Based on Light Metals

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The aim of the present study is to establish a correlation between the experimental results on the reaction of hydrogen with nanostructured alloys and compounds based on the light metals (Mg, Al, Ti) and the results of the theoretical quantum chemical calculations, focused on the clusters of the mentioned metals, including those doped with other atoms. Such a combined approach will allow optimizing search of the novel materials based on light metals with improved H storage performance.

Experimental studies involved measurements of hydrogen absorption and desorption properties of the nanostructured materials obtained by intensive plastic deformation of the eutectic alloys of Mg with La, Mn and Ni, by using *in-situ* high temperature X-ray diffraction, programmed thermodesorption and metallographic examination. The materials with optimized microstructure, phase composition, amount of catalytic additives, and crystallite sizes demonstrate substantially improved hydrogen absorption and desorption performance [1]. Kinetics of hydrogen absorption-desorption by the metal hydride composites based on the ternary eutectic alloys Mg-Mn-Ni with nano-carbon additives was successfully modeled using an Avrami-Erofeev approach. It was shown that the carbon additives alter the mechanism of hydrogen release from the MgH₂ phase in the composites at temperatures $\leq 300^\circ\text{C}$ [1–3].

On the other hand, precise *ab-initio* quantum chemical calculations were employed to study the hydrides of light metals and elementary hydrogenation reactions. Thus, the Møller–Plesset perturbation theory was used to calculate structure and properties of low-lying isomers of the elementary and hydrided forms of the doped aluminides with icosahedral [Al₁₂] cage and endohedral *closo*-alanes with the light cations inside *closo*-alane and related dianions Al₁₂X₁₂²⁻ were predicted to be stable [4]. The potential energy surfaces (PES) of the elementary catalytic cycle of early stages of the H₂ + MAl₁₂ reaction of dissociative addition of an H₂ molecule to aluminum clusters MAl₁₂ doped with light 3d and 4d transition metal atoms (Sc, Y, Ti, Zr, V, Nb) in the states of different multiplicity were calculated by the density functional theory method. The effect of the dopant nature and the electronic state multiplicity of the cluster on the energies and activation barriers of hydrogenation reactions of aluminum clusters were considered [5]. The calculated PES corresponding to the early stages of the H₂ + TiAl₁₂ reaction indicate a similar behavior of the titanium dopant as compared to such transition metals as Zr and V.

The work is supported by RFBR (grants № 13-08-00642 and 14-03-01060).

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In-situ and time-resolved measurement on hydrogen absorption/desorption processes of hydrogen absorbing alloys using synchrotron radiation x-rays

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Hydrogen absorbing alloys are widely investigated as potential hydrogen storage materials for several applications including fuel cell vehicles as well as stationary energy storage system. To develop high-performance hydrogen absorbing alloys, it is essential to elucidate detailed mechanism of hydrogen absorption and desorption processes. The hydrogen absorbing states of materials usually arise under the pressurized hydrogen gas environment. Hence, in-situ measurement is necessary to investigate the hydrogen absorbing states as well as hydrogen absorption/desorption processes. In order to investigate the structural changes during the hydrogen absorption/desorption processes, we have developed an in-situ x-ray diffraction measurement setup at the Japan Atomic Energy Agency Beamline BL22XU in SPring-8. The in-situ x-ray diffraction measurement has been performed for the several hydrogen absorbing alloys under equilibrium and non-equilibrium pressure of hydrogen gas. In addition, by using a large area detector and high energy x-ray about 70 keV, we are capable of performing x-ray total scattering experiments ($Q_{\max} \sim 25 \text{ \AA}^{-1}$) to obtain the atomic pair distribution function (PDF) [1]. From the Rietveld and PDF analyses on x-ray diffraction data, we can investigate the change in both average and local structures during the hydrogen absorption/desorption processes. In this presentation, we will introduce our measurement setup and show some preliminary results.

This work is supported by Photon and Quantum Basic Research Coordinated Development Program from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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Hydrogen Storage Properties in Pd-based Nanoalloys

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Recently, Pd-based nanoalloys have been successfully synthesized through a chemical method[1]. The finding provides a new understanding of interaction between hydrogen (H) and nanostructured solid, which could contribute to the development of practical H storage materials. In order to enhance understanding in the nature of H storage behaviour in Pd-based nanoalloy, we performed calculations of H storage energy of possible interstitial sites at subsurface and inner-site regions.

The calculations were performed using the VASP based on the density functional theory. The generalized gradient approximation of Perdew-Burke-Emzerhof was introduced to describe the exchange and correlations interactions. The cutoff energy was 400 eV with the k-points of 1x1x1. Projector augmented wave method was also employed.

Pd-based nanoalloy as shown in Figure 1, with dopant metals of Rh, Ag, Ir, Pt and Au, was used in the calculations. H storage energy for various nanoalloys at two different regions, subsurface and inner-site are presented in Figure 2. We observed, subsurface region is more favorable for H as compared to inner-site region for all nanoalloys. Dopant metal also give a large contribution for H stability, as the most stable nanoalloy is Pd-Ag, for both regions, whereas Pd-Pt and Pd-Ir do not show any H absorption properties.

We also studied the local site and whole structure configurations dependence for H storage energy, which will be presented.

Acknowledgement

Activities of INAMORI Frontier Research Center are supported by KYOCERA.

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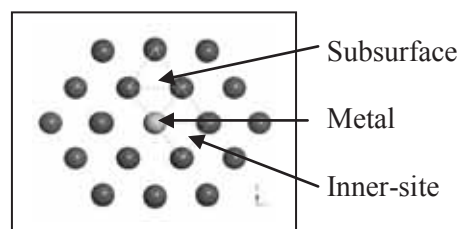


Figure 1. Pd₅₄-M₁ nanoalloy

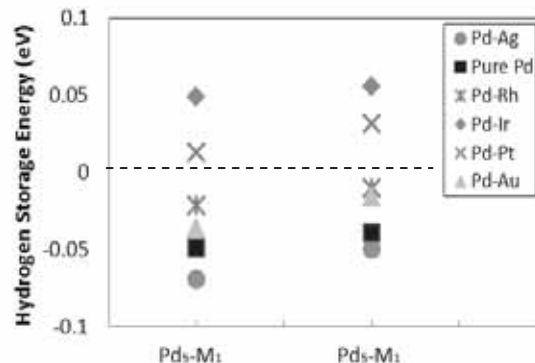


Figure 2. The H storage energy for Pd-based nanoalloy

Effect of hydrogen on generation of lattice defects in shock-loaded Pd

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Pd is widely used as a model system for investigations of hydrogen in metal lattice since Pd can absorb a relatively large amount of hydrogen, its kinetic response to hydrogen is fast and it can be easily charged with hydrogen at room temperature. In a perfect fcc Pd lattice hydrogen occupies octahedral interstitial sites and causes remarkable volume expansion. In a non-perfect Pd lattice hydrogen can be trapped at open-volume defects like vacancies, dislocations and grain boundaries. It was reported that segregation of hydrogen at open volume defects can reduce the defect formation energies and facilitate the creation of the defects [1].

The effect of hydrogen absorbed in fcc Pd lattice on the generation of dislocations and vacancy clusters during plastic deformation was investigated in this work. Well annealed bulk Pd samples were firstly charged with hydrogen up to various hydrogen concentrations. Subsequently the samples were shock-loaded on a Split-Hopkinson apparatus. Shock-loading yields extremely high strain rate up to 8000 s^{-1} and causes intensive plastic deformation of the samples. Lattice defects of the shock-loaded samples were characterized by positron annihilation spectroscopy (PAS) combined with X-ray diffraction.

It was found that shock-loaded pure Pd samples (i.e. samples deformed without hydrogen) exhibit high density of dislocations ($\approx 10^{15} \text{ m}^{-2}$). Shock-loaded Pd-H samples contain even higher dislocation density which increases with increasing hydrogen concentration in the samples. This indicates that introduction of hydrogen facilitate the creation of dislocations. Moreover, PAS studies revealed that shock-loaded Pd-H samples contain not only dislocations, but also small vacancy clusters which were not observed in the shock-loaded pure Pd. The vacancy clusters were likely created by agglomeration of deformation-induced vacancies. In pure Pd vacancies are very mobile at room temperature and quickly disappear by diffusion to sinks at grain boundaries. On the other hand in Pd-H the deformation-induced vacancies are stabilized by segregated hydrogen atoms. Some fraction of vacancies disappears in sinks but the remaining vacancies agglomerate and form vacancy clusters which are surrounded by hydrogen. The concentration of vacancy clusters increases with hydrogen concentration due to the reduction of vacancy formation energy by hydrogen.

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Static and dynamic response of a Pd-coated microcantilever exposed to hydrogen

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The study of the static and dynamic response of functionalized microcantilevers reacting with their gaseous environment is of fundamental interest for understanding the absorption-desorption mechanisms of systems such as Pd-hydrogen. We used an *in situ* technique developed [1] to simultaneously measure the static deflection and the resonance frequency of samples under hydrogen static pressure. The measurements were performed on microfabricated silicon cantilevers coated with thin films of Pd (10, 30 or 60 nm thick).

Experiments have shown that the resonance frequency and deformation states of the cantilever exhibit clear correlations with the hydriding process. Pd-H absorption experiments suggest that the cantilever bending response can be deciphered into three different regimes corresponding to the classical α , $\alpha + \beta$, β phases of the Pd-H system. The cantilever initially bends with a linear slope in α phase while an exponential change occurs in $\alpha + \beta$ phase. No significant change is monitored in the β phase.

The resonance frequency shows no change in α phase but undergoes a dramatic decrease in $\alpha + \beta$ phase. Most of these deflection and frequency changes are correlated to the elastic properties change of the Pd-H film.

These results help in discerning the parameters that control the cantilever response as well as the relationships between these parameters, namely Young's modulus, swelling, mass intake, surface stress. The comparison with other systems such as various gas sensors or biological molecular adsorption on thin films is interesting.

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In-situ Nanoindentation of Palladium-Hydrogen Alloys

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The influence of hydrogen on the formation of dislocations during plastic deformation is studied with an in-situ setup for nanoindentation. For this purpose a defined hydrogen concentration can be kept within the palladium.

Nanoindentation of an initially defect free material often shows a sudden increase in displacement, the so-called pop-in. This marks a transition of elastic to plastic deformation, where a new dislocation loop is formed.

Other experiments [1] show that hydrogen affects defect formation. Hydrogen solved in palladium facilitates the formation of dislocations, leading to an increase in dislocation density.

These experiments can be analyzed using the defactants concept [2], the basis of which is the assumption that a decrease of the overall free energy by the segregation of solute atoms to a defect can be ascribed to a decrease of the defect formation energy.

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Theoretical analysis for interface interaction and hydrogen absorption of Pd@HKUST-1 hybrid material

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The hydrogen absorption properties of Pd@HKUST-1 significantly improved compared with pure Pd nanoparticle [1]. This result will lead to the spread of the hydrogen storage materials. In this study, to explain hydrogen absorption mechanism of Pd@HKUST-1 hybrid material, we analyze the interface conformation and hydrogen absorption energy of Pd@HKUST-1 by using density functional theory calculation.

All calculations were performed under GGA-PBE functional in DMol³ program package. DNP with ECP was used as basis sets.

We assumed two terminated models (Cu and O terminals) of HKUST-1. As adsorption site of HKUST-1 on Pd, 4-fold and on top sites on Pd(1 0 0) surface are analyzed. Table 1 shows the result about interaction energy between Pd and model of HKUST-1. The most stable site was on top in Pd surface with O terminal model of HKUST-1. Then we added hydrogen atom into the octahedral site of Pd in the optimized structure, and calculated hydrogen absorption energy. Table 2 shows the hydrogen absorption energy for each octahedral site (Figure 1). Site 1 and 2 under the coordinated oxygen of HKUST-1 were more stable than Pd slab model. Same calculation was applied to CH₃COO⁻, because HKUST-1 and CH₃COO⁻ have the same functional group, carboxyl. There is no significant difference of hydrogen absorption energy in two models.

Table 1 : Interaction energy of Pd and model of HKUST-1[eV]

	4-fold	On top
Cu terminal	-2.11	-
O terminal	-2.41	-2.60

Table 2 : Hydrogen absorption energy[eV]

	HKUST-1	CH ₃ COO ⁻
Site1	-0.18	-0.19
Site2	-0.17	-0.17
Site3	-0.12	-0.12

Only Pd model = -0.13

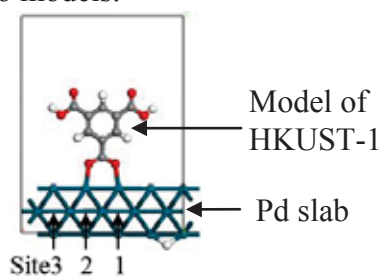


Figure 1. Hydrogen absorption site

Acknowledgement

Activities of INAMORI Frontier Research Center are supported by KYOCERA Corporation.

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Hydrogen sorption behaviour of carbon-supported Pd nanoparticles

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Palladium has exhibited interesting properties when at the nano-scale such as fast kinetics for dissociation and association of hydrogen molecules on metal surfaces [1]. This has led to a range of applications such as fuel cell catalysts, sensors, and hydrogen storage media [2]. In this work, the hydrogen / deuterium sorption behaviour of Pd nanoparticle samples (on their own and carbon-supported) has been studied.

The structure of the Pd powder samples (Pd and Pd supported on carbon) have been characterised by XRD, Raman spectroscopy, and temperature programmed desorption-mass spectrometry (TPD-MS). A series of activated carbon samples with 1, 3, 5, 10 and 30 wt% loadings of Pd were obtained (Sigma Aldrich), in which the Pd particles were estimated to have a grain size of about 10-100 nm, using Williamson-Hall analysis of the XRD patterns.

Hydrogen absorption occurred at room temperature upon exposure to 5 bar hydrogen, as shown by the formation of a Raman peak associated with Pd hydride. The dehydrogenation (hydrogen and deuterium) properties of the series of carbon-supported Pd samples were studied by TPD-MS, by heating from 77 to 773 K in flowing Ar. The dehydrogenation results are discussed in terms of the Pd loading, the effect of the carbon substrate, Pd particle size, and Pd grain size.

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Crystal structure and hydrogen absorption-desorption property of Gd_2Ni_7 with Ce_2Ni_7 -type structure

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The intermetallic compounds $\text{RNi}_{3\sim 3.8}$ (R = rare earth) [1] with superlattice structure have been investigated as a hydrogen storage material. These compounds consist of cells with MgZn_2 - and CaCu_5 -type cells stacked along the c -axis. The phase diagram of the GdNi system shows nine phases in the equilibrium state: Gd_3Ni , Gd_3Ni_2 , GdNi , GdNi_2 , GdNi_3 , Gd_2Ni_7 , GdNi_5 , and $\text{Gd}_2\text{Ni}_{17}$ [2]. Gd_2Ni_7 has two types of crystal structures: a hexagonal Ce_2Ni_7 -type structure (space group $P6_3/mmc$) at high temperature and a rhombohedral Gd_2Co_7 -type structure (space group $R\bar{3}m$) at low temperature [3]. They consist of cells with MgZn_2 - and CaCu_5 -type structures stacked along the c axis at ratios of 1:2. This study focused on Ce_2Ni_7 -type Gd_2Ni_7 to study the hydrogen absorption-desorption property. The hydrogenation properties of Gd_2Ni_7 have not yet been fully elucidated. The behavior of the MgZn_2 - and CaCu_5 -type cells during hydrogenation should be closely related to the hydrogenation properties.

The crystal structure and hydrogenation properties of Ce_2Ni_7 -type Gd_2Ni_7 were investigated by X-ray diffraction (XRD) and the hydrogen pressure–composition (P – C) isotherm. Ce_2Ni_7 -type Gd_2Ni_7 was obtained by annealing at 1523 K for 12 h and quenching in ice water. The refined lattice parameters were $a = 0.49662(9)$ nm and $c = 2.4255(3)$ nm, respectively. Two plateaus were clearly observed during the absorption–desorption process in the P – C isotherm. The first and second plateaus were at 0.015 and 0.13 MPa, respectively, in the first desorption. The maximum hydrogen capacity reached was 1.13 H/M. After the P – C isotherm, the GdNi_5 cell volume expanded by 2.15%, but the Gd_2Ni_4 cell volume shrank by 2.83%.

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Simulating the Surface Stress Effects due to the Initiation and Growth of Uranium Hydride

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The mechanism of uranium hydriding is of interest as an ideal model of a metal-hydrogen system since there is very low solubility of hydrogen in the metal and only stoichiometric UH₃ is formed. The main focus of this study is to understand the relationship between stress and the corrosion site growth in the early reaction stages.

A model has been constructed, using the Finite Element package *COMSOL*, to investigate the stress generated by the nucleation of hydride close to the metal-oxide boundary. Additional stresses induced by the presence of a representative elastic-plastic UO₂ oxide overlayer have been included. Investigations have focussed on the effect of precipitate size, depth and shape on resultant stress regions around the hydride site. It has been determined from these simulations that the presence of the hydride site induces a compressive field at the surface of the metal but that this compressive field is surrounded by a tensile region. The size and intensity of these regions are functions of precipitate size, depth and shape. This work is in fair agreement with the work of Greenbaum and co-workers, (1, 2) in that the central compressive region is surrounded by tensile regions, however significant differences remain and these may be attributable to differences in the model (i.e. shape and depth of the hydride, the oxide to hydride size ratio, a residual stress within the oxide, and the fact that Greenbaum models PdH which has a volume expansion of 17% over the metal compared to 71% for UH₃). We consider that the stress distribution is important to an understanding of the ultimate development of these nuclei: both in terms of shapes and location of nucleation but also in terms of ultimate size. (3) These relationships will be discussed, as will possible relationships between diffusivity, solubility and phase transformation with stress.

We have used recent AFM data on uranium exposed to a low pressure of hydrogen (4) comparing shapes and sizes of surface protrusions, resulting from the growth of small (μm sized) sub-surface nucleation of uranium hydride, to compare to the model. These comparisons will be discussed.

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Influence of Hydrogen and Mechanochemical Activation on the Properties of Nd-Fe-B- and Sm-Fe-N-Type Magnetic Materials

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In spite of the fact that a lot of works are devoted to hydrogen interaction with $\text{Sm}_2\text{Fe}_{17}$ and $\text{R}_2\text{Fe}_{14}\text{B}$ intermetallic compounds and alloys of Nd-Fe-B system, a number of aspects, such as influence of hydrogenation and absorption-desorption cycling on magnetocrystal anisotropy and mechanism of its formation, are studied insufficiently. The relationship between the quantity of absorbed hydrogen and the dimensions and morphology of hydride particles is not found out, though this data is necessary for correct design of reactors for hydriding of magnetic alloys.

In present work the influence of hydriding-dehydriding procedures on the phase composition, structure and powder morphology of mechanoactivated $\text{R}_2\text{Fe}_{14}\text{B}$ -based alloys. It was found that the high-energy milling leads to increase of coercitivity of dehydrided powders up to 2.4 kOe, that is almost 10 times higher than coercitivity of the as-cast alloy. Also, mechanoactivation of as-cast $\text{R}_2\text{Fe}_{14}\text{B}$ alloy results in formation of two types of amorphous regions with different composition.

In case of Sm-Fe-N alloys the phase composition, structure and magnetic properties of $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ nitrides, obtained by nitridation of $\text{Sm}_2\text{Fe}_{17}$ both as milled powder and HD powder, are almost the same. However, HD process significantly accelerates the nitride formation. Additional mechanoactivation of hydrides leads to increase of coercitivity of nitrides.

The analysis of the changes of the remagnetisation and partial hysteresis loop curves, depending on the obtaining conditions and the duration of milling, shows that the limiting stage of the remagnetisation processes in nitrides is the generation and growth of reverse magnetisation domains.

Investigation of nanocrystalline and epitaxial Gd films loaded with hydrogen

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The Gd–H system attracts attention of researchers because it can absorb a large amount of hydrogen and exhibits a negative enthalpy of solution for atomic hydrogen. However, the knowledge about the Gd–H phase diagram is yet incomplete, especially at low temperatures. It is well known that hydrogen in metals strongly interacts with open-volume defects. Hydrogen absorption is therefore influenced by microstructure of the sample and understanding of hydrogen interaction with defects is essential for a proper design of materials suitable for hydrogen based technologies.

The present work reports on microstructure studies of hydrogen-loaded thin Gd films prepared by cold cathode beam sputtering on single crystalline sapphire (11.0) substrates. Two sets of Gd films with different microstructures were compared: (i) films deposited at room temperature which exhibit nanocrystalline grains with the mean size of ≈ 50 nm and (ii) epitaxial films deposited on the substrate heated at 800°C. The Gd films were electrochemically step-by-step charged with hydrogen and the structural development with increasing concentration of absorbed hydrogen was studied by *in-situ* X-ray diffraction using synchrotron radiation. Defect studies of Gd-H films were performed by variable energy slow positron annihilation spectroscopy. The relaxation of hydrogen-induced stresses was examined by acoustic emission.

The nanocrystalline Gd films contain a high density of vacancy-like defects at grain boundaries. Absorbed hydrogen occupies preferentially grain boundaries. When grain boundaries are filled hydrogen penetrates also to grain interiors. With increasing hydrogen concentration the film transforms into the dihydride phase (GdH₂). Precipitation of GdH₂ introduces very high density of dislocations. Finally at high hydrogen concentrations $x_H > 2.0$ H/Gd, the film structure becomes almost completely disordered. Contrary to bulk Gd specimens, trihydride phase (GdH₃) is not formed in the nanocrystalline Gd films.

The virgin epitaxial Gd film exhibits high density of misfit dislocations compensating for the lattice mismatch between the film and the substrate. During hydrogen charging hydrogen-induced stresses grow with increasing hydrogen concentration and from a certain critical hydrogen concentration plastic deformation of the film takes place. Similarly to the nanocrystalline film high density of dislocations is introduced during formation of GdH₂ phase.

Enhanced joint catalysis of $\text{YH}_2/\text{Y}_2\text{O}_3$ on dehydrogenation of MgH_2

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Doping catalytic additives by mechanical milling have been shown to greatly improve the hydrogen storage properties of MgH_2 . Various catalysts such as transition metal hydrides, oxides, nitrides and fluorides have been widely explored. The catalytic mechanism is normally related to the enhanced H_2 dissociation/recombination as well as H atom diffusion. Herein, we investigate the joint catalytic effect of YH_2 and Y_2O_3 on the dehydrogenation of MgH_2 .

The casted $\text{Mg}_{93.3}\text{Y}_{6.8}$ ingot was grinded and then milled for further characterization of hydrogen storage properties and microstructure. The hydrogenated products consist of MgH_2 , nanosized YH_2 and YH_3 . The YH_3 partially decomposed into YH_2 after dehydrogenation. With longer hydriding time, more YH_2 was transformed to YH_3 , but the dehydrogenation properties of MgH_2 remained almost unchanged. This result indicates that $\text{YH}_3 \rightarrow \text{YH}_2$ phase transformation has no catalytic role on the dehydrogenation of MgH_2 . Similar conclusion should also work for other multi-valence metal hydrides, such as $\text{LaH}_3/\text{LaH}_2$, $\text{CeH}_3/\text{CeH}_2$.

After unexpected oxidation, the $\text{Mg}_{93.3}\text{Y}_{6.8}$ alloy showed better properties, the hydrogen desorption rate at 300 °C increased by nearly three times, but the improvement in hydrogenation kinetics is not significant (Figure 1). It is found that YH_3 was oxidized to Y_2O_3 , which is accompanied with nanoscale YH_2 (Figure 1). Therefore, the coexistence of YH_2 and Y_2O_3 played better catalytic effect than YH_2/YH_3 . Similar phenomena is also found in a Mg-Ce-Ni alloy containing nanoscale $\text{CeH}_2/\text{Ce}_2\text{O}_3$ [1]. This synergetic catalysis is possibly related to hydrogen spillover mechanism over the oxide surface. To maximize the catalytic effect, the milling process under H_2 atmosphere mixed with air is investigated.

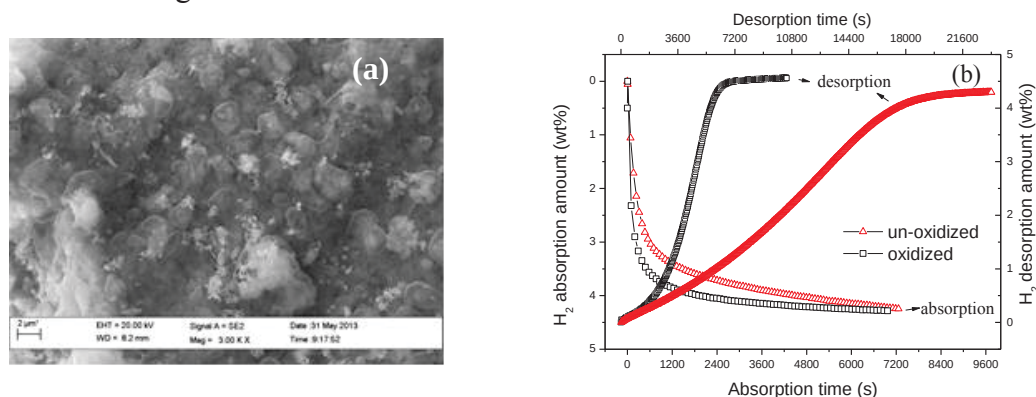


Figure 1. SEM image showing bubble-like microstructure of Y_2O_3 accompanying with nanoscale YH_2 after hydrogenation and oxidation (left). The comparison on hydrogen sorption kinetic properties of oxidized and un-oxidized samples showing greatly improved dehydrogenation kinetics (right).

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Preparation and Electrochemical Properties of $\text{La}_2(\text{Ni}, \text{Co}, \text{M}, \text{Mg})_{10}$ (M=Al or In) hydrogen storage alloys

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The performance of Ni-MH batteries depends on the characteristics of the negative hydride electrode. Currently, the negative electrode of the most batteries are based on the AB_5 family of intermetallic compounds. The archetype material of the AB_5 alloys is LaNi_5 , a compound which has been thoroughly investigated due to its utility in conventional hydrogen storage applications. Unfortunately, LaNi_5 is too unstable and mechanically-sensitive to be used as a battery electrode. The partial substitution of Ni by certain elements increases the thermodynamic stability of the hydride phase and, sometimes, its corrosion resistance. Recent investigations [1-3] have shown that the Mg-doped compounds may serve as promising materials for hydride electrodes owing to their high hydrogen storage capacity and good electrochemical properties. In this report the effect of the technology fabrication of $\text{La}_2(\text{Ni}, \text{Co}, \text{Mg}, \text{M})_{10}$ alloys doped with M = In or Al on their electrochemical properties are presented. Three different metallurgy procedures were applied: i) melting of $\text{La}_2\text{Ni}_{9-x}\text{M}_x$ (M = Co and Al or In) alloy precursor and Mg in sealed molybdenum crucibles in induction or in resistance furnaces and ii) by powder metallurgy route consisting of the mechanical alloying of $\text{La}_2\text{Ni}_{9-x}\text{M}_x$ precursor and Mg powder followed by sintering process at high temperatures. The electrochemical characteristics of the alloys including the discharge capacity, the $\text{H}_2\text{O}/\text{H}_2$ exchange current density, and the hydrogen diffusivity have been studied as function of the number of charge/discharge cycles. Electrochemical measurements have been carried out using chronopotentiometric and chronoamperometric methods. It has been proved that the metallurgical process applied in the alloy manufacturing has a significant effect on electrochemical hydrogenation properties. Our investigations indicate that the best results have been obtained for electrodes synthesized by powder metallurgy route followed by sintering process. Multi-cycled hydrogenation experiments for the tested electrodes at $400 \text{ mA} \cdot \text{g}^{-1}$ charge/discharge rate revealed the maximum discharge capacities as large as $325 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$.

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XPS Studies of Nanocrystalline $\text{La}_x\text{Ni}_{1-x}$ and $\text{LaNi}_{5-x}\text{Al}_x$ ($x = 0.2, 0.5, 1$) Alloy Thin Films

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Several semi-empirical models [1, 2] have been proposed for the heat of formation and heat of solution of metal hydrides and attempts have been made for justifying the maximum hydrogen absorption capacity of the metallic matrices. These models showed that the energy of the metal - hydrogen interaction depend both on geometric and electronic factors. In this contribution, we study experimentally the electronic properties of polycrystalline and nanocrystalline $\text{La}_x\text{Ni}_{1-x}$ and $\text{LaNi}_{5-x}\text{Al}_x$ thin films using X-ray photoelectron spectroscopy (XPS). The structure of the samples has been studied by X-ray diffraction (XRD). Their bulk chemical compositions were measured using X-ray fluorescence (XRF) method.

$\text{La}_x\text{Ni}_{1-x}$ and $\text{LaNi}_{5-x}\text{Al}_x$ ($x = 0.2, 0.5, 1$) alloy thin films were prepared onto glass and oxidised Si(100) substrates in the temperature range 285 – 700 K using computer-controlled ultra high vacuum (UHV) magnetron co-sputtering. Ni (Al) and La targets were sputtered using DC and RF modes, respectively. The base pressure before the deposition process was lower than 5×10^{-10} mbar. The chemical composition and the cleanness of all layers was checked *in-situ*, immediately after deposition, transferring the samples to an UHV (4×10^{-11} mbar) analysis chamber equipped with XPS [3].

Structural studies showed that the samples deposited at 295 K are nanocrystalline with average grain size $D \sim 15 - 20$ nm. Thin films deposited at about 700K are polycrystalline with $D \sim 200$ nm. The total thickness of the samples was about 1000 nm. XPS results showed that the shape of the valence band measured for the polycrystalline LaNi_5 thin film is practically the same compared to that reported earlier for the single crystalline sample [1]. On the other hand, the XPS valence bands of the nanocrystalline $\text{La}_x\text{Ni}_{1-x}$ and $\text{LaNi}_{5-x}\text{Al}_x$ thin films are considerably broader compared to those measured for the polycrystalline samples. This is probably due to a strong deformation of the nanocrystals. Normally the interior of the nanocrystal is constrained and the distances between atoms located at the grain boundaries are expanded [3]. In conclusion, the different microstructure observed in polycrystalline and nanocrystalline alloy thin film leads to significant modifications of their electronic structure. Especially, the observed modifications of the valence bands of the nanocrystalline alloy thin films are in good accordance with hydrogenation properties reported recently for bulk LaNi_5 – type nanomaterials [3].

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Composition changes of structural and hydrogenation properties of ZrM_2 type intermetallics for high pressure hydrogen storage applications

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Several series of pseudo-binary compounds such as $Zr(Fe, M)_2$ with $M = Cr, Mn$ and Nb and $Ti_{1-x}Zr_x(Cr, M')_2$ with $M' = Fe, Mn$ and V , mostly exhibiting the C14 hexagonal type of Laves phase compounds were considered for the large span of plateau pressure they can exhibit when forming reversible metal hydrides.

The samples were synthesized by using either the arc melting technique or the high frequency in cold crucible technique, or even both methods. Most of materials were prepared at lab scale (a few gr. to a few tens gr.) for further advanced characterization procedures mainly by using XRD, SEM/EDX analysis and PCT measurements undertaken before and after forming (when stable in normal conditions) metal hydrides.

The different samples were studied and classified for their reversible characteristics in terms of hydrogen absorption kinetics, plateau pressure level, maximum hydrogen uptake and amplitude of hysteresis effect in between absorption and desorption pressure.

For the most interesting and performant materials several kg size batches were also processed and characterised.

The aim of the present collaborative study is to provide a series of materials having successive equilibrium plateau pressures enabling to cover step by step the H_2 pressure range from 0 to 30 MPa when submitted to typical temperature variation between RT and $\sim 90^\circ$ - $100^\circ C$. Also the potential decrepitation and demixion process were studied. The target application is building a multistep and high dynamics hydrogen compressor with close enough structural, microstructural and heat conduction properties mainly composed of the cheapest and easily available metals.

Detailed characterisations will be presented and discussed as well as the main features of the tank systems developed in parallel.

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Impact of hydrogen absorption on crystal structure and magnetic properties of $\text{RE}_2\text{T}_2\text{X}$ compounds

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We have been studying some members of large family of $\text{A}_2\text{T}_2\text{X}$ (A = Rare-Earth (RE) or actinide, T = transition metal, X = *p*-metal) compounds crystallizing in the Mo_2FeB_2 structure type (space group $P4/mbm$) [1]. In $\text{U}_2\text{T}_2\text{X}$, the H concentration up to 2 H atoms/f.u. can be reached in pressures up to 150 bar, producing a lattice expansion, while the tetragonal structure is preserved. The H atoms presumably enter the 8*k* position inside the U_3T tetrahedra occupied randomly up to 50 % [2]. We have shown that some $\text{RE}_2\text{Pd}_2\text{In}$ compounds can absorb more hydrogen compared to their U-counterparts. The amorphization of the structure upon hydrogenation was found for $\text{RE}_2\text{Pd}_2\text{In}$ with light RE (La, Nd). $\text{RE}_2\text{Pd}_2\text{In}$ with heavy RE behave similar way as was found for $\text{U}_2\text{T}_2\text{X}$ compounds (2 H/f.u., crystal structure type not changed). For the $\text{RE}_2\text{Pd}_2\text{In}$ compounds, the lattice parameters *a* and *c* and unit cell volume *V* decrease linearly with increasing atomic number of RE due to lanthanide contraction. Crystal lattice reacts to hydrogenation by anisotropic expansion, which becomes progressively concentrated into the *c*-direction with increasing atomic number. Therefore the initial expansion in *a* turns actually into a compression behind Gd. The RE_3T tetrahedra, presumably accommodating the H atoms, become very much elongated along *c* for late RE's, while their basis shrinks. This has apparently no impact on H storage capacity. The volume expansion decreases with increasing atomic number from 6 to 3.5 %.

The magnetic ordering temperatures of all RE-compounds studied are dramatically reduced by the hydrogenation, typically to the *T*-range below 1.8 K. Such general dramatic weakening of the RKKY exchange interaction should have a strong reason – most likely the impact of hydrogenation on the system of conduction electrons. Few percent volume expansion cannot have such a dramatic consequence. The effect of H-bonding is more probable.

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Structural impacts of Transition Metal Fluorides on the Reactive Hydride Composites (RHC)

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In order to understand the catalytic effect of transition metal fluoride additives on the nano-structure of the Reactive Hydride Composites (RHC), several techniques such as powder X-ray diffraction (in situ SP-XRD), X-ray absorption spectroscopy (XAS), anomalous small angle X-ray scattering (ASAXS) and small angle neutron scattering (SANS) were applied. The main attention of this research is focused on the contrast variation techniques [1]. By varying the anomalous dispersion factors (ASAXS) the nanoscopic heavy transition metal structures can be revealed and via isotope exchange, for instance H/D (SANS), the nano-structure of light hydride-matrix can be resolved. The results of this investigation contribute to further optimization of kinetics and capacity of RHCs.

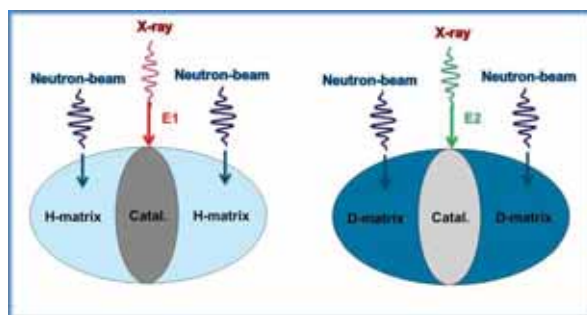


Figure 1. Contrast variation by variation of X-ray energy and isotope exchange via ASAXS and SANS, respectively.

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Deuterium Exchange Dynamics in $\text{Zr}_2\text{NiD}_{4.8}$ Studied by ^2H MAS NMR Spectroscopy

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Variable temperature (VT) ^2H magic angle spinning (MAS) spectroscopy was employed to measure deuterium diffusion behavior in interstitial $\text{Zr}_2\text{NiD}_{4.8}$ phase. The Zr_2Ni phases when highly saturated with deuterium were initially studied by powder diffraction methods [1,2] a while ago, but the dynamical behavior among deuteride site occupancies has never been accessed. ^2H MAS NMR spectrum at 190 K provides with well resolved 4 different site occupancies which can be assigned based on the crystal structure (16*k* (Zr_2Ni_2), 32*m* (Zr_3Ni), Zr_4 (16*l* and 4*b*)). As the temperature rises, the ^2H peaks sensitively reflect the exchange behavior among the sites with evident change at around 230 K and reaching a uniform distribution of site occupancies above 245 K. This behavior is reflected by the collapse of the ^2H MAS spectrum into a single peak as shown in Figure 1. From lineshape analysis of VT MAS NMR spectra, we were able to extract hopping rates between 32*m* and 16*l* sites (e.g., $\tau_c = 2.06 \times 10^{-4} \text{ s}$ at 245 K) with a corresponding activation energy of 58 kJ/mol.

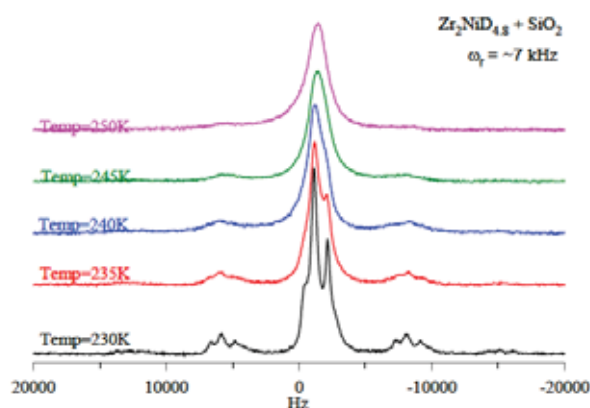


Fig. 1. ^2H MAS-NMR Spectra for $\text{Zr}_2\text{NiD}_{4.8}$ obtained between 230 K and 250 K

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Preferred Hydride Growth Orientations on Oxide-coated Gadolinium Surfaces

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The initial development of hydrides on polycrystalline Gadolinium (Gd), as on some other hydride forming metals, is characterized by two sequential steps. The first step involves the rapid formation of a dense pattern of small hydride spots (referred to as the "small family" of hydrides) below the native oxidation layer. The second stage takes place when some of the "small family" nucleants (referred to as "growth centers", GC's) break the oxide layer, leading to their rapid growth and finally to the massive hydriding of the sample.

In the present study, the texture of the two hydride families was studied, by combining X-ray diffraction (XRD) analysis with a microscopic analysis of the hydride, using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). It has been observed that for the "small family", a preferred growth of the (100)_h plane of the FCC GdH₂ takes place, whereas for the GC's, a change to the (111)_h plane of the cubic hydride dominates. These preferred growth orientations were analyzed by their structure relation with the (00.1)_m basal plane of the Gd metal.

It has been concluded that the above texture change is due to the surface normal compressive stress component exerted by the oxidation overlayer on the developing hydride, preventing the (00.1)_m || (111)_h growth orientation. This stress is relieved upon the rupture of that overlayer and the development of the GC's, leading to the energetically favorable mode of growth.

Investigation of Crack Formation in High-purity Iron

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Hydrogen embrittlement is a current problem in various applications of metals and it becomes more relevant with respect to hydrogen as a solution for energy storage.

The mechanism of damage due to hydrogen was studied in high-purity iron by loading hydrogen with different current densities and evaluating the microstructure using scanning electron microscopy. Cracks inside the bulk of iron and coves on the surface above cracks were observed.

The hydrogen content in the samples was measured directly after loading and the pressure in the cracks was deduced from Sievert's law. This made it possible to identify a mechanism of crack formation.

In iron samples of different purity the crack formation was located either at the grain boundaries or inside the grains, both together was not observed. A dependence on the purity of iron is likely.

Hydrogen in V: isotope effects and site occupancy

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Abstract

We discuss the influence of site occupancy on the absorption of the hydrogen isotopes H and D in thin V(001) layers. By growing V(001) under biaxial compressive strain in a Fe/V(001) superlattice, the hydrogen is forced to reside exclusively in octahedral sites, even at the lowest concentrations. Two layer thicknesses of V(001) are used to elucidate the effect of confinement on the absorption of the two isotopes. Significant weakening of the isotope effects is observed, when the hydrogen resides in tetrahedral sites as compared to octahedral sites.

Apparatus for In-situ Defect Analysis (AIDA) Investigations on Fe₆₀Al₄₀ Phase transition

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We performed in-situ annealing investigations of 250 nm Fe₆₀Al₄₀ thin films. The magnetic properties of disorderd Fe₆₀Al₄₀ thin films change from the ferromagnetic to paramagnetic state du to annealing. No conclusive discussion of that phase transtion as a function of the open volume defects exists in the literature. First results on the Fe₆₀Al₄₀ annealing driven magnetic phase transition between the ferromagnetic A1 phase and the paramagnetic B2 phase as a function of the open volume defects will be shown. The magnetization of the film after each annealing step indicates its progress reflecting chemical ordering of the alloy and dinishing of ferromagnetism [1]. Fig. 1 shows the temperature dependence of the positron annihilation spectroscopy (PAS) S-parameter indicating the open volume defects evolution during annealing. The defects are very stable with respect to annealing and do not directly relate to the change of magnetic properties. Our results indicate that Fe₆₀Al₄₀ could be a promising candidate for Hydrogen storage due to a large amount of stable defects. Through hybridisation the electronic structure can be modified, combined with a local lattice distortion. Hydrogen can therefore be viewed as a tool to modify the electronic structure, allowing tuning of the magnetic properties as a consequence.

For the in-situ annealing we have utilized a unique high vacuum system combining material evaporation and ion beam modification with positron annihilation spectroscopy. The system has been developed and installed in the Helmholtz-Zentrum Dresden-Rossendorf. The system is capable to perform Doppler broadening spectroscopy as well as resistometry and provides a monoenergetic positron beam pre-accelerated in the range of 80 eV to 35 keV thus enabling sample depth profiling.

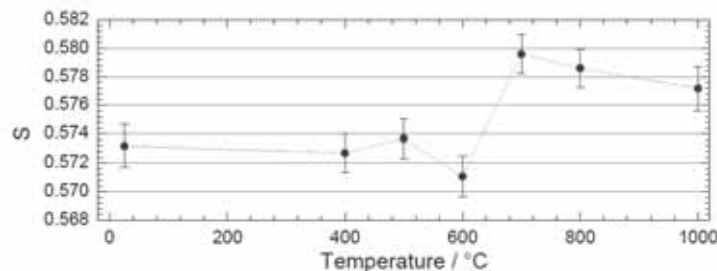


Figure 1. S-parameters (S scales with the amount and the size of defects) of Fe₆₀Al₄₀ as a function of the annealing temperature. The open volume defects prove stability and insensitivity to annealing.

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Structural properties of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17-x}\text{Mn}_x$ alloys and its deuterides

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Titanium based amorphous and quasicrystalline materials have very desirable properties, like high strength, high corrosion resistance and good soft magnetic properties. Moreover, such alloys containing Zr and Ni have a potential to be used for hydrogen storage tanks and M-NiH batteries because in such alloys it is possible to obtain high hydrogen concentrations (above 2 wt.%) that can be achieved under reasonable thermodynamic conditions.

Our work is focused on amorphous and quasicrystalline $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17-x}\text{Mn}_x$ alloys ($x=2, 4$). These materials were produced at ambient temperature by mechanical alloying using high energy planetary ball mill. The basic alloys and the resulting deuterides were examined by in-situ X-ray and neutron diffraction in ambient and non-ambient temperatures. Deuterium sorption measurements in Sieverts apparatus were made, as well. In appropriate conditions it was possible to deuteride these amorphous materials without losing of their amorphous state. According to the neutron diffraction data, that enable tracking of deuterium within the material, interesting phase transitions caused by deuterium were evidenced. Namely, amorphous deuterides transform into very unusual phase, where only two sharp maxima in diffraction pattern were visible. Positions of these reflections are similar to the main reflections observed for deuterided quasicrystalline material what proves, that the material after deuterization remains amorphous.

Formation in Ternary Ti-V-Mn Alloy in the Hydride Cycle, Their Interaction With Hydrogen

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Abstract

Formation in Ternary Ti-V-Mn Alloy in the Hydride Cycle, Their Interaction With Hydrogen

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In recent years, the study of Ti based BCC phase alloys, due to their remarkable hydrogen absorbing ability, take up a special place in investigations of some laboratories and research centers in the world. Of particular interest are the hydrogen absorbing, α , β , γ phase alloys in Ti-V, Ti-V-Mn, Ti-V-Cr systems [1-7].

In the Institute of Chemical Physics after A.B. Nalbandyan of Armenian NAS, a new “Hydride Cycle” (HC) method has been developed for synthesis of binary and multicomponent alloys [3]. The essence of HC consists in combination of two methods: self-propagating high-temperature synthesis (SHS) of transition metal hydrides, and dehydrogenation-sintering. The present work provides the results of study of the mechanism of formation of the ternary Ti-V-Mn alloys in HC.

TiV1.2Mn0.8; TiV0.8Mn1.2; Ti0.37V0.25Mn0.25 alloys were synthesized. The peculiarities of interaction of these alloys with hydrogen were studied. It was shown that the synthesized alloys interacted with hydrogen a) in the combustion mode and b) at rather low temperature, 25-50°C, after short-time activation of alloy (400°C, 30 min.) This interaction resulted in forming high hydrogen content (2.5-3.5 wt %) TiV1.2Mn0.8H3.7; TiV0.8Mn1.2H2.35 and Ti0.37V0.38Mn0.25H1.56 hydrides. The phase composition of the synthesized alloys and their hydrides were determined by X-ray analysis. The lattice parameters were defined. In the synthesized alloys the main was BCC phase. XRD of hydrides showed that at interaction of alloys with hydrogen, a BCC phase transition to FCC structure occurred [4, 6, 7]. Such a phase transition is peculiar also for BCC binary alloys, such a phase transition is peculiar also for BCC binary alloys. For example, it occurs at interaction of Ti-V and Ti-Nb alloys with hydrogen [3]. The identity of structure, hydrogen content and thermal properties of alloy hydrides, synthesized by both the SHS combustion and short-term activation methods, was manifested by X-ray diffraction, chemical and DTA analyses.

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IMPEDANCE SPECTROSCOPY FOR CHARACTERIZATION OF OXIDIZED TITANIUM HYDRIDE POWDERS

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The results of studying of electroconductive properties of titanium hydride powders, oxidized by air oxygen in different oxidation conditions with the aim to create oxide and oxohydride coatings on the particles' surface, improving the hydride thermal stability, are presented [1-3]. Using the impedance spectroscopy the contribution of the formed coatings' resistance, as well as titanium hydride grains particles' resistance, in the total resistance of powder was defined. The methodical aspects of powder materials impedance measurements by step by step compression of the sample [3-6], as well as a general approach to processing of experimental data in relation to metal hydrides studies, which containing shielding films on the particles' surface with different chemical composition, are considered.

The obtained data show wide possibilities for using impedance spectroscopy to solve various fundamental and applied problems connected with studying of properties of powder materials particles' coatings.

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Hydrogen Storage in Nanostructured TiFe Processed by High-Pressure Torsion

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When TiFe is plastically deformed by high-pressure torsion under a pressure of 6 GPa, it absorbs and desorbs ~2 wt.% hydrogen at room temperature for many cycles without any requirement to activation process, whereas TiFe usually does not absorb hydrogen without a sophisticated activation process. The absorption pressure is 2 MPa in the first hydrogenation cycle, but it decreases to 0.7 MPa in the latter cycles. The HPT-processed TiFe is not deactivated even after storage for several hundred days in the air or even after repeated hydrogenation/dehydrogenation and exposure to air. The HPT-processed TiFe exhibits heterogeneous microstructures composed of nanograins and rather coarse-grains and amorphous-like phases. The mechanism for easy activation and high resistance to deactivation of HPT-processed TiFe is proposed in details at the presentation (see Fig. 1).

Details of this work were published in Refs. [1,2].

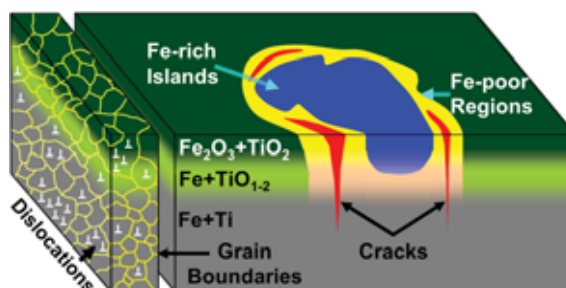


Figure 1. Schematic illustration of activation mechanism by high-pressure torsion. Generation of lattice defects (dislocations and grain boundaries) by high-pressure torsion and resultant enhanced atomic diffusion result in surface segregation and formation of catalytically active Fe-rich islands, Fe-poor regions and cracks. Grain boundaries and cracks serve as pathways to transport hydrogen to interior of sample through oxide layer.

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Reduction and Unusual Recovery in the Reversible Hydrogen Storage Capacity of $V_{1-x}Ti_x$

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Vanadium (V) is considered one of promising hydrogen storage materials since it can absorb and desorb a large amount of hydrogen at ambient conditions [1]. For practical application, its relatively high cost is a bottleneck, and for that reason alloying V with other inexpensive elements is necessary. However, alloying V with other elements often leads to unfavorable changes in hydrogen storage properties like reduction in an initial maximum hydrogen storage content [2,3] and poor cyclic stability [4].

Titanium (Ti) is an essential element for lowering the hydrogen absorption and desorption pressure of V-based body-centered cubic (bcc) alloys without diminishing the initial maximum hydrogen content significantly and therefore it is important to understand how Ti affects on the cyclic stability of V-based bcc alloys. For this purpose, we investigated how the hydrogen storage properties of $V_{1-x}Ti_x$, $x=0.2$ and 0.5 change during hydrogen cycling and evaluated whether the cyclic stability of $V_{1-x}Ti_x$ strongly depends on the V-content or not [5].

$V_{1-x}Ti_x$, $x=0.2$ and 0.5 samples were hydrogenated and dehydrogenated at 410 K and 553 K respectively, for more than 100 times. During hydrogen cycling, reduction in the reversible hydrogen storage capacity was clearly observed from both samples. Unlike V-Ti-Cr ternary alloys, whose cyclic stability is strongly dependent on the V-content [4], no prominent V-effect was found in $V_{1-x}Ti_x$. In fact, the reduction rates of two samples were similar. In addition, the absorption and desorption plateaus got more slanted and hysteresis became noticeably smaller as hydrogen cycling progressed. We found that even after the reversible hydrogen storage capacity of $V_{0.8}Ti_{0.2}$ at 410 K was reduced to 66% of the initial value, at low enough temperature, it could absorb hydrogen as much as it did at the first cycle. In fact, no sign of mono-hydride or secondary phases was seen in the X-ray diffraction data of cycled $V_{1-x}Ti_xH_2$ suggesting that the structure of $V_{1-x}Ti_x$ was retained but heavily distorted by hydrogen cycling. Furthermore, after the low temperature hydrogenation tests, the reversible hydrogen storage capacity of $V_{0.8}Ti_{0.2}$ at 410 K was recovered from 66% to 82% of the initial value. It is most likely that when the cycled sample was fully hydrogenated at low temperatures, metal lattice distorted during hydrogen cycling was restored to a certain degree so that some of tetrahedral sites could accommodate hydrogen even at high temperatures, resulting in an unusual recovery in the capacity.

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Decaying Behavior of $V_{40}(TiCr)_{51}Fe_8Mn$ Hydrogen Storage Alloy with Different Particle Sizes

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The decaying behavior of $V_{40}(TiCr)_{51}Fe_8Mn$ hydrogen storage alloys with different particle sizes from 60 to 500 meshes was investigated systematically in this work. XRD results showed that the main phase of the alloy with different particle sizes before hydrogen absorption is BCC phase and then transformed to BCT phase after hydrogen absorption-desorption cycles. The hydrogen desorption capacity of the alloys decreases when the number of hydrogen absorption-desorption cycles increases, but the decaying rate of hydrogen desorption capacity can be obviously restrained as the particle sizes become finer, varying from 60 up to 400 meshes. The decay of hydrogen desorption capacity has similar exponential rule to the variation of the micro-strain in the alloy lattice during cycling. However, a superfine alloy with 500 meshes showed larger decaying rate, which was possibly attributed to the poisoning by foreign gases. The smaller the particle sizes(60~400 meshes in this work), the smaller the micro-strain in the lattice, namely, the alloy powders with finer size have less micro-stress and correspondingly better cycling stability.

Keywords: hydrogen storage alloy, BCC, BCT, particle size, cycling stability, micro-strain

Improvement in Cyclic Stability and Resistance to Water Impurity in Hydrogen of TiFe-Based Alloy by V Substitution

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We have worked toward the application of TiFe-based alloy to storage of hydrogen produced from water electrolysis using surplus electricity. TiFe requires high temperature for activation treatment and relatively high pressure for assumed operating conditions. Mn substitution for a part of Fe enables both activation at room temperature and plateau pressure adjustment [1]. Plateau pressure between β -hydride and γ -hydride (0.5 to 1 H/M) of TiFe rises and becomes aslope with hydrogen absorption and desorption cycles resulting in decrease of effective hydrogen capacity. In addition, the alloy is expected to be poisoned by water possibly contained in the hydrogen produced from water electrolysis. We preliminarily tried substitution of several elements for a part of Mn in $\text{TiFe}_{0.8}\text{Mn}_{0.2}$, which has an equilibrium pressure in the required range. Among the elements, substitution of V was found to improve cyclic stability. Therefore, in the present study, cyclic property of $\text{TiFe}_{0.8}\text{Mn}_{0.2-x}\text{V}_x$ ($x = 0, 0.05, 0.1$) was investigated using pure hydrogen and hydrogen containing water of 40 ppm (hereinafter wet hydrogen) focusing on the effect of V.

With absorption and desorption cycles using pure hydrogen, the β - γ plateau pressures for $\text{TiFe}_{0.8}\text{Mn}_{0.2}$, $\text{TiFe}_{0.8}\text{Mn}_{0.15}\text{V}_{0.05}$ and $\text{TiFe}_{0.8}\text{Mn}_{0.1}\text{V}_{0.1}$ increased. The increment was reduced with increase of V content. Lattice strain of α -solid solution, β -hydride and γ -hydride of each sample was evaluated from X-ray diffraction. Lattice strain of α -solid solution, β -hydride and γ -hydride increased in accordance with increase of the β - γ plateau pressure. Increase of the plateau pressure is related to formation of lattice strain. Pulverization during cycles was enhanced in V-containing samples. The above results suggest that V substitution promotes pulverization and releases stress due to lattice expansion upon hydrogen absorption, which prevents increase of lattice strain.

Absorption and desorption cycles using wet hydrogen raised the β - γ plateau higher than the pure hydrogen cycles. Ti-rich segregation was observed in the samples after the wet hydrogen cycles by SEM. The results suggested that the water contained in hydrogen caused segregation of Ti and reduction of the Ti content in main phase increased the plateau pressure. The observed number of segregated grains were smaller in samples with a higher V content. It is reported that vanadium ion disperses into TiO_2 and prevent crystallization of the oxide [2]. The V substitution is expected to have an effect on preventing Ti from crystallization and segregation.

Acknowledgement: This research was conducted in collaboration with Takasago Thermal Engineering Co. Ltd., and Integrated Hydrogen System Group of AIST.

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Modification of Interlayer Exchange Coupling in Fe/V/Fe Trilayers Using Hydrogen

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Fe/V/Fe trilayers with either wedged Fe or wedged V sublayers were prepared using UHV (5×10^{-10} mbar) magnetron sputtering [1]. A capping layer of 5 nm Pd was used to prevent oxidation. As a substrate we have used Si(100) wafers with an oxidised surface. The chemical composition and the cleanness of all layers was checked *in-situ*, immediately after deposition, transferring the samples to an UHV (4×10^{-11} mbar) analysis chamber equipped with X-ray photoelectron spectroscopy (XPS). From the exponential variation of the XPS Fe-2p and V-2p integral intensities with increasing layer thickness we conclude that the Fe and V sublayers grow homogeneously. The coercive (H_c) fields were determined from the in-plane hysteresis loop measurements at room temperature.

In the case of the wedged Fe/V/Fe trilayer, the bottom and top Fe layers were deposited in different deposition conditions to obtain relatively high difference in their coercive fields. For a sufficiently small V thickness, the exchange coupling energy is large enough for the simultaneous magnetisation reversal of the bottom and top Fe layers [1]. The magnetisation reversal processes of the two Fe layers are independent for very weak or zero interlayer exchange energy. In that case we have observed two different coercivities H_{c1} and H_{c2} . The observed two significantly different coercive fields are originated from the soft and hard magnetic Fe layers, respectively. In the intermediate case between the fully coupled and the independent (i.e. fully decoupled) Fe layers, the exchange field felt by each layer due to the presence of the second layer decreases (increases) the observed switching field of the soft (hard) magnetic layer in the case of AFM coupling, and vice versa for FM [1]. Results on the coercivity studies as a function of the V interlayer thickness showed near $d_V \sim 3$ nm weak minimum and maximum of H_{c1} and H_{c2} values, respectively. The above behaviour could indicate a weak AFM coupling between Fe layers in agreement with results published very recently in Ref. [2]. Furthermore, we have studied interlayer exchange coupling across vanadium after hydrogenation. It is well known that after hydrogen uptake of Fe/V multilayers, the H atoms reside exclusively in V layer [3]. Therefore the observed modification of the interlayer exchange coupling could be explained in terms of Fermi surface modification [3] and/or change in V thickness.

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Ti-V-Mn Based Metal Hydrides for Hydrogen Compression Applications

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Metal hydride compressors take advantage of the thermodynamic properties of metal hydrides and provide: ultra-high purity hydrogen, have no associated emissions, contain no moving parts and allow for silent operation^[1]. A future application for metal hydride compression may be as part of the hydrogen refuelling network for fuel cell vehicles.

For effective compression, the important requirements for metal hydrides are small hysteresis, large volumetric capacity and the ability to tune plateau pressures^[2].

The technology behind metal hydride compression was first demonstrated in the 1970s with a hydrogen refrigerator using LaNi₅^[3]. Since these early studies, there has been much R&D interest surrounding metal hydride compression, with a focus on both the fundamental and practical considerations - a review of which has been given by Lototsky et al^[4]. However, to be commercially viable, the overall energy efficiency of such systems needs to be increased and the capital cost reduced.

It has been shown that Ti-V-Mn alloys, with C14 Laves and BCC phases, possess good volumetric hydrogen storage capacities, fast reaction kinetics at ambient temperatures and the plateau pressure can be influenced by V substitutions^[5]. In this work, the synthesis of Ti-V-Mn based alloys for use in hydrogen compression applications, was investigated. Alloys were synthesised by arc melting, after which heat treatment was performed at 1233 K for 6 h in vacuum (10⁻⁶ mbar). The effects of composition, microstructure, and crystallography on the hydrogen sorption properties were then examined using SEM-EDS, XRD and Sieverts-PCT measurements.

After studying compositions based on Ti-V-Mn (i.e. Ti_{0.5}V_{0.4}TM_{0.1}Mn, where TM = Nb, Cr, Mo, Ta and Ti_{0.5}V_{0.5-x}Nb_xMn, where x = 0.05, 0.2 and 0.5) it was found that small amounts (0.05 - 0.1 at%) of Nb substituted for V resulted in: a reduction in hysteresis between hydrogen absorption and desorption; a reversible hydrogen storage capacity of 0.8 H/M; and higher hydrogen dissociation pressures of 40 to 45 bar.

This finding has led to the design and construction of a two-stage metal hydride compressor utilising a Ti-V-Nb-Mn alloy in the high pressure stage and an AB₅ type alloy in the low pressure stage. Trials on the system show it is capable of pressurising a 2 L cylinder up to 650 bar from an input pressure of < 10 bar, at a rate of 0.5 g H₂/min.

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Simulation of behavior hydrogen in titanium hydrogen systems TiH_x.

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Study of the behavior of hydrogen in metals and alloys is of great importance due to the practical uses of hydrogen-metal systems for absorption of nuclear radiation, in neutron sources, for storage of hydrogen. This work is devoted to simulation of behavior hydrogen in titanium hydrides.

Atomistic study is based on classical molecular dynamics (MD) and density functional theory (DFT) calculations. LAMMPS [1] is involved for molecular dynamics simulations and VASP [2, 3] as a density-functional code. For macro kinetic simulation of behavior hydrogen in TiH_x we are using OpenFOAM software.

In a classical molecular dynamics inter atomic interactions in titanium are described within angle depended potential (ADP). Hydrogen-metal potential is produced by means of force matching method, taking into account stability of basic Ti-H crystalline structures (calculated within DFT approach). The applicability of different potentials for the description of hydrogen-metal systems is discussed. Diffusion coefficients of hydrogen are estimated from the simulations for different temperatures and hydrogen concentrations in titanium and titanium hydrides. Corresponding migration energies are evaluated and compared with estimates from DFT and experimental data.

For macro kinetic simulation we get Thermal Desorption Spectrum which good corresponding with experimental data.

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Effect of Non-stoichiometry on AB₂ - type Alloys for Improved Hydrogen Storage Properties

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Development of hydrogen technologies is important in order to meet the growing demands for a green energy future. Hydrogen storage studies in metal hydride families have been the focus of attention due to its high volumetric and gravimetric energy density and its practical working conditions [1-3]. Among the different types of metal hydrides, AB₂ type Laves phase alloys are promising due to their easy activation, kinetics and that their operating temperature and pressure conditions are close to ambient. The present work is aimed at developing a hydrogen store based on AB₂ type alloys for a village in West Bengal, India. A challenge for the research project has been to optimise a hydridable alloy which can reversibly store hydrogen at ambient temperature (30 - 35 °C) and in an operating pressure range of 1-15 bar hydrogen. In order to optimise a material for this application, the effect of stoichiometry on the hydrogen storage properties of non-stoichiometric AB₂ type Laves phase (Ti_yZr_{1-y})_{1+x}MnCr_{0.8}M_{0.2} (x = 0, 0.05, 0.075 and 0.1) (M is transition metal) alloys have been studied. X-ray diffraction patterns of these AB₂ type alloys reveal a single phase formation which crystallizes in hexagonal structure with the space group of P6₃/mmc. From isotherm measurements, the maximum hydrogen storage capacity is found to be around 2.2 wt% at 35 bar and 32 °C (Fig. 1), which is approximately 16 % higher than that of the commercially available Hydralloy C (TM). The maximum working capacity (i.e. in the pressure range 1 to 15 bar) was found to be 1.55 wt % which compares favourably with the working capacity of Hydralloy C (TM) which is only 1.3 wt % at these temperature. The hydrogenation kinetics of these alloys are relatively fast reaching full capacity within 10 min and the as prepared alloy requires no special activation procedure. Thermodynamic properties for this range of alloys have been measured by high pressure DSC method ($\Delta H = -26$ to -29 kJ/mol H₂ and $\Delta S = -96$ to -100 J/K/mol H₂) and show good agreement to values calculated from the isotherm experiments.

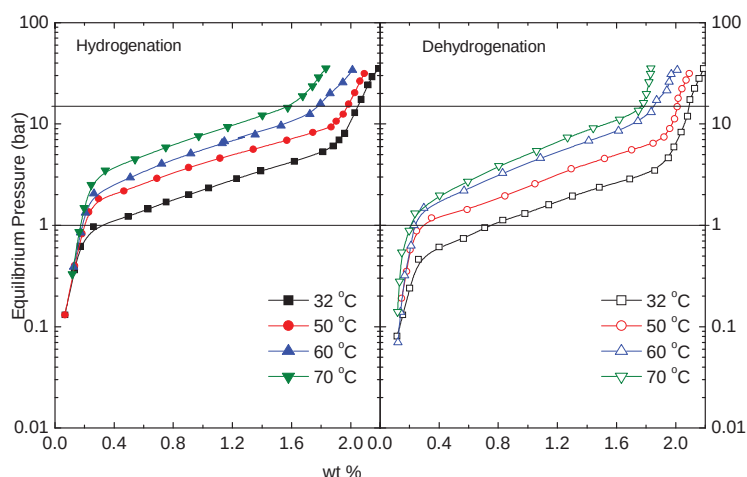


Figure 1. Hydrogenation/dehydrogenation isotherms of (Ti_yZr_{1-y})_{1+x}MnCr_{0.8}M_{0.2}

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A STUDY OF SURFACE OF TITANIUM TARGETS FOR NEUTRON GENERATORS

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The development of tritium and deuterium targets for neutron tubes and generators is a part of the activities in All-Russia Research Institute of Experimental Physics (RFNC-VNIIEF). These items contain a metal substrate (for example, copper) with a titanium film with a few microns thickness deposited on it. Then these metal films are saturated with tritium, deuterium or their mixtures. The significant problem in neutron tubes and neutron generators is the characterization of substrate surface before a deposition of titanium film on it, and analysis of the deposited titanium film's surface before hydrogenation and after a saturation of the film with hydrogen isotopes. The performance effectiveness of neutron tube and generator depends also upon the quality parameters of the surface of initial substrate, deposited metal film and hydrogenated target.

The objective of our work is to study of the target prototype samples, that have differ by various approaches to preliminary chemical processing of copper substrate, and to analyze the integrity of titanium film after its saturation with deuterium.

The research results of copper substrate and of the surface of deposited titanium film with the use of electron microscopy, X-ray spectral microanalysis and laser-spark methods of analyses are presented. The causes of surface defects appearance have been identified. The distribution of deuterium and some impurities (oxygen and nitrogen) along surface and across the height of the hydrogenated film in the target has been established.

This allows us to evaluate the composition homogeneity of the samples and consequently to estimate the quality of hydrogenated samples. As the result of this work the propositions on the advancement of production technology and characterization of target's surface have been presented.

Interesting Hydrogen Storage Capability in Manganese Oxide

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Hydrogen is the lightest element and the most abundant of all the universe. For many years, we are studying different techniques to be able to store hydrogen which remains one of the main problems that hinder its spread as an energy vector. The hydrogen storage in solid phase is emerging as one of the most promising. Among all the studied materials particular consideration should be directed toward the class of polymers[1].

In this work, a Poly(ether ether ketone) (PEEK) was chosen as a base polymeric matrix with the aim of producing a low cost and weight hydrogen storage material. The polymer acts as a support for the anchoring of a manganese oxide, through a substitution in situ reaction between the chloride of the chlorine-sulphonic group of the PEEK and potassium permanganate used to produce the above mentioned oxide. The functionalised and composite polymer were characterized by CHNS-O, BET, SEM-EDX, XRD and TEM.

The manganese oxide content was related to the potassium permanganate concentration, time and temperature reaction. The oxide introduction modifies the starting material in terms of XRD profile, the morphology and the surface area. In fact, a slight increase was registered revealing the possibility to store hydrogen up to a 1.2%wt in cryogenic conditions (77 K)[2]. This profile is recorded for the sample containing 15%wt manganese oxide. On the same typology material a gravimetric measurement at T> room temperature a pressure range between 2-60bar was conducted obtaining encouraging results (0.3wt% at 50°C and 80bar). Very promising results were obtained with a polymer containing 78wt% manganese oxide, reaching a value of about 1wt% through Sievert apparatus at 110°C/60bar. Increasing the temperature reaction of the manganese oxide was recorded 1.1%wt in less drastic conditions (110°C/10bar) (fig. 1).

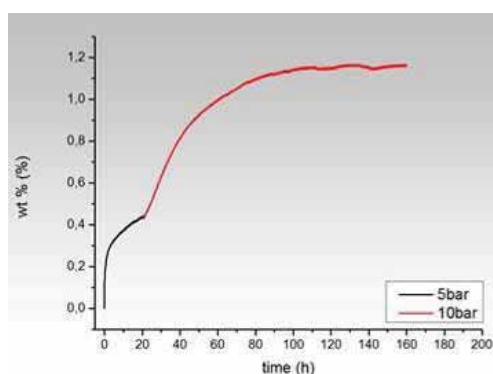


Figure 1. H₂ sorption profile at 110°C.

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HREM Observation and High-Pressure composition Isotherm Measurement of $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ Quasicrystal Powders Synthesized by Mechanical Alloying

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Icosahedral (i) quasicrystals have a new type of translational long-range order, and possess more tetrahedral interstitial sites, where hydrogen atom can locate [1]. Ti and Zr have a strong chemical affinity for hydrogen, while Ni is catalysis to decompose hydrogen molecules into the atoms. Therefore, Ti-Zr-Ni quasicrystals seem to have a large hydrogen capacity and good hydrogen desorption characteristics. One of the authors (AT) previously measured the pressure-composition (PC) isotherms at low-hydrogen pressure (measurable upper limit was 0.13MPa) [2]. In this study, we focus on HREM observation and measurement of PC isotherms at high-hydrogen pressures (up to 2 MPa) for Ti-Zr-Ni powder mixtures after mechanical alloying (MA) and subsequent annealing. The measurements of PC isotherm were performed at temperatures of 523 K, 573 K and 623 K using a Sieverts' type apparatus. Powder X-ray diffraction measurements were also made before and after PC measurements. The powders after MA were amorphous, but a subsequent annealing caused the formation of the i-phase with Ti_2Ni type crystal phase as a minor phase. Fig. 1 shows a digital diffractogram of an observed high-resolution image of the powder sample after MA and subsequent annealing (FFT image of an high-resolution lattice one), which exhibits ten-fold symmetry. The maximum hydrogen storage capacity (H/M) at 523 K was about 1.3, which decreased with increasing hydrogenation temperatures. All the PC isotherms were steep, and no plateau pressure was detected.

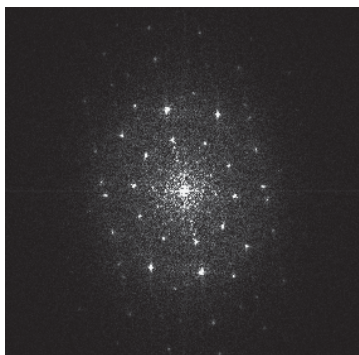


Figure 1. Digital diffractogram of an observed high-resolution image.

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The hydrogen storage performance of $\text{LaMg}_{11}\text{Ni}+x\%\text{Ni}$ ($x = 100, 200$) alloys prepared by mechanical alloying

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In order to improve the hydrogen storage performances of REMg_{12} type alloys, ball milling technology was used for preparing nanocrystalline/amorphous $\text{LaMg}_{11}\text{Ni}+x\%\text{Ni}$ ($x = 100, 200$) composite. Thermal stability of the as-milled alloy after hydrogenated was studied by means of differential scanning calorimetry (DSC). The gaseous hydrogen absorption capacity and kinetics of the as-milled alloys were measured by an automatically controlled Sieverts apparatus. The electrochemical hydrogen storage characteristics of the alloys were tested by an automatic galvanostatic system. The electrochemical impedance spectra (EIS), Tafel polarization curves and potential-step curves were also plotted by an electrochemical workstation (PARSTAT2273). The results indicate that the as-milled alloys exhibit a nanocrystalline and amorphous structure, and the amorphization degree of the alloys visibly increases with the milling time growing. The thermal stability of the metal hydride clearly decline with the milling duration pronging. The gaseous hydrogen absorption capacity and kinetics of the as-milled alloys first augment and then drop with the milling time rising, and the optimal milling time is 20 h. Prolonging the milling duration markedly enhances the electrochemical discharge capacity and cyclic stability of the alloys, but the electrochemical hydrogen storage kinetics of the alloys has a maximum value with the milling time varying.

Formation Mechanism of Micro/nano-structures through Competitive Reactions in Mg/Cu Super-laminate Composites during Initial Hydrogenation

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Mg is one of the promising candidates among hydrogen storage materials because of its abundance, inexpensiveness, light weight, and hydrogen absorption capacity of 7.6 mass% to form MgH₂. However, the standard formation enthalpy of MgH₂ is -76 kJ(mol H₂)⁻¹ and too low to achieve hydrogen desorption under moderate conditions. Another problem is the sluggish reaction of Mg with H₂ gas. Thus, various Mg-based alloys and compounds have been investigated to improve the rate and to lower the temperature of hydrogen sorption. Super-laminate composites (SLCs) have been attracting attention since Ueda et al. reported that Mg/Cu SLCs showed reversible hydrogen sorption at 473K [1].

The improvement of hydrogen sorption kinetics, its relations with microstructures, and the effect of initial structures of Mg/Cu SLCs on hydrogen sorption properties have been reported in previous papers for Mg₂Cu-H₂ system [2, 3]. However, these are not fully understood yet. In this paper, we propose the formation mechanism of micro/nano-structures through competitive reactions in Mg/Cu SLCs during initial hydrogenation.

We expect that micro/nano-structures of Mg/Cu SLCs after initial hydrogenation change depending on whether hydrogenation of Mg starts before alloying Mg with Cu or after. In order to ascertain it, Mg/Cu SLCs, pellets of MgH₂ and Cu, and those of MgH₂ and Mg₂Cu powder as references were prepared and their micro/nano-structures were examined with a scanning electron microscope (SEM). Mg/Cu SLCs were hydrogenated at 573 K and 3.3 MPa of H₂ for 86.4 ks with a Sieverts' type instrument, whereas two kinds of pellets were heated at various temperatures and hydrogen pressures for 86.4 ks with a Sieverts' type instrument. SEM observations revealed that our expectation was correct to show references representing the characteristic micro/nano-structures of Mg/Cu SLCs after initial hydrogenation..

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Microstructures and Hydrolysis Behaviors of Mg-Ca Hydrides Synthesized by Different Ball-milling Processes

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Microstructures and hydrolysis properties of Mg-Ca hydrides obtained by different synthetic methods, including direct hydrogenation after ball-milling (DHBM) and ball-milling in H_2 atmosphere (BMIH), were investigated in this paper. The products were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). It was found that two different kinds of ternary alkaline earth hydrides, namely $Ca_4Mg_3H_{14}$ and $Ca_{10}Mg_8H_{54}$, with Mg-Ca alloy as starting material were synthesized by DHBM and BMIH, respectively. Their hydrolysis properties, mainly hydrogen yields and the rate of hydrogen evolution were studied in deionized water near room temperature. The results showed that the Mg-Ca hydride prepared by BMIH has faster hydrogen generation rate (hydrolyzed 100% in 20 min) and higher overall hydrogen yield (1512 ml g^{-1} in 20 min) than that prepared by DHBM. This phenomenon is due to the different components and microstructures of the hydrides made by various processes. The synthesis mechanisms of Mg-Ca hydrides prepared by different means are also discussed from kinetics point of view.

Keywords: hydrolysis; hydrogen generation; Mg-Ca hydride; microstructure

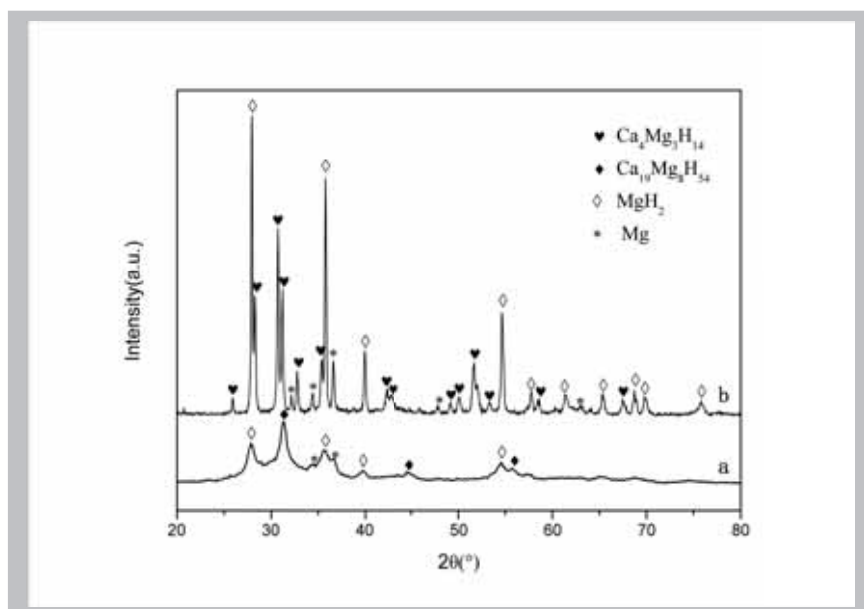


Figure 1. XRD patterns of Mg-Ca hydrides synthesized by (a) ball-milling in H_2 atmosphere (BMIH); (b) direct hydrogenation after ball-milling (DHBM).

Mg–Al–H Hydrogen Storage Systems: Preparations, Reaction Mechanisms and Hydrogen Desorption Properties

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MgH₂ possesses a high hydrogen capacity (7.6 wt%), but suffers from high thermal stability ($\Delta H_f = -74$ kJ/mol) and low sorption kinetics. In this work, the as-received metallic Al and the as-prepared AlH₃ were ball milled respectively with MgH₂ to tailor the hydrogen storage properties of MgH₂. Hydrogen desorption measurements show that both Al and AlH₃ can reduce the onset desorption temperature and improve the desorption kinetics of MgH₂. Moreover, AlH₃ is better regarding its ability to improve the desorption properties (see Figure 1b). This superiority is ascribed to the fact that AlH₃ is a brittle metal hydride, which makes it easier to mix with MgH₂ well by short-term milling. Besides, the oxide-free Al* formed *in situ* from the decomposition of AlH₃ is high in chemical activity and will benefit the reaction kinetics with MgH₂. Further investigations on the structures evolution of the MgH₂–1/4AlH₃ during desorption process demonstrates that desorption is composed of two stage with the self-decomposition of AlH₃ as the Stage I and the decomposition of MgH₂ as the Stage II. In addition, the Stage II is a two-step process with the reaction of MgH₂ and Al* forming Mg₁₇Al₁₂ as the Step I and the self-decomposition of the residual MgH₂ as the Step II (see Figure 1a). Under the conditions of 300 °C and 5 MPa H₂, the MgH₂–1/4AlH₃ composite can uptake hydrogen of 5.82 wt% (H/M) within 1 h. The absorption kinetics of MgH₂ in the MgH₂–AlH₃ composites are also improved compared with the pure MgH₂.

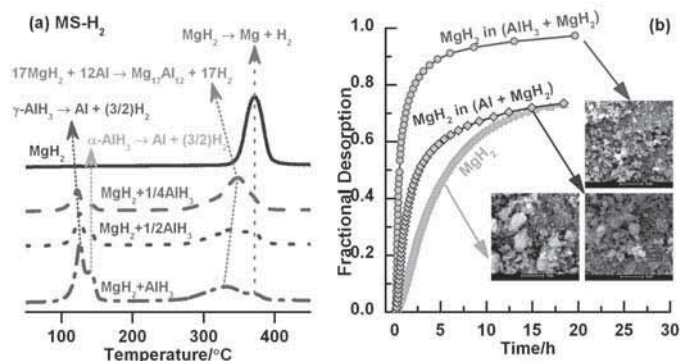


Figure 1. Hydrogen desorption properties of the Mg-Al-H systems.

Acknowledgements: This work was supported by the National 973 Program (NO.2010CB631304) and National NSFC (NO.51171168).

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Study of the hydrogenation/dehydrogenation process in the Mg-Ni-C-Al system

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Magnesium hydride (MgH₂) has been extensively studied due to its high hydrogen capacity (7.6 wt.%) and low manufacture costs. Despite these interesting properties, its practical use as hydrogen storage material is prevented by high dehydrogenation temperatures (around 620 K) and slow kinetics. The addition of metal elements and catalysts improves the kinetics and decrease the hydride stability. In particular, it has been reported that carbon materials act as efficient catalysts in H₂ sorption reactions and are good anti-sticking agents towards Mg [1]. Moreover, the activation barrier of H desorption is reduced in aluminium doped MgH₂ [2].

In this work we present a detailed study of the hydrogenation and dehydrogenation processes of a nanostructured Mg-Ni-C-Al obtained via High Energy Ball Milling. The sample doped with TiO₂ catalyst, has been characterized by means of pressure-composition isothermal analyses, concomitant thermogravimetric and differential scanning calorimetry analysis and anelastic spectroscopy.

The dehydrogenation takes place in two steps likely due to the formation of two different phases during the hydrogenation process. The enthalpy and the activation energy measured for the main hydrogen desorption are lower than those ones reported for magnesium hydride [3]. Possible models to explain the nature of the different hydrides phases and of the decomposition steps are discussed.

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Hydrogen Decrepitation of Mg Rich Intermetallics

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The production of metal hydride canisters may involve mechanical milling of the alloy powders under protective atmosphere and filling them into the canister in a glove-box environment. Such processes are often quite costly, and it is desirable to find a process which does not necessitate the use of protective atmosphere. Hydrogen decrepitation is one such process which involves in-situ pulverization of hydrogen storage alloys. The process starts with coarse alloy powders filled into a canister in open atmosphere and then subjected to several cycles of severe hydrogenation and dehydrogenation treatments which reduce the particles into submicron sizes[1]. Two alloys were selected in the current study; Mg₂Ni and Mg₂Cu. The alloys were prepared by skull melting in an induction furnace using a cold crucible. Both Mg₂Ni and Mg₂Cu were melted under high pressure argon atmosphere due to high partial pressure of Mg. Solid alloys obtained in this way were pulverized by crushing them in a mortar and sieved to yield particles within 63-53 µm range. The alloy powders were then subjected to 10 hydrogenation cycles in a custom-made apparatus. Samples from hydrogenation cycles were examined by SEM, laser diffraction and BET analysis techniques so as to follow the decrepitation process. Results showed that Mg₂Ni alloy powder was pulverized easily upon cycling reaching to submicron sizes with no more than three hydrogenation cycles. Mg₂Cu, on the other hand, was resistant to pulverization. This was despite the fact that the alloy was dissociated upon hydriding to MgH₂ and MgCu₂ with 24.6% volume expansion.

The Phase Transition and Hydrogen Storage Properties of $\text{Mg}_{17}\text{Ba}_2$ compound

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Mg-based hydrogen storage alloys are considered as one of the most promising hydrogen storage alloys due to their high hydrogen storage capacity, abundance resources and environment-friendly. However, MgH_2 is limited in practical application for its demerits of high desorption temperature and sluggish kinetics. Many methods have been used to solve these problems. Among them, either changing the reaction method or alloying is an effective way to improve its thermodynamic and/or kinetic properties[1]. Low melting point metal alloying may lead to the high atomic diffusion rate in the alloy and accelerate the de/hydrogenation kinetics. On the other side, the reaction between the different Mg base hydrides could change the enthalpy change. In this paper, $\text{Mg}_{17}\text{Ba}_2$ compound has been prepared using vacuum induction melting. The phase transition and hydrogen storage properties of $\text{Mg}_{17}\text{Ba}_2$ compound during the de/hydrogenation process have been investigated.

XRD patterns show that $\text{Mg}_{17}\text{Ba}_2$ compound reacted with hydrogen and transformed into MgH_2 and Ba_2MgH_6 and then $\text{Ba}_6\text{Mg}_7\text{H}_{26}$. While for the dehydriding process, MgH_2 and $\text{Ba}_6\text{Mg}_7\text{H}_{26}$ transforms into Ba_2MgH_6 and Mg and further formed $\text{Mg}_{17}\text{Ba}_2$. The results show that the reversible hydrogen storage capacity of $\text{Mg}_{17}\text{Ba}_2$ alloy is 4.2wt% H_2 . The alloy could hydrogenate at 543K and dehydrogenate at 633K, which is about 50K lower than pure MgH_2 . The kinetic properties of $\text{Mg}_{17}\text{Ba}_2$ compound was also measured. The hydrogenation activation energy and dehydrogenation activation energy are calculated to be 126kJ/mol and 173.92kJ/mol, respectively.

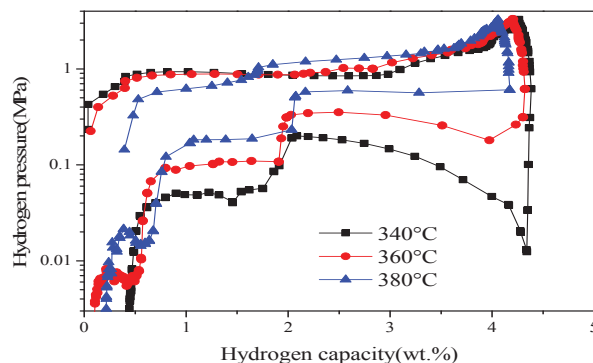


Fig.1 PCI curves of $\text{Mg}_{17}\text{Ba}_2$ alloy measured at different temperatures.

Fig.1 is the PCI curves of $\text{Mg}_{17}\text{Ba}_2$ alloy measured at temperatures of 613, 633, and 653 K. As shows, two dehydrogenation platforms have been found, which indicates two-step dehydrogenation reaction mechanism. The in-situ XRD results showed that the dehydrogenation reaction mechanism of the hydrogenated $\text{Mg}_{17}\text{Ba}_2$ hydrides contains two steps. For the first step, $\text{Ba}_6\text{Mg}_7\text{H}_{26}$ and MgH_2 reacted with each other and release hydrogen, and then transformed into $\text{Mg}_{17}\text{Ba}_2$ and Ba_2MgH_6 . For the second step, Ba_2MgH_6 further reacted with MgH_2 and transformed into $\text{Mg}_{17}\text{Ba}_2$ and release hydrogen. The retained MgH_2 transformed into Mg and H_2 at last was also observed at 633 and 653 K as shown in Fig 1 as indicated by the arrow.

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Novel Mg-In-Ni Ternary Alloys for Reversible Hydrogen Storage

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Mg is considered to be a promising metallic hydrogen storage material mainly because of high capacity (theoretically 7.6 wt.% for MgH₂). However, stable thermodynamics of MgH₂ hinders its practical applications. Composition and structure modification have been proven to be effective in improving its hydrogen storage properties. For example, we found that Mg(In) and Mg(In,Al) solid solutions could be reversibly formed by dehydrogenating from their hydrogenated products with lowered desorption enthalpy [1]. Herein we investigate the reversible phase transformation of Mg-In-Ni ternary alloys during de-/hydrogenation cycles, and their dehydrogenating thermodynamic and kinetic properties.

The Mg₉₀In₅Ni₅ alloy was prepared by mechanical milling Mg(In) solid solution and Ni powders. The result indicates Ni could not get dissolved in Mg. Upon hydrogenation, the milled Mg₉₀In₅Ni₅ sample transforms to MgH₂ and a ternary alloy phase. After dehydrogenation, Mg and another ternary alloy phase with tetragonal structure are formed. Those two new unknown ternary alloy phases are fully reversible in the de-/hydrogenation cycles. Therefore, the reversible phase transformation in the Mg-In-Ni ternary system is different from that previously found in the Mg-In binary alloy. The Ni addition also greatly improves the dehydrogenation kinetic of MgH₂. The dehydrogenating activation energy of Mg₉₀In₅Ni₅ alloy decreased to 92.8 kJ/mol, and the PCI testing could be carried out at a lower temperature of 230 °C (Figure 1).

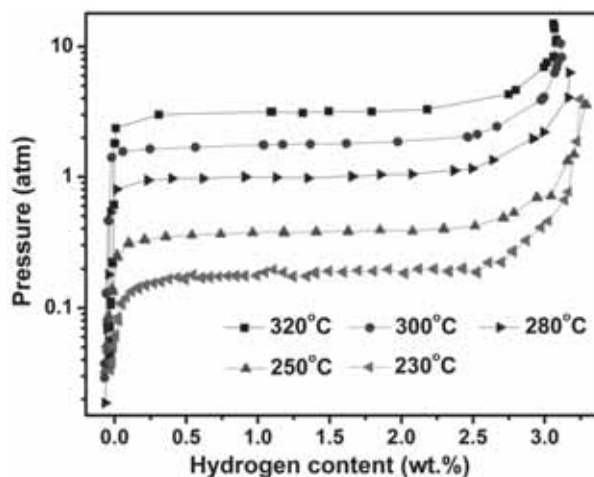


Figure 1. The PCI curves for hydrogen desorption of Mg₉₀In₅Ni₅ alloy.

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Structure and Hydrogen Storage Properties of the NdMg T_4 ($T = \text{Co, Ni}$) Compounds

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Recently, ternary RE-Mg-Ni intermetallic compounds (IMC) attracted much interest as potential hydrogen storage materials and electrodes of Ni-MH batteries [1]. Hydrogenation properties of REMg T_4 (RE=Y,Ce; $T = \text{Co, Ni, Cu}$) intermetallics were studied and substantial peculiarities for different transition metals were demonstrated [2,3]. In this work, new ternary NdMgCo $_4$ and pseudo-ternary NdMgCo $_2$ Ni $_2$ IMC have been obtained. Their hydrogenation behavior has been studied in detail and compared with that of the isostructural NdMgNi $_4$ compound [4].

The alloys were prepared by powder metallurgy method from the Nd T_4 alloy precursor and Mg powder. The mixtures were annealed under argon atmosphere at 800 °C for 8 h and quenched to room temperature. Powder XRD analysis showed formation of single phase alloys with cubic $MgCu_4Sn$ structure type (sp.gr. $F-43m$; $a = 7.0947(5)$ Å, 7.1184(1) and 7.0742(1) Å for NdMgNi $_4$, NdMgCo $_2$ Ni $_2$ and NdMgCo $_4$, respectively).

The NdMg T_4 compounds readily absorb hydrogen at room temperature and 1-2 MPa H_2 pressures. NdMgCo $_4$ compound shows significantly higher hydrogenation capacity (6.5 at.H/f.u.) than NdMgNi $_4$ (4 at.H/f.u.) and NdMgCo $_2$ Ni $_2$ (4.8 at.H/f.u.). More stable hydride was observed at 5.2 at.H/f.u. content for NdMgCo $_4$. Structural parameters of NdMgNi $_4$ H $_4$ hydride are in good agreement with those of NdMgNi $_4$ D $_{3.6}$ [4], with a lowering of crystal symmetry from the cubic structure of the parent compound towards an orthorhombic structure ($Pmn2_1$ space group) for the hydride.

The same cubic structure as the parent compound was maintained for NdMgCo $_2$ Ni $_2$ and NdMgCo $_4$ hydrides. We obtained the following lattice parameters for NdMgCo $_2$ Ni $_2$ H $_{4.8}$ and NdMgCo $_4$ H $_{5.2}$ hydrides: $a = 7.5345(4)$ Å, $\Delta V/V = 18.6\%$ and $a = 7.5035(2)$ Å, $\Delta V/V = 19.3\%$, respectively. PCT measurements showed the existence of lower hydride phase in the NdMgCo $_4$ - H_2 system with H content ~ 4 at.H/f.u., however, its structure has not been solved yet.

The influence of the hydrogen absorption on the magnetic properties of NdMg T_4 compounds ($T = \text{Ni, Co}$) has been investigated. A significant magnetic order is observed below 50 K for the intermediate NdMgNi $_2$ Co $_2$ compound, which disappears upon H absorption. On the other hand, an increase of the magnetization is observed for both NdMgNi $_4$ and NdMgCo $_4$ upon H absorption.

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Hydrogen Storage Properties of the RE₄MgCo (RE=Y, Nd, Tb) Compounds

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The ternary Rare Earth metal - Transition metal - Magnesium systems have been studied intensively in the last years in order to obtain new intermetallic compounds (IMC) and investigate their crystal structure and properties. Special attention was paid to the hydrogenation of the selected binary and ternary compounds. Hydrogen storage properties have been studied for RE₄MgNi compounds [1]. The existence of the RE₄MgCo intermetallics [2] was confirmed in this work and their hydrogen storage and magnetic properties were investigated.

The RE₄MgCo alloys were prepared by powder metallurgy route from the mixture of RE₄Co alloy and Mg. The powder mixtures were pressed into pellets, sintered at 800...900 °C and then annealed at 500 °C for 300 h. The prepared alloys were characterized by powder X-ray diffraction (DRON-2.0, Fe K α -radiation).

RE₄MgCo (RE = Y, Tb) hydrides have been synthesized by gaseous hydrogenation at room temperature and 10-20 bar pressure. Tb₄MgCo compound absorbed 10 at.H/f.u., however, XRD data has demonstrated only partial hydrogenation. The corresponding hydride (str. type Gd₄RhIn, sp. gr. *F*-43m, *a*=14.5322(3) Å, $\Delta V/V=23$ %) was observed together with the initial IMC and TbH₃. Y₄MgCo compound has absorbed 12 at.H/f.u. (*a*=14.5507(19) Å, $\Delta V/V=20.9$ %). We analyzed the interstices and possible blocking between H-atoms in the Y₄MgCoH₁₂ structure. It was shown that the H occupancy occurs into 3 types of octahedral and 5 types of tetrahedral sites. The calculated hydrogen storage capacity is equal to 11.75 at. H/f.u., which is very close to the experimentally observed value. The corresponding deuteride will be studied by neutron diffraction to confirm this hypothetical structure. The Nd₄MgCo hydride has been synthesized by gaseous hydrogenation at 120 °C temperature and 0.3-1 bar pressure and is characterized by ~12 at.H/f.u. capacity (*a*=14.979(4) Å, $\Delta V/V=25$ %).

The magnetic properties of the RE₄MgCo compounds have been studied with a Physical Properties Measurement System. We have observed that the magnetic properties of RE₄MgCo compounds depends substantially on the RE element. Y₄MgCo shows a ferromagnetic behaviour from 2 to 300 K, with a small decrease of the saturation magnetization upon heating. Both Nd₄MgCo and Tb₄MgCo display magnetic transitions at low temperature, which can be attributed to RE order. At 2K, the hysteresis cycle of Tb₄MgCo presents several abrupt transitions, whereas a soft variation is observed for Nd₄MgCo.

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HYDROGEN ASSISTED PHASE TRANSITION IN A TRIHYDRIDE MgNi₂H₃ SYNTHESISED AT HIGH H₂ PRESSURES: THERMODYNAMICS, STRUCTURE AND CHEMICAL BONDING

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MgNi₂ intermetallic alloy was synthesized by powder metallurgy and crystallizes with a Laves type C36 hexagonal structure (Sp.gr. *P6₃/mmc*; *a*=4.826; *c*=15.832 Å). MgNi₂ was loaded with hydrogen or deuterium at 300 °C and a gas pressure from 2.7 to 7.2 GPa. The resulting powders with compositions close to trihydrides MgNi₂H₃ and MgNi₂D₃ were quenched to the liquid N₂ temperature, recovered to ambient pressure and examined by X-ray and neutron diffraction, magnetization measurements and hot extraction. Rietveld profile analysis of the X-ray diffraction pattern showed that formation of MgNi₂H₃ is associated with a complete rebuilding of the initial hexagonal structure into the orthorhombically distorted MoSi₂-type sublattice (Sp.gr. *Fmmm* (No. 69); *a*=4.56; *b*=4.69; *c*=8.80 Å; Mg in 4*a* and Ni in 8*i*). Neutron diffraction of the MgNi₂D₃ was performed at 100 K at the DN-2 time-of-flight diffractometer installed at the IBR-2M pulsed nuclear reactor, Joint Institute for Nuclear Research in Dubna, Russia. D atoms fill 4*b* and 8*f* sites having octahedral Mg₄Ni₂ (D1/4*b*) and planar Ni₂ (D2/8*f*) coordinations. The closest interatomic distances are: Mg–D 2.30; Ni–D 1.71 and D–D 2.30 Å. In the frame of the DFT, calculations of the electronic structure showed a charge transfer from Mg (–1.55 e[–]) to Ni (+0.18 e[–]), H1 (+0.6 e[–]) and H2 (+0.3 e[–]). Calculated DOS revealed the formation of a structure around –10 to –6 eV caused by the chemical bonds of H with 3*d*-states of Ni (Figure 1). Calculated enthalpy of formation of MgNi₂H₃ is about –40 kJ/mol-H₂, which is consistent with the fact that the hydride is rather stable at normal conditions and its quick decomposition starts only upon heating above 100 °C (Figure 2).

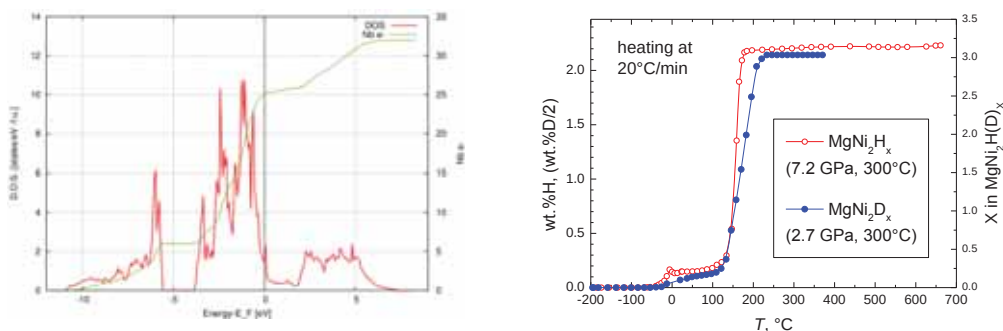


Figure 1 (left). Total DOS of MgNi₂H₃. Figure 2 (right). Hot extraction curves of H₂/D₂. The event at around 0 °C manifests decomposition of a NiH(NiD) impurity.

Thermodynamic Properties of Borohydrides Destabilized by Hydrides of Mg-TM Alloys

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Light metal tetrahydroborates attracted growing attention in the field of solid state hydrogen storage in recent years [1]. Their high gravimetric hydrogen storage capacity makes them attractive candidates for mobile applications. The major obstacle for practical usage of these compounds is the high thermal stability resulting in high desorption temperatures. The introduction of reactive hydride composites (RHCs) [2, 3] meant a substantial progress: The destabilization of the borohydrides by other compounds such as MgH_2 promised a significant decrement of equilibrium temperatures. However, due to kinetic constraints the common desorption temperatures are still rather high.

To address this issue, transition metal hydrides and hydrides of Mg-TM alloys were applied to tailor thermodynamic properties of borohydrides. The approach of this study was to further decrease desorption temperatures by reducing the overall reaction enthalpy. Since the (re-)absorption of systems with low reaction enthalpies requires usually high pressures, hydrogen pressures up to 1000 bar and temperatures up to 300 °C were used to enhance the probability of (re-)absorbing the investigated systems. Furthermore, such high pressures can act as driving force and help to overcome kinetic barriers [4]. The considered systems were characterized by means of ex situ X-ray diffraction analyses at different stages of sorption, coupled differential thermal and thermogravimetric analyses as well as volumetric analyses.

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The $\text{Mg}_2\text{Ni}_{1-x}\text{Co}_x\text{H}_y$ ($0 < x < 1$) Hydrides Obtained by Reactive Milling

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Reactive ball milling is a useful technique to obtain hydrogen storage materials. A compilation of different families among the hydrides synthesised by mechanochemical methods is discussed in [1]. Ternary magnesium based hydrides have been successfully prepared with many transition metals using ball milling techniques [2]. Mg_2MH_y ($y = 4-6$) compounds with $M = \text{Ni}, \text{Fe}, \text{Co}$ have been widely studied with respect to synthesis, structure and hydrogen storage properties [3]. Additionally, the quaternary $\text{Mg}_2(\text{FeH}_6)_{0.5}(\text{CoH}_5)_{0.5}$ hydride has been recently described in literature, where authors claimed on coexistence of two different transition metal complex anions [4] in the same crystalline structure. In present work, we report on the preparation, structure and properties of the complex $\text{Mg}_2\text{Ni}_{1-x}\text{Co}_x\text{H}_y$ ($0 < x < 1$) hydrides.

Hydrides were prepared by reactive ball milling using elemental metal powders in hydrogen atmosphere. Syntheses were performed in Fritsch 4 and 6 apparatus. Obtained materials were characterized by power X-ray diffraction using Bruker D8 and Dron 3M diffractometers. Phase and structural analysis were done by Rietveld refinement using FullProf code. Thermodesorption properties were studied by UGS-3 controlled system. Electrochemical properties were performed in galvanostatic regime at 100 mA/g.

It was found that $\text{Mg}_2\text{Ni}_{0.5}\text{Co}_{0.5}\text{H}_{4.4}$ hydride forms after 2 h of milling at 73 bar initial H_2 pressure. The synthesized quaternary hydride adopts the tetragonal low-temperature Mg_2CoH_5 structure type (space group $P4/nmm$). Refined lattice parameters were found to be $a = 4.5344(6) \text{ \AA}$, $c = 6.5156(13) \text{ \AA}$, $V = 133.97(4) \text{ \AA}^3$. Composition of this hydride is very close to that suggested for $\text{Mg}_2(\text{FeH}_6)_{0.5}(\text{CoH}_5)_{0.5}$, as an equal mixture of the ternary Mg_2NiH_4 and Mg_2CoH_5 hydrides. The hydrogen peak desorption temperature from $\text{Mg}_2\text{Ni}_{0.5}\text{Co}_{0.5}\text{H}_{4.4}$ hydride is 210°C under vacuum. The maximum discharge capacity of the as-prepared hydride is 66.4 mAh/g. These results are discussed and compared with new data for other $\text{Mg}_2\text{Ni}_{1-x}\text{Co}_x\text{H}_y$ ($x = 0.25; 0.75$) mixed complex hydrides.

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Effects of Cu on microstructural evolution and hydrogen storage properties of the $\text{Mg}_{77}\text{Ni}_{20-x}\text{Cu}_x\text{La}_3$ ($x=0, 5, 10$) alloys

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Mg-based hydrogen storage alloys have received considerable interest due to their low cost, high hydrogen storage capacity (7.6wt% for MgH_2 and 3.6wt% for Mg_2NiH_4), lightweight and great abundance [1, 2]. However, high hydrogen desorption temperature (300 °C) and relatively slow kinetics of H-absorption/desorption make them still far from being practically applicable [3]. It is reported that Cu-addition is effective in enhancing the reaction thermodynamics and H-sorption kinetics [4]. In the present paper, the effect of Cu on microstructural evolution and hydrogen storage properties of $\text{Mg}_{77}\text{Ni}_{20-x}\text{Cu}_x\text{La}_3$ ($x=0, 5, 10$) (mole fraction) is studied. The as-cast Mg-based alloys were prepared by a simple and low-cost two-step method of pre-alloying and vacuum induction melting. The phases consist of Mg, Mg_2Ni and $\text{La}_2\text{Mg}_{17}$ phases (see Fig.1). With the substitution of Cu for Ni, all the phases structure do not change expect for a slightly change in lattice parameters of Mg_2Ni phase. The P-C isotherm of the Mg-based alloys were carried out on a sievert-type apparatus, as shown in Fig.2, it has two distinct hydrogen absorption plateaus, which attribute to the Mg and Mg_2Ni phases, respectively. The addition of Cu improves the thermodynamic properties. The formation enthalpy of alloys were calculated by the van't Hoff equation, showing the values of -55.0, -50.4 and -40.0 kJ/mol. H_2 for Mg_2NiH_4 in the $\text{Mg}_{77}\text{Ni}_{20-x}\text{Cu}_x\text{La}_3$ ($x=0, 5, 10$) alloys, respectively.

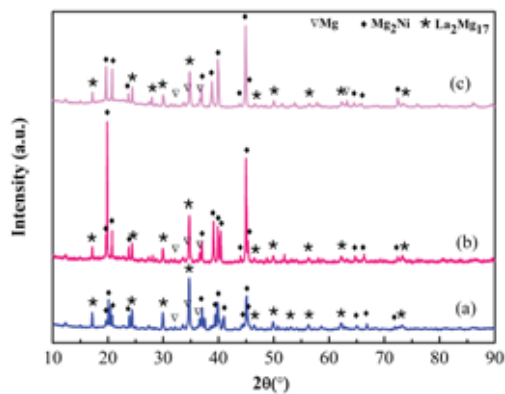


Figure 1. XRD patterns of the $\text{Mg}_{77}\text{Ni}_{20-x}\text{Cu}_x\text{La}_3$ ($x=0, 5, 10$) alloys: (a) $x=0$; (b) $x=5$; (c) $x=10$.

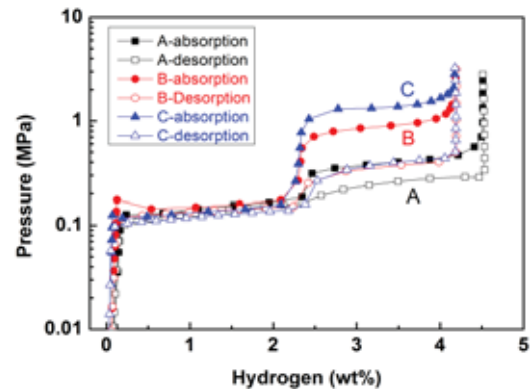


Figure 2. PCI curves of the $\text{Mg}_{77}\text{Ni}_{20-x}\text{Cu}_x\text{La}_3$ ($x=0, 5, 10$) alloys at 300 °C: (a) $x=0$; (b) $x=5$; (c) $x=10$.

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Microstructure evolution and hydrogen storage properties for Mg-Zn-Y ternary alloy

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A new ternary Zn-Mg-Y alloy system for hydrogen storage has been investigated for the first time. SEM images (figure 1) show the microstructure evolution of the Zn-Mg-Y alloys during the first hydrogenation/dehydrogenation cycle. A dendritic structure appeared on the surface of the as-prepared sample particles, and the cross section SEM-BSE image showed that it contained three phases (figure 1, a). XRD results proved that the as-prepared sample was composed of α -Zn-Mg-Y, β -Zn-Mg-Y alloys and Mg_7Zn_3 phases, which upon hydrogenation at 350 °C became $\text{Mg}_x\text{Zn}_y\text{Y}_{(1-x-y)}$ (the major phase) and YH_2 , YH_3 , MgH_2 (minor phases). An interesting morphology with micro-sized spherical protrusions from the surface of the particles was observed for the hydrogenated sample (Figure 1, b). More interestingly, the α -Zn-Mg-Y alloy was reformed after the dehydrogenation, along with the formation of a eutectic structured Mg_7Zn_3 (figure 1, c), showing reversibility for the Zn-Mg-Y system.

The pressure-composition-isotherm (PCI) curve under low H_2 pressure (< 10 bar) showed a plateau (*ca.* 3 bar) with a corresponding capacity of 0.6 wt.% at 300 °C which supported by TGA result. Further investigations are in progress to complete the PCI at high pressure (*ca.* 100 bar H_2).

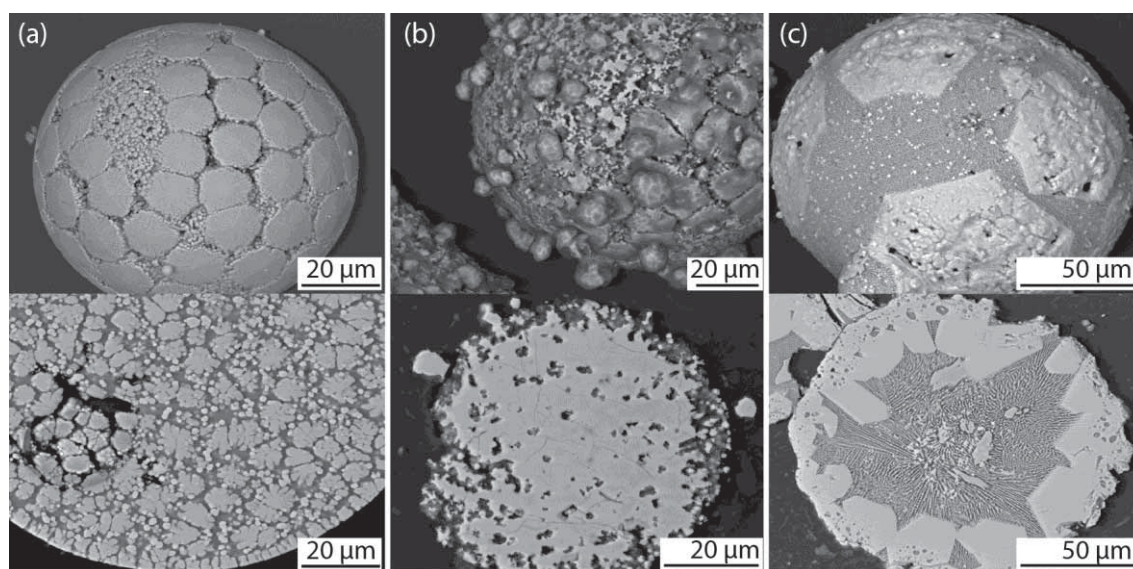


Figure 1. SEM-BSE images of the Zn-Mg-Y alloy particles (top) and their cross-section (bottom): (a) as prepared; (b) hydrogenated at 350 °C; (c) post DSC with decomposition temperature up to 500 °C.

Enhanced hydrogen storage properties in Mg-based hybrids synthesized by severe plastic deformation

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Magnesium with a 7.6 wt.% hydrogen capacity, exceeds the expectations imposed by DOE norms of 5.5 wt.%. However, high pressures (3-10 bar) and temperatures (above 300°C) are required for the absorption of hydrogen and the kinetics of absorption in bulk Mg is slow. To enhance the hydrogen absorption properties (of Mg), Mg based hybrids are synthesized by accumulative roll bonding (ARB). LaNi₅, Mg₂Ni and carbon are incorporated between the layers in the ARB process. After 30 cold rolling passes (with 50% reduction in each pass), the layer thickness decreases below 20 nm. The ARB samples are drilled to impart further severe plastic deformation. It is seen that the hybrid absorbs more than 4.5 wt.% H₂ at 250°C (at a plateau pressure less than 1.5 atm). Kinetics of absorption is also considerably enhanced (~4 wt.% H₂ in 2 min). A fine scale microstructure (with a fine distribution of the phases) along with the strain introduced is expected to be responsible for the enhanced hydrogen absorption properties.

Keywords: Mg-alloy, Hydrogen storage, LaNi₅, Mg₂Ni, Accumulative roll bonding (ARB).

Structural Rearrangement of Mg-containing Superlattices for Superior Hydrogen Storage

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As compared to highly H-containing chemical hydrides such as NaAlH_4 , LiBH_4 , BH_3NH_3 , and their related derivatives, the advantages of using the hydride-forming intermetallics as hydrogen storage materials lie in simpler chemical process, better reversibility, higher hydrogen purity and lower working temperature. However, to meet the demands for practical onboard application, the development of new intermetallics with higher capacity is quite necessary, which could be achieved by the substitution of light metals for heavy ones. For instance, ternary X-Mg-Ni (X = Ca, Y and rare earth metals) compounds have been developed from corresponding binary X-Ni compounds. The X-Mg-Ni have layered structures where $[\text{XMgNi}_4]$ and $[\text{XNi}_5]$ units stack along the c-axis alternatively according to certain combination.^[1] In this work, a systematic study of ternary X-Mg-Ni compounds was carried out to determine the structural features and absorption-desorption characteristics. First, the crystal structure of the ternary X-Mg-Ni compounds derived from XNi_3 and X_2Ni_7 are presented for comparison (see Figure 1). In the meantime, the existence of the 2H and 3R variants was confirmed by crystallographic analyses. The polymorphic transition between the 2H and 3R phases was subsequently revealed by quenching the X-Mg-Ni samples at various temperatures, and a crystallographic model for this transition was proposed. The possibility of improving the hydrogen storage properties by adjusting the X(Ca)/Mg ratio is also reported. Finally, both gaseous and electrochemical hydrogen absorption and desorption behaviors were analyzed to reveal the change in the hydriding/dehydriding process.

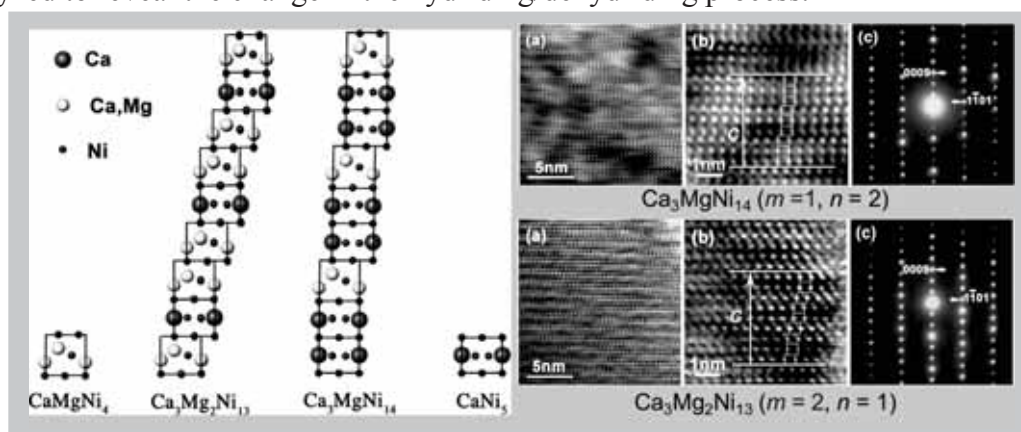


Figure 1. Structure stacking models, low- and high-magnification HRTEM images and the corresponding SAED pattern for $\text{Ca}_3\text{Mg}_2\text{Ni}_{13}$ and $\text{Ca}_3\text{MgNi}_{14}$.

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Evaluations of hydrogenation properties on MgH_x -transition metal fluoride composites by planetary ball milling

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Metal hydrides based on magnesium are interesting materials for hydrogen storage system because it has high hydrogen capacity (7.6wt.%), lightweight, low cost materials [1]. However mercantile application of the magnesium hydride currently inhibited by its high absorption/desorption temperature, poor reaction kinetics, high activation energy and high oxidation reactivity. Yavari et al. and Ma et al. reported that MgF_2 formed from the MgH_x -transition metal fluorides system can be replaces the initial surface oxide layer and provides a reactive and protective fluorinated surface for hydrogen uptake. Thus, the absorption/desorption kinetics will be enhanced [2,3]. In this research, the MgH_x -transition metal fluoride composites (CoF_2 , TiF_3 , CeF_3) has been prepared by planetary ball milling under argon atmosphere. MgH_x containing 5 and 10 vol% of each fluoride was charged with 17.7mm diameter Cr-steel ball into BPR 66:1. The powders synthesized were characterized by XRD, SEM, EDS, BET and simultaneous TG/DSC analysis. The hydrogenation behaviors were measured by using a sievert's type automatic PCT equipment. The results of XRD patterns indicated that MgH_x - CoF_2 composites (5 and 10 vol%) contain MgH_2 , Mg and MgF_2 ; and MgH_x - TiF_3 composites contain MgH_2 , MgF_2 , Mg, $\text{TiH}_{0.66}$, $\text{TiH}_{1.7}$ and TiH_2 (fig.1); and MgH_x - CeF_3 composites contain MgH_2 , CeH_2 , CeF_3 and MgF_2 respectively, after milling for 96 hours. SEM observation revealed that MgH_x -transition metal fluoride composites has both small and large particles with fine particles on their surfaces. EDS image mapping of MgH_x -transition metal fluoride composites shown that, each element is distributed homogeneously.

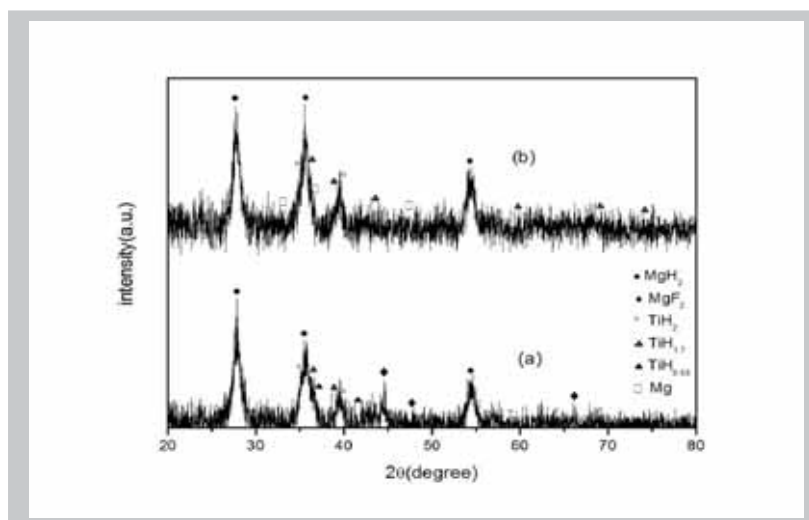


Figure 1. XRD patterns of MgH_x - TiF_3 composites (a) MgH_x - TiF_3 5vol%. (b) MgH_x - TiF_3 10vol%.

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Hydrogen Storage Property of MgH_2 Doped with Ce-fluorides

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MgH_2 is considered as a promising vector for hydrogen storage due to the hydrogen density of 7.6 wt.%, abundant resource and environmental friendly etc. However, the sluggish kinetics and operating temperatures as high as 300-400 °C hurdle its practical application. Doping additives/catalysts via high energy ball-milling, very often together with nanostructuring, is an efficient method for fabricating Mg-based materials with superior hydrogen storage properties. In the present study, Ce-based fluorides with different valences and addition amounts are doped into MgH_2 via ball-milling under different atmospheres, including H_2 and Ar. Microstrual transition, valence evolution and de/hydrogenation performances of the composites are studied via XRD, TEM, XPS, DSC, TG and DTA etc. It is found that the nano Ce-fluorides are homogeneously embedded in the MgH_2 matrix and remarkably improve the de/hydrogenation kinetics of MgH_2 , which should be largely attributed to the formation of F-species on the $\text{CeF}_x/\text{MgH}_2$ interface and the easy electron transfer induced from the Ce-based cations. Higher valence compounds present much better catalysis than that of the lower valence ones. We found that 2 mol% addition of CeF_4 lowers the desorption activation energy of MgH_2 to 110.6 KJ/mol, which is quite smaller than that induced from 2 mol% CeF_3 (168.9 KJ/mol).

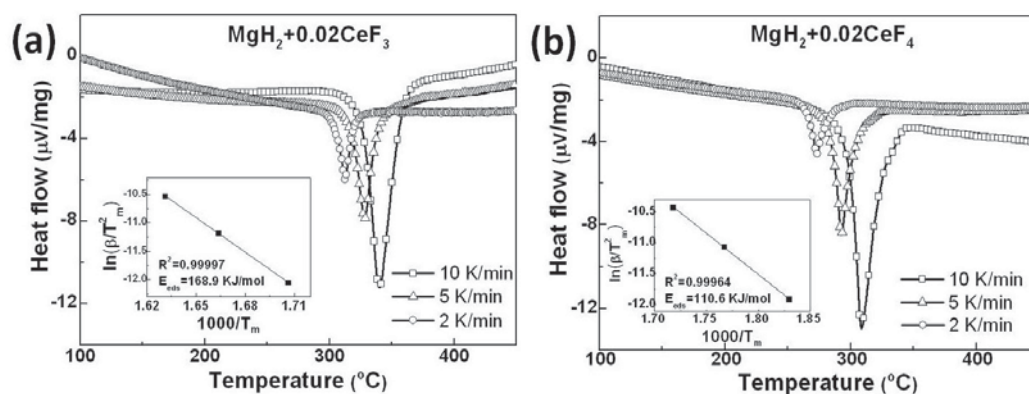


Figure 1. DTA traces of MgH_2 doped with 2 mol% CeF_x (a) $x=3$ and (b) $x=4$) at different heating rates, the insets show the Kissinger's plots.

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Size Effects on the Hydrogen Storage Properties of Mg Nanoparticles Synthesised by Eletroless Reduction Method

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Magnesium has attracted extensive attention as a promising material for hydrogen storage because of its high storage capacity and good reversibility. However, its application in hydrogen storage is limited due to the relative high thermodynamic stability of magnesium hydride and slow kinetics during hydrogen desorption. One potential solution to these problems is to decrease particle size to the nano-scale range [1].

In this study, magnesium nanoparticles were prepared by reducing organomagnesiums with lithium in the presence of naphthalene as an electron transfer agent. The nucleation-growth process, controlled by varying the ratio of the reactants, led to magnesium nanoparticles with different sizes and morphologies (Figure 1a).

Interestingly, high-pressure DSC demonstrated that these materials except $\text{MgLi}_{4.6}\text{Napht}_{4.6}$ were capable of low-temperature hydrogen sorption ($< 100\text{ }^{\circ}\text{C}$). However, desorption remained at relatively high temperatures ($\sim 250\text{--}300\text{ }^{\circ}\text{C}$) due to altered enthalpy and entropy. Indeed, additional PCT measurements revealed not only a decrease in enthalpy but also entropy impairing hydrogen desorption at low temperatures (Figure 1b) [2].

The challenge in using such nanosized effects to improve the hydrogen sorption properties of magnesium is thus to better understand how to control any evolution of ΔS while simultaneously optimising ΔH to around $40\text{ kJ}\cdot\text{mol}^{-1}\text{ H}_2$ to allow reversible storage of hydrogen under practical conditions of temperatures, i.e. $100\text{ }^{\circ}\text{C}$ for an equilibrium pressure of 0.1 MPa .

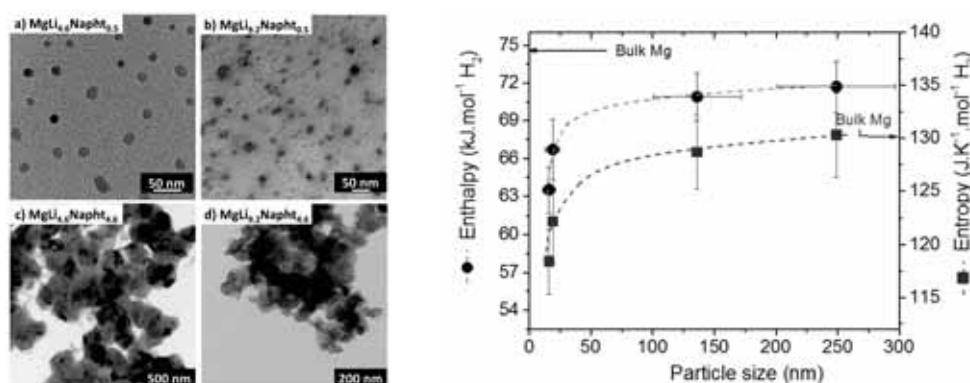


Figure 1. (a) TEM images of magnesium nanoparticles and (b) size effects on enthalpy and entropy of their hydride. $\text{MgLi}_x\text{Napht}_y$ correspond to different molar ratio of lithium (x) and naphthalene (y).

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Magnesium Hydrides Nano-objects: Novel Physical and Hydrogen Storage Properties Relationships

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Nanostructuring metal hydride has been identified as the potential approach to overcome kinetics and thermodynamic limitations. Several reports have now shown that such approach could lead to better hydrogen sorption kinetics and possibility alter the thermodynamics due to the large surface area and high surface energy of nanomaterials.¹ However, in practice the synthesis of such nanosized materials with controlled properties is a real challenge. In particular, the high reactivity of magnesium – a promising material for hydrogen storage – challenges its synthesis at the nanoscale.

Here, different strategies based on wet synthesis methods to synthesize magnesium hydrides nanoparticles will be reported. We have found that the morphologies of the nanosized magnesium can be altered through changing the chemical synthetic the environment.² Since, these differences also affected the hydrogen sorption properties of nanosized-magnesium, these findings provide a new mean to control the hydrogen sorption properties of magnesium hydride.

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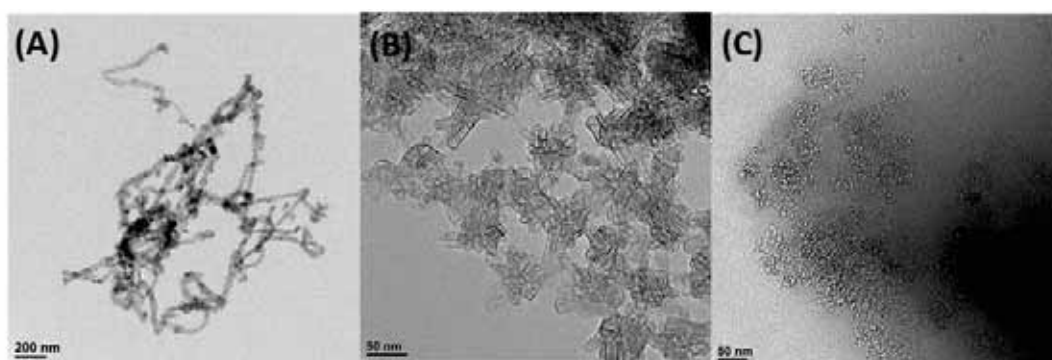


Figure 1. TEM images of magnesium hydride synthesized by various techniques (A) Thermal decomposition of organomagnesium leading to nano-wires, (B) Decomposition of magnesium anthracene, and (C) Through colloidal approaches.

Effect of Rolling Atmosphere on Sorption Kinetics of MgH_2

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In previous reports we have shown that cold rolling in air could be as effective as ball milling for the enhancement of hydrogen sorption kinetics [1]. However, large number of rolling in air resulted in formation of oxide which greatly reduced the hydrogen capacity of the material. A rolling apparatus was modified in order to be able to perform cold rolling in argon as well as in air. As shown in Figure 1, after five rolling passes the sample rolled in argon has a much higher hydrogen capacity than the sample rolled in air. However, the intrinsic kinetic is the same for both samples. X-ray diffraction patterns of samples after rolling in air and in argon are very similar: crystallite sizes of the $\beta\text{-MgH}_2$ phase are about 15 nm for both samples. After complete dehydrogenation at 350°C there is strong grain growth for the two samples, and crystallite size reached a value of 81 nm. Therefore, powder diffraction alone could not explain why the argon processed material has more capacity than the air processed one. Surely, the amount of oxide plays a role and as this oxide is probably in the form of a thin layer on particle's surface (less than a few nm) it is essentially impossible to see by X-ray diffraction. Tests on the effect of more rolling passes will be shown.

This investigation was supported in part by the Ministry of Education of Perm Region (Russia), funding project C-26/211 and by NSERC Canada.

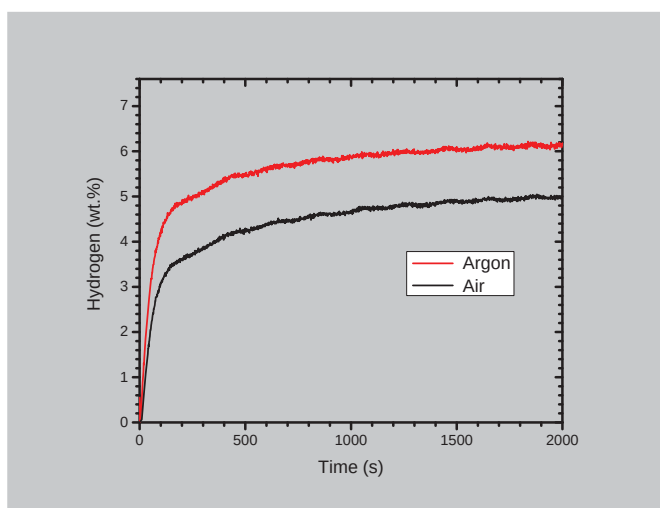


Figure 1. Hydrogen sorption kinetics at 350°C under 20 bar of hydrogen of MgH_2 cold rolled five times under argon and under air.

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Different catalytic effects of Ti-based compounds on dehydrogenation properties of MgH_2

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Due to its high hydrogen storage capacity (7.6 wt%), low cost and good reversibility, MgH_2 has been considered as an ideal hydrogen storage material. However, MgH_2 is still suffers from high dehydrogenation temperature and sluggish sorption kinetics[1, 2]. In this work, a series of Ti-based compounds (Ti, TiF_3 , TiB_2 -commercial, TiN-commercial, TiB_2 -prepared and TiN-prepared) are doped into MgH_2 and their different catalytic effects on dehydrogenation properties of MgH_2 are systematically investigated. It is found that ionic TiF_3 shows better improvements on MgH_2 than covalent TiB_2 , TiN and atomic Ti. The onset dehydrogenation temperature of $\text{MgH}_2\text{-TiF}_3$ sample is 147 °C lower than that of pure MgH_2 . And 6.0 wt.% hydrogen is released within 6.5 min at 300 °C for the $\text{MgH}_2\text{-TiF}_3$ sample, which is several times faster than that of pure MgH_2 . In addition, TiB_2 -prepared and TiN-prepared have superior catalytic effects on MgH_2 than their commercial competitors. The apparent activation energy (E_a) of different Ti-based compounds doped MgH_2 composites, as shown in Fig. 1, are calculated by Kissinger equation. Further more, the thermodynamic events during the dehydrogenation are determined by using high-pressure differential scanning calorimetry (HP-DSC) equipment.

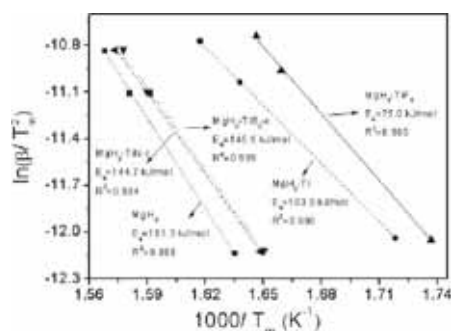


Figure 1. The dehydrogenation Kissinger plots of different Ti-based compounds doped MgH_2 samples.

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MgH₂/Pd Nanoparticles Embedded in Silica Aerogel Monoliths

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Hydrogen is an ideal energy carrier which is considered for future transport, such as automotive applications. In this context, storage of hydrogen is one of the key challenges in developing hydrogen economy. A group of Mg-based hydrides stand as promising candidate for competitive hydrogen. The main disadvantages of MgH₂ as a hydrogen store is the high temperature of hydrogen discharge. The kinetics have been improved by adding an appropriate catalyst (TiO₂, AlO, Ni, Pd etc.) into the system [1]. Another option in order to enhance the kinetics is the reduction of Mg to the size of nano, which reduces the diffusion distances and increases the surface area to bulk volume ratio [2].

Aerogels are a class of materials with extraordinary properties like high porosity, high specific surface and low density. In this work, they are proposed as storage medium for metal nanoparticles. Hydrophilic silica alcogels were produced following the two step sol-gel process. After it, Mg and Pd nanoparticles were impregnated in the aerogel matrix using supercritical carbon dioxide properties. Magnesium acetyl acetonate and palladium acetyl acetonate were used as metal precursors [3]. The organic part of the precursors was eliminated by calcination. It was followed by the hydrogenation of the metals in order to obtain MgH₂. The hydrogenation and dehydrogenation kinetics were studied for several cycles and the changes in the behaviour was studied when the Pd particles were present. The structural and textural properties of the obtained materials were also characterized.



Figure 1. Pure silica aerogels monoliths (on the right); impregnated with magnesium acetyl acetonate (in the center); impregnated with palladium acetyl acetonate (on the left)

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Impact of Severe Plastic Deformation and Additives on the Stability of MgH_2

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Magnesium is one of the best candidate for hydrogen storage technology. More particularly, during the last year, it was demonstrated that: 1- severe plastic deformation (reducing particle and crystallite sizes), and 2- addition of various types additives, both applied to MgH_2 led to very fast H-sorption reactions.

Here we report on the impact of different additives (Ni, V, TiC and TiVCr) to MgH_2 , first submitting the mixture to intense Ball Milling (BM), ECAP and Fast Forging (FF) processes. The resulting materials were checked by XRD, SEM and DSC/TGA.

It appears that very important changes in the dehydrogenation process occur immediately after the SPD cycle. They result from both the two type situations: from additive reaction and from deformation processes. However the kinetic trace of the dehydrogenation process presents particular insights depending on the materials and the applied SPD treatments. For example, impact of the additives on the H-reaction with the Mg-matrix is either the formation of additional endothermic peaks or the rise of a shoulder on the maximum heat absorption peak immediately after the first hydrogenation cycle. Besides it has been shown that application of intense plastic deformation process modifies as well the temperature interval where starts hydrogen desorption.

Using TGA/DSC experiments, granulometry measurements, SEM and XRD analyses, lead considering that the size and the morphology of the additives on one side, the amount and the chemical nature of these elements, play a determining role on the stabilization/destabilization of MgH_2 during the first H/D cycles. The origins of such dramatical changes in the hydrogen desorption kinetics are discussed.

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Micronized MgH_2 and MgO by Supercritical Anti Solvent process

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The development of materials for hydrogen storage is still one of the most important challenges. Magnesium hydride is one of the light metals most used due to its high content in hydrogen (7.6%wt). However, it has some limitations due to it requires high desorption temperature and the kinetic is slow which can be improved by the reduction of the size of the hydride.

In this work, MgH_2 and magnesium oxide (MgO) has been obtained using magnesium acetate as precursor. Micronization of magnesium acetate tetrahydrate from methanol solutions has been performed by Supercritical Antisolvent (SAS) process using supercritical carbon dioxide at different conditions of operation obtaining spherical particles with an average particle size of less than $1\mu\text{m}$. Several process parameters: concentration of the solution, temperature and carbon dioxide molar fraction have been studied analyzing their influence on the properties of particles produced, including its size and morphology, analyzed by laser diffraction and SEM microscopy, and structural parameters, characterized by FT-IR spectroscopy and X-ray diffraction.

First, micronized magnesium acetate has been treated with hydrogen at high temperature obtaining magnesium hydride. The utilization of micronized magnesium acetate induces several advantages such as the reduction of diffusion distances enhancing the rate at which hydrogen is distributed. Moreover, hydrogen bond dissociation is also favored enhancing the hydrogen diffusion rate, properties that will improve the kinetic of hydrogen desorption compared to bulk samples [1].

On the other hand, MgO is of interest in different applications such as catalyst in order to speeding-up the hydrogen releasing from the hydride [2]. Its nanostructure is expected to have novel properties superior to the bulk material due to the quantum confinement effect which influence reactivity, catalytic and electrochemical activity. Magnesium oxide is obtained after calcination at 648K for several hours in a muffle furnace. Dehydration is followed by decomposition of the material removing the organic part resulting in magnesium oxide with a more defined and not agglomerated structure in contrast to unprocessed calcinated magnesium acetate.

Both products (MgH_2/MgO) obtained from the same micronized precursor, magnesium acetate, have been characterized using Sievert's method to determine the improvement in the kinetic of hydrogen release compared to the bulk hydride.

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Electrocatalytic Activity of Mg in Hydrogen Evolution Reaction

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The most promising solution for storage and transportation of hydrogen can be a way to MH. One way of obtaining low-cost energy-metal hydrides is by electrolysis. In this case it is necessary to know the mechanism of hydrogen evolution reaction (HER) on the metal (or alloy) and catalytic properties of the original components that were investigated by cathodic polarization curves. The main kinetic parameters of the stages of hydrogen penetration and diffusion were determined by using the electrochemical extraction. Such kinetic parameters as the amount of absorbed hydrogen (C_H), the effective diffusion coefficient (D_H) and the reaction rate constant of the hydrogen atom transfer from the metal surface (k_{bs}) were determined.

The comparison of electrochemical (cathodic) behavior magnesium (in initial state) with samples of magnesium after severe plastic deformation (SPD) showed that the rapidity of the cathodic process for deformed magnesium sample is 2-3 times higher.

Moreover, the amount of hydrogen absorbed in the surface layer - V_H (the surface of the sample) of the deformed pattern is about 14 times higher as for magnesium in initial state. For example, $V_H = 1,66 \cdot 10^{-4} \text{ sm}^3/\text{sm}^2$ - for the magnesium in initial state and $V_H = 22,93 \cdot 10^{-4} \text{ sm}^3/\text{sm}^2$ for the sample after SPD. Thus, the method allows to increase catalytic activity of the deformed material.

Electrochemical studies allow suggesting that the alloys Mg-Ni with 22 wt% of nickel have electrocatalytic activity in the HER higher as Mg. It should be noted that the effect of SPD on the amount of adsorbed hydrogen magnesium alloy is similar. For example, it can be shown that ECAP significantly improves the first hydrogenation of magnesium. However, this benefit greatly depends on ECAP processing temperature. If the processing temperature is above room temperature there are no significant improvement of kinetics while ECAP performed at room temperature makes magnesium absorbs and desorb a higher amount of hydrogen than unprocessed magnesium.

The results show that the proposed method allows to saturate by hydrogen at a room temperature and normal atmospheric pressure. This makes it possible to increase the efficiency of hydrogen saturation of alloys by electrochemical method and to form a hydride layer on the surface of the alloy. The obtained hydrides can be used for storage of hydrogen.

The present work was supported by grants of Ministry of Education and Sciences of the Perm Region C-26/211.

Magnesium hydride - Magnesium nanoparticles confined in carbon aerogels

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Magnesium has been for a long time a promising material for hydrogen storage applications due to its low cost, abundance, low density and high storage capacity of 7.6 wt% [1]. However, it exhibits some well known drawbacks: high stability and slow dehydrogenation kinetics [2].

Some theoretical studies predict that thermodynamic stability of MgH_2 would be decreased in the form of nanoparticles or clusters. In addition, nanosized Mg/MgH_2 exhibit other advantages derived from their small size: increased surface area, shortened hydrogen diffusion distances, increased number grain boundaries to enhance the hydrogen diffusion rates [3].

In our work, we have chosen nano-confinement within porous carbon aerogels as a means to altering the thermodynamics and dehydrogenation kinetics of magnesium hydride. A wet impregnation method is being developed which involves ionic exchange within a solution of magnesium nitrate hexahydrate. The size of the Mg is directly influenced by the pore size of the carbon aerogels and can be varied from 5 to 20 nm. The optimized preparation method and the sorption properties of Mg-based hydrogen storage materials will be presented in detail.

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Rapid Dehydrogenation of Chemically-Synthesized MgH_2 Nanocomposites

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A new MgH_2 nanocomposite can be synthesized *via* a simple wet chemical route with tetrahydrofuran (THF) as a solvent. The effect of variations in the synthetic process on hydrogen desorption performance has been investigated systematically. Ball-milling MgH_2 using LiCl as buffering agent (in the *absence* of hydrogen) and treating with THF at room temperature produces a fine powdered material characterised as comprising of orthorhombic γ - MgH_2 and tetrahedral β - MgH_2 . The β -/ γ - MgH_2 nanocomposite exhibits a capacity of 6.6 wt.% H_2 and starts to release hydrogen at $\sim 260^\circ\text{C}$; *ca.* 120°C lower than that of commercial MgH_2 (Figure 1a). No other gas-phase products were observed during desorption (Figure 1b). Analysis reveals that the metastable γ - MgH_2 component first transforms into stable β - MgH_2 followed by dehydrogenation to Mg . The improved dehydrogenation kinetics can be ascribed both to the existence of nanoscale MgH_2 and to the exothermic process associated with the γ - MgH_2 to β - MgH_2 phase transition. Developing a fundamental understanding of the dehydrogenation mechanism and of the synthesis process itself should prove of considerable value in chemically designing new Mg-based hydrogen storage materials.

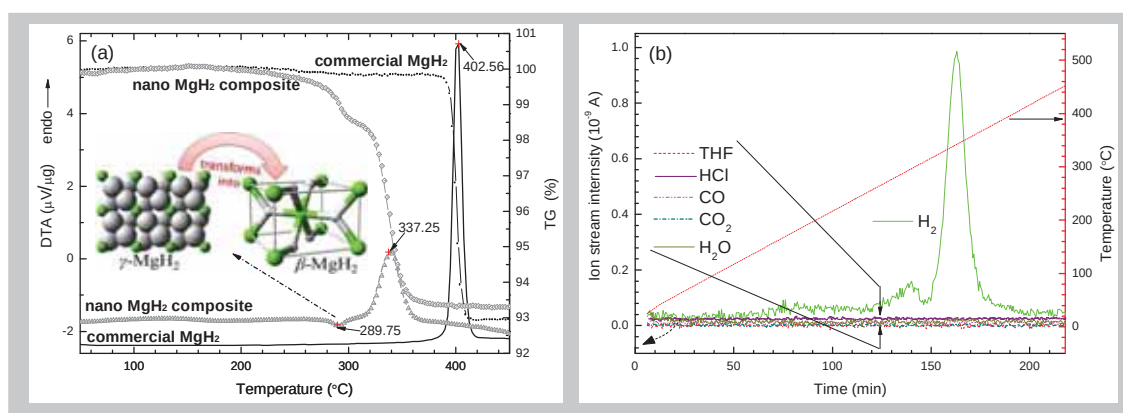


Figure 1. (a) TG-DTA curves of the MgH_2 nanocomposite and commercial MgH_2 ; (b) Evolved gas analysis (by MS) from the decomposition of the MgH_2 nanocomposite.

Hydrogen Storage Properties of Mg and Mg-alloys after Severe Plastic Deformation

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Mg and Mg alloys are attractive hydrogen storage materials in view of their favourable volumetric and gravimetric densities. However, the slow kinetics of hydrogen absorption and desorption in conventionally processed industrial metals present a major drawback for practical applications. This problem can be overcome through nanostructuring of the starting materials by means of various techniques of Severe Plastic Deformation (SPD) such as Ball Milling (BM), Equal Channel Angular Pressing (ECAP), High Pressure Torsion (HPT) or Accumulated Roll Bonding (ARB). Application of these methods results in strongly reduced grain size and thereby leads to significantly improved hydrogen diffusion and absorption (see e.g. [1]).

While BM frequently entails contamination of materials and, most notably, is excessively time and energy consuming other SPD techniques yield ultrafine grain sizes in bulk shape and thus in a much more economic way. In earlier work of our group ECAP was used to refine the grain size of a commercially available ZK60 magnesium alloy to about 250 nm resulting in rapid hydrogen desorption kinetics allowing for discharging in less than 5 min at 350 °C. In a cyclic sorption/desorption test no deterioration with regard to storage capacity or kinetics was found after 1000 cycles [2].

In the present investigation the employment of SPD techniques is extended to HPT and ARB. In order to facilitate the application of these methods MgH₂ is used as starting material. MgH₂ is considerably more resistant to oxidation than pure Mg or Mg alloys and, therefore, can be entirely processed and handled in air. We present a comparison of the results achieved by applying different SPD techniques and discuss their respective advantages and drawbacks with respect to efficient nanostructuring of the starting materials, kinetics of hydrogen absorption/desorption and long-term stability of storage properties.

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Catalytic Effect of MgF_2 on hydrogenation properties of MgH_2

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In the last decade, improvement in hydrogen sorption kinetics of Mg has been achieved by reducing the particle or grain size using mechanical milling. However, this method has a limitations to achieve nanocrystalite size (<5nm) that is required for destabilization of MgH_2 . Further improvements in sorption behavior were achieved using a wide variety of transition metals and their compounds [1]. Recently, it has been reported that addition of transition metal fluorides during milling helps to lower the hydrogen release temperature and increase the rate of hydrogen uptake by MgH_2 . Many groups [2-4] have shown that during milling of MgH_2 with transition metal fluorides, the formed MgF_2 phase replaced the original oxide layer and provides a reactive and protective fluorinated surface for hydrogen uptake. This compound possesses high affinity with hydrogen because of the F-anion, which weakens the Mg-H bonding and improves the sorption properties [7]. However, not much work has been done on direct use of MgF_2 , as additive for MgH_2 .

In this work, new results on the catalytic behaviour of MgF_2 on hydrogen storage properties of MgH_2 are presented. It was found that the sorption properties of MgH_2 can be improved by mechanical milling with 5mol% MgF_2 . particularly in the temperature range of 350-300C were sample absorbs in less than 30 mins. Complete reversibility of ~6wt% hydrogen was achieved at 300°C with absorption occurring in less than 30min under 10b H_2 pressure and desorption taking place in 2 hours under 1b H_2 . Morphological results suggest uniform distribution of protective and reactive magnesium fluoride layer on the MgH_2 matrix. Structural investigation reveals that MgF_2 phase does not decompose upon hydrogen cycling.

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MgH₂ destabilization by the anodic porous alumina impregnation

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The limited resources of natural gas, coal and oil as well as a visible increase of greenhouse gases emission force to search of alternative energy sources. The idea of hydrogen economy treats hydrogen produced using renewable energy and transformed to the electricity by fuel cells as an energy carrier. The most important drawback in implementation of hydrogen economy is the safe and effective method of hydrogen storage.

The aim of this paper is to investigate the dehydrogenation properties of nanocomposites obtained by infiltration of the porous alumina impregnated by magnesium hydride. Nanorefinement is a way to improve not only the kinetics of hydrides decomposition, but also to modify the thermodynamic of the reaction. Modeling has shown that magnesium hydride particles which have diameter below 10 nm can have a different enthalpy of decomposition in comparison to bulk or micrometer size powder [1]. One of the possibilities allowing to obtain nanoparticles with very small size is the use of matrixes in the form of AAO nano templates, which can be filled through various techniques of infiltration with liquid hydrides precursors, which in turn to become the hydride nanoparticles after specific treatment [2].

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Hydrogen generation from Mg-hydride system

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Recently, producing hydrogen from the hydrolysis of light weight metal has attracted much attention because it is convenient, cheap and clean. The theoretical hydrogen yield of Mg-H₂O reaction is 8.2 wt.% (no water included in the calculation). However, the dense by-product Mg(OH)₂ formed covers the surface of Mg and block the hydrolysis reaction. In order to overcome this problem, different hydrides and salts are added into and milled with Mg powder in this paper. The sample handling is carried out in a glove box and the hydrogen generation is test under standard situation (1 atm, 298 K) with a flowmeter (ADM 2000, Angilent Technologies).

The experimental results show that among the hydrides tested, LiBH₄ turns out to be an effective additive to promoter the hydrolysis of Mg powder with the yield and maximum hydrogen generation rate (mHGR) of 18 % and 309.4 ml min⁻¹g⁻¹. However, the hydrolysis can be further promoted by adding salts into the original Mg-LiBH₄ system. The addition of AlCl₃ proves to be an effective method to improve the overall hydrolysis reaction. The Mg-9 wt.%LiBH₄-1 wt.%AlCl₃ composite reaches a conversion yield of 87%, corresponding to 1083.5 ml H₂ g⁻¹ (composite), and the mHGR is 1256.9 ml min⁻¹g⁻¹ in 60 min at 298 K. The synergistic effect between Mg and LiBH₄ as well as the catalytic effects of LiBH₄-AlCl₃ additives both contribute to the improved hydrolytic performances. What's more, NiCl₂ can also promote the hydrogen generation performances of Mg-LiBH₄ composite greatly. The Mg-18 wt.%LiBH₄-15 wt.%NiCl₂ sample ball-milled for 6 h reaches a yield of 96.1 % with an mHGR of 1113.3 ml min⁻¹g⁻¹. The milling conditions and the *in situ* deposition of metallic Ni are both believed to be important factors that benefit the overall hydrolysis process.

Acknowledgments

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Effect of ZrCrCo alloy on hydrogen storage properties of Mg

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Mg - x wt% ZrCrCo ($x = 25, 50$) composites are prepared by high energy milling. These composites are studied in terms of their structural, morphological, and hydrogenation properties. XRD results suggest no reaction between Mg and ZrCrCo not only after milling but also after hydriding treatment. Both counterparts are found to be converted in their hydride state on hydrogen exposure. The maximum storage capacity is found to be 5.4 and 3.8 wt% at 300°C for $x = 25$ and 50 respectively in Mg-x wt% ZrCrCo composite. The presence of alloy phase greatly enhances the sorption kinetics even at lower temperature. The composite with 50% ZrCrCo content could desorb 90% of its total hydrogen capacity within 60 min at 250°C, while it takes less than 10 min to desorb its total capacity at 300°C.

Dual-tuning Effects of In, Al and Ti on the Dehydrogenation Thermodynamic and Kinetic Properties of MgH₂ using DBDP Milling

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MgH₂ has shown promise as an energy carrier medium due to its high hydrogen content (7.6 wt.%) and low cost. However, its on-board applications are obstructed by its sluggish desorption kinetics ($E_a=160$ kJ/mol) and high thermodynamic stability ($\Delta H = 75$ kJ/mol H₂). We found that the ΔH of MgH₂ could be substantially altered by reversibly forming an Mg(In) solid solution, but the kinetic property required to be further improved and the synthesis process is the combination of ball milling, sintering and prolonged ball milling ^[1]. Our recent work demonstrated that dielectric barrier discharge plasma assisted milling (P-milling) could simultaneously accomplish efficient synthesis of Mg(In) solid solution and *in situ* generation of the catalyst MgF₂ as a dispersed dopant, which enhanced the dehydrating thermodynamics and kinetics of Mg simultaneously ^[2]. In this work, to further lower the dehydrogenation enthalpy change of Mg(In) solid solution, Al was introduced into it through P-milling, meanwhile Ti was also added to further improve the kinetics of this system. The as-obtained Mg-In-Al-Ti composite was composed of Mg(In) solid solution, MgF₂, Al and Ti. MgF₂ was formed due to the reaction between Mg and polytetrafluoroethylene under the influence of the plasma-assisted ball milling process. Compared with pure Mg or the *in situ* formed MgF₂ catalysed Mg(In) solid solution, the addition of Ti could improve the kinetic property and counteract the negative effect brought by the introduction of Al, hence the composite exhibited better thermodynamic and kinetic properties. The decreased dehydrogenation enthalpy change and reduced activation energy were 65.2 kJ/mol H₂ and 125.2 kJ/mol, respectively.

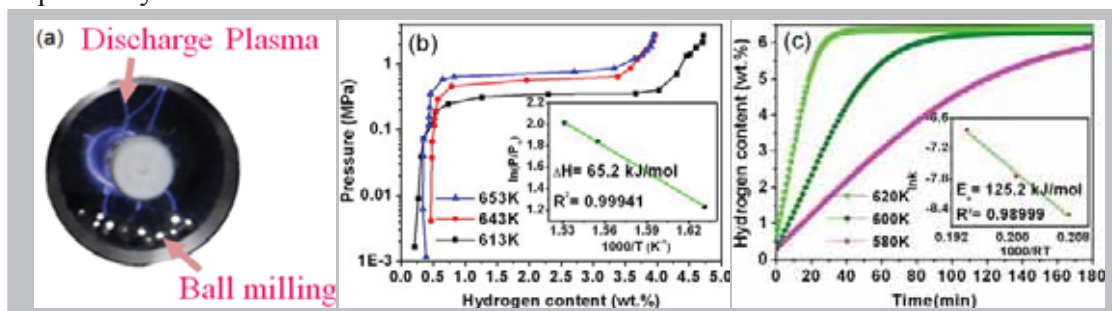


Figure 1. Shows (a) the dielectric barrier discharge plasma-assisted ball milling, (b) dehydrogenation PCT curves and (c) kinetic curves of Mg-In-Al-Ti composite.

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Hydrogen Sorption Properties of Magnesium Hydride Catalized Multiply with Carbon and Silicon

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Magnesium hydride (MgH_2) is considered as potential hydrogen storage material because it exhibits a high theoretical hydrogen capacity up to 7.6 wt.% and relatively low cost. Nevertheless, the practical application is limited by slow hydrogen kinetics at low temperature ($<300^\circ\text{C}$) and the high thermodynamic stability of its hydride. Recently, many efforts have been made to improve its hydrogen sorption properties by addition of some kinds of catalysts such as metals and oxides, etc. We have previously reported that the hydrogen desorption temperature of MgH_2 was reduced more by the multiple addition of oxides than by the single addition of an oxide. On the other hand, many researchers have reported that among light elements, carbon, such as graphite and carbon nanotubes, exhibited prominent catalytic effect on the hydrogen storage properties of Mg.

In this study, multiple addition of light elements (C (graphite) and Si) was attempted to improve the properties further because Si is in the same group (IVB) in the periodic table. MgH_2 powders were mechanically alloyed with both/either C and/or Si powders. X-ray diffraction and scanning calorimetric measurements were made after mechanical alloying, and activation energies for hydrogen desorption were also calculated by a Kissinger method. Multiple addition of C and Si decreased the hydrogen desorption (onset and peak) temperatures than single addition, and the lowest activation energy for hydrogen desorption was obtained from the sample powders ($2\text{mol MgH}_2 + 0.5\text{mol C} + 0.5\text{mol Si}$).

Hydrolysis Mechanism of Lithium Hydride

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Lithium hydride, LiH, and its derivatives are very attractive materials, particularly in the field of new energy technologies such as controlled fusion, the hydrogen fuel cells and neutron shielding. Lithium hydride appears, for example, as a potential candidate for the storage of hydrogen. With an absorption capacity of about $2000 \text{ cm}^3_{\text{NTP of H}_2} \cdot \text{cm}^{-3}$, a low density ($0.8 \text{ g} \cdot \text{cm}^{-3}$) and a decomposition process that does not require thermal activation, LiH is particularly attractive for small sized mobile applications, such as cellular phone batteries.

However, lithium hydride is a material whose implementation requires a stringent control of the air handling and/or air storage. Indeed, this material is extremely hygroscopic: the reaction of lithium hydride with water is highly exothermic and generates the release of molecular hydrogen. As a consequence it must be handled in a glove box, under dry atmosphere and inert gas, to prevent any risk of inflammation.

Due to the high reactivity of this material with air, many hypotheses are suggested to describe the overall reaction scheme of the LiH hydrolysis. The different results obtained until now in the literature do not lead to a unanimous agreement regarding the products formed during the reaction (Li_2O and/or LiOH).

The aim of this work is to elucidate the hydrolysis mechanism of LiH. Two experimental setups were specifically designed for achieving experiments in a large range of water vapor pressure ($10^{-4} - 30 \text{ hPa}$) and at room temperature. The first setup is based on the manometric technique which allows performing hydrolysis in a closed system. After activation under vacuum or under pure hydrogen at 350°C , LiH is put in contact with a fixed amount of water vapor and the hydrolysis reaction is studied by measuring the total pressure as a function of time. In the second setup, an open system was developed to monitor the hydrolysis of LiH by combining manometry and differential scanning calorimetry. Thus the reaction occurred under constant water vapor pressure. The measurements of the total pressure in the system and the heat released during the reaction allowed us to determine the extent of the hydrolysis reaction.

After hydrolysis, the samples were characterized by X-ray diffraction and FTIR-ATR spectroscopy under vacuum. Our first results show that the hydrolysis of LiH is not complete and occurs following a two-step mechanism. It involves the production of lithium oxide, Li_2O , as a first step and the formation of lithium hydroxide, LiOH , as a second step. Furthermore, the experiments have shown a threshold pressure below which LiOH is not produced. Diffusion of hydrogen through the oxide or hydroxide layer formed at the surface of LiH particles is suspected to be the limiting step of the reaction.

Synthesis and Characterization of LiBH_4 confined in Mg-Coated Mesoporous Carbon for Reversible Hydrogen Storage

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An important challenge for the use of hydrogen as an energy carrier is its compact and safe storage. A promising option is reversible storage in metal hydrides^[1]. The lighter alkali and alkaline-earth borohydrides are appealingly hydrogen-dense, but the removal of hydrogen requires high temperatures, and the "recharging" of hydrogen is slow and requires high pressures of hydrogen gas. The nanoconfinement^[2] and reactant destabilization^[3-4] are the two important strategies to improve the dynamic, thermodynamic and cycling properties.

We seek to synthesize composite materials using ball-milling and melt-infusion. This study will be helpful to the research of fabricating the material system of LiBH_4 - MgH_2 -MC and studying the mechanism of strategies. The crystal, local and electronic structure are investigated systemically by Synchrotron Radiation XRD, XAFS and XPS. Any knowledge of the structure and properties associated with destabilized nanoconfined LiBH_4 will contribute to a more comprehensive understanding of why nanoconfinement and destabilization can enhance the hydrogen properties compared to those of the bulk material.

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Alkali metal borohydride/ LiH composites for Energy Storage Applications

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Borohydride compounds are of interest for energy storage applications such as hydrogen storage and batteries. In addition, the thermal energy storage applications may be of interest, however, this will require the identification of phase changes in suitable temperatures with appropriate enthalpy values (1).

Planetary ball milling of alkali metal borohydrides (ABH_4 , $A = Na$ or K) milled with lithium hydride (LiH) in various ratios (1:1, 1:2 and 1:19) has been undertaken as well as the starting materials. Deformation and impurities are introduced to the compounds. The effect of this process is studied on the structure and the properties of the compounds. Raman and XRD was carried out to investigate changes in structure and bonding in ambient and sub-ambient temperatures. Thermal desorption spectroscopy has been carried out at high temperatures to study the dehydrogenation behaviour.

Both $NaBH_4$ and KBH_4 have a face-centred cubic structure (space group $Fm-3m$) at room temperature. At $-83\text{ }^{\circ}C$ and $-203\text{ }^{\circ}C$, respectively, they transform into a tetragonal structure (2). Lithium hydride also has face-centred cubic structure (space group $Fm-3m$) which is stable to 252 GPa (3). An unidentified phase was observed in ball milled LiH between $-110\text{ }^{\circ}C$ and $-188\text{ }^{\circ}C$ according to Raman and XRD. This new phase is dependent on the time of ball-milling.

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Effect of Ni- alloys on thermal decomposition of ammonia borane

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Hydrogen has the potential to be an alternative solution to the current problems related to the depleting fossil fuels as well as environmental issues. Despite its bright prospect, hydrogen storage suffers from considerable drawback due to its inefficient method of storage. Among the various chemical hydrides being considered for hydrogen storage, and ammonia borane seems to be very promising, due to its high theoretical hydrogen storage capacity, and lower decomposition temperature compared to complex hydrides (e.g., Sodium borohydride, lithium borohydrides, etc.). However, ammonia borane also suffers from severe drawbacks like release of unwanted gaseous by products, such as, borazine during thermolysis. The borazine release, is in principle triggered by the highly exothermic nature of ammonia borane decomposition reaction which leads to uncontrollable decomposition of ammonia borane. In the current work, Ni alloys, e.g. ZrNi, FeNi, and CuNi were synthesized by co-precipitation of oxides followed by charcoal reduction method. These catalysts were employed to facilitate the decomposition reaction. ZrNi was prepared by phase propagation method. The catalysts as synthesized were well characterized with XRD and FTIR spectroscopy. The effect of the alloys on thermal decomposition of ammonia borane were studied with help of TG-DTA and FTIR spectroscopy. It was observed that, ZrNi and FeNi were highly influential in facilitating Ammonia borane decomposition. From Fig. 1 it may be observed that, total mass loss for AB+ZrNi and AB+FeNi are substantially lesser compared to pure ammonia borane. This reduction in mass loss is principally accorded with reduction in borazine release. Such characteristics may be attributed towards the intrinsic hydrogen storage properties of the Ni alloys and their influence in decreasing the exothermicity of the reaction.

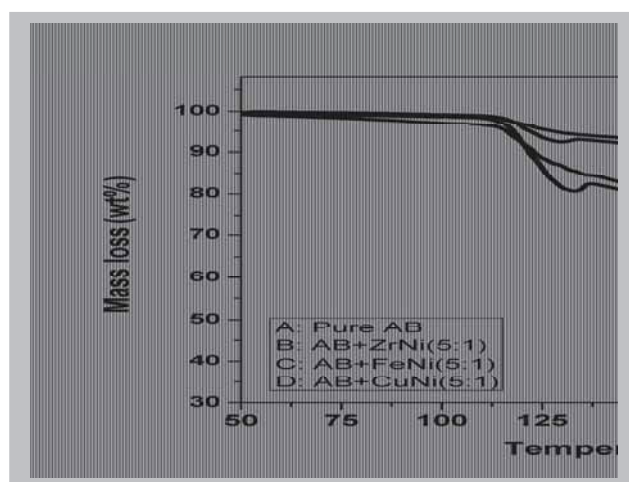


Figure 1. TGA plot of Pure AB, AB+ZrNi, AB+FeNi and AB+CuNi

A Novel Synthesis Process of Anhydrous Alkali Metal Dodecaborate $M_2B_{12}H_{12}$ ($M = Li, Na, K$) Using Decaborane $B_{10}H_{14}$

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Metal tetrahydroborate $M(BH_4)_n$, possessing high hydrogen density of approximately 10 mass%, has been investigated as potential hydrogen storage materials [1, 2]. Most of $M(BH_4)_n$ dehydrogenates via multistep reactions accompanied with the formation of intermediate compounds including metal dodecaborate- $M_{2/n}B_{12}H_{12}$. The strong B-B bond in the icosahedral boron cage of $M_{2/n}B_{12}H_{12}$ is considered to be one of the main reasons which degrade the regeneration of $M(BH_4)_n$. Fundamental investigation of thermodynamic and kinetic properties of $M_{2/n}B_{12}H_{12}$ are in high demands, in order to substantially improve the hydrogen storage performance of $M(BH_4)_n$.

General synthesis of $M_{2/n}B_{12}H_{12}$ via multistep liquid phase reactions [3] using triethylamineborane (Et_3NBH_3) and $M(OH)_n$ solution requires a careful dehydrating process at the end, and results in some $M_{2/n}B_{12}H_{12}$ decomposition through reacting with crystal water [4]. Therefore, development of non-solvent synthesis processes of anhydrous $M_{2/n}B_{12}H_{12}$ is in great need.

In this study, we propose a novel solvent-free synthesis process of dodecaborates using $B_{10}H_{14}$ with a low melting point of 99.6 °C. As a case study, we have successfully synthesized anhydrous alkali metal dodecaborate $M_2B_{12}H_{12}$ ($M = Li, Na$ and K) through optimizing heat treatment conditions of starting materials (a) $2MH + 1.2B_{10}H_{14}$ or (b) $2MBH_4 + B_{10}H_{14}$ [5], based on the following equations.



In this presentation, we will discuss the synthesis mechanism of $M_2B_{12}H_{12}$ and its relationship with the de/rehydrogenation of $M(BH_4)_n$.

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Synergetic Effect of Nano-confinement and Nano-catalysis for the Reversible Hydrogen Storage of LiBH_4

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LiBH_4 is an attractive material for hydrogen storage owing to its high gravimetric and volumetric hydrogen capacities. However, its high thermostability, sluggish kinetics, and undesirable rehydrogenation conditions limit its practical application as an onboard hydrogen storage medium. In this work, LiBH_4 has been infiltrated into highly ordered mesoporous carbon scaffold containing dispersed NbF_5 nanoparticles to investigate the possible synergetic effect between nano-confinement and nano-catalysis on the reversible hydrogen storage of LiBH_4 . Temperature-programmed desorption-mass spectroscopy measurements show that the onset desorption temperature for nano-confined $\text{LiBH}_4@\text{MC-NbF}_5$ system is reduced to 150 °C, 225 °C lowered than the bulk LiBH_4 . Furthermore, rehydrogenation of LiBH_4 is achieved under mild conditions (200 °C and 60 bar H_2). The activation energy of hydrogen desorption is reduced from 189.4 kJ mol^{-1} for bulk LiBH_4 to 97.8 kJ mol^{-1} for $\text{LiBH}_4@\text{MC-NbF}_5$ sample. All these have demonstrated that there is a favorable synergetic effect between nano-confinement and NbF_5 nano-additive on the reversible hydrogen storage performance of LiBH_4 as compared to either nano-confinement or adding NbF_5 alone. These results are attributed to the active Nb-containing species and the function of F^- anion, as well as the nanosized pores and high specific surface area of the MC scaffold, which facilitates the dissociation, diffusion and recombination of hydrogen molecules on its surface and grain boundaries. The combination of nano-confinement and functionalized catalytic scaffold may develop to become an important strategy within the nanotechnology for improving reversible hydrogen storage properties of various complex hydrides.

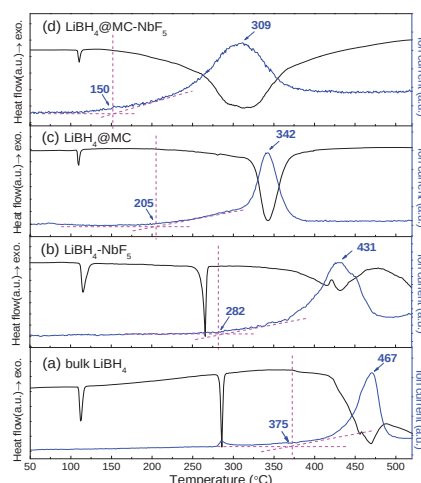


Figure 1. DSC-MS profiles of the bulk LiBH_4 (a), $\text{LiBH}_4\text{-NbF}_5$ (b), $\text{LiBH}_4@\text{MC}$ (c) and $\text{LiBH}_4@\text{MC-NbF}_5$ (d) at a heating rate of 5 °C/min. DSC profiles and MS spectra ($m/z = 2$) are shown in black and blue curves, respectively.

Thermal decomposition of $\text{Mn}(\text{BH}_4)_2 - \text{M}(\text{BH}_4)_x$ and $\text{Mn}(\text{BH}_4)_2 - \text{MH}_x$ composites with $\text{M} = \text{Li}, \text{Na}, \text{Mg}$ and Ca

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Within transition metal hydrides, manganese borohydride, $\text{Mn}(\text{BH}_4)_2$, with a theoretical hydrogen capacity of 9.53 wt% H_2 is an interesting candidate for hydrogen storage, because of high stability at room temperature, low decomposition temperature ($T = 137^\circ\text{C}$) and the high abundance of manganese in the lithosphere. A drawback is, that the decomposition of $\text{Mn}(\text{BH}_4)_2$ is accompanied by diborane in the hydrogen gas and that the solid decomposition products are not yet fully identified [1,2].

In this study we investigated the thermal decomposition of halide free $\text{Mn}(\text{BH}_4)_2$ composites with metal hydrides and metal borohydrides of lithium, sodium, magnesium and calcium. Combined thermogravimetry (TG), differential scanning calorimetry (DSC) and mass spectrometry (MS) were performed to measure and analyze the released gas; *in situ* synchrotron powder X-ray diffraction was employed to investigate the reaction mechanisms.

The thermal analysis of $\text{Mn}(\text{BH}_4)_2 - \text{M}(\text{BH}_4)_x$ ($\text{M} = \text{Li}, \text{Na}, \text{Mg}, \text{Ca}$) samples showed a lower onset of the decomposition in all samples, but large amounts of diborane were released together with hydrogen in the samples $\text{Mn}(\text{BH}_4)_2 - \text{M}(\text{BH}_4)_x$ ($\text{M} = \text{Li}, \text{Na}, \text{Mg}$). The ball milling of $\text{Mn}(\text{BH}_4)_2 - \text{Ca}(\text{BH}_4)_2$ lead to a partial decomposition of the sample, reducing the total gas release.

Reactive hydride composites of $\text{Mn}(\text{BH}_4)_2$ with LiH or NaH released up to 5.8 wt % of pure hydrogen gas at about 130°C . The decomposition of $\text{Mn}(\text{BH}_4)_2$ in presence of LiH , NaH and CaH_2 lead to the *in situ* formation of the thermodynamically more stable borohydrides $\text{M}(\text{BH}_4)_x$ ($\text{M} = \text{Li}, \text{Na}, \text{Ca}$). This provides a way to maintain all boron in the system, since no diborane is released and thereby addresses one mayor challenge in the use of metal borohydrides as storage materials. The reaction is fast and strongly exotherm in case of Na and slower in the Li or Ca system.

We furthermore found a new high pressure polymorph of $\text{Mn}(\text{BH}_4)_2$ with tetragonal symmetry, that has an exceptionel high volumetric hydrogen content of 142.0 g H_2/L , compared to 117.9 g H_2/L in trigonal $\text{Mn}(\text{BH}_4)_2$, corroborating the structural similarities of $\text{Mn}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$ [3].

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Nanoconfinement of $\text{LiBH}_4\text{-KBH}_4$ Eutectic Composite Systems

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The eutectically melting composite of $\text{LiBH}_4\text{-KBH}_4$ has been determined to be 0.725 LiBH_4 - 0.275 KBH_4 and has a remarkably low melting point of $T = 105^\circ\text{C}$. This property makes it attractive to melt infiltrate $\text{LiBH}_4\text{-KBH}_4$ into a Resorcinol-formaldehyde-carbon aerogel (CA), in which other systems has shown a decrease in decomposition temperature.[1-2] The aerogels are solvent infiltrated with magnesium dibutyl in heptane, $\text{Mg}(\text{Bu})_2$, and hydrogenated to MgH_2 . The MgH_2 in the aerogel is heated under vacuum to form nanodispersed Mg particles. The aerogel samples are mixed with molar ratio 2(0.725 $\text{LiBH}_4\text{-0.275 KBH}_4$)-Mg. In bulk samples of $\text{LiBH}_4\text{-KBH}_4$ a small hydrogen release is observed after melting at $T = 105^\circ\text{C}$, however major hydrogen release is initiated at 400°C (similar to pure LiBH_4). The nanoconfined samples show major hydrogen release already at 175°C , hence a clear decrease in decomposition temperature of the eutectic mix is observed. Subsequent hydrogen cycles reveal improved cyclic stability in the nanoconfined samples, where hydrogen release initiates at 275°C . In Figure 1 the improved hydrogen release and cyclic stability obtained by nanoconfinement is illustrated as the desorbed hydrogen shown for both the bulk and nanoconfined sample of the $\text{LiBH}_4\text{-KBH}_4$ eutectic system. Similar effects are observed in the bulk and nanoconfined samples with Mg particles.

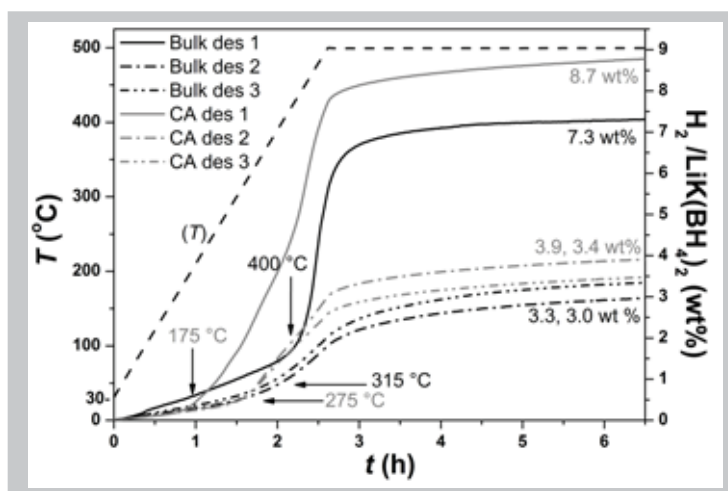


Figure 1. Sieverts desorption measurements of bulk $\text{LiBH}_4\text{-KBH}_4$ (black lines) and nanoconfined $\text{LiBH}_4\text{-KBH}_4$ (grey lines). The temperature profile is shown as a dashed line (T).

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Synthesis of Trimetallic Core-Shell Catalysts for Hydrolytic Dehydrogenation of Ammonia Borane

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With the future shortage of petrochemical energy, hydrogen is considered to be an ideal alternative. Ammonia borane (AB) is deemed to be a potential candidate because of its high hydrogen content (19.6 wt %) and stability in water. However, the kinetic property of hydrolysis of AB is very low in the absence of catalysts. Therefore, efficient catalysts with high catalytic activity are essential to facilitate the hydrolysis of AB. In this work, triple-layered Ag@Co@Ni core-shell nanoparticles (NPs) were synthesized and employed in the hydrolysis of AB. It was found that Ag@CoNi core-shell NPs contained a Ag core, a Co inner shell and a Ni outer shell. The thickness of CoNi double shells varied with different contents of Co and Ni. Ag_{0.04}@Co_{0.48}@Ni_{0.48} core-shell NPs displayed the distinctest core-shell structure and showed an excellent catalytic activity towards the hydrolysis of AB. What's more, the particle size of the NPs can be well controlled by using graphene (rGO) with different reduction degree as substrates. The number of C=O and C-O functional groups on the rGO played a vital role in controlling the growth of the NPs. The strong steric hindrance effect of C=O led to the growth of large particles, while C-O was conducive to forming small particles. The particle size of the NPs supported on the rGO with different reduction degree decreased with the reduced number of C=O functional groups (solvochemical>NaBH₄>high temperature). The decreased particle size probably led to the increased catalytic activity during the hydrolysis of AB. The smallest Ag_{0.04}@Co_{0.48}@Ni_{0.48} core-shell NPs supported on rGO reduced by high temperature method displayed the highest catalytic activity. It was proved that rGO with different reduction degree was a suitable support in controlling the particle size of catalysts for the on-board application of hydrogen storage materials. These promising catalysts may bring about a bright future for AB in application of fuel cells.

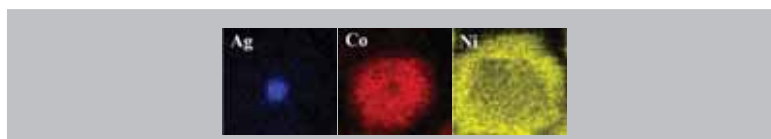


Figure 1. Elemental mapping of Ag, Co and Ni in Ag_{0.04}@Co_{0.48}@Ni_{0.48} core-shell NPs.

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Revisiting the Role of Dodecaborates

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Due to the high hydrogen densities, metal borohydrides $M(\text{BH}_4)_n$ (n is valence of M) have been widely investigated for solid-state hydrogen storage.

The hydrogen sorption of $M(\text{BH}_4)_n$ were reported to go through the formation of dodecaborate, e.g. $[\text{B}_{12}\text{H}_{12}]^{2-}$ compounds, as the main intermediates.^[1, 2] For example, $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and/or its derivatives has been identified by Raman, FTIR and NMR spectroscopic methods in the decomposition of LiBH_4 .^[3, 4] Due to its high stability, $\text{Li}_2\text{B}_{12}\text{H}_{12}$ is considered to be a boron sink in the hydrogen sorption cycles and to reduce the reversibility.

However, other borohydrides such as $\text{Y}(\text{BH}_4)_3$ show different decomposition pathways. We identified yttrium octahydrotriborate, i.e. $\text{Y}(\text{B}_3\text{H}_8)_3$, rather than the stable $\text{Y}_2(\text{B}_{12}\text{H}_{12})_3$ as the main intermediate in the decomposition process of $\text{Y}(\text{BH}_4)_3$ (Figure 1)^[5]. We also addressed the formation of $[\text{B}_{12}\text{H}_{12}]^{2-}$ compounds in the decomposition processes of $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$ by using solution-state and solid-state NMR. We reviewed the formation of $[\text{B}_{12}\text{H}_{12}]^{2-}$ compounds and compared their roles between different metal borohydrides $M(\text{BH}_4)_n$ ($M = \text{Li}, \text{Mg}, \text{Ca}, \text{Y}$).

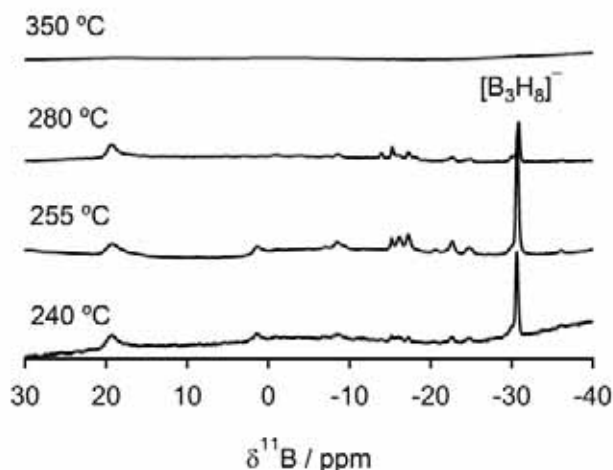


Figure 1. Solution-state $^{11}\text{B}\{^1\text{H}\}$ NMR spectra of D_2O soluble intermediates after decomposition of $\text{Y}(\text{BH}_4)_3$ at 240 to 350 °C in vacuum.

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Bimetallic Borohydrides Synthesized from $\text{Sr}(\text{BH}_4)_2$ and Alkali Metal Borohydrides

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Bimetallic borohydrides synthesized from alkali, alkali earth and transition metal borohydrides by mechanochemical treatment have received significant attention, because of their structural diversity and very high volumetric density of hydrogen [1-3]. Recently, new bimetallic compounds were found in the $\text{KBH}_4\text{-M}(\text{BH}_4)_2$ ($\text{M} = \text{Mg}$ or Mn) system. Particularly, the novel perovskite structure of $\text{KMn}(\text{BH}_4)_3$ is interesting as it seem to occur with other compositions as well.

Recently, strontium borohydride, $\text{Sr}(\text{BH}_4)_2$, has been reported. $\text{Sr}(\text{BH}_4)_2$ decomposes at 350 °C into SrB_6 and SrH_2 [4]. Here, we study the formation and properties of new $\text{MSr}(\text{BH}_4)_3$ from $\text{MBH}_4\text{-Sr}(\text{BH}_4)_2$, $\text{M} = \text{Na}, \text{K}, \text{Rb}$ and Cs mixtures using mechanochemical treatment i.e. ball milling.

We discovered new bimetallic compounds, $\text{KSr}(\text{BH}_4)_3$, $\text{RbSr}(\text{BH}_4)_3$ and $\text{CsSr}(\text{BH}_4)_3$, which have an orthorhombic perovskite crystal structure, similar to $\text{KMn}(\text{BH}_4)_3$. These new bimetallic compounds have been investigated by *in situ* synchrotron radiation X-ray powder diffraction (SR-PXD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

As reported in [4] the decomposition of $\text{Sr}(\text{BH}_4)_2$ is very difficult to analyze. Unfortunately, the new bimetallic compounds behaves similar to $\text{Sr}(\text{BH}_4)_2$ as the decomposition is very complex thus decomposition products have been determined *ex situ*. Additionally, reversibility has been tested using a Sieverts apparatus by conducting a desorption-absorption-desorption cycle. However, thermal stability of solid borohydride compounds owing to strong covalent and ionic bonding nature often provides high decomposition temperatures alongside slow kinetics and poor reversibility[5]. Indeed, this might be an advantage in respect to other applications e.g. ion conductors.

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Investigation Of γ -Mg(BH₄)₂-X Composites, X = LiH, NaH, CaH₂, MgH₂

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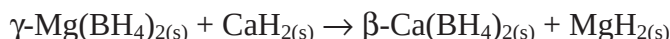
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In order to have hydrogen fuel vehicles in the future a compact, safe, efficient, and affordable way of storing hydrogen is needed. Metal borohydrides are considered suitable hydrogen storage materials as they have high gravimetric and volumetric hydrogen capacities. Recently Filinchuk et al.^[1] discovered a new polymorph of magnesium borohydride, γ -Mg(BH₄)₂, which has a large permanent porosity and is the first borohydride capable of storing molecular hydrogen, thus making it very interesting for hydrogen storage. However, as most of the metal borohydrides the temperature-pressure conditions and the rate at which the hydrogen can be released is not appropriate for on-board hydrogen storage. The decomposition of γ -Mg(BH₄)₂ is complex and occurs in several steps with the first hydrogen release around ~280 °C. One possible way of destabilising the borohydride and thus lowering the desorption temperature for hydrogen is by combining it with other compounds.

In order to examine how the presence of different metal hydrides influence the decomposition and hydrogen desorption compared to the pristine γ -Mg(BH₄)₂, we have investigated samples of γ -Mg(BH₄)₂-X, X = MgH₂, LiH, NaH, or CaH₂ with the molar ratios; 2:1, 1:1, 1:2. The samples has been studied with *in situ* synchrotron radiation powder X-ray diffraction (SR-PXD) while heating the samples from room temperature to 300-500 °C. Also Thermogravimetric Analyses coupled with Mass Spectroscopy (TGA-DSC-MS) has been performed aiding to the understanding of the decomposition behaviour of the samples.

Unfortunately preliminary results show that the addition of metal hydrides have no positive effect on the temperature of hydrogen release. The samples containing NaH and CaH₂ even have a negative effect increasing the temperature of hydrogen release with ~30 °C. However, results from the SR-PXD and TGA-MS experiments, indicate that the following cation substitution reactions are taking place during heating:



Thus the only effect of adding the metal hydrides is the making of the more stable borohydride. However, one interesting thing from these experiments is observed, namely the fact that a crystalline γ -Mg(BH₄)₂ sample had turned amorphous over time (months). This is currently investigated by Richter and Jensen^[2].

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Synthesis and Stability of Dodecaborates $M(B_{12}H_{12})_n$ ($M = Mg, Y$)

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Dodecaborates, e.g. $[B_{12}H_{12}]^{2-}$ compound, were considered to form as the main intermediate in the decomposition process of metal borohydrides.^[1, 2] For some of them (e.g. $MgB_{12}H_{12}$ and $Y_2(B_{12}H_{12})_3$), the properties such as stability and reactivity are still unknown and their roles in the de-/re-hydrogenation processes have not yet been fully understood.

Generally, metal dodecaborates such as $Li_2B_{12}H_{12}$ and $CaB_{12}H_{12}$ can be synthesized through the thermohydrolysis of their hydrated salts. However, the synthesis of some other dodecaborates such as $MgB_{12}H_{12}$ suffer from the desolvation process. For example, the $[B_{12}H_{12}]^{2-}$ species in $Mg(H_2O)_6B_{12}H_{12} \cdot 6H_2O$ collapse in the drying process, owing to the dihydrogen bonds between H_2O and the $[B_{12}H_{12}]^{2-}$ anion.^[3]

Here, we present the synthesis of solvent-free $MgB_{12}H_{12}$ and $Y_2(B_{12}H_{12})_3$ via gas-solid reaction in yields of 92.5 mol% and 60 mol%, respectively, according to the following equation.^[4, 5]



$MgB_{12}H_{12}$ and $Y_2(B_{12}H_{12})_3$ were identified by solution-state ^{11}B NMR, as shown in Figure 1. Their stabilities were investigated by NMR and their roles in the decomposition processes of $Mg(BH_4)_2$ and $Y(BH_4)_3$ were discussed.

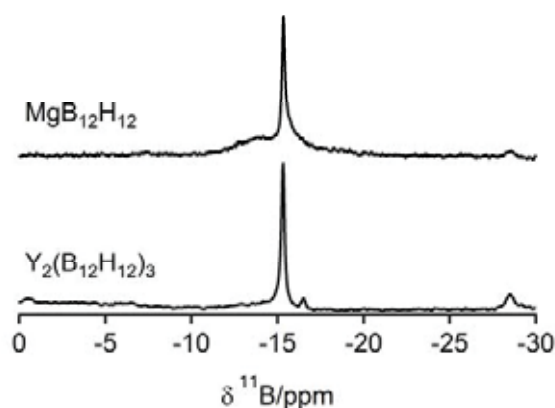


Figure 1. $^{11}B\{^1H\}$ NMR spectra of $M(B_{12}H_{12})_n$ in $DMSO-d_6$ solutions

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Hydrogen Desorption and Cycling Properties of Eutectic Borohydrides - Mesoporous Carbons Composites

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Complex hydrides have a high hydrogen content and may in principle be used as solid hydrogen stores. However their application is hampered by both slow kinetics and inconvenient thermodynamics. It has been proposed that nanosizing of complex hydrides by means of infiltration within nanopores may kinetically (and in some cases thermodynamically) enhance hydrogen release upon heating. Additionally it is believed that pore confinement of the hydrides may drastically improve their cycling stability by protecting them from e.g. agglomeration. In this respect we have used two eutectic mixtures of borohydrides, namely $\text{LiBH}_4 - \text{Mg}(\text{BH}_4)_2$ [1] and $\text{LiBH}_4 - \text{Ca}(\text{BH}_4)_2$ [2] and two different nanoporous carbons (noted as CMK-3 and ASM) to prepare borohydride-carbon composites and study their hydrogen desorption behaviour and cycling stability. The carbon materials used were predominantly mesoporous, with size distributions centred at ~ 5 nm for CMK-3 and ~ 20 nm for ASM, while their specific surface area and pore volume differ significantly. By combining the materials, a series of composites (8 in total) were prepared by either physically mixing the borohydrides with the carbons at room temperature or by heating their physical mixtures above the melting points of the eutectic mixtures under ~ 100 bar of H_2 . Furthermore, in order to investigate possible catalytic effects of carbonaceous surfaces, an extra set of composites was prepared by using a non-porous carbon material.

The bulk eutectic mixtures as well as all the composites were characterized by means of X-ray diffraction and N_2 sorption measurements at 77K, while their hydrogen desorption properties were studied by temperature programmed desorption coupled with mass spectrometry up to 500°C . In order to study their cycling behaviour, all materials were additionally subjected to 3 cycles of hydrogen loading (100 bar, 400°C) and release (1.5 bar 500°C) by using a Sievert-type apparatus. As also reported before [3] the hydrogen release properties as well as the cycling stability of the composites differ significantly from the bulk borohydrides mixtures. However based on our results the differences cannot be directly related neither to the size of the pores nor to the available surface areas, while surface catalytic effects cannot be excluded.

The present work is partially supported by the FCH JU project BOR4STORE (GA No. 303428) and the COST Action MP1103.

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Investigation into the destabilisation of LiBH_4 with CaNi_5

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Currently complex metal hydrides are of great interest for hydrogen storage and one example is lithium borohydride which has a high hydrogen storage capacity (18.5 wt%). However, its high dehydrogenation temperature, $>400^\circ\text{C}$, makes it impractical for automotive applications. Because there has been success in using CaH_2 to destabilise LiBH_4 [1] and in using Ni-based hydrides such as Mg_2NiH_4 [2], this work has focussed on the use of CaNi_5 to reduce the enthalpy of dehydrogenation for LiBH_4 .

Thermal decomposition using TGA, figure 1, showed that the decomposition temperature, of the $2\text{LiBH}_4\text{:CaNi}_5$ system has been reduced to 200°C . DSC results showed no evidence of melting of LiBH_4 , further proof that this phase had been fully decomposed. Powder XRD and neutron diffraction were both used to investigate the structure and the decomposition pathway of the system. XRD was used to confirm borides of Ni had been formed after thermal decomposition and neutron diffraction, figure 2, was able to shed light on the reaction pathway. Neutron diffraction experiments also demonstrated the reversibility for the system.

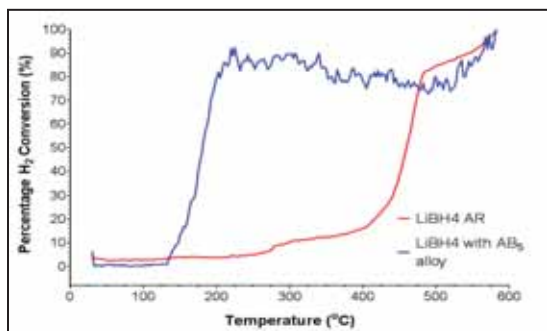


Figure 1 – Hydrogen conversion, from TGA data, of the as-received LiBH_4 and $2\text{LiBH}_4\text{:CaNi}_5$ system demonstrating the reduction in decomposition temperature to 200°C .

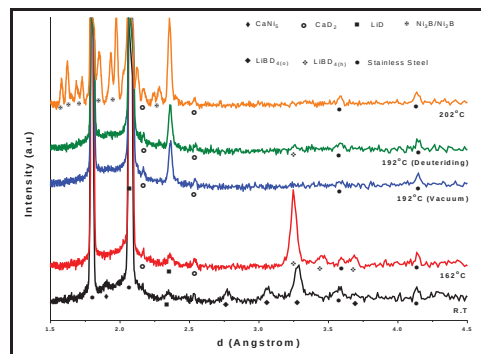


Figure 2 – In situ neutron powder diffraction data for the $2\text{LiBD}_4\text{:CaNi}_5$ system upon heating and deuteriding at different steps in the procedure.

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Magnesium-Based Hydrogen Storage Nanomaterials Prepared by High Energy Reactive Ball Milling in Hydrogen at the Presence of Mixed Titanium – Iron Oxide

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High Energy Reactive Ball Milling in Hydrogen (HRBM) is a very efficient route for the preparation of hydrogen storage materials on the basis of nanostructured magnesium hydride ($n\text{-MgH}_2$). In combination with catalysts (including easily hydrogenated alloys), HRBM of Mg was shown to be a good method for the production of the hydride materials suitable for large-scale weight efficient hydrogen storage [1]. Further improvement on performances of the $n\text{-MgH}_2$ can be achieved by the addition of carbon which, apart from intensification of heat transfer in the MH bed [1], also improves the H_2 absorption / desorption kinetics and operation lifetime, even when the carbon additive loading is below 5 wt. % [2].

This work presents the results of experimental study of the preparation and physical characterisation (XRD, SEM / EDS, TEM, volumetric H_2 sorption studies, TDS, TGA / DSC) of Mg-based hydrogen storage materials prepared by HRBM of Mg ($P_{\text{H}_2} \leq 30$ bar, $T_0 \sim 293$ K) with mixed oxide, TiFeO_3 [3]. It was shown that the addition of ≥ 5 wt.% of this “cheap” and easy available material (ilmenite) dramatically facilitates and improves H absorption in Mg during HRBM (Figure 1; *left*) and reduces the temperature of further H desorption by more than 50 degree C. Further addition of carbon, including Graphite (G), Activated Carbon (AC) and Multi-Wall Carbon Nanotubes (MWCNT) results in some slowing the H absorption down (see Figure 1; *left*) but significantly improves re-hydrogenation performances of the material, which in time is able to re-absorb about 5 wt% H in less than 5-7 minutes (15 bar H_2 / 250 °C). These improvements are mainly due to the reduction of TiFeO_3 yielding TiFe(Hx) ; in the presence of the carbon additives, the reduction is already taking place during the HRBM process (Figure 1; *right*).

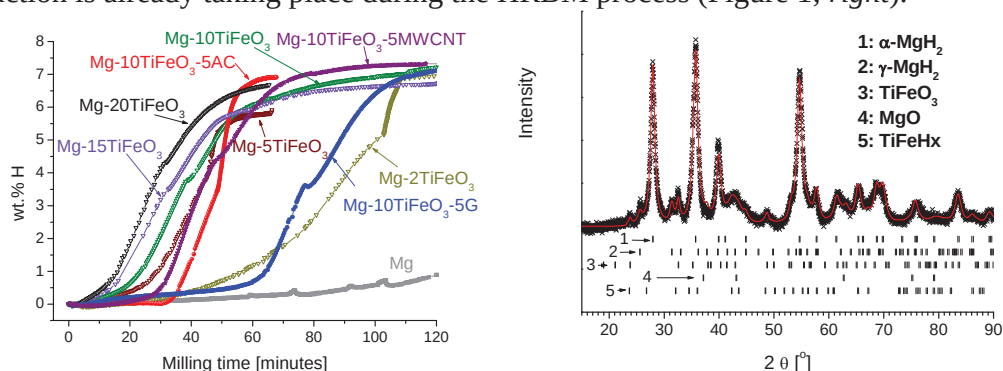


Figure 1. *Left:* H absorption during HRBM of Mg with x wt% of TiFeO_3 and carbon. *Right:* XRD pattern (Cu-K α) of the as milled Mg-10 TiFeO_3 -5 G.

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Electrochemical performance of $\text{LiM}(\text{BH}_4)_3\text{Cl}$ ($M = \text{La, Ce, Gd}$)

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Rare earth metal borohydrides are potential hydrogen storage materials as well as lithium ion conductors and luminescent materials. In this work, we present improved synthesis methods for rare earth metal borohydrides and discuss properties and results regarding lithium ion conductivity.

Recently, we discovered a system of novel rare earth metal borohydrides $\text{LiM}(\text{BH}_4)_3\text{Cl}$ ($M = \text{La, Ce or Gd}$), that show high Li ion conductivity ($\sigma \sim 1 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$) at room temperature [1,2]. By developing a synthesis for halide-free $M(\text{BH}_4)_3$ ($M = \text{La, Ce}$) and using those as starting materials, a route for producing $\text{LiM}(\text{BH}_4)_3\text{Cl}$ without excess LiCl has been developed. This holds promise for further optimising $\text{LiM}(\text{BH}_4)_3\text{Cl}$ ($M = \text{La, Ce}$) as solid state electrolytes. Reactions of $M(\text{BH}_4)_3$ ($M = \text{La, Ce}$) with alkali metal borohydrides have also been studied in the search for halide-free ionic conductors and the compounds have been structurally characterised using *in situ* SR-PXD.

$\text{LiM}(\text{BH}_4)_3\text{Cl}$ ($M = \text{La, Ce or Gd}$) have a high decomposition potential ($E_{\text{dec}} > 7 \text{ V}$). We have investigated the electrochemical performance of a Li-ion battery assembled with $\text{LiGd}(\text{BH}_4)_3\text{Cl}$ as the electrolyte. The lithium insertion-extraction from LiCoO_2 is possible at room temperature showing the good conduction of the $\text{LiGd}(\text{BH}_4)_3\text{Cl}$ compound, see Figure 1. However, the battery suffers from capacity decay due to large interfacial resistances, most likely caused by the partial reduction of LiCoO_2 .

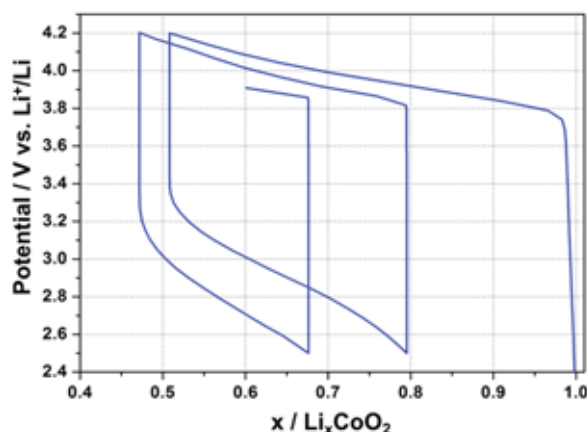


Figure 1. Galvanostatic charge-discharge curves (C/10, 25°C) of an all-solid-state battery consisting of a LiCoO_2 cathode, a $\text{LiGd}(\text{BH}_4)_3\text{Cl}$ electrolyte and a lithium metal anode.

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Supercritical Nitrogen Processing: a Route to Clean Hydrogen Storage in γ -Mg(BH₄)₂

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Diborane was detected as a prominent desorption product of samples of γ -Mg(BH₄)₂, which has significant implications for its applicability as a hydrogen storage material and is crucial information used in determining the reaction pathways relevant to the decomposition of magnesium- and related borohydride systems. However, the release of diborane is unexpected thermodynamically given the relative stability of Mg(BH₄)₂ [1], and indeed is not observed (or is minimally present) during the decomposition of the α - and β -phases. By pretreating the highly porous γ -Mg(BH₄)₂ using novel supercritical nitrogen drying (NScD) techniques, we report that the presence of diborane among the gaseous decomposition products can be suppressible to obtain a clean, impurity-free dehydrogenation (yielding 7.6 mass% H₂) of γ -Mg(BH₄)₂ under moderate conditions (see Figure 1). The diborane released therefore originates from impurities on the surface and within the pores of Mg(BH₄)₂, merely a remnant of wet chemical synthesis, which also explains its absence with respect to the nonporous α -phase and heat-treated β -phase.

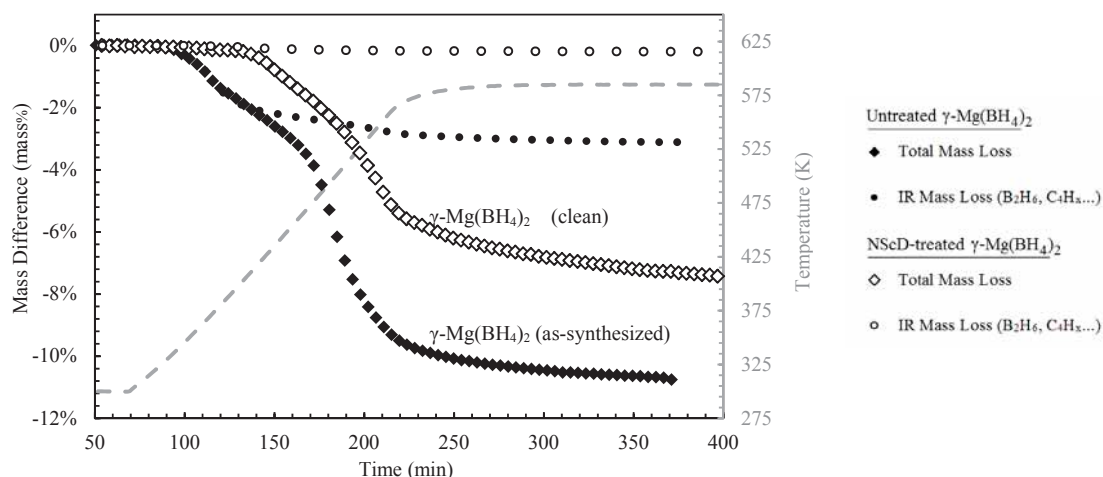


Figure 1. The total mass loss upon decomposition of untreated and NScD-treated samples of γ -Mg(BH₄)₂ under a heating ramp of 2 K min⁻¹ up to 590 K in flowing H₂. The total mass loss (measured by gravimetry) is deconstructed using IR spectroscopic analysis of the gaseous products giving specific quantities of mass loss from each species evolved [2], predominantly B₂H₆ and n-butane/THF.

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Improving dehydrogenation of LiBH_4 via modification with poly(methylmethacrylate)

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Due to the unfavorable high thermal stability, the practical utilization of lithium borohydrides as hydrogen storage material is hampered. In the previous study, we had found that the dehydrogenation temperature of LiBH_4 (loading weight was 28 wt%) could be decreased via modification LiBH_4 within poly(methylmethacrylate) (PMMA), also the air stability of LiBH_4 was increased significantly [1].

In order to further increase the hydrogen capacity of the LiBH_4 -PMMA composite, the loading weight of LiBH_4 increased from 28 wt% to 60 wt%. In this work, the 60 wt% LiBH_4 @PMMA composite (abbreviated as 60LP) which prepared by solution method presented a low onset dehydrogenation temperature of 263 °C, and the main dehydrogenation peak centered at 355 °C. The released gas of 60LP was significantly improved from 0.020 mol/g for the pure LiBH_4 to 0.035 mol/g at 360 °C (figure 1b). Compared with 28 wt% LiBH_4 @PMMA composite, the microstructure in the 60LP showed that LiBH_4 distributed in the relatively large network pore of PMMA, which led to the relatively high desorption temperature. Judging from the FTIR and XRD results, the dehydrogenation mechanism was that LiBH_4 reacted with PMMA to produce LiBO_3 during the dehydrogenation process. In order to confirm the dehydrogenation mechanism at the main dehydrogenation peak centered at 355 °C, bulk LiBH_4 was ball milled with PMMA for dehydriding test. The dehydrogenation temperature of bulk LiBH_4 decreased after ball milling with PMMA and product further demonstrated the interaction of LiBH_4 with PMMA. It could be concluded the dehydrogenation property of LiBH_4 was significantly improved through the destabilization by PMMA.

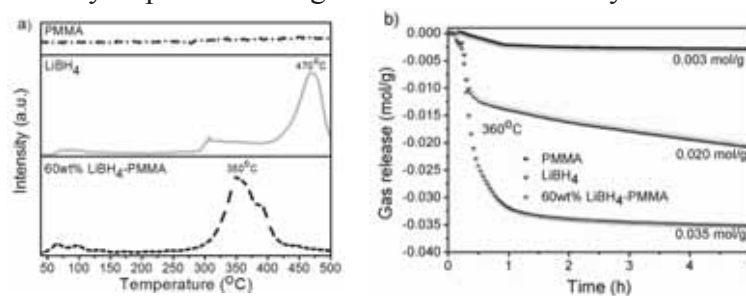


Figure 1. (a) MS hydrogen signals and (b) Isothermal TPD results of pure PMMA, LiBH_4 and 60 wt% LiBH_4 @PMMA composite.

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Study on dehydrogenation kinetics of LiBH_4 via confinement in modified carbon nanotubes

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Borohydrides are potential candidates for on-board hydrogen storage because of their high gravimetric hydrogen densities [1]. Among all borohydrides, lithium borohydride (LiBH_4) is attracted considerable attention as a hydrogen storage material, due to its extremely high gravimetric hydrogen density (13.8 wt%). However, the practical use of LiBH_4 is limited by the high dehydrogenation temperature and the complexity of the recycling mechanism [2]. In order to improve thermodynamics and kinetics of dehydrogenation of LiBH_4 , Au et al. [3] observed that element substitution and additive interaction are effective in reducing dehydriding temperatures, but the reversibility of oxide-modified lithium borohydrides deteriorate due to increasing formation of Li_3BO_3 . In the present work, we proposed confining LiBH_4 in carbon nanotubes exploiting the favourable properties of nanostructured materials and avoiding oxidation during desorption. The dehydrogenation kinetics of LiBH_4 incorporated within various carbon nanotubes by melt infiltration has been studied, as shown in Fig. 1. The structural properties of confined samples were demonstrated by means of Transmission electron microscopy, powder X-ray diffraction and Raman spectroscopy.

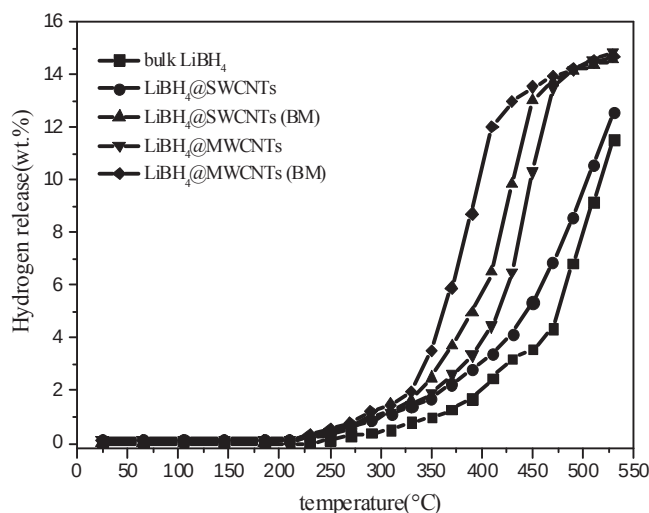


Figure 1. Thermal programmed desorption curves of bulk and nanoconfined samples.

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Dehydriding Property of Metal Borohydrides Combined with Mg_2FeH_6

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Recently, we reported that combining LiBH_4 with Mg_2FeH_6 results in a marked decrease in the dehydriding temperature of LiBH_4 , along with the observation of a unique single-step dehydriding process [1]. To investigate whether combination with Mg_2FeH_6 is generally effective for reducing the dehydriding temperature of metal borohydrides, the dehydriding property of NaBH_4 combined with Mg_2FeH_6 was measured.

$x\text{NaBH}_4 + (1-x)\text{Mg}_2\text{FeH}_6$ ($x = 0.1-0.75$) were prepared by mechanical milling under the identical condition as that of LiBH_4 . The dehydriding property was investigated by thermogravimetric analysis-mass spectrometry (TG-MS) and the results illustrated in Figure 1. The dehydriding process of pure NaBH_4 and Mg_2FeH_6 occurred at approximately 720 and 450 K, respectively. A drastic alteration of the dehydriding behavior was observed in $x\text{NaBH}_4 + (1-x)\text{Mg}_2\text{FeH}_6$. Within the composition range of $0.1 \leq x \leq 0.125$, a single-step dehydriding process was observed in which NaBH_4 and Mg_2FeH_6 released hydrogen simultaneously. The dehydriding temperatures and quantity of hydrogen released increased proportionally with x . When $x \geq 0.25$, a multi-step dehydriding process was observed. With *ex-situ* powder X-ray diffraction, the presence of NaH and MgB_2 in the Mg_2FeH_6 partially dehydrided products was confirmed which indicates that NaBH_4 dehydrided simultaneously with Mg_2FeH_6 . These results indicate that by combining with Mg_2FeH_6 , the dehydriding temperature of NaBH_4 was decreased by at least 150 K and infer a possible formation of solid solution similar to that observed in $x\text{LiBH}_4 + (1-x)\text{Mg}_2\text{FeH}_6$.

This research is funded by JSPS KAKENHI Grant number 25220911, Integrated Project of ICC-IMR of Tohoku University and the CONCERT-Japan Joint Call on Efficient Energy Storage and Distribution/Resilience against Disasters.

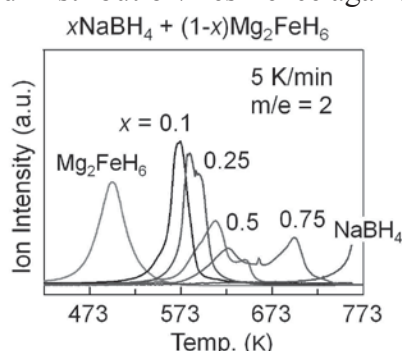


Figure 1. Mass spectrometry of $x\text{NaBH}_4 + (1-x)\text{Mg}_2\text{FeH}_6$.

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Destabilization of LiBH_4 by nanoconfinement in PMMA-co-BM polymer matrix for reversible hydrogen storage

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Destabilization of LiBH_4 by nanoconfinement in poly (methyl methacrylate)-co-butyl methacrylate (PMMA-co-BM), denoted as nano LiBH_4 -PMMA-co-BM, is proposed for reversible hydrogen storage. The onset dehydrogenation temperature of nano LiBH_4 -PMMA-co-BM is reduced to $\sim 80^\circ\text{C}$ ($\Delta T = 340$ and 170°C as compared with milled LiBH_4 and nanoconfined LiBH_4 in carbon aerogel, respectively). At 120°C under vacuum, nano LiBH_4 -PMMA-co-BM releases 8.8 wt. % H_2 with respect to LiBH_4 content within 4 h during the 1st dehydrogenation, while milled LiBH_4 performs no dehydrogenation at the same temperature and pressure condition. Moreover, nano LiBH_4 -PMMA-co-BM can be rehydrogenated at the mildest condition (140°C under 50 bar H_2 for 12 h) among other modified LiBH_4 reported in the previous literatures. Due to the hydrophobicity of PMMA-co-BM host, deterioration of LiBH_4 by oxygen and humidity in ambient condition is avoided after nanoconfinement. Although the interaction between LiBH_4 and the pendant group of PMMA-co-BM leads to a reduced hydrogen storage capacity, significant destabilization of LiBH_4 is accomplished.

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Cycle Durability and Factors Disturbing Rehydrogenation for $\text{LiBH}_4\text{-MgH}_2\text{-Al}$ Composites

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$\text{LiBH}_4\text{-MgH}_2$ composites were promising materials for hydrogen storage because of their high hydrogen content. However, rate of the dehydrogenation was very slow in the range from room temperature to 623 K[1]. To solve the problem, $\text{LiBH}_4\text{-MgH}_2\text{-Al}$ composites were proposed[2]. Rate of the dehydrogenation and reversible hydrogen storage property were improved by addition of Al[2]. Therefore the Al added composites are expected as practical hydrogen storage materials in term of reversible hydrogen storage property. The cycle stability and the adverse factors for hydrogenation and/or dehydrogenation should be clear for applying the composites as practical materials. Therefore the objectives of this study were to clear the factors which should be affect the rehydrogenation through cycle process.

Mixtures of $2\text{LiBH}_4\text{-(1-x)MgH}_2\text{-xAl}$ ($x=0, 0.1, 0.2, 0.3, 0.4$ and 0.5) were prepared by mechanical milling with a planetary ball milling machine from LiBH_4 powder (Sigma-Aldrich, 90% in purity), MgH_2 powder (A Johnson Matthey, 98% in purity) and Al powder (Wako, 99.5% in purity). Dehydrogenation/rehydrogenation properties were carried out with a Sieverts' type apparatus. The mixtures were heated up at a rate of 5 K min^{-1} from room temperature to 773 K and held at 773 K for 1.8 ks (initial pressure of 0.1 MPa of H_2) in dehydrogenation. To evaluate the rehydrogenation properties, the mixtures were heated at the rate of 5 K min^{-1} from room temperature to 623 K and held at 623 K for 7.2 ks (initial pressure of 8 MPa of H_2).

From calculation of the hydrogen capacity of mixtures, the dehydrogenation was almost completed in all of the samples, however the rehydrogenated capacity was lower than the value of calculated capacity. The reasons why the rehydrogenated reaction was not finished were proposes as follows; (1) thermodynamics problems, (2) separation among phases by partial melting in dehydrogenation, (3) kinetics problems of formation of the stable phase of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ in dehydrogenation[3].

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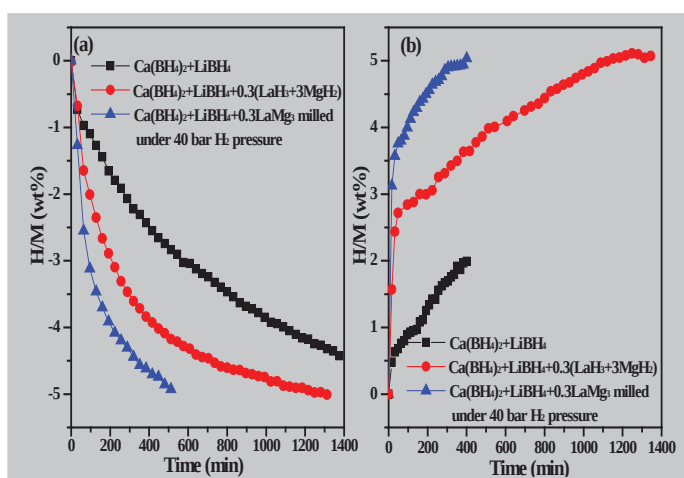
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Improved Hydrogen Storage properties of $\text{Ca}(\text{BH}_4)_2 + \text{LiBH}_4$ composite motivated by LaMg_3 alloy

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The utilization of complex hydrides for reversible hydrogen storage in mobile applications is beneficial in terms of safety and hydrogen density. $\text{Ca}(\text{BH}_4)_2$ contains 11.4 wt.% hydrogen and possesses favorable thermodynamics. LiBH_4 has a high hydrogen density of 18.5 wt.%. Both of them are regarded as ideal candidates for hydrogen storage. However, their application is hindered by their high dehydrogenation temperature and poor reversibility. A mixed borohydride composite $\text{Ca}(\text{BH}_4)_2 + \text{LiBH}_4$ is found to have lower temperature and much favorable reversibility than either LiBH_4 or $\text{Ca}(\text{BH}_4)_2$.^[1] Our previous work^[2] revealed that $\text{Ca}(\text{BH}_4)_2$, LiBH_4 and MgH_2 reacted with each other, resulting in lowered operating temperature and favorable cyclic performance. However, it is still necessary to further improve the hydrogen storage property of the $\text{Ca}(\text{BH}_4)_2 + \text{LiBH}_4$ system. In the present work, we find that the hydrogen storage property of the $\text{Ca}(\text{BH}_4)_2 + \text{LiBH}_4$ can be evidently improved by introducing a LaMg_3 alloy *via* ball milling under an H_2 pressure. The system retains 70% of the initial hydrogen content after 5 cycles. Mechanism study reveals that the *in situ* formed MgH_2 and LaH_3 during milling improve the thermodynamics of the $\text{Ca}(\text{BH}_4)_2 + \text{LiBH}_4$ system, resulting in an evident decrease in de-/hydrogenation temperatures.



Isothermal dehydrogenation (a) at 280 °C and hydrogenation curves (b) at 350 °C and 90 bar H_2 pressure of the samples

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M(BH₃NH₂BH₂NH₂BH₃) – the missing link in the mechanism of thermal decomposition of light alkali metal amidoboranes

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Metal amidoboranes constitute an important family of solid state hydrogen stores [1]. Due to their high hydrogen capacity and low temperature of H₂ desorption they are promising H₂ source for low temperature fuel cells. Up to now amidoboranes of several metals (Li, Na, K, Ca, Sr, Y) have been characterised. Alkali metal amidoboranes are efficient and low-temperature sources of H₂ gas but they exhibit endothermic process preceding the hydrogen evolution which is related to evolution of NH₃ impurity [2,3].

We have now synthesised and characterised oligomeric salts of light alkali metals related to amidoboranes: Li(BH₃NH₂BH₂NH₂BH₃) and Na(BH₃NH₂BH₂NH₂BH₃) [4]:



We have also observed formation of these derivatives upon heating of alkali metal amidoboranes (Fig. 1) which explains the evolution of NH₃ during thermal decomposition of metal amidoboranes:



The oligomeric phases exhibit high hydrogen content (lithium salt 15%, sodium salt 12.5%) and evolve H₂ at temperatures of ca. 140°C; they are kinetically stable at ambient (p.T) conditions. Formation of such phases was postulated in recent works [5,6,7].

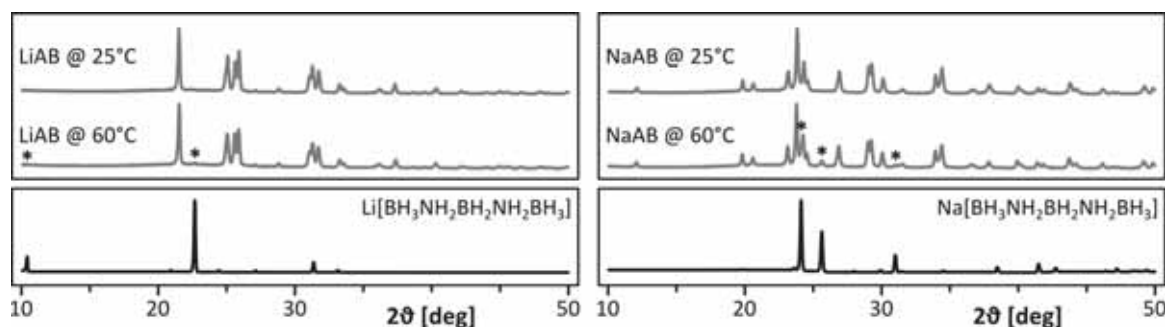


Figure 1. Comparison of X-ray powder diffraction patterns of lithium and sodium amidoboranes with those for respective M(BH₃NH₂BH₂NH₂BH₃) phases.

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Hydrogen desorption properties of a LiBH_4 - C_{60} composite

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Lithium borohydride has a high intrinsic hydrogen content (18.4 wt%). However, it needs to be heated to above 450 °C for desorption to occur (11 wt%) [1], and subsequent recombination (e.g. under 100 bar H_2) is very slow.

The catalytic effects of C_{60} upon the decomposition of LiBH_4 have been shown [2], in a sample produced using a solvent-based method. More recently recombination was demonstrated at 330 °C in 100 bar H_2 [3]. This paper explores the use of a melting method to produce a composite mixture of $\text{LiBH}_4 + \text{C}_{60}$, and investigates the decomposition and recombination mechanisms.

DSC of $\text{LiBH}_4 + \text{C}_{60}$ heated to 300 °C is shown in Figure 1. The phase change temperature for LiBH_4 exhibits multiple peaks upon cooling, indicating multiple LiBH_4 environments. While XRD shows that C_{60} transforms from a cubic to a hexagonal structure.

Decomposition of LiBH_4 occurred between 355 and 480 °C, with the evolution of hydrogen. This is about 100 °C lower than for as-received LiBH_4 . A study of the reversibility properties and mechanisms is underway.

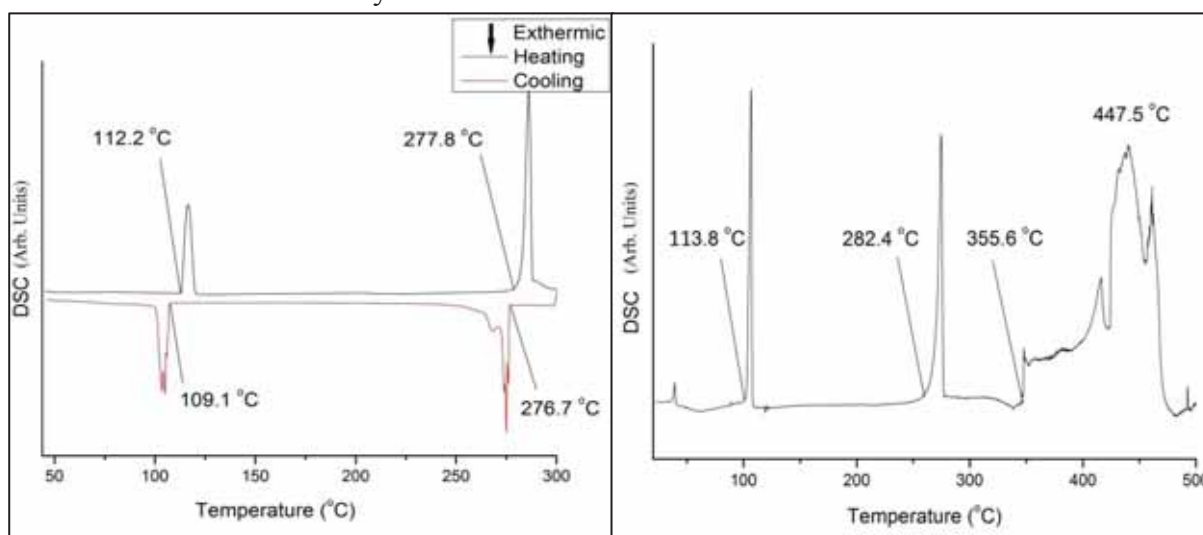


Figure 1 DSC of $\text{LiBH}_4 + \text{C}_{60}$ heated at 2 °C/min in 3 bar Ar: a) up to 300 °C and then cooled, and b) up to 500 °C.

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Altering the Structural Properties of $A_2B_{12}H_{12}$ Compounds via Cation and Anion Modifications

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While materials involving the tetrahydroborate (BH_4^-) anion are of interest for hydrogen-storage, hydroborate-based compounds, including the overly stable dehydrogenation by-products comprised of decahydro-*closo*-decaborate ($B_{10}H_{10}^{2-}$) and dodecahydro-*closo*-dodecaborate ($B_{12}H_{12}^{2-}$) anions, also have the potential to be fast ion conductors. For example, recent diffraction results have indicated that both $Li_2B_{12}H_{12}$ (near ~ 615 K) and $Na_2B_{12}H_{12}$ (near ~ 530 K) undergo unusual entropy-driven order-disorder structural transitions [1,2]. The high-temperature disordered phases possess cation vacancies amenable to facile cation diffusional jumps between the large, reorientationally mobile anions [3]. Indeed, AC impedance measurements have confirmed dramatic Na^+ superionic conductivity in the cation-vacancy-rich disordered phase of $Na_2B_{12}H_{12}$ [4], and it is expected that $Li_2B_{12}H_{12}$ exhibits similar conductivity behavior. In order to improve the properties of these types of materials as next-generation, solid electrolytes in Li-ion and Na-ion batteries, it is desirable to lower the order-disorder transition temperature. To do this, different cationic or anionic modifications of the $A_2B_{12}H_{12}$ phases are viable options, *e.g.*, with the incorporation of alkali halides or other hydroborate-based ionic compounds. This talk highlights the different synthesis methods and characterization techniques used on various substituted dodecahydro-*closo*-dodecaborate phases, some of these resulting in favorable changes in the structural properties that may translate into improved ion conductivity.

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Mechanochemical synthesis of new rare-earth borohydrides.

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Metal borohydrides usually exhibit large gravimetric hydrogen content and as such they could be used as materials for chemical hydrogen storage [1,2]. Some could also serve as precursors towards refractory metal borides, *e.g.* those containing transition or rare-earth metals. Moreover, a high lithium ion conductivity has been lately reported for lanthanide borohydride chlorides [3] which is of use in lithium batteries. These features, along with traditional role of lithium and sodium borohydrides as reducing agents in chemical synthesis, render metal borohydrides a valuable group of chemical compounds.

Here we focus on synthesis and characterisation of several rare-earth borohydrides: $\text{Ho}(\text{BH}_4)_3$, its composites with LiBH_4 , and mixed-metal $\text{M}[\text{Ln}(\text{BH}_4)_4]$ compounds, $\text{M} = \text{Na}, \text{K}$, $\text{Ln} = \text{Ho}, \text{Yb}$. These borohydrides were prepared mechanochemically from LnCl_3 ($\text{Ln} = \text{Ho}, \text{Yb}$), LiBH_4 and MBH_4 ($\text{M} = \text{Na}, \text{K}$). We have found that holmium borohydride can be obtained in two polymorphic forms, $\alpha\text{-Ho}(\text{BH}_4)_3$ and $\beta\text{-Ho}(\text{BH}_4)_3$, which are isostructural to the corresponding polymorphs of $\text{Y}(\text{BH}_4)_3$. Interestingly, the relative amount of polymorphs can be controlled by the composition of reagents, *Figure 1* [4,5]. The investigated materials decompose thermally with emission of pure hydrogen; the thermal decomposition of LiBH_4 is significantly influenced by addition of $\text{Ho}(\text{BH}_4)_3$. The structural and thermal properties of these borohydrides are compared to the known rare earth borohydrides prepared via mechanochemical or wet chemistry methods [6,7].

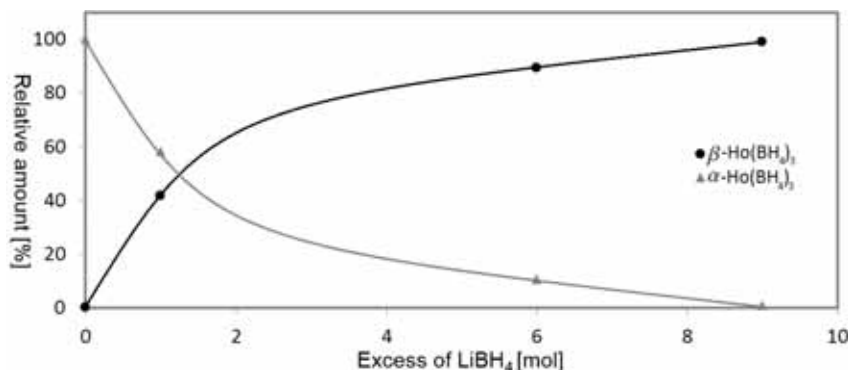


Figure 1. The relative amount of $\alpha\text{-Ho}(\text{BH}_4)_3$ and $\beta\text{-Ho}(\text{BH}_4)_3$ as a function of the composition of reagents used for mechanochemical synthesis.

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New eutectic $x\text{LiBH}_4 - 1-x\text{KBH}_4$ ($x = 0.7 - 0.75$)

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Eutectic melting occurs in several mixtures of alkali and alkaline earth metal borohydrides [1]. Here, we examine a new eutectic metal borohydride mixture, $x\text{LiBH}_4 - 1-x\text{KBH}_4$ ($x = 0.7 - 0.75$).

We have determined the novel eutectic composition $x\text{LiBH}_4 - 1-x\text{KBH}_4$ ($x = 0.7 - 0.75$) ($T_{\text{melt}} \sim 105^\circ\text{C}$), which has the lowest melting point of all alkali and alkaline earth metal borohydride mixtures [2]. The correct eutectic composition has been found using *in situ* SR-PXD, DSC and temperature programmed photographic analysis. The data from the different techniques has been used to construct a phase diagram, see Figure 1. Crystalline KBH_4 is observed by *in situ* SR-PXD after melting of a KBH_4 rich sample with an incorrect ratio of the eutectic mixture, while DSC records the polymorphic transition for LiBH_4 in a LiBH_4 rich sample. Mechanochemistry and manual mixing of LiBH_4 and KBH_4 facilitate the formation of $\text{LiK}(\text{BH}_4)_2$ from $\text{LiBH}_4 - \text{KBH}_4$ 1:1 [3]. *In situ* SR-PXD reveals that the bimetallic borohydride $\text{LiK}(\text{BH}_4)_2$ disassociates at 90°C into LiBH_4 and KBH_4 followed by incomplete melting at 105°C . The solidification process of the eutectic mixture has also been studied by *in situ* SR-PXD.

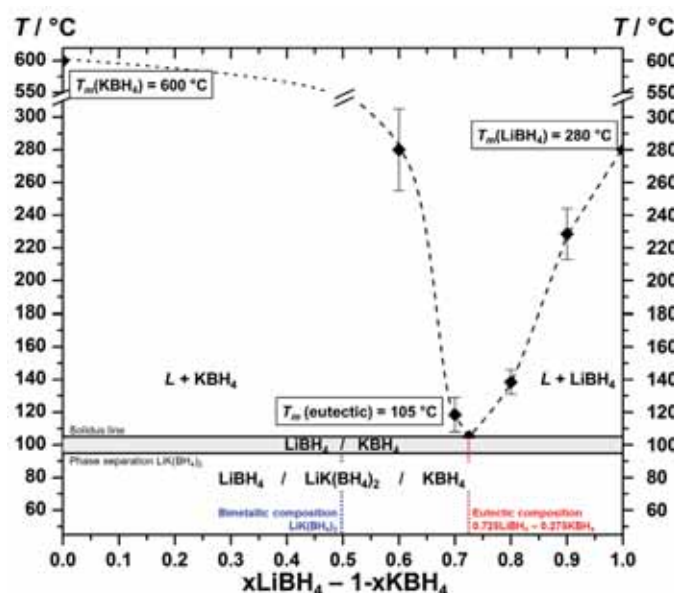


Figure 1. Binary phase diagram of the $\text{LiBH}_4 - \text{KBH}_4$ system.

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Hydrogen storage properties of nanoconfined $\text{LiBH}_4\text{-NaBH}_4$

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LiBH_4 is one of the promising candidates for hydrogen storage materials due to its high gravimetric hydrogen capacity. However, LiBH_4 possesses a high dehydrogenation temperature and has limited reversibility. It is possible to destabilize LiBH_4 by mixing with other complex borohydrides such as $\text{Mg}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2$ and NaBH_4 [1-3] to form eutectic melting composite.

In this study the eutectic melting composite $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ (LiNa) forms an eutectic melt at $T_{\text{melt}} \sim 240^\circ\text{C}$. The composite has been melt infiltrated into a nanoporous resorcinol formaldehyde carbon aerogel scaffold with a pore size of $D_{\text{max}} = 35\text{ nm}$, a specific surface area $S_{\text{BET}} = 702\text{ m}^2/\text{g}$ and a total pore volume of $V_{\text{tot}} = 1.03\text{ mL/g}$. The hydrogen desorption temperature of bulk LiNa is exhibited at 350°C , which is reduced $\sim$ by 150°C with the presence of carbon. Bulk LiNa has a very poor reversibility during continuous hydrogen release and uptake cycling maintaining 18% of the initial hydrogen storage capacity after four hydrogen desorptions. However, nanoconfinement into carbon aerogel scaffold stabilizes the hydrogen storage capacity significantly, maintaining 51% of the initial hydrogen capacity after four cycles, see Figure 1. Considering 100 vol% pore filling of $0.62\text{LiBH}_4\text{-}0.38\text{NaBH}_4$ into CA, would give rise to an available hydrogen release of $>6\text{ wt\% H}_2$ after the first desorption equivalent to $3.5\text{ wt\% H}_2$ after four desorptions. Recent nanoconfinement studies report that CO_2 -activation of carbon aerogel scaffold facilitate increase surface area and pore volume, allowing incorporation of larger hydride content [1,4]. The effect of surface area needs to be investigated of the $\text{LiBH}_4\text{-NaBH}_4$, however this is work in progress.

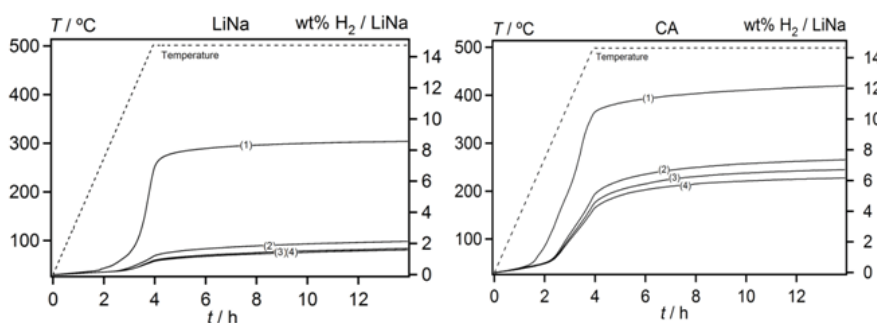


Figure 1. Sieverts' measurements showing hydrogen desorption cycles 1 to 4 of bulk LiNa (left) and melt infiltrated (60 vol%) in into carbon aerogel CA (right). Hydrogen desorption was performed at 500°C ($\Delta T/\Delta t = 2^\circ\text{C}/\text{min}$)

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Hydriding and Dehydriding Kinetics of RbH- Doped 2LiNH₂/MgH₂ Hydrogen Storage System

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In recent years, complex metal hydrides have been widely studied as promising hydrogen storage materials. The 2LiNH₂/MgH₂ system has been recognized as an attractive system for hydrogen storage. This is because it can release significant amounts of H₂ at temperatures below the high temperature-PEM fuel cell operating temperature of 200 °C [1]. However, there is a need to increase the reaction rate of hydrogen with this system and lower the desorption temperatures. In a previous study, alkali metal hydride catalysts (KH and RbH) were added to the 2LiNH₂/MgH₂ system and their effects on desorption temperatures and dehydriding rates were compared [2]. Thermodynamic and kinetic studies showed RbH to be the best catalytic additive for the 2LiNH₂/MgH₂ system so far.

In this current paper, further analyses have been done on the RbH-doped lithium amide/magnesium hydride system in order to compare the thermodynamics and kinetics of absorption and desorption at lower temperature range from 140-180 degrees. All kinetics measurements were done using constant pressure thermodynamic driving forces. The results in Figure 1 show that, under the same conditions, absorption is faster than desorption. In addition, modeling studies were done to determine what controls the hydriding and dehydriding rates. These were based on the shrinking core, Johnson Mehl Arvami, and Hancock and Sharp models. The results all show that diffusion controls the rate-limiting step for both absorption and desorption kinetic studies. Cycling studies have also been done to determine what, if any, changes would occur in the sample upon repeated hydriding/dehydriding cycling at 200°C. It was found that the amount of hysteresis increased and there was also some decrease in the hydrogen capacity after 70 cycles.

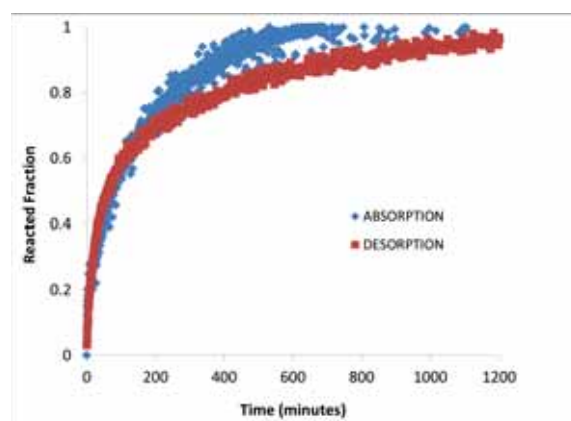


Figure 1 Absorption and desorption kinetics results for 2LiNH₂/MgH₂ doped with RbH at 160 °C.

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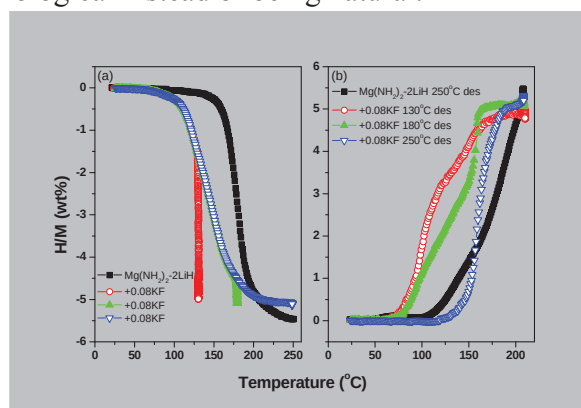
Mechanistic investigations of the high-temperature failure of K-based additives for $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ systems

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Metal-N-H systems have attracted much attention as a new family of high-density complex hydrides. Among them, the Li-Mg-N-H system composed of $\text{Mg}(\text{NH}_2)_2$ and LiH exhibits moderate thermodynamics, good reversibility and a relatively high capacity of 5.6 wt%, and is therefore regarded as a promising candidate for on-board applications. However, a rather high kinetic barrier induces that a reasonable rate for hydrogen desorption/absorption was achieved only at a temperatures up to 200 °C. K-based compounds are currently some of the most effective additives used to decrease the dehydrogenation/hydrogenation temperature of the $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ systems. The onset dehydrogenation temperature of $\text{Mg}(\text{NH}_2)_2\text{-2LiH-0.08KF}$ sample is only 80 °C; this is a ~50 °C reduction relative to that of the pristine $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ sample. Such a temperature falls into the operating temperature range of PEMFCs. However, the positive effects of K-based additives decrease when the hydrogen desorption and absorption of the K-modified $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ samples are performed at higher temperatures, seriously hindering its practical applications for long-term on-board hydrogen storage. In this paper, we report the high-temperature failure mechanism of K-based additives in a $\text{Mg}(\text{NH}_2)_2\text{-2LiH}$ system for the first time. The changes in the crystal structure of the dehydrogenation product, the enlargement in the grain and particle size of the dehydrogenation/hydrogenation products, and the increased inhomogeneous degree of mixing and distribution of the K-based additive are three most important reasons for the increased operating temperature in the follow-up cycles. More interestingly, the positive effects of K-based additives can be sufficiently recovered after further ball milling. We therefore believe that the failure of K-based additives after high-temperature treatment is only phenomenological instead of being natural.



De-/hydrogenation curves of the $\text{Mg}(\text{NH}_2)_2\text{-2LiH-xKF}$ samples.

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Synthesis, characterization and reaction kinetics on the K/Mg amides-based system

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The important role of the K₂Mg(NH₂)₄ phase as intermediate in the KH-doped Mg(NH₂)₂-2LiH system was recently investigated.[1,2] In this work, a multiphase system containing dipotassium-magnesium tetraamide, potassium amide, magnesium hydride and magnesium amide was prepared by ball milling. The thermal evolution of the system was determined by in-situ synchrotron X-ray diffraction.

Opposite to the 2Li/Mg amide-based systems, which showed similar sorption properties starting both from 2LiNH₂-MgH₂ and 2LiH-Mg(NH₂)₂, the K-Mg-N-H composite was strongly modified by using reversed reactants. Indeed, while the reaction between Mg(NH₂)₂ and KH occurred already at 120 °C, in our system KNH₂ and MgH₂ did not react below 170 °C, confirming that KNH₂ does not play the same key role of KH in lowering the desorption temperature by promoting low energy pathways.[2]

The recently solved KMg(NH)(NH₂) phase was the major component after 200 °C and around 330 °C the Mg₃N₂ was the dominating crystalline phase. (Fig. 1) It is worth mentioning that K₂Mg(NH₂)₂(NH), K₂Mg(NH)₂ and KMgN phases were not observed in the kinetics pathways investigated.[1,3]

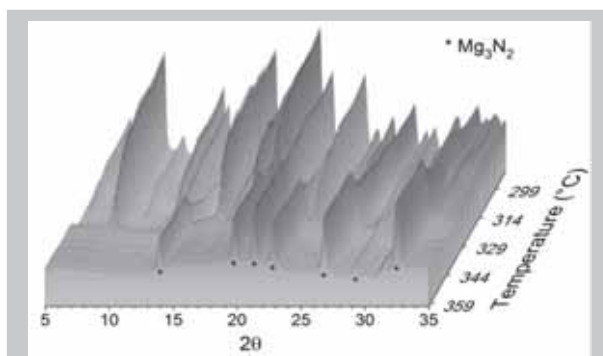


Figure 1. In Situ XRD patterns collected above 300 °C for the K/Mg-based system.

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***In situ* hybridization of LiNH₂-LiH-Mg(BH₄)₂ nano-composites for enhanced hydrogen storage properties^[1]**

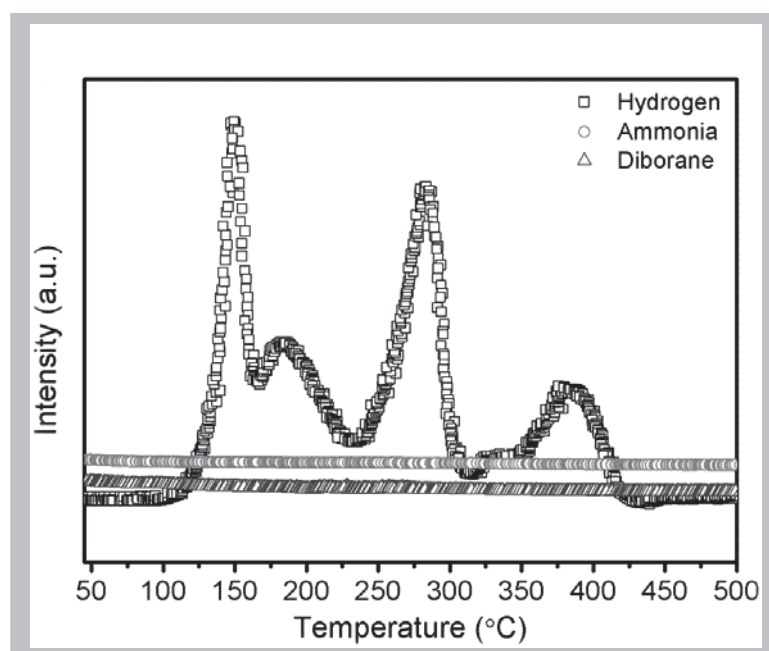
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Magnesium borohydride (Mg(BH₄)₂) is widely concerned as a promising hydrogen storage material due to its high gravimetric hydrogen capacity (14.8 wt %).^[2] However, its decomposition temperature is relatively high and it releases diborane at elevated temperature. Recently, nano-confinement and hybridization with protonic hydrogen-containing compounds are reported to be effective in enhancing the performance of borohydrides.^[3,4]

We developed a new method to synthesize LiNH₂-LiH-Mg(BH₄)₂ nano-composites through in situ hybridization of LiNH₂-LiH nano-hollowspheres and Mg(BH₄)₂ solution. This composite exhibits lower hydrogen desorption temperature and superior gas purity as shown in Figure 1. 5.3 wt % hydrogen desorption can be recorded at 150 °C and 2.2 wt % can be rehydrogenated.



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Hydrogen Storage Properties and Ionic Conductivity in Lithium nitride Bromide Systems

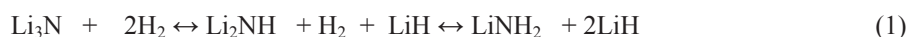
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Hydrogen is an ideal fuel to use, as it has a high energy density, light weight and is a highly abundant element. Hydrogen can be stored as either as a liquid or as a gas, although both require significant energy to allow it be stored in large quantities safely. Research into alternative ways of storing hydrogen has been carried out worldwide. This has led to developments in metal hydrides and metal complex hydrides as potential solid state hydrogen storage materials.

The first step of Equation 1 [1] shows a reversible reaction of Li_3N to Li_2NH and LiNH_2 . The hydrogenation of Li_3N step can occur at relatively low temperatures reaction time can be slow, however, the reverse reaction back to Li_3N requires a large amount of energy and is impractical in hydrogenation storage applications.



Incorporating halides into lithium amide systems resulted in hydrogen being released at a lower temperature and the release of ammonia not being detected as a side product [2]. Also these materials showed improved hydrogen absorption properties by being hydrogenated faster than Li imide. It was proposed that halide doping improves Li ion conductivity which aids in the dehydrogenation and rehydrogenation processes. This work investigates whether it is possible to improve the kinetics and thermodynamics of the first part of equation 1 with halide doping in Li_3N . In this poster we examine the hydrogen storage properties and Li ionic conductivity (figure 1) of Li_6NBr_3 (figure 2).

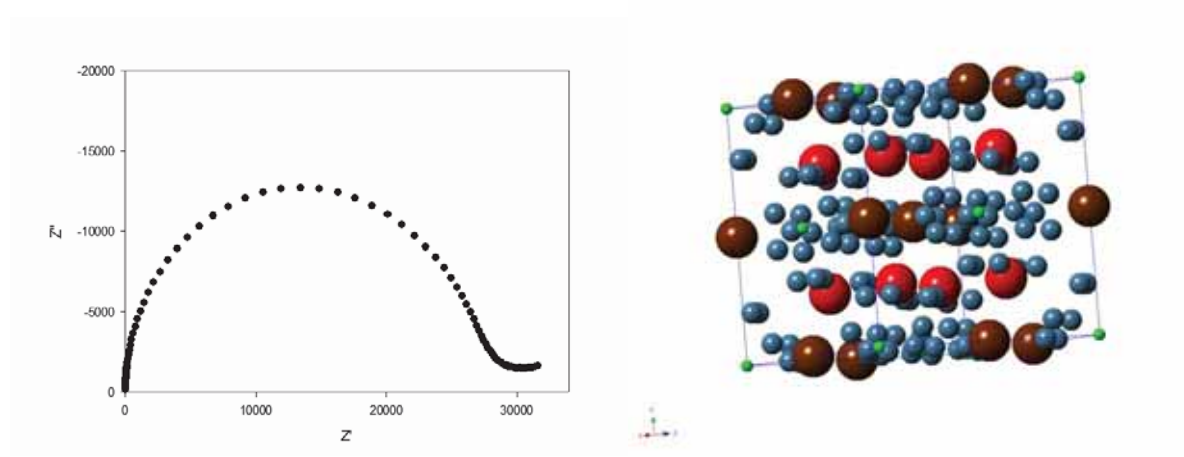


Figure 1. A.C. Impedance Nyquist plot for Li_6NBr_3

Figure 1. Crystal structure of Li_6NBr_3

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Preparation of Carbon Supported Lithium Amide

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Lithium amide has garnered much interest in the field of hydrogen storage in recent years since its ability to reversibly store 10.5 wt% of hydrogen was demonstrated [1]. Several other hydrogen storage materials have shown changes in kinetics and sometimes thermodynamics upon decreasing the particle size to the nano-scale that aid reversible hydrogen storage [2], but as of yet very little work of this kind has been carried out on lithium amide. For this reason lithium amide nanoparticles have been prepared on a carbon support for hydrogen/ammonia storage or catalysis.

The synthesis consists of 2 steps: the first is solution impregnation of LiH onto carbon using butyllithium, which is an adaptation of a previously reported method for magnesium [3]. A solution of butyllithium is added to the carbon support. The butyllithium decomposes at 300 °C, 50 bar to form LiH and butene gas. The second step is the treatment with ammonia gas to form LiNH₂.

Characterization was performed using X-ray diffraction, nitrogen physisorption and temperature programmed desorption in conjunction with mass spectrometry. This method yielded LiNH₂ with a crystallite size around 50 nm. Upon heating decomposition of lithium amide starts at 150 °C, which is 150 °C lower than for the bulk system, and ammonia is released in the process.

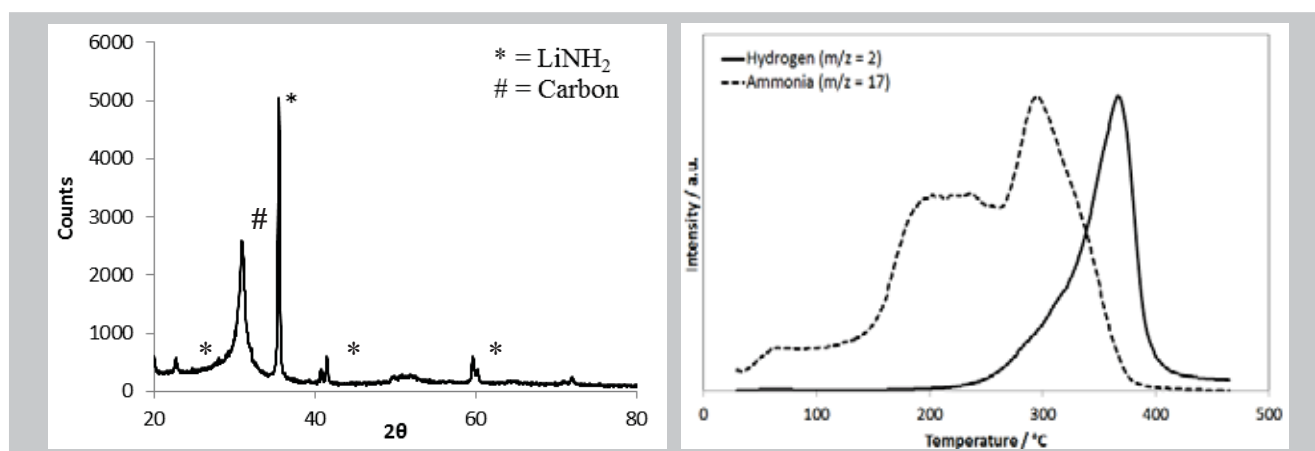


Figure 1. Results for lithium amide on carbon Left: X-ray diffraction pattern. Right: Release of H₂ ($m/z = 2$) and NH₃ ($m/z = 16$ and 17) upon heating with a ramp rate of 5 °C min⁻¹, measured using temperature programmed desorption coupled to MS.

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Catalytic Effects of ZrC Additions on the Hydrogen Storage Properties of LiAlH_4

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Abstract: Sustainable and renewable alternative energy storage systems are proposed, attributing to the environmental contamination impacted from combusting fossil fuels and dwindling energy resources[1]. As a promising hydrogen storage material, LiAlH_4 , is limited by its slow kinetics, high desorption temperature, and poor reversibility[2]. To solve these crucial drawbacks, extensive studies of catalysts incorporated by ball milling to ameliorate hydrogen storage performance of LiAlH_4 , have been conducted recently[3]. The catalysis of ZrC on the dehydrogenation properties of LiAlH_4 , prepared by designed mixing and milling processes, are systematically investigated for the first time. The results of thermal desorption measurement indicate that these factors, e.g. the particle size, ball milling time and mixed conditions, are evidently affect the improvement of hydrogen storage of LiAlH_4 . The onset dehydrogenation temperature for the 10 mol% ZrC-doped sample prepared by high-energy ball milling for 1h, are 85.3 and 148.4 °C for the first two dehydrogenation stages and released 6.88 wt.% hydrogen, which are 90.7 and 57.8 °C lower than those of as-received LiAlH_4 , respectively. Isothermal volumetric measurements reveals that $\text{LiAlH}_4 + 5 \text{ mol\% ZrC}$ sample can release about 5.62 wt.% hydrogen in 3h at 145 °C, whereas as-received LiAlH_4 releases only 1.49 wt.% hydrogen under the same condition. From differential scanning calorimetry (DSC) and Kissinger desorption kinetics analyses, the apparent activation energies (E_a) of dehydrogenation are considerably lowered by adding ZrC particles. The microstructures of the powder mixtures are characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR).

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Assessing the Performance of Sodium Aluminium Hexahydride as a Hydrogen Storage Material for an Al-alloy Based Tank.

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Sodium alanate, NaAlH₄, has gained much attention as a potential hydrogen storage material since it was reported to be reversible through doping with small amounts of Ti-catalysts [1]. Na₃AlH₆, an intermediate in the two step decomposition reaction of NaAlH₄, has a lower dissociation pressure than NaAlH₄ (6 bar vs. 66 bar at 150 °C respectively) with a theoretical hydrogen capacity of 3 wt.%. In this study Na₃AlH₆ is used as a hydrogen storage material for the development of an aluminium alloy based storage tank (3 L and 0.4 L) in the presence of a Ti-catalyst, activated carbon and metallic Al to improve the systems' hydrogen storage capacity, cycle stability and thermal conductivity. Na₃AlH₆ is synthesized through reactive ball milling of pre-doped NaAlH₄ and NaH, whereas heat transfer was realised by thermal oil flowing through a heat exchanging structure inside of the tank.

It has been found that upon cycling (170 °C) of Na₃AlH₆ doped with 4 mol% TiCl₃ a hydrogen capacity of 1.65 wt.% was obtained (0.4 L tank) which could be significantly increased to 2.2 wt.% (3 L tank) by the addition of activated carbon and metallic Al. Both systems showed no decrease in hydrogen capacity upon cycling for 13 and 188 cycles respectively (each cycle consists of 2 h dehydrogenation, 2 h hydrogenation).

Furthermore, no rupture of the tank or corrosion of the alloy was observed under the experimental conditions demonstrating that doped Na₃AlH₆ can be operated in a light weight hydrogen storage tank at 170 °C making it compatible with HT-PEM fuel cells which operate between 120 -190 °C.

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Enhanced Dehydrogenation in LiAlH_4 via Nanoconfinement in Porous Carbons

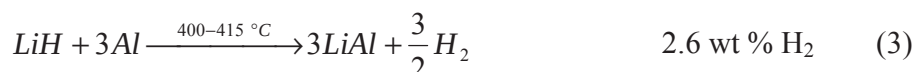
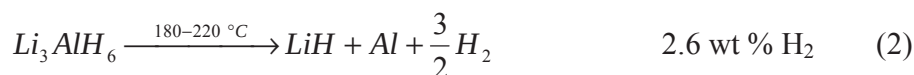
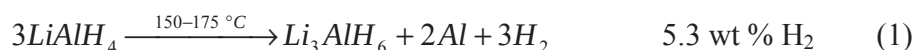
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Ideally a viable storage system will be built around materials that can uptake and release hydrogen reversibly quickly at reduced operating temperatures. No material so far meets all of the US DoE targets. Various approaches can be adopted with the aims of improving the kinetics and thermodynamics of hydrogen sorption. The nanostructuring of materials is one of the more promising strategies to achieve these aims.

LiAlH_4 is a promising high capacity material for H_2 storage[1]:



The theoretical hydrogen storage capacity of LiAlH_4 is 10.5 wt.%. However, only the first (1) and second step (2) take place at temperatures suitable for practical mobile applications providing a theoretical hydrogen release of 7.9 wt. %.

Reduction of the particle size of hydrides by nanoconfinement in forms of porous matrix leads to an increased surface area of the active material, and shorter diffusion distances for hydride to travel in the solid state. Kinetic barriers can be overcome and thermodynamics manipulated. An enhanced dehydrogenation rate and a reduced dehydrogenation temperature can be achieved by impregnating metal hydrides into porous scaffolds [2].

In this work, LiAlH_4 has been impregnated in different types of commercial and synthesised porous carbon scaffolds for the first time. We demonstrate how the design of the carbon scaffold (as manifested for example, by the surface area and the pore volume and pore size distribution) influences the dehydrogenation behavior of the impregnated complex hydride. By judicious selection of an appropriate porous host, we show how it is possible to induce faster H_2 desorption and substantially reduce the desorption temperature.

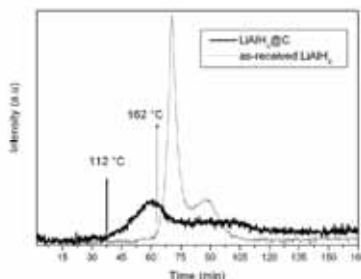


Figure 1. TPD of bulk LiAlH_4 and LiAlH_4 impregnated in a porous carbon matrix..

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Direct Mechanochemical Synthesis of the Complex Aluminum Hydrides of Rb and Cs

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Although LiAlH_4 and NaAlH_4 are widely investigated over the last decade, only limited information is known about the homologues RbAlH_4 and CsAlH_4 , with crystal structures built from $[\text{AlH}_4]^-$ tetrahedra. The synthesis of RbAlH_4 and CsAlH_4 is usually done in the liquid phase. One possible synthesis starts from the elements at 270 bar of hydrogen pressure, a temperature of 150 °C and in the presence of triethylaluminum as a catalyst in toluene.^[1] The second way is the metathesis reaction of LiAlH_4 with the corresponding metal halide in toluene with triethylaluminum as a catalyst.^[2] The corresponding hexahydrides (Rb_3AlH_6 and Cs_3AlH_6) are unknown. Here we present the mechanochemical direct synthesis^[3] of the complex aluminum hydrides CsAlH_4 , RbAlH_4 , Rb_3AlH_6 , and Cs_3AlH_6 from the elements at room temperature under hydrogen pressure. During the milling process the pressure evaluation inside the milling vial was recorded continuously. The compounds were characterized with ^{27}Al -NMR MAS spectroscopy and powder diffraction. The new crystal structures were solved from powder diffraction data, structure refinements were performed by the Rietveld method.

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Hydrogen Release and Uptake in the Li-Zn-N System

Trang T. T. Nguyen^{1*}, Paul A. Anderson¹, David Book² and Daniel Reed²

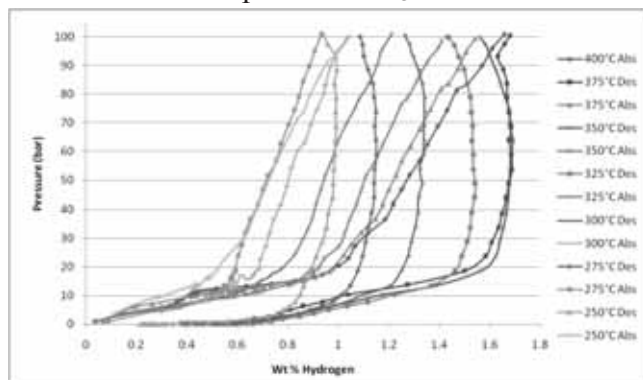
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The Li-N-H system has attracted considerable attention as one of the most promising materials for hydrogen storage [1]. Although a large number of studies have been carried out on this system, the low absorption kinetics and relatively high operating temperature currently limit its practical application [2]. Amide halide systems have recently been found to release hydrogen on heating and rehydrogenate more rapidly than LiNH_2 [3].

In the present work, reactions of ZnCl_2 with LiNH_2 under different conditions were investigated and the molar ratios of 1:2 and 1:3 were confirmed as stoichiometric ones with different reaction products Zn_3N_2 and LiZnN . Temperature programmed desorption with mass spectrometry (TPD-MS) showed that the main gas emitted was ammonia. The addition of LiH changed the main gaseous product from NH_3 to H_2 , which was released at a low temperature beginning around 90°C .



form LiNH_2 and Zn metal in a molar ratio of 1:1. Reversible properties of the Li-Zn-N system have been tested using HTP. The results show that up to 2 wt % hydrogen could be stored reversibly from 250°C .

Figure 1. Absorption/desorption of the Li-Zn-N system studied using HTP at 400°C (1st), 375°C (2nd), 350°C (3rd), 325°C (4th) and 300°C (5th), 275°C (6th), 250°C (7th).

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Rb₃AlD₆ an unusual alanate featuring an interstitial hydrogen atom position in addition to a well ordered octahedral AlD₆ complex and 3 disordered complexes.

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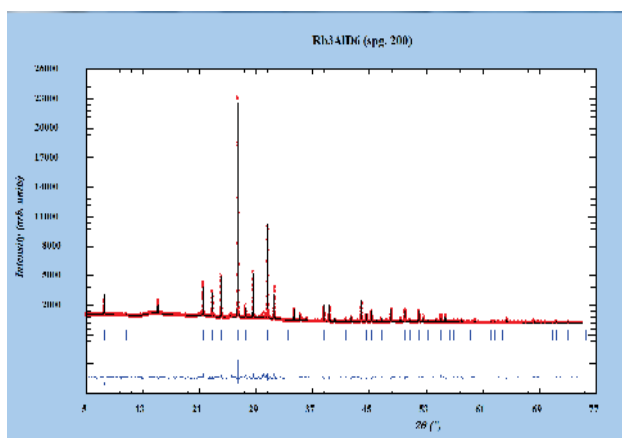
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Abstract

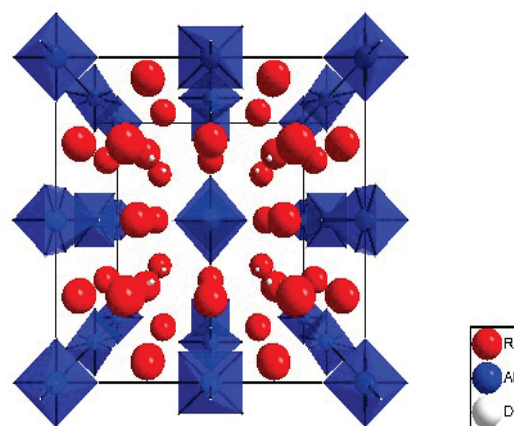
Gallium hydride clusters have been found with larger rubidium and caesium counter ions.¹⁻³ Such complexes could facilitate practical hydrogen storage by acting as stable intermediates in absorption/desorption reactions as exemplified by:²



In this work we aimed at finding similar clusters based on aluminium. These could make practical hydrogen storage systems based on alanates possible. So far we have not been successful, but during our attempts we discovered a new type of alanate structure in Rb₃AlD₆. The refinement was made in two steps. X-ray powder as well as single crystal diffraction data yielded the metal atom positions. But during the refinement of the neutron diffraction data we found one eight fold interstitial hydrogen site. This has consequences for the anticipated AlD₆ complexes. Only one was well ordered and the other three both orientation disordered as well as lacking deuterium atoms.



Observed and calculated XRD pattern



Structure of Rb₃AlD₆ in spgr 200

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Inelastic Neutron Scattering Studies on Water Exposed Sodium Alanate: Is "S105" Relevant to Enhanced Hydrogen Cycling Kinetics?

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In situ ²⁷Al NMR studies of Sc and Ti-doped NaAlH₄ have detected a mobile, Al-bearing species (aka S105) that forms at elevated temperatures. Initially it was reported that this species was “highly defective NaAlH₄ likely having a large AlH₃ vacancy concentration” that persists only at elevated hydrogen pressures ⁽¹⁾. It has subsequently been found that this species arises simply upon exposure of either doped or un-doped NaAlH₄ to H₂O ⁽²⁾. However, despite this revision, Conradi and co-workers still assert that S105 is a facilitator of Al-atom transport in NaAlH₄ and is essential for the induction of enhanced dehydrogenating kinetics⁽²⁾.

In order to further clarify this, the identity of S105 and its possible connection to the enhanced hydrogen cycling kinetic of Ti-doped NaAlH₄, we have conducted inelastic neutron scattering (INS) studies on Ti-doped and un-doped NaAlH₄ that was exposed to water vapour.

The INS studies confirm that mild interaction with air/water introduces defective structural bulk changes in undoped NaAlH₄ that are quite similar in character to those resulting from Ti doping. However, following complete dehydrogenation to NaH/Al, the water-exposed materials fail to undergo re-hydrogenation to NaAlH₄ under the same moderate conditions that are well established for Ti-doped NaAlH₄. We conclude that while S105 is associated with a stoichiometric hydrolysis event that leads to the elimination of hydrogen and generation of a stoichiometric amount of Na₃AlH₆, the formation S105 is not associated with the celebrated enhanced hydrogen cycling kinetics of Ti-doped NaAlH₄. The details of the INS studies will be presented together with a detailed discussion of the dehydrogenation reaction associated S105.

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Composites of Light-metal Amides and Hydrides as Hydrogen Storage Systems

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A hydrogen storage system, which can fulfill all the necessary selection criteria for commercial use in a fuel-cell vehicle, remains a challenge despite several decades of intense research that has, however, been able to identify a number of promising light-metal hydrides capable of satisfying some of the selection criteria. As a result, use of composite systems comprising these promising hydrides was suggested with the aim to improve the kinetic and the thermodynamics properties suitable for reversibly storing hydrogen in these composites [1]. One of the parameters that often proved useful to control the sorption properties is the mole ratio of the components. A systematic study of such composites with different mole ratios, which may be able to identify the optimum combinations of the hydrides, therefore, is important.

We here report hydrogen desorption properties of the systems comprised of three compounds taken from light metal hydrides $[MH_x]$ and amides $[M(NH_2)_y]$ where $M=Li, Mg$ and $x,y=1,2$ giving four possible three-component systems, viz., (i) $LiH-MgH_2-LiNH_2$, (ii) $LiH-MgH_2-Mg(NH_2)_2$, (iii) $MgH_2-LiNH_2-Mg(NH_2)_2$ and (iv) $LiH-LiNH_2-Mg(NH_2)_2$. For each of the systems, we mechanically mixed the compounds (ball milling for 20h under Ar environment) in different molar ratios; and the thermal decompositions of the composite powders were studied by the Thermogravimetric Analysis combined with Differential Thermal Analysis (TG-DTA) supported by XRD and Raman spectroscopy to identify the phases present in the composites.

Our study reveals that $Mg(NH_2)_2$ mixed with LiH and MgH_2 (system (ii)) in 1:1:1 mole ratio undergoes a distinct endothermic decomposition $\sim 300^\circ C$ resulting 4 wt% mass-loss with onset temperature $\sim 150^\circ C$. A mass-loss of 5 wt% with the onset temperature $\sim 100^\circ C$ is achieved by replacing $Mg(NH_2)_2$ with $LiNH_2$ (system (i)). System (iii) appeared to be unstable even at room temperature, presumably, due to the reaction between MgH_2 and $Mg(NH_2)_2$ releasing a large amount of H_2 gas. As a result, we noticed increase of gas pressure inside the milling pot and a very less mass-loss during TPD (typically < 1 wt% for a 3:1:1 composition). On the other hand, study with system (iv) suggests that there may be an intermediate concentration of LiH in this composition that could maximize the desorbed gas within 200 C.

The present study initiates a systematic screening for the promising composite systems as well as the range of the molar ratios of the systems for fast hydrogenation kinetics within the fuel-cell operating temprature without compromising the hydrogen storage capacities.

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Formation in Ternary Ti-V-Mn Alloy in the Hydride Cycle, Their Interaction With Hydrogen

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In recent years, the study of Ti based BCC phase alloys, due to their remarkable hydrogen absorbing ability, take up a special place in investigations of some laboratories and research centers in the world. Of particular interest are the hydrogen absorbing, α , β , γ phase alloys in Ti-V, Ti-V-Mn, Ti-V-Cr systems [1-7].

In the Institute of Chemical Physics after A.B. Nalbandyan of Armenian NAS, a new "Hydride Cycle" (HC) method has been developed for synthesis of binary and multicomponent alloys [3]. The essence of HC consists in combination of two methods: self-propagating high-temperature synthesis (SHS) of transition metal hydrides, and dehydrogenation-sintering. The present work provides the results of study of the mechanism of formation of the ternary Ti-V-Mn alloys in HC.

TiV_{1.2}Mn_{0.8}; TiV_{0.8}Mn_{1.2}; Ti_{0.37}V_{0.25}Mn_{0.25} alloys were synthesized. The peculiarities of interaction of these alloys with hydrogen were studied. It was shown that the synthesized alloys interacted with hydrogen a) in the combustion mode and b) at rather low temperature, 25-50°C, after short-time activation of alloy (400°C, 30 min.) This interaction resulted in forming high hydrogen content (2.5-3.5 wt %)

TiV_{1.2}Mn_{0.8}H_{3.7}; TiV_{0.8}Mn_{1.2}H_{2.35} and Ti_{0.37}V_{0.38}Mn_{0.25}H_{1.56} hydrides. The phase composition of the synthesized alloys and their hydrides were determined by X-ray analysis. The lattice parameters were defined. In the synthesized alloys the main was BCC phase. XRD of hydrides showed that at interaction of alloys with hydrogen, a BCC phase transition to FCC structure occurred [4, 6, 7]. Such a phase transition is peculiar also for BCC binary alloys, such a phase transition is peculiar also for BCC binary alloys. For example, it occurs at interaction of Ti-V and Ti-Nb alloys with hydrogen [3]. The identity of structure, hydrogen content and thermal properties of alloy hydrides, synthesized by both the SHS combustion and short-term activation methods, was manifested by X-ray diffraction, chemical and DTA analyses.

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Hydrogen Sorption in Metal Intercalated Fullerenes

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It has been shown that in metal intercalated Fullerenes (M_xC_{60} , $M=Li, Na, K, Mg$) hydrogen can be reversibly absorbed and desorbed. In $Na_{10}C_{60}$ up to 3.5 mass% of hydrogen can be reversibly absorbed at a hydrogen pressure of 200 bar and a temperature of 200 °C [1]. In $Li_{12}C_{60}$ it is even possible to absorb up to 5 mass% of hydrogen [2]. The metal fullerenes were investigated by XRD, NPD, FTIR. Infrared spectroscopy has shown C-H stretching modes, indicating that the hydrogen is covalently bonded to the C_{60} . XRD and NPD investigations revealed that during hydrogenation metal atoms deintercalate from the M_xC_{60} and form metal hydride MH which decomposes during dehydrogenation and the metal atoms reintercalate in the metal atom depleted $M_{x-y}C_{60}$ phase (see Figure 1).

In order to improve the hydrogen sorption kinetics of the M_xC_{60} samples different transition metals were added and the influence on the kinetics investigated.

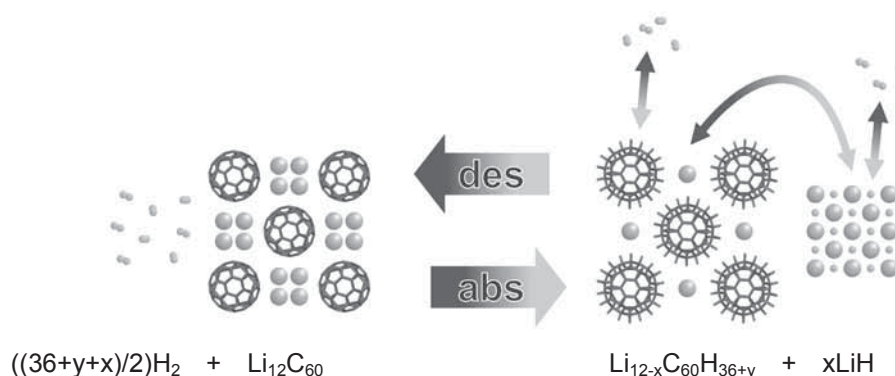


Figure 1. Illustration of the hydrogen sorption mechanism shown for $Li_{12}C_{60}$.

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Catalytic Modification in Hydrogenation properties of KSiH_3

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Recently KSiH_3 has been proposed as an attractive contender towards hydrogen storage media, owing to its high storage capacity i.e. 4.3 wt% within a good P-T window [1]. Although thermodynamic parameter i.e. $\Delta H = -28 \text{ kJ mol}^{-1}$ allows hydrogen absorption at reasonable working conditions; the slow sorption kinetics hinders its practical use at the same time. The high activation energy for desorption ($\sim 121 \text{ kJ mol}^{-1}$) allows KSiH_3 to desorb hydrogen slowly only at 200°C . Moreover, the efforts to improve the kinetics by means of milling with carbon powder disproportionate KSiH_3 into KH, Si & K-Si intermetallic phases [2]. In the present work, a number of known catalysts, which are proven very effective for several hydrogen species, were attempted in order to see the effect on sorption properties of KSiH_3 . Among all the catalysts used in this work, mesoporous Nb_2O_5 is found to be quite effective with a reduction in activation energy from 132 kJ mol^{-1} for pristine KSi to 63 kJ mol^{-1} for meso- Nb_2O_5 doped KSi. Any disproportionation is not observed in controlled hydrogenation process. The mechanism for this improvement is also proposed in details.

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Enhanced Catalytic Effects of Co@C Additive on Dehydrogenation Properties of LiAlH₄

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Hydrogen is regarded as one of the most promising energy candidates for on-board fuel cell applications owing to its high energy density and free of pollutants. Catalyst usually has a stronger selective for the acceleration of the reaction. Lithium aluminum hydride (LiAlH₄) is considered as an attractive candidate for hydrogen storage owing to its favorable thermodynamics and high hydrogen storage capacity. However, its reaction kinetics and thermodynamics have to be improved for the practical application. The dehydrogenation thermodynamics and kinetics of LiAlH₄ after adding Co@C additive can be significantly increased. In our present work, the dehydrogenation thermodynamics and kinetics properties of the as-synthesized Co@C-doped LiAlH₄ have been systematically investigated. The dehydrogenation behaviors of 10 wt%Co@C-doped LiAlH₄ (10%Co@C-LiAlH₄) have been investigated using temperature programmed desorption (TPD), differential scanning calorimetry (DSC) and fourier transform infrared spectroscopy (FTIR). The dehydrogenation kinetics of 10%Co@C-LiAlH₄ can also be significantly increased with the increase of dehydrogenation temperature. Interestingly, the onset hydrogen desorption temperature of 10%Co@C-LiAlH₄ sample gets lower from 151.0 °C to 100.0 °C with a faster kinetics, and the dehydrogenation rate reached a maximum value at 156.9 °C. Moreover, 10%Co@C-LiAlH₄ displays a substantially reduced activation energy for LiAlH₄ dehydrogenation.

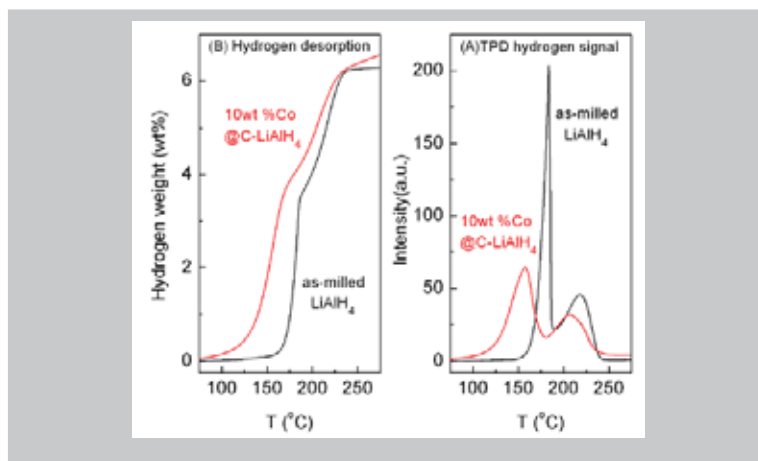


Figure 1. Thermal desorption profiles of H₂ for the as-milled LiAlH₄ and 10%Co@C-LiAlH₄ samples under an Ar atmosphere (heating ramp 2 °C min⁻¹).

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Hydrogen Solubility in Silica and Silicate Compounds

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The paper reports on results of our experimental investigation of the solubility of molecular hydrogen in amorphous and crystalline phases of silica at pressures up to 75–90 kbar and a temperature of 250°C and also in forsterite (Mg_2SiO_4) at $P = 50$ kbar and $T = 250^\circ\text{C}$. The samples synthesized under high hydrogen pressure and elevated temperature were quenched to the temperature of liquid nitrogen and further studied by powder X-ray diffraction, Raman spectroscopy and thermal desorption analysis at ambient pressure. The molar ratio $X = \text{H}_2/\text{SiO}_2$ of the obtained solid hydrogen solutions in amorphous silica was shown to linearly increase with the synthesis pressure from $X = 0.16$ at $P = 6$ kbar to $X = 0.53$ at $P = 75$ kbar. The maximal value of $X = 0.53$ reached in our experiments much exceeds the limiting value of $X = 0.05$ predicted earlier [1]. The Raman spectra collected from the sample synthesized at 56 kbar show two H_2 vibron lines at 4160 and 4362 cm^{-1} . We suppose that the two different H_2 vibron lines correspond to two different positions of the hydrogen molecules in the silica network. Also, our X-ray diffraction studies showed that the hydrogen molecules penetrated in the silica glass network at a hydrogen pressure of 75 kbar prevented the sample from the significant irreversible densification occurring at this pressure in the absence of hydrogen.

A sample of a low-pressure cristobalite I phase exposed to $P = 90$ kbar and $T = 250^\circ\text{C}$ had $X \sim 0.10$. An X-ray examination showed the hydrogenated sample to consist of a mixture of the cristobalite I phase (70%) and a high-pressure cristobalite II phase (30%). Also, X-ray diffraction revealed a hydrogen-induced expansion of the cristobalite I unit cell by 0.26 and 0.61 $\text{\AA}^3$, respectively, in the samples hydrogenated at $P = 28$ and 75 kbar. The Raman spectroscopy showed that the hydrogen-induced lattice expansion occurred in both cristobalite-I and cristobalite II phases and that the hydrogen is dissolved in these phases mostly in the form of H_2 molecules weakly interacting with the silica network.

The hydrogen solubility in two other crystalline phases of silica, quartz and coesite, does not exceed $X = 0.01$ at $P = 28$ kbar and $X = 0.025$ at $P = 50$ kbar, respectively.

The hydrogen solubility in amorphous forsterite (Mg_2SiO_4) has also been investigated for the first time. The H_2/SiO_2 ratio of the forsterite sample exposed to $P = 50$ kbar and $T = 250^\circ\text{C}$ reached $X = 0.58$. Studies on the hydrogen solubility in some other silica compounds are in a progress.

The work was supported by Grant No. 12-02-00871 from the Russian Foundation for Basic Research and by the Program “Elementary Particle Physics, Fundamental Nuclear Physics and Nuclear Technologies” of the Russian Academy of Sciences.

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Raman spectroscopy and imaging of lithium hydride and corrosion products

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Lithium hydride (LiH) is the lightest metal hydride and has many applications including as a reducing agent and potential hydrogen storage material. LiH readily reacts with atmospheric moisture to produce hydroxide (LiOH) and hydrogen gas, which is undesirable from both a quality and safety standpoint.

Diffuse Reflectance IR Fourier Transform (DRIFT) spectroscopy is commonly used in LiH corrosion studies to detect the presence of surface LiOH [1]. However, the role of lithium oxide (Li₂O - which is also a decomposition product of LiOH) in the hydrolysis is less well understood, partially because the only IR active Li₂O vibration is typically obscured in the DRIFT spectrum. More recently, it has been shown that Raman spectroscopy using a UV excitation source allows observation of Li₂O, whilst mainly avoiding regions of the EM spectrum that cause fluorescence [2].

This study utilises a Renishaw InVia Raman instrument with 325 nm UV laser to characterise the surface corrosion layer of LiH compacts following exposure to atmospheric H₂O and CO₂. Standard Raman spectra were recorded using both fibre optic delivery (to an inert atmosphere glovebox) and microscope setups, whilst the microscope stage was also used to carry out Raman imaging of corroded LiH surfaces.

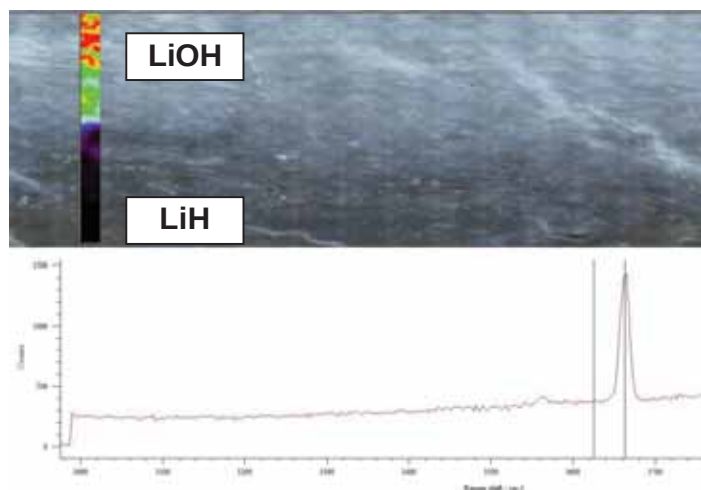


Figure 1. White light montage image of partially corroded LiH sample with overlaid Raman image map (top), Raman spectrum showing hydroxide peak at 3676 cm⁻¹ (bottom). Image © British Crown Owned Copyright 2014/AWE

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Cunning	Benjamin	ThP-075			
Czujko	Tomasz	MoOD-033			
Daemen	Luke	ThP-033			
Daio	Takeshi	WeOC-123			
Daku	Latévi Max Lawson	MoOD-034	TuOQ-060	TuOD-076	TuOC-085
Dam	Bernard	TuOC-086	TuOC-087	TuP-102	WeOQ-098
		WeOC-123			
		TuP-022			
D'Anna	Vincenza	TuP-023			
Danzberger	Jürgen				
Dao	Dzung				

David	Bill	MoOQ-003	TuP-008	WeOH-102	WeOH-105
Davids	Moegamat Wafeeq	TuP-020	ThP-095		
Davies	Rosalind	WeOH-104			
De Bonis	Angela	TuOH-072			
de Jongh	Krijn	TuOQ-053	ThP-115		
de Jongh	Petra	TuOQ-053	ThP-115		
de Rango	Patricia	TuOQ-050	TuOQ-058	ThP-022	ThP-068
		ThP-070			
Deavin	Oliver	ThP-094			
Degtyareva	Valentina	TuP-113			
Dekura	Shun	TuP-084			
Deledda	Stefano	TuP-062	WeOC-124	ThOQ-135	ThP-100
Delmelle	Renaud	MoOD-035	TuOC-089	ThOD-152	
Demmel	Franz	ThOC-164			
Denis	Jean-Benoît	ThP-004			
Denys	Roman	TuOQ-049	TuOH-061	TuOH-063	TuP-034
		TuP-080	ThP-052	ThP-053	ThP-054
		ThP-012	ThP-027		
Deutges	Martin	ThOQ-127			
Devillers	Michel	TuP-029			
Dey	Tapobrata	ThOQ-136			
Di Sarcina	Ilaria	TuP-054			
Dieterich	Mila	MoOD-027			
Dionne	Jennifer	ThP-005			
Dittmeyer	Roland	ThP-074			
Dixit	Vinay	TuP-027			
Djerdire	Abdesslem	ThP-018			
Dobron	Patrik	TuOH-063			
Dobrotvorskiy	Mstislav	MoOD-033			
Dolan	Michael	WeOH-103			
Dolci	Francesco	ThP-031	ThP-124		
Dolukhanyan	Seda	TuOD-083	TuP-099		
Dong	Hanwu	MoOQ-011	TuP-025	TuP-030	WeOH-107
Dornheim	Martin	ThOH-137	ThP-101	ThP-112	FrOH-183
		ThOQ-127	ThOH-143		
Dovgaliuk	Iurii	TuP-067	TuP-086	ThP-028	
Droulias	Sotirios	ThP-020			
Drulis	Henryk	TuP-017			
Dundar-Tekkaya	Ezgi	ThOH-139			
Dupuis	Cédric	ThP-110			
Durojaiye	Tolulope	MoOD-034			
Dutta	Sarmila	TuP-115			
Dye	David	MoOH-019	MoOC-047	TuOQ-052	
Eastwick	Carol	ThP-033			
Edalati	Kaveh	MoOC-037			
Edalati		WeOH-102			
Edwards	Peter	ThP-128			
Efimchenko	Vadim	TuP-102			
Egger	Werner	TuOD-079			
Ehlers	Georg	TuOD-075	TuOD-076	TuP-102	
Eijt	Stephan W. H.	ThOH-138			
Elie	Manon	TuP-027			
Elkedim	Omar	MoOQ-002			
Elsaesser	Thomas	TuP-055			
Emami	Hoda	TuP-063			
Emery	Sam	TuOD-080	TuOD-081	TuP-114	
Endo	Naruki	TuP-050	ThP-034	ThP-036	
Enoki	Hirotooshi	WeOH-103	WeOH-107	ThP-112	
Enzo	Stefano	ThP-121			
Eriksson	Lars	MoOH-023			
Eriksson	Olle	TuP-105	ThOC-163	ThP-011	
Fabre	Arnaud	ThP-121			
Fahlquist	Henrik	ThP-059			
Faisal	Mohammad	ThP-085			
Fan	Xiulin	TuP-099			
Fang	Fang	MoOC-041			
Fang	Zak				

Fedotov	Vladimir	ThP-054	ThP-128		
Felderhoff	Michael	MoOC-042	ThP-117	ThP-119	
Fell	Helen	TuP-074			
Fenineche	Nourdine	TuP-027			
Fichtner	Maximilian	MoOC-045	TuP-080	WeOD-111	ThOD-155
		ThP-005			
Figiel	Henryk	ThOH-140	ThP-030	ThP-079	
Fijalkowski	Karol	ThP-104			
Filinchuk	Yaroslav	WeOQ-099	ThOQ-127	ThOQ-128	ThOQ-131
		ThOQ-134	ThOH-143		
Filipek	Stanislaw	TuP-112			
Findlay	Ian	WeOD-116			
Finot	Eric	ThP-011			
Fischer	Roland A.	ThOC-165			
Florian	Paolo	MoOC-046			
Fokin	Valentin	TuP-103			
Fokina	Evelina	TuP-103			
Fouldavind	Marjan	TuOQ-050			
Francisco Fernandez	José	TuOD-082	FrOQ-172		
François	Julien	TuP-066			
Fréchette	Nicolas	ThP-065			
Friedrich	Theo	TuP-053	WeOC-119		
Frommen	Christoph	ThOQ-125			
Fruchart	Daniel	TuOQ-050	TuOQ-058	TuP-076	TuP-083
		ThP-022	ThP-065	ThP-068	ThP-070
		TuOQ-056	ThP-113		
Fu	He	TuP-068			
Fujisaki	Fumika	TuP-060			
Fukai	Yuh	TuP-060			
Fukumuro	Naoki	ThP-007			
Fursikov	Pavel	TuP-028	ThP-001		
Fuura	Tatsuya	MoOD-032	TuOH-063		
Gabis	Igor	TuP-006			
Gaboardi	Mattia	TuOQ-050	ThP-068	ThP-070	
Gabov	Andrei	MoOC-046			
Gagliano	Salvatore	ThP-103	ThP-111		
Gao	Mingxia	TuP-061			
Garanin	Georgy	WeOH-107	ThP-112		
Garroni	Sebastiano	ThP-042			
Gatto	Irene	MoOC-044			
Gaudin	Etienne	WeOQ-098			
Geerlings	Hans	TuP-053			
Gehrer	Carmen	ThOD-152			
Gehrig	Jeffrey	TuP-090	ThP-018		
Gemma	Ryota	ThP-122			
Georgiev	Peter	FrOQ-176			
Gerger	Joachim	TuOC-092			
Getzlaff	Mathias	TuP-029			
Ghosh	Prakash C	TuP-016			
Giasafaki	Dimitra	ThOH-138	ThOH-139		
Gillia	Olivier	TuP-006			
Girella	Alessandro	ThP-026			
Giyora	Kimmel	ThP-020			
Giza	Krystyna	ThOQ-136			
Gizer	Gokhan	ThOH-148			
Gkanas	Evangelos	ThP-095			
Goh	Jonathan	ThP-041			
Golubeva	Valentina	ThOH-140	ThP-030	ThP-079	
Gondek	Łukasz	ThP-101			
Gosalawit-Utke	Rapee	TuOD-084	TuP-036		
Goubault	Lionel	TuP-010	ThP-110		
Goudy	Andrew	TuP-046			
Grabovetskaya	Galina	MoOC-046			
Graizzaro	Alessandro	TuOD-079			
Granroth	Garrett	MoOH-019	TuOQ-052	TuOQ-059	ThOH-148
Grant	David	ThP-040	ThP-058	ThP-094	

Gray	Evan	MoOD-026 TuP-101	MoOC-048 ThOH-144	TuP-011	TuP-023
Greenbaum	Yeuda	TuP-093 FrOH-181			
Greenway	Scott	ThP-072	ThP-118		
Gregory	Duncan	TuOD-077 TuOH-068	TuOD-078	TuP-115	
Gregoryanz	Eugene	MoOH-015 ThP-073			
Griessen	Ronald	WeOC-119			
Grill	Andreas	WeOC-122	ThP-104	ThP-107	
Grimmer	Christoph	ThP-091 TuOH-103			
Grochala	Wojciech	ThOH-139			
Grube	Elisabeth	ThP-080 TuOD-077			
Grzech	Anna	MoOQ-007	TuP-007	ThP-082	
Gu	Jian	MoOD-029 ThP-059			
Guenoux	Lise	MoOH-024			
Guichard	Jordan	TuP-038			
Guillaume	Christophe	ThP-020			
Guo	Sheng	TuP-053	WeOC-119		
Guo	Zheng Xiao	TuP-095	WeOC-123	ThOC-167	
Gupta	Anshul	MoOD-034			
Gupta	Michèle	ThP-031			
Habaguchi	Hiroki	TuOD-078			
Hackemer	Alicja	MoOQ-002			
Hacker	Viktor	TuP-107			
Hagemann	Hans	MoOQ-011	ThP-087		
Haije	Wim	WeOH-103			
Hakobyan	Hasmik	TuP-052			
Halsall	Matthew	TuP-069	TuP-070		
Hamm	Peter	FrOQ-175			
Hansen	Thomas	TuP-027			
Hansen	Bjarne R. S.	ThP-016			
Hansen	Thomas	MoOD-025			
Hara	Masanori	MoOD-033			
Haraki	Takeshi	MoOQ-003			
Hardy	Bruce	TuOC-088	WeOH-106	ThOD-158	
Harel	Fabien	TuOD-080			
Harker	Robert	FrOH-182			
Harris	Rex	MoOQ-004	MoOC-045	TuP-062	WeOD-111
Hartl	Minonka	WeOC-124	ThOQ-125	ThOQ-135	ThP-025
Hartly	Jon	ThP-100			
Hashimoto	Naoyuki	WeOD-114 WeOD-112	ThP-023		
Hattori	Takanori	MoOQ-007	TuP-007		
Hauback	B.C.	ThP-110 ThP-084			
Hauback	Bjørn C.	ThOC-165	ThOC-166		
		ThOH-140 TuOC-091			
Havela	Ladislav	FrOQ-170			
Havranek	Vladimir	WeOH-104			
Hayden	Brian	TuP-087			
Hayes	Jalaal	TuP-031			
He	Liqing	ThOH-140			
Heine	Thomas	TuP-022			
Herbrig	Kai	TuOC-088			
Heubner	Felix	TuOC-088 WeOQ-097	TuP-003	ThOQ-135	
Heuser	Brent	ThOC-165	WeOQ-098	WeOQ-099	ThOQ-134
Hewett	David	MoOH-014	MoOH-023	TuOQ-060	TuP-067
Hideaki	Kasai	TuP-086	WeOD-109	ThP-028	
Higuchi	Eiji	ThP-022			
Hilger	André				
Hingerl	Kurt				
Hino	Ryutaro				
Hino	Satoshi				
Hirscher	Michael				
Hjörvarsson	Björgvin				
Hlil	El Kebir				

Hoelzel	Markus	WeOH-103			
Holtz	Marcel	MoOQ-002			
Horita	Yoshinobu	MoOC-037			
Horita	Zenji	MoOC-037	TuP-077	ThP-033	
Horky	Jelena	ThP-073			
Hoser	Andreas	ThP-030			
Hosono	Minako	TuP-051			
Howard	Matthew	ThP-114			
Howie	Ross	TuOD-077			
Hruška	Petr	ThP-018			
Hu	Weikang	TuOH-061	TuOH-063		
Huang	Cunke	TuOD-083			
Huang	Jianmei	ThP-098			
Huang	Liwu	TuOH-070			
Huang	Wen	TuP-086	ThP-028		
Huang	Zhenguo	ThOQ-130			
Hudson	Matthew R.	WeOQ-099			
Hugenschmidt	Christoph	TuP-102			
Hughes	Luke	TuP-091			
Hulvey	Zeric	TuP-013			
Hummel	Stefan	FrOQ-176			
Humphries	Terry D.	MoOQ-004	ThOQ-125	ThOQ-135	
Hunter	Hazel	TuP-008	WeOH-102	WeOH-105	
Huot	Jacques	TuOQ-050	ThP-065	ThP-070	ThP-074
Hutcheon	Ian	FrOH-180			
Huthwelker	Thomas	TuP-094			
Hwang	Sonjong	WeOC-121	ThOD-156	ThP-025	ThP-084
Ichikawa	Takayuki	TuOH-069	TuP-005	TuP-033	TuP-071
		ThP-126			
Iizuka	Riko	TuOD-080			
Ikarashi	Yudai	TuP-003			
Ikeda	Kazutaka	TuP-068			
Ikeda	Ryuichi	TuP-084			
Ikeda	Suguru	TuOH-069			
Ikeshoji	Tamio	MoOQ-006	TuOH-066		
Ikeuchi	Shuki	ThP-045			
Iles	Gail N.	WeOQ-099			
Ino	Shuichi	TuP-050	TuP-051		
Inokawa	Hitoshi	TuP-031	TuP-071		
Iosub	Vasile	ThOH-139			
Iriowen	Esosa	TuP-010			
Isheim	Dieter	MoOD-033			
Ishikawa	Kazuhiro	TuP-038	TuP-040		
Ishikiriya	Mamoru	TuOH-067			
Ishimoto	Takayoshi	TuP-096	ThP-009	ThP-013	FrOQ-171
Isobe	Shigehito	TuOQ-055	TuOC-088	TuP-003	WeOH-106
		TuP-088			
		ThP-102			
Ito	Yohei	TuP-077	ThP-033		
Iwaoka	Hideaki	ThOH-146	ThP-015		
Iwase	Kenji	FrOH-177			
Jacob	Isaac	ThP-077	ThP-126		
Jain	Ankur	ThP-077			
Jain	I.P.	ThP-074	ThP-077		
Jain	Pragya	ThP-077			
Jangir	Mukesh	MoOQ-009	MoOQ-010		
Janot	Raphaël	ThP-096			
Janot	Raphaël	WeOC-122	ThP-107		
Jaroń	Tomasz	ThP-093	ThP-109		
Javadian	Payam	ThOQ-129	ThP-122		
Jensen	Craig	TuP-009			
Jensen	Peter	ThP-091			
Jensen	Steffen Riis Højbjerg	MoOQ-008	MoOQ-011	WeOQ-099	ThOQ-125
Jensen	Torben René	ThOQ-131	ThOQ-134	ThP-086	ThP-087
		ThP-090	ThP-091	ThP-093	ThP-096
		ThP-097	ThP-108	ThP-109	FrOQ-174

Jepsen	Julian	TuP-030	ThOH-137		
Jepsen	Lars H.	MoOQ-008	ThOQ-131	ThOQ-134	
Jiao	Lifang	ThP-066	ThP-088		
Jimenez	Isabel	TuOD-082			
Johansson	Robert	MoOH-023			
Joiret	Suzanne	TuP-036			
Jones	Martin	MoOQ-003	TuP-008	WeOH-102	WeOH-105
Jorgensen	Scott W.	WeOQ-099			
Jothi	Sathiskumar	MoOH-018	ThOD-159		
Joubert	Jean-Marc	MoOH-021			
Ju	Xin	ThP-081	ThP-099		
Juvé	Vincent	MoOQ-002			
Kalb	Roland	WeOC-119			
Kaneko	Naokatsu	TuP-068			
Kaneko	Takehiro	WeOQ-100			
Kanlidindi	Suresh B.	ThOC-165			
Karagiorgis	George	ThP-022			
Kardjilov	Nikolay	ThOH-140			
Karimi	Fahim	ThP-024			
Katayama	Yoshinori	TuOD-080	TuOD-081	TuP-114	ThP-008
Kato	Nobuyuki	ThP-001			
Kato	Shunsuke	TuP-094			
Kawahito	Koji	TuP-033			
Kawahito	Koji	TuOH-069			
Kazakovskiy	Nikolay	ThP-041			
Khasanov	Salavat	ThP-124			
Kieback	Bernd	TuOC-091	ThOH-140		
Kiehn	Rüdiger	TuP-025			
Kikuchi	Shiomi	ThP-045			
Kim	Chul	ThOD-156	ThP-025		
Kim	Hyunjeong	TuP-050	WeOD-110	ThOH-146	ThP-008
		ThP-034	ThP-036		
Kim	Sang-Mun	MoOD-033			
Kimijima	Tubasa	TuP-032			
Kimura	Tomonori	ThOD-158			
Kirchheim	Reiner	ThP-012	ThP-027		
Kirk	Andrew	ThP-129			
Kitagawa	Hiroshi	TuP-012	TuP-084		
Kiyobayashi	Tetsu	TuP-092			
Klassen	Thomas	MoOQ-011	TuP-030	ThOH-137	ThP-101
Klein	Markus J.	TuOD-075			
Klimkowicz	Alicja	TuP-082	ThP-079		
Klyukin	Konstantin	TuP-076			
Knight	Kevin	MoOD-026			
Knowles	John	MoOH-016	TuP-072	TuP-074	TuP-107
		WeOD-116			
Knudsen	K.D.	FrOH-182			
Kobayashi	Hirokazu	TuP-012	TuP-084		
Kobori	Yoshihiro	TuP-038			
Koh	Ai Leen	MoOD-027			
Kojima	Saeka	TuP-060			
Kojima	Yoshitsugu	TuOH-069	TuOC-088	TuP-005	TuP-033
		TuP-071	ThP-126		
Kojima	Yoshiyuki	WeOQ-100			
Kolesnikov	Alexander	TuOD-079	TuP-024		
Kolomiets	Aleksander	ThP-023			
Komeda	Osamu	TuOH-067			
Koncar	Michael	WeOC-119			
Kondo	Ryota	TuP-092	ThP-045	ThP-102	
Königshofen	Samuel	TuOC-092			
Korshunov	Kirill	ThP-032			
Kosciuczyk	Ewelina	ThP-075			
Kotani	Norihiro	TuP-031			
Koultoukis	Evangelis	ThP-022			
Koyama	Michihisa	TuP-096	ThP-009	ThP-013	FrOQ-171
Kozhakhmetov	Serik	MoOD-032			

Krech	Daniel	ThP-119	FrOH-178		
Krexner	Gerhard	ThP-073			
Krishnamurthy	Nagaiyar	ThOH-145			
Kudiiarov	Victor	TuP-047	TuP-061		
Kulakov	Valery	ThP-054			
Kumar	Sanjay	ThOH-145			
Kunisada	Yuji	TuP-104			
Kuznetsov	Anatoliy	TuP-045			
Kuzovnikov	Mikhail	ThP-054			
Kuzovnikov	Mikhail	TuOD-079	ThP-128		
Lafont	Ugo	TuOD-075			
Laipple	Daniel	ThP-101			
Lampimäki	Markus	TuP-094			
Lang	Julien	TuOQ-050	ThP-065	ThP-070	
Langhammer	Christoph	TuOD-073	TuP-049		
Langhans	Volker	TuP-025			
Langmi	Henrietta	TuP-001	WeOQ-096		
Laptev	Roman	TuP-061			
Latroche	Michel	MoOH-024	TuOH-061	TuOH-063	TuOH-070
		TuOH-071	TuOD-084	TuP-036	WeOQ-094
Laversenne	Laetitia	FrOQ-172			
Le Duff	Cécile	ThOQ-127			
Lecoq	Hervé	ThP-080			
Lee	Hyun-Sook	WeOC-121	ThOD-156		
Lee	Ming-Tao	TuP-039	TuP-094		
Lee	Young-Su	WeOC-121	ThOD-156		
Lehmberg	Annegret	ThP-027			
Léonel	Eric	TuOH-071	WeOQ-094		
Ley	Morten Brix	ThOQ-131	ThP-087	ThP-090	ThP-096
		ThP-108			
Li	Chao	ThP-111			
Li	Gao Ran	TuP-035			
Li	Guangqin	TuP-012			
Li	Guanqiao	MoOQ-004	MoOQ-011	ThP-100	
Li	Hai-Wen	ThP-084	ThP-123		
Li	Li	ThP-066	ThP-088	ThP-127	
Li	Ping	ThP-116			
Li	Shouquan	ThP-047			
Li	Xingguo	TuOQ-051	TuOQ-056	ThP-113	
Li	Yongtao	ThP-060			
Li	Zhou Peng	TuP-002	TuP-035		
Li	Ziliang	ThP-116			
Liang	Li	ThOC-162	FrOH-179		
Lider	Andrey	TuP-047	TuP-061		
Lidström	Emil	TuP-049			
Liedke	Maciej Oskar	ThP-029			
Lin	Huai-Jun	ThP-062			
Linder	Marc	MoOC-038	MoOC-045	TuP-054	
Liu	Bin Hong	TuP-002	TuP-035		
Liu	Feng	ThP-010			
Liu	Haizhen	ThP-047	ThP-076		
Liu	Hang	ThP-014			
Liu	Jiangwen	TuOQ-054	ThP-050	ThP-051	ThP-078
Liu	Peipei	ThP-046			
Liu	Wei	ThP-063			
Liu	Yongan	ThP-047	ThP-076		
Liu	Yongfeng	ThP-103	ThP-111		
Llewellyn	Gwynfor	ThP-129			
Lohstroh	Wiebke	ThOD-155			
Lototsky	Mykhaylo	MoOC-043	TuP-020	TuP-024	ThOH-147
		ThP-095			
Lozano	Gustavo	TuP-030			
Lu	Yanshan	ThP-051			
Luetto	Carlo	MoOC-045	MoOC-046		
Lukáč	František	MoOD-036	TuP-106		
Lumley	Simon	TuP-115			

Luo	Linshan	ThP-035			
Luo	Xuanli	ThP-058			
Lushnikov	Stepan	TuP-057	TuP-058		
Lutz	Matthias	FrOQ-176			
Lux	Susanne	TuP-053			
Lv	Yujie	ThP-057			
Lyth	Stephen	TuP-015			
Lyutyy	Pavlo	TuP-034			
Ma	Mingwang	ThOC-162	FrOH-179		
Machida	Akihiko	TuOD-080	TuOD-081	TuP-114	WeOD-110
		ThP-008	ThP-034		
Maekawa	Yasunari	TuOC-088			
Maesato	Mitsuhiko	TuP-084			
Majzoub	Eric	MoOH-017	ThOH-146	ThOD-149	
Makepeace	Joshua	TuP-008	WeOH-102	WeOH-105	
Makridis	S.S.	ThP-022			
Malfatti	Célia	TuP-014			
Malkov	Igor	TuP-045			
Malysenko	Stanislav	ThP-003			
Manassen	Yishay	TuP-093			
Manickam	Kandavel	ThP-040			
Manke	Ingo	ThOH-140			
Mann	Vicky	MoOD-025			
Manna	Joydev	ThP-083			
Marini	Amedeo	TuP-006	WeOH-107	ThP-112	
Marni	Amedeo	ThP-101			
Marques	Miriam	TuOD-077			
Martin Martinez	Angel	ThP-067	ThP-069		
Martins	Leandro	ThOD-157			
Marty	Philippe	TuOQ-058			
Marzaroli	Vittoria	TuP-006			
Maskova	Silvie	ThP-023			
Masolo	Elisabetta	WeOH-107	ThP-112		
Matei-Ghimbeu	Camelia	TuOH-071	WeOQ-094		
Matej	Zdenek	WeOD-114			
Mathe	Mkhulu	TuP-001	WeOQ-096		
Matsuda	Hitoshi	TuP-060			
Matsuda	Junko	MoOC-037	ThOD-150	ThP-033	
Matsumoto	Takashi	TuP-052			
Matsumoto	Yoshihisa	MoOD-031	TuP-042	TuP-085	
Matsumura	Daiju	TuP-073			
Matsunaga	Tomoya	TuOH-067			
Matsuo	Motoaki	MoOQ-004	MoOQ-011	TuOH-066	TuOD-080
		WeOH-106	ThP-100	ThP-106	
Matsuyama	Masao	TuP-052			
Matzel	Jennifer	FrOH-180			
Mauermann	Sebastian	TuOC-091			
Mauron	Philippe	ThP-125	FrOH-184		
Mauroy	Henrik	WeOD-111	ThP-005		
Mayer	Nicole	WeOC-119			
Mays	Tim	TuOC-090	TuP-108		
McGee	Randolph	WeOC-117			
McLean	William	FrOH-180			
Medvedeva	Nataliya	ThP-068	ThP-070		
Meethom	Sukanya	ThP-101			
Meggouh	Mariem	ThP-117			
Meletov	Konstantin	ThP-128			
Melikhova	Oksana	ThOD-160	ThP-010		
Melnichuk	Maximiliano	TuP-026			
Meng	Xianhe	ThP-081	ThP-099		
Menushenkov	Vladimir	TuP-059	ThP-017		
Merritt	Christopher	TuP-011			
Merson	Dmitriy	TuP-048			
Merson	Evgeniy	TuP-048			
Mertens	Florian	WeOC-120			
Metz	Oliver	TuP-025	ThOH-137	FrOH-183	

Michael	Felderhoff	FrOH-178			
Middelkoop	Joost	TuOD-075			
Milanese	Chiara	TuP-006	WeOH-107	ThP-101	ThP-112
Mintz	Moshe	TuP-093	ThP-026		
Mirabile Gattia	Daniele	TuP-016	ThOQ-136		
Mishin	Ivan	TuP-046			
Mistry	Priyen	TuOQ-059			
Mitrokhin	Sergey	ThP-003	ThP-017		
Miwa	Kazutoshi	TuP-056			
Miyaoka	Hiroki	TuOH-069	TuP-005	TuP-033	TuP-071
Mizuki	Jun'ichiro	TuP-073			
Mnatsakanyan	Nune	ThP-031	ThP-124		
Mohammadshahi	Shahrazad	MoOC-048	TuP-023		
Mohtadi	Rana	TuOH-065			
Mokrushin	Valeriy	ThP-032	ThP-041	TuP-045	
Møller	Kasper	ThP-090			
Monnier	Judith	TuP-036			
Montealegre	Felipe	TuP-097	TuP-098		
Montone	Amelia	TuP-016	ThOQ-136		
Mooij	Lennard	MoOH-014	TuOQ-060	TuP-067	TuP-086
		ThP-028			
Morelle	Fabrice	ThOQ-128	ThOH-143		
Moretto	Pietro	MoOC-045	WeOH-103		
Morgante	Gianluca	Plenary 5			
Mori	Kazuhiro	ThP-015			
Moropeng	Mapula Lucey	TuP-024			
Morozov	Yury	ThP-054			
Morozov	Boris	TuP-058			
Morrison	Ian	TuP-019			
Moser	David	TuOD-083	TuP-019		
Moskura	Melanie	TuP-105			
Motyka	Theodore	FrOQ-175			
Movlaev	Elshad	TuP-057	TuP-058	ThP-017	
Mücklich	Arndt	ThP-018			
Mulas	Gabriele	WeOH-107	ThP-112		
Mulder	Fokko M.	TuOH-068	TuOD-075		
Munaõ	David	TuOH-072			
Murai	Mikako	TuP-052			
Muraki	Keita	TuP-070			
Murata	Yoshinori	TuP-042	TuP-085		
Murray	Allen	WeOC-117			
Musyaev	Rafael	TuP-111			
Musyoka	Nicholas	WeOQ-096			
Muthukumar	Palanisamy	ThOH-147			
Nachev	Simeon	TuOQ-058	ThP-068		
Nagai	Hiroyuki	ThP-102			
Nakagawa	Yuki	TuP-003	TuP-088		
Nakamura	Jin	TuP-028	WeOD-110	ThP-001	
Nakamura	Yuki	TuP-042			
Nakamura	Yumiko	TuP-050	TuP-051	WeOD-110	ThOH-146
		ThP-008	ThP-034	ThP-036	
Nambu	Tomonori	MoOD-031	TuP-042	TuP-085	
Napolitano	Emilio	WeOH-103			
Narayan	Tarun	MoOD-027			
Nardin	Philippe	MoOC-040			
Nayebossadri	Shahrouz	MoOD-030	TuP-041	TuP-044	ThOH-148
Neiner	Doinita	WeOC-118			
Nestl	Stephan	TuP-053			
Ngene	Peter	MoOD-034	TuOD-076	TuOC-085	TuOC-086
Nguyen	Trang	ThP-120			
Nicholson	Kelly	MoOQ-005			
Nishihata	Yasuo	TuP-073			
Nishimiya	Nobuyuki	WeOQ-100			
Nishimura	Katsuhiko	TuP-052			
Noguchi	Kazuo	ThP-034	ThP-036		
Noréus	Dag	TuOH-064	TuOD-083	ThP-121	

North	Brian	TuP-001	WeOQ-096		
Nugroho	Ferry	TuP-049			
Obata	Nanako	TuP-038			
Obermayr	Markus	TuP-022			
Odysseos	Marios	ThP-022			
Ogawa	Hiroshi	TuP-079	WeOD-110		
Oguchi	Hiroyuki	TuOH-066			
Oh	Hyunchul	WeOQ-097	WeOQ-099	ThOQ-134	ThOC-165
Ohata	Yuki	TuP-069			
Ohnuki	Somei	TuOQ-055	TuP-003	TuP-088	WeOH-106
		ThOD-158			
Ohshita	Hidetoshi	TuP-068			
Okamura	Yuka	TuP-073			
Olafsson	Sveinn	TuP-081			
Olsen	Jørn Eirik	ThOQ-125			
Oñoro	Moises	TuOD-082			
Orefuwa	Samuel	TuP-010			
Orimo	Shin-Ichi	MoOQ-006	MoOQ-011	MoOQ-004	Plenary 3
		TuOH-066	TuOD-080	TuOD-081	TuP-062
		WeOH-106	ThOQ-129	ThP-100	ThP-106
		TuP-068			
Otomo	Toshiya	TuOH-070	TuOH-071	WeOQ-094	
Oumellal	Yassine	TuOQ-054	ThP-019	ThP-050	ThP-051
Ouyang	Liuzhang	ThP-078	ThP-098		
		TuP-108			
Owens	Simon	MoOC-039	TuP-043	ThP-049	
Oztürk	Tayfur	TuP-087			
Padama	Allan	ThP-006			
Paidar	Vaclav	ThP-123			
Paik	Biswajit	MoOD-033			
Pal	Narendra	MoOH-014	TuOQ-060	ThP-028	TuP-086
Pálsson	Gunnar	ThP-048			
Palumbo	Oriele	ThP-103	ThP-111		
Pan	Hongge	TuP-002			
Pan	Wei Yuan	TuOH-072			
Panero	Stefania	TuP-022			
Panholzer	Martin	TuOH-072	ThP-048		
Paolone	Annalisa	ThP-022			
Papapanagiotou	Theodoros	MoOQ-008	FrOQ-174		
Paskevicius	Mark	TuOD-074			
Pasquini	Luca	ThP-011			
Passian	Ali	ThP-082			
Paterakis	Christos	MoOH-019	TuOQ-052		
Patman	Andrew	WeOD-114			
Paukov	Mykhaylo	TuP-112	ThOC-168	ThP-052	ThP-053
Paul-Boncour	Valérie	ThP-056			
		TuP-094			
Paun	Cristina	FrOQ-176			
Pawelke	Roland	Plenary 5			
Pearson	David	ThP-042			
Pedicini	Rolando	ThP-117			
Peil	Stefan	ThP-117			
Peinecke	Kateryna	TuOQ-060			
Perkisas	Tyché	FrOQ-175	FrOH-181		
Peters	Brent	TuOD-075			
Pfeiffer	Tobias V.	ThOH-148	ThP-038		
Pickering	Lydia	MoOH-022	MoOC-046		
Pinatel	Eugenio R.	TuP-037			
Piskin	Berke	TuP-043			
Pişkin	Fatih	MoOQ-011	WeOH-107	ThP-101	ThP-112
Pistidda	Claudio	MoOD-032			
Piven	Vladimir	TuOD-079			
Podlesnyak	Andrey	ThP-005			
Pohl	Alexander	TuOC-091	ThOH-140		
Pohlmann	Carsten	TuP-020	TuP-024	ThOH-147	ThP-095
Pollet	Bruno	FrOH-178			
Pommerin	Andre				

Ponthieu	Marine	TuOD-074	FrOQ-172		
Pontiroli	Daniele	TuP-006			
Porch	Adrian	MoOQ-003			
Postnikov	Alexey	ThP-041			
Potekhina	Yuliya	ThP-041			
Potzger	Kay	ThP-029			
Powell	George	WeOD-115			
Pranzas	Philipp Klaus	TuP-025			
Privalov	Alexei	TuP-083			
Prochazka	Ivan	WeOD-112	ThOD-160	ThP-010	
Proctor	John	TuOD-078	TuP-115		
Proffen	Thomas	WeOD-110			
Proost	Joris	MoOD-035			
Provost	Karine	ThOC-168			
Psycharis	Vassilis	ThP-022			
Pundt	Astrid	MoOD-036	TuP-090	TuP-106	ThOD-151
		ThP-018			
Pushilina	Natalia	TuP-047			
Pyle	Darryl	TuP-011			
Qaade	Ulrich	TuP-009			
Qiu	Fangyuan	ThP-066	ThP-088	ThP-127	
Qu	Xuanhui	ThP-116			
Ramirez-Cuesta	A. J. Timmy	TuOC-089	ThOH-142		
Ramón Ares	Jose	TuOD-082	FrOQ-172		
Ramos	Silvina	TuP-026			
Ravelli	Luca	TuP-102			
Raybaud	Pascal	MoOQ-009	MoOQ-010		
Reale	Priscilla	TuOH-072			
Realpe	Henry	TuP-093			
Reed	Daniel	MoOQ-007	TuP-007	ThOQ-132	ThP-014
		ThP-038	ThP-082	ThP-105	
Reguera	Edilso	ThP-071			
Reissner	Alexander	FrOQ-176			
Reiter	Joseph W	Plenary 5			
Reller	Christian	WeOC-120			
Rellinghaus	Bernd	TuP-100			
Remhof	Arndt	TuOH-066	ThP-089	ThP-092	FrOH-184
Ren	Jianwei	TuP-001	WeOQ-096		
Rentsch	Daniel	ThP-089	ThP-092		
Riabov	Alexander	ThP-053			
Riccò	Mauro	TuP-006			
Richter	Bo	WeOQ-099	ThOQ-134	ThP-093	ThP-097
Riktor	Marit D.	ThOQ-125			
Riley	Duncan	TuP-019			
Rizzi	Paola	MoOC-046			
Roach	Daniel	TuOQ-057			
Robeyns	Koen	ThOQ-127			
Robinson	Ian	TuP-110			
Roedern	Elsa	ThP-086	ThP-108		
Rogers	David	WeOQ-098			
Röhm	Eva	ThOD-155			
Rokhmanenkov	Alexander	ThP-039			
Romanov	Ivan	ThP-003			
Röntzsch	Lars	TuOC-091	ThOH-140		
Ross	Keith	TuP-107	ThOC-164		
Rothensteiner	Matthäus	TuP-094			
Roy	Binayak	ThP-083			
Rueda Norieg	Miriam	ThP-067	ThP-069		
Rush	John	ThOD-154	ThP-106		
Rusinek	Dariusz	ThP-030			
Ruta	Beatrice	MoOD-033			
Saccà	Ada	ThP-042			
Sadikin	Yolanda	TuP-078	ThOH-143		
Sadykov	Ravil	TuOD-079			
Saeki	Yoshihide	TuP-040			
Saisopa	Thanit	ThP-101			

Saita	Itoko	ThP-034	ThP-036		
Saitoh	Hiroyuki	MoOQ-006	TuOD-080	TuOD-081	TuP-114
Sakaguchi	Norihito	TuP-104			
Sakaki	Kouji	TuP-050	TuP-051	WeOD-110	ThOH-146
		ThP-008	ThP-034	ThP-036	
Saldan	Ivan	ThOQ-135			
Salque	Bruno	ThOH-139			
Salvio	Filipe	ThOD-157			
Samelyk	Anatoly	FrOH-184			
Sánchez	Carlos	TuOD-082	FrOQ-172		
Sano-Furukawa	Asami	TuOD-080			
Santoru	Antonio	WeOH-107	ThP-112		
Santosntos	Dilson	ThOD-157			
Sanz Moral	Luis Miguel	ThP-067	ThP-069		
Sarker	Suchismita	MoOD-033			
Sartori	Sabrina	FrOH-182			
Sato	Toyoto	MoOQ-004	TuOD-080	TuP-062	
Savaris	Israel	TuP-014			
Savchenko	Aleksandr	TuP-059	ThP-017		
Savchenko	Levgeniia	ThOC-165			
Scheicher	Ralph H.	MoOH-023			
Scheler	Thomas	TuOD-077			
Schiavo	Benedetto	TuP-030			
Schiavone	Emily	FrOQ-170			
Schlichtenmayer	Maurice	WeOQ-097			
Schmidt-Ott	Andreas	TuOD-075	TuP-102		
Schouwink	Pascal	TuP-075	ThOQ-126	ThOH-143	ThOC-167
		ThP-090			
Schreuders	Herman	TuOQ-060	TuOD-076		
Schubert	David	WeOC-118			
Schultz	Ludwig	TuP-100			
Schut	Henk	TuP-102			
Schweke	Danielle	ThP-026			
Sciora	Elisabeth	ThP-080			
Segales	Marc	ThP-118			
Segard	Mathieu	TuP-105	ThOC-163		
Seifert	Bernhard	FrOQ-176			
Sengmany	Stéphane	TuOH-071	WeOQ-094		
Sethio	Daniel	TuP-095	ThOC-167		
Setijadi	Eki	ThP-064			
Seya	Tomohiro	TuP-068			
Sgroi	Mauro	MoOC-045			
Shalimov	Artem	MoOD-036			
Shamir	Noah	TuP-093			
Shao	Huaiyu	TuOQ-051	TuP-015		
Shao	Jie	ThP-085			
Shapovalov	Alexandr	ThP-032			
Sharma	Manish	TuP-095	ThOC-167		
Sharma	Pratibha	ThP-083			
Shcherbakova	Larisa	FrOH-184			
Shchetinin	Igor	TuP-059	ThP-017		
Shekhtman	Veniamin	ThP-031	ThP-124		
Shelyapina	Marina	TuP-076	TuP-083		
Sheppard	Drew	MoOQ-008	FrOQ-174	FrOQ-175	
Sheptyakov	Denys	TuOH-061			
Sheridan	Richard	MoOD-025			
Shervani	Suboohi	ThP-059			
Sheverev	Stanislav	ThP-054			
Shibata	Kazuya	ThP-045			
Shibato	Tsuyoshi	ThP-043			
Shin	Hyeon Man	ThP-061			
Shinozawa	Tamio	TuOH-067			
Shneck	Roni	TuP-093			
Sholl	David	MoOQ-005			
Shtender	Vitalii	TuP-034	ThP-052	ThP-053	
Sibanyoni	Johannes Mlandu	ThP-095			

Sidorov	Nikolay	MoOD-032			
Siekhaus	Wigbert	WeOD-115	FrOH-180		
Silin	Nicolas	TuP-026			
Silva	Bruno	ThOD-157			
Silvestri	Laura	TuOH-072			
Silvi	Luca	ThOD-155			
Singdeo	Debanand	TuP-029			
Sinnaeve	Marc	MoOD-035			
Sipatov	Ivan	MoOD-032			
Skoryna	Juliusz	ThP-021	ThP-037		
Skoryunov	Roman	TuP-075			
Skipov	Alexander	TuOH-066	TuP-075	ThOD-153	ThOD-154
		ThP-106			
Skryabina	Nataliya	TuOQ-050	TuOQ-058	ThP-065	ThP-068
		ThP-070			
Slaman	Martin	TuOC-086			
Slater	Peter	ThP-114			
Smardz	Lesław	ThP-021	ThP-037		
Smith	Dean	TuOD-078	TuP-115		
Smith	Robert	ThOC-161			
Solis	Hugo	TuP-097	TuP-098		
Solonin	Yurii	FrOH-184			
Soloninin	Alexei	TuP-075			
Solorza	Omar	ThP-071			
Song	Yun	TuP-099			
Sørby	Magnus H.	MoOQ-004	WeOD-111	ThOQ-125	ThP-005
		ThP-025	FrOH-182		
Sorte	Eric	TuP-063	ThOD-149		
Soulié	Jean-Philippe	MoOQ-007	TuP-007		
Speight	John	MoOD-030	TuP-041	TuP-044	
Spodaryk	Mariana	FrOH-184			
Stadie	Nicholas	TuOC-089	ThP-097		
Stamatakis	Manos	ThP-022			
Stavila	Vitalie	ThOD-154	ThP-106		
Steel	Simon	TuP-107	ThOC-164		
Stepanova	Ekaterina	TuP-046	TuP-047		
Steriotis	Theodoros	TuP-016	ThP-022	ThP-093	
Stetson	Ned	Plenary 4			
Stevens	Nicholas	ThP-016			
Stolboushkina	Oxana	TuOC-092			
Stuart	Alastair	MoOH-019	TuOQ-052	ThOH-148	
Stubos	Thanos	ThP-022			
Subramaniam	Anandh	ThP-059			
Suh	Jin-Yoo	WeOC-121			
Sun	Dalin	TuP-099			
Sun	Tai	TuP-021			
Suo	Tao	ThP-010			
Surrey	Alexander	TuP-100			
Suwarno	S.	TuOQ-053			
Suzuki	Asuka	TuP-042	TuP-085		
Suzuki	Tetsuya	ThP-015			
Suzuya	Kentaro	TuP-068			
Svoboda	Pavel	ThP-023			
Swierczek	Konrad	TuP-032	TuP-082	ThP-043	ThP-079
Szilagy	Petra	WeOQ-098			
Tajima	Ikko	TuP-069			
Takada	Masayuki	ThP-102			
Takagi	Shigeyuki	MoOQ-004	MoOQ-006	TuOD-081	TuP-062
Takahashi	Keisuke	TuP-088			
Takamatsu	Yu	ThP-001			
Takamura	Hitoshi	TuOH-066			
Takasaki	Akito	TuP-032	TuP-082	ThP-030	ThP-043
		ThP-079			
Takeichi	Nobuhiko	TuP-092			
Takeshita	Hiroyuki T.	TuP-092	ThP-045	ThP-102	
Tamehiro	Ko	TuP-069			

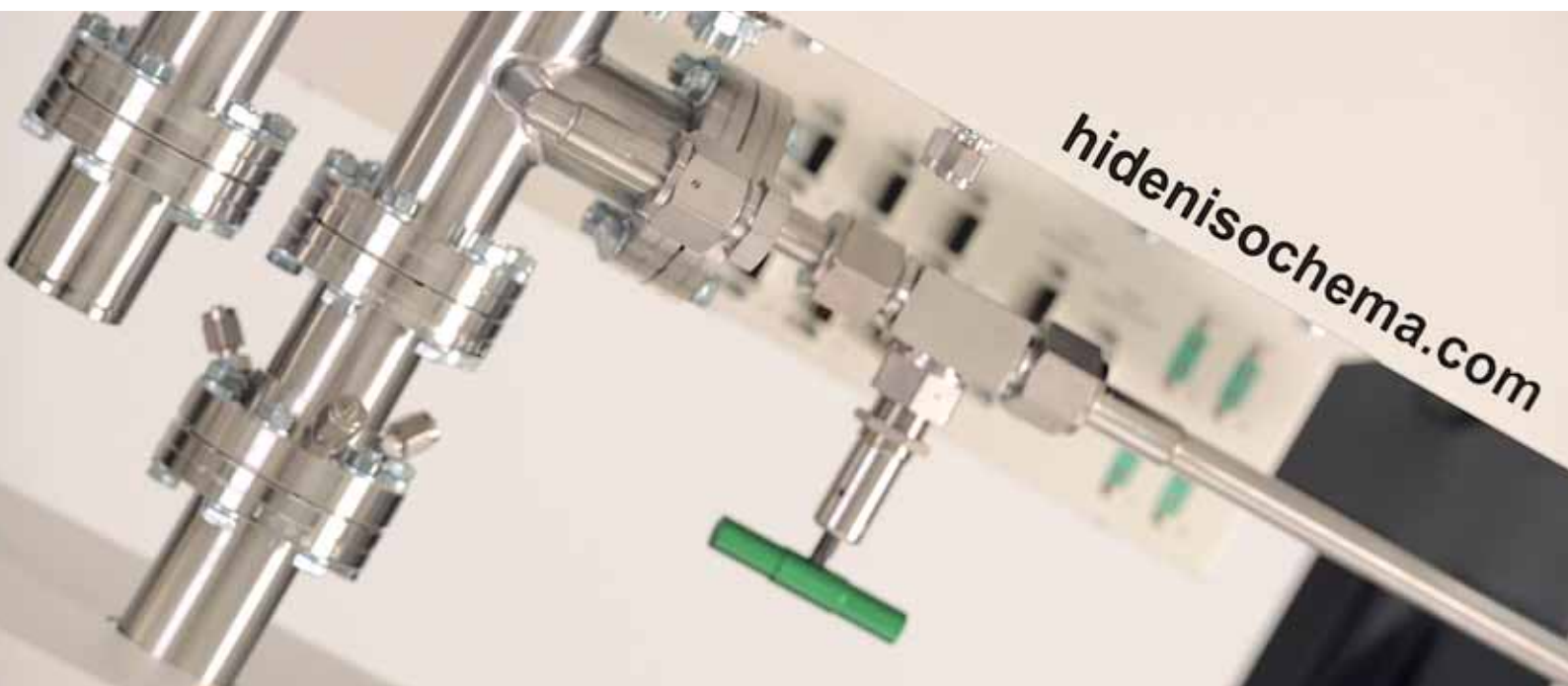
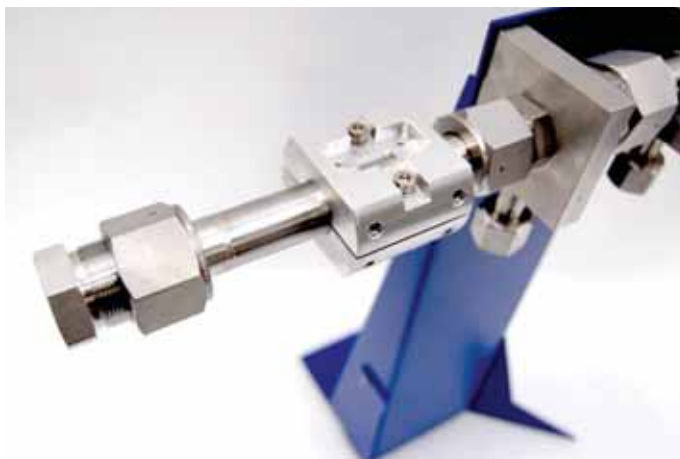
Tampaxis	Christos	TuP-016			
Tan	Serdar	MoOC-039			
Tan	Xiaohua	ThOC-162	FrOH-179		
Tanaka	Koji	TuP-092	ThP-045		
Tang	Renheng	TuP-021			
Tang	Wan Si	MoOQ-009	MoOQ-010	ThOD-154	ThP-106
Tarasov	Boris	TuOH-063	TuP-080	TuP-103	ThP-007
		ThP-054			
Tashiro	Suguru	ThP-015			
Tayeh	Toufic	TuP-089			
Taylor	James	TuP-008			
Teprovich	Joseph	FrOQ-175	FrOH-181	FrOH-182	
Teresov	Anton	TuP-047			
Ter-Galstyan	Ofeliya	ThP-031	ThP-124		
Teslich	Nick	WeOD-115			
Thundat	Thomas	ThP-011			
Tihonov	Vasilii	TuP-111			
Tkach	Ilya	WeOD-114			
Tkacz	Marek	TuP-109			
To	Magnus	ThOD-156			
Toh	Shoichi	ThP-033			
Tokoyoda	Kazuhiko	TuOC-088			
Tokuhira	Shinnosuke	TuP-070			
Tolj	Ivan	TuP-020			
Tominaga	Tomoki	TuP-082	ThP-043		
Toyama	Takeshi	WeOQ-100			
Trasova	Anna	TuP-045			
Trequattrini	Francesco	ThP-048			
Trinh	Thu Trang	ThP-029			
Trinkle	Dallas	FrOQ-170			
Trynogga	Marie	ThP-027			
Tsarev	Maxim	TuP-045	ThP-032	ThP-041	
Tsareva	Irina	ThP-041	TuP-045		
Tsirlina	Galina	TuP-080			
Tsunokake	Shigeru	TuP-028	ThP-001		
Tsutsumi	Tatsuki	ThP-013			
Tumanov	Nikolay	WeOQ-099	ThOH-143		
Turner	Stuart	WeOQ-098			
Uchida	Helmuth	MoOD-036	TuP-106	ThP-018	
Uchida	Hirohisa	TuP-069	TuP-070		
Uchiyama	Naoki	ThOD-150			
Udovic	Terrence	MoOD-033	TuOH-066	ThOD-154	ThP-106
Ulivi	Lorenzo	WeOQ-095			
Ulmer	Ulrich	WeOD-111	ThP-005		
Unemoto	Atsushi	TuOH-066			
Urbanczyk	Robert	ThP-117			
van Bokhoven	Jeroen A.	TuP-094			
van Hassel	Bart	WeOC-117			
Vargas	Claudia	ThP-071			
Vargas	William	TuP-097	TuP-098		
Vegge	Tejs	TuOH-066	TuP-009		
Verbetsky	Victor	TuP-057	TuP-058	TuP-059	ThP-017
Verbovytskyy	Yuriy	TuP-034	ThP-056		
Verdal	Nina	ThOD-154			
Verdal	Nina	ThP-106			
Viano	David	MoOD-033			
Viano	Maddury S.	MoOD-033			
Vinogradov	Alexei	TuP-048			
Vitillo	Jenny G.	WeOC-124			
Vitucci	Francesco Maria	TuOH-072	ThP-048		
Vix-Guterl	Cathie	TuOH-071	WeOQ-094		
Vlach	Martin	MoOD-036	TuP-106		
VIček	Marián	MoOD-036	TuP-106		
Voitic	Gernot	TuP-053			
Volodin	Alexey	TuP-080			
Voyshnis	Svetlana	ThOC-168			

Voyt	Alexey	TuOH-063			
Vyas	Devendra	ThP-077			
Vyvodtceva	Anna	TuP-083			
Wadell	Carl	TuP-049			
Wagner	Stefan	MoOD-036	TuP-106	ThOD-151	ThP-018
Walker	Gavin	MoOH-019	MoOC-047	TuOQ-052	TuOQ-059
		ThOH-148	ThP-040	ThP-058	ThP-094
Walton	Allan	MoOD-025			
Wan	Chubin	ThP-081	ThP-099		
Wan	Qi	ThP-116			
Wan	Ruiyun	ThOC-162	FrOH-179		
Wang	Haitao	ThP-044			
Wang	Hui	TuOQ-054	ThP-019	ThP-050	ThP-051
		ThP-078	ThP-098		
Wang	Jianhui	ThP-123			
Wang	Junzhi	ThOQ-129			
Wang	Lei	MoOQ-012			
Wang	Qidong	ThP-085			
Wang	Xiaojuan	ThP-113			
Wang	Xinhua	ThP-047	ThP-076		
Wang	Yijing	ThP-066	ThP-088	ThP-127	
Wang	Ying	ThP-066	ThP-127		
Wang	Yongmei	ThP-088			
Wang	Yongming	TuP-088	WeOH-106		
Wang	Yuan	ThOC-162	FrOH-179		
Wang	Yuting	ThP-081	ThP-099		
Wanjelik	Sara	TuOC-092			
Ward	Patrick	FrOH-181			
Watanuki	Tetsu	TuOD-080	WeOD-110	ThP-008	ThP-034
Webb	Colin	MoOD-026	MoOC-048	TuP-011	TuP-023
		TuP-101	ThOH-144	ThP-002	
Webb	Timothy	MoOD-026	ThOH-144		
Weber	Peter	FrOH-180			
Weekes	Hannah	TuP-115			
Wegner	Wojciech	WeOC-122	ThP-107		
Weidenthaler	Claudia	ThP-119	FrOH-178		
Weinrauch	Ingrid	WeOQ-098			
Wenman	Mark	TuP-115			
Werner	Per Erik	ThP-121			
Westerwaal	Ruud	MoOD-034	TuOD-076	TuOC-085	TuOC-086
		TuOC-087			
Whittemore	Sean	WeOC-118			
Wilkinson	David	TuP-107			
Woerner	Michael	MoOQ-002			
Woisetschlaeger	Dieter	WeOC-119			
Wolff	Max	MoOH-014	TuOQ-060	ThP-028	TuP-067
		TuP-086			
Wood	Thomas	WeOH-102			
Wood	Tom	WeOH-105			
Wood	Tom	TuP-008			
Wosylus	Aron	FrOH-178			
Wu	Chaoling	ThP-035	ThP-046		
Wu	Cong	ThP-050			
Wu	Daifeng	ThP-050			
Wu	Guotao	WeOH-101			
Wu	Hui	MoOH-013			
Wu	Ying	TuP-004	ThP-057		
Xao	Xin	MoOH-014			
Xiang	Wei	ThOC-162	FrOH-179		
Xiao	Xin	TuP-086			
Xiao	Fangming	TuP-021			
Xiao	Jinsheng	WeOQ-093			
Xiao	Xin	ThP-028			
Xiao	Xuezhang	ThP-072	ThP-085		
Xie	Lei	TuOQ-056			
Xin	Gongbiao	ThP-113			

Xu	Yaolin	TuOH-068			
Yae	Shinji	TuP-060			
Yafyasov	Adil	TuOH-063			
Yamada	Yoshinori	TuP-040			
Yamagami	Ryo	TuOQ-055			
Yamaguchi	Shotaro	ThP-126			
Yamamoto	Kousuke	TuP-092			
Yan	Mi	ThP-047			
Yan	Yigang	ThP-089	ThP-092		
Yan	Youhua	TuP-004	ThP-098		
Yang	Junzhi	ThP-113			
Yang	Tai	ThP-044			
Yanilkin	Alexey	ThP-039			
Yano	Ken-Ichi	TuOC-088			
Yartys	Volodymyr	MoOC-043	TuOQ-049	TuOH-061	TuOH-063
		TuP-080	TuP-103	ThP-007	ThP-054
Yasuoka	Shigekazu	TuOH-062			
Yayama	Tomoe	TuP-096	ThP-009	ThP-013	FrOQ-171
Ye	Zhou	TuOH-064			
Yokota	Hitoshi	ThP-015			
Yoshida	Kenta	ThOD-150			
Yoshimura	Shin-Ichi	TuP-050			
Yoshitake	Tsukasa	ThP-102			
Young	Kwo	TuOH-062			
Yu	Xuebin	ThOQ-133			
Yuan	Huatang	ThP-066	ThP-088		
Yuan	Zeming	ThP-044			
Yuhimchuk	Arkadiy	TuP-111			
Yukawa	Hiroshi	MoOD-031	TuP-042	TuP-085	
Yürüm	Yuda	TuP-017			
Zabavin	Evgeniy	ThP-032			
Zacharia	Renju	WeOQ-093			
Zakaznova-Herzog	Valentina	FrOH-184			
Zamponi	Flavio	MoOQ-002			
Zavaliy	Ihor	TuP-034	ThP-052	ThP-053	ThP-056
Zavorotynska	Olena	WeOC-124	ThOQ-135		
Zeaiter	Ali	MoOC-040			
Zehetbauer	Michael	ThP-073			
Zhai	Fuqiang	ThP-116			
Zhai	Tingting	ThP-044			
Zhang	Bao	TuP-004	ThP-057		
Zhang	Junxian	TuOD-084	ThP-056		
Zhang	Shiling	WeOC-117			
Zhang	Tengfei	WeOH-106			
Zhang	Xuanzhou	TuOQ-056			
Zhang	Yanghuan	ThP-044			
Zhang	Yinghe	TuP-018			
Zhao	Dongliang	ThP-044			
Zhao	Ji-Cheng	ThOQ-130			
Zhao-Karger	Zhirong	ThOD-155			
Zheng	Jie	TuOQ-056			
Zheng	Kun	TuP-082			
Zhou	Jingjing	ThP-035			
Zhu	Min	TuOQ-054	TuOD-083	ThP-019	ThP-050
		ThP-051	ThP-062	ThP-078	ThP-098
Zidan	Ragaiy	FrOQ-175	FrOH-181	FrOH-182	
Zlotea	Claudia	TuOH-070	TuOH-071	WeOQ-094	
Zulkifli	Nor Diana	ThP-009			
Züttel	Andreas	PLENARY 1	MoOQ-002	TuOH-066	TuOC-089
		WeOQ-098	ThOD-152	ThP-089	ThP-092
		ThP-097	FrOH-184		
Zverkova	Irina	ThP-124			

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A tradition of innovation in sorption measurement technology



Hidden Isochema has been manufacturing gravimetric gas sorption analyzers for over 20 years.

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The Salford Energy House testing facility

Background

A unique testing asset, the Energy House is the only full-scale building in an environmental chamber in Europe and the only full-scale, brick-built test facility in a controlled environment in the world. The test facility (Energy House) has been designed and developed to allow leading academics and researchers to conduct scientific research, to improve the energy efficiency of "hard to treat" properties, in collaboration with industry.

This includes the development and testing of new materials, systems and products as well as looking at behaviour change associated with the adoption of energy efficiency measures in the home.

The Energy House is also breaking new ground in terms of Building Physics, carrying out many verification tests for methodologies that are currently used (and being developed) to test the energy performance of buildings and address the gap between design and as-built performance.

Construction

The house is a traditionally constructed, terraced building (with a neighbouring property). It has solid brick walls, suspended timber floors, lath and plaster ceilings and single glazed windows. In its current state it is uninsulated. The heating is provided by a wet central heating system, fired by a gas condensing combination boiler. All of this can be changed to suit the testing requirements required by clients.

Chamber environment

The external environment surrounding a dwelling can potentially make a significant difference to how much energy is required to heat the building. It is for this reason that we have developed the chamber to recreate a series of external weather conditions:

- Rain (up to 200mm each hour)
- Temperature ranges from -12°C to +30°C (with an accuracy of +/- 0.5°C)
- Wind (localised and chamber wide) upto 10 m/s
- Snow.

Monitoring

The test facility uses several different monitoring equipment, all logging and displayed through a custom time series program. This provides live data feeds and real time analysis of the following data points. Currently the Energy House has over 200 sensors which are able to read down to 1 second resolution. This can generate over 2.8 Gigabytes in a week-long test.

Past tests

Since opening, the following funded testing has taken place

- Performance of building controls (TRV and thermostats)
- Performance of insulation solutions (of all kinds)
- Testing of various building performance tests (Coheating, in situ U value monitoring etc.)
- Door and window heat loss testing
- Monitoring the performance of electrical heating systems.

The Energy House, a traditional style terrace house, with two rooms on the ground floor (living room and kitchen diner), the upstairs consist of two bedrooms and a bathroom.

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