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Hydrogen-based materials for energy storage roadmap

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Abstract

Driven by the increasing global demand for sustainable energy, hydrogen-based materials have been extensively explored for a range of energy storage solutions. The 12 sections of this roadmap span multiple fields and applications, providing an assessment of the current worldwide landscape of hydrogen-based materials for energy storage. Each section first summarises the current status of research in each field, before identifying current and future challenges to be addressed. Subsequently, an assessment is made of advances in science and technology to meet those challenges, finishing with concluding remarks. The sections of the roadmap cover nanoporous materials, magnesium-based compounds, intermetallic hydrides, complex hydrides, liquid hydrogen carriers, compression and purification, thermal energy storage, electrochemical energy storage and solid-state electrolytes, experimental characterisation, and computational approaches. Overall, hydrogen-based materials show amazing properties for a wide variety of energy storage technologies and have an exciting role to play in the future energy transition, providing many benefits over current alternatives as solid-state and liquid energy stores, thermal energy stores, hydrogen compressors, negative battery electrodes and solid-state electrolytes.

Keywords: hydrogen storage, hydrogen compression, thermal energy storage, metal hydride, complex hydride, batteries, solid electrolytes, computational material science

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Contents

1. Overview of the roadmap: hydrogen-based materials for energy storage 4
2. Nanoporous materials for hydrogen storage 8
3. Magnesium-based hydrides for energy storage 12
4. Intermetallic hydrides for energy storage 16
5. Complex hydrides for hydrogen storage 20
6. Materials-based hydrogen compression and purification 24
7. Hydrogen storage in liquid hydrogen carriers 28
8. Metal hydride materials for thermal energy storage 32
9. Metal hydrides for electrochemical energy storage 35
10. Metal hydridoborates as electrolytes for solid state batteries 39
11. Experimental methods for characterization 43
12. Computational methods 46
13. Conclusions 51
References 54

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1. Overview of the roadmap: hydrogen-based materials for energy storage

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Overview

Hydrogen has been globally recognised as a highly promising carrier for clean energy. As such, hydrogen-based materials have been intensely investigated for a range of sustainable energy solutions. This roadmap spans multiple fields and applications, providing an overall evaluation of the present international landscape and state-of-the-art in hydrogen-based materials for energy storage.

Firstly, solid-state hydrogen storage materials are considered, including nanoporous materials, magnesium-based compounds, intermetallic and complex hydrides. These materials can store large amounts of hydrogen by volume, and in many cases also by weight, and offer several advantages over compressed gas and liquid H_2 alternatives such as safety, cost and energy efficiency. Liquid hydrogen carriers are also addressed, which store hydrogen through chemical reactions at near-ambient temperatures and pressures. These materials have the key benefit of being able to take advantage of the current liquid handling infrastructure making them promising candidates for hydrogen transport.

In addition to storing hydrogen, hydrogen-based materials have been utilised in hydrogen technologies for compression and purification, where they offer significant improvements in operating efficiencies, reduced system complexities, reliability and costs compared to traditional techniques. Due to their high energy density and ability to store heat through reversible reactions with hydrogen, these materials can also be used to store thermal energy, with prototypes now under development.

Another exciting field for sustainable energy is battery technologies. Since hydrogen can interact with materials electrochemically, hydrogen-based materials can be used as negative electrodes in batteries such as Ni-MH and Li-ion, benefitting from high energy storage capacities. Hydrogen-based materials are also advantageous as solid-state electrolytes for use in solid-state batteries. In particular, boron-based complex hydrides have demonstrated extremely high cationic conductivities.

The final two sections of the roadmap consider broad topics which extend across the development of all hydrogen-based materials for energy storage: experimental characterization methods and computational modelling and simulation. Experimental methods for characterizing hydrogen-based materials are key to understanding and developing their applications in energy storage. Through a series of advanced complementary techniques, the structures, properties, and performances of the materials can be assessed. Computational modelling and simulation, including the more recent use of artificial intelligence, has become a crucial method to design, discover and understand hydrogen-based materials and their reactions. These computational methods can often be used in conjunction with experimental data to more fully interpret results and to suggest the directions for new experiments.

Each section of this roadmap first summarises the current status of research in the particular field, before secondly identifying current and future challenges being faced. Following that, advances in science and technology needed to meet those challenges are assessed, finishing with some concluding remarks. An infographic overview of the roadmap topics is provided in Figure 1. Across all the sections of this roadmap, it is clear that hydrogen-based materials have had many exciting developments across energy storage applications. These materials provide many benefits over current alternative technologies, and can play a key role in facilitating the future energy transition.

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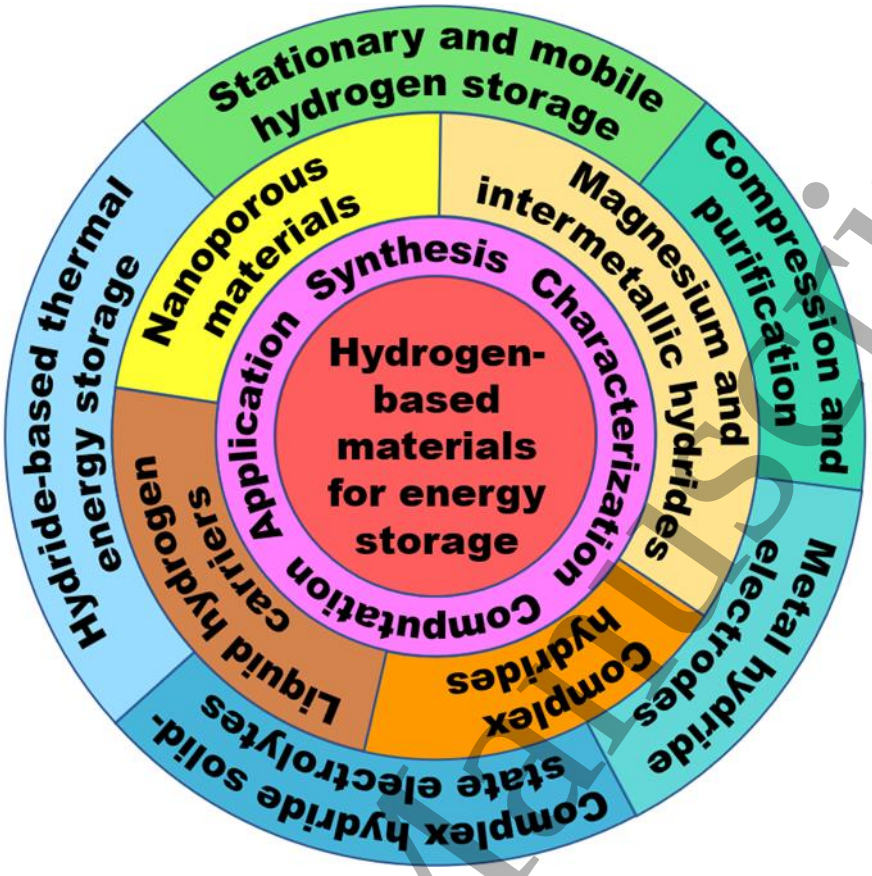


Figure 1: An infographic overview of the roadmap. At the core is the development of novel hydrogen-based materials for energy storage, which is performed by a combination of experimental and computational studies on synthesis, characterization and application. The next ring contains the four main material classes investigated, and the outer ring represents major areas of application.

Roadmap summary

A summary of each section of the roadmap and associated figures is given below. The reader is invited to see the individual full sections for detailed explanations and references.

- Nanoporous materials (section 2) such as MOFs and COFs offer a promising solution for hydrogen storage with high hydrogen capacity and energy efficiency. Key challenges identified include balancing gravimetric and volumetric capacities, improving thermal conductivities, optimising adsorption temperatures, uncovering more sustainable syntheses and reducing boil off when storing and transporting liquid H_2. Current avenues for further research incorporate shaping/densifying nanoporous powders, using composites or tank design strategies to improve heat conduction, hierarchical pore structures, solvent free and waste-derived syntheses and utilising cryo-adsorbents to reduce boil-off. A schematic of the optimisation steps required for nanoporous materials for hydrogen storage is shown in Figure 2.

- Magnesium (section 3) is a lightweight and abundant material with a high capacity for storing hydrogen both by weight and by volume. Significant advances have been made to improve kinetics of hydrogen sorption through additives, catalysts and structural enhancement. Ongoing research seeks to reduce dehydrogenation temperatures, develop scalable syntheses and processing routes, and ensure long-term cycling stability. Exciting developments include destabilised Mg-based amorphous alloys, MgH_2/TiH_2 nanocomposites and adding small amounts of oxygen-stabilised intermetallic compounds as catalysts, scalable drop-forge manufacturing and carbon-based additives to stabilise microstructures while cycling. An illustration of various strategies to improve thermodynamic and kinetic properties of Mg-based hydrides is given in Figure 3.

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- Intermetallic hydrides (section 4) offer advantages as materials for hydrogen storage, hydrogen gas compression and advanced battery anodes. Current challenges to the further advancement of the field include understanding hysteresis and plateau slopes in PCI measurements, material cyclability and resistance to amorphization or degradation, experimentally determining thermodynamic properties, and understanding initial material activation. Future work to address these challenges should focus on better understanding H-H interactions, considering the impact of impurities on cycling behaviour, direct calorimetry, particle size effects and multielement alloys. Figure 4 presents an illustrative sketch of idealized improvements compared to suboptimal performance of intermetallic hydrides for hydrogen storage.

- Complex hydrides (section 5) have extremely high gravimetric and volumetric hydrogen densities, ideal for onboard hydrogen storage applications. Some complex hydrides, such as ammonium borohydride (NH_4BH_4) and light metal borohydrides have hydrogen densities similar to that of liquid natural gas. However, these compounds and their derivatives often do not store hydrogen reversibly, and kinetics of sorption can be slow. Attempts continue to be made to tune the thermodynamics and further the cyclability of such compounds under practical conditions by altering the chemistry, developing suitable additives and catalysts, combining different metal and complex hydrides in Reactive Hydride Composites, or by taking completely new approaches such as designing new complex hydrides for hydrogen physisorption. A summary of the key challenges faced by complex hydrides and some exciting recent advancements is shown in Figure 5.

- Hydrogen-based materials for compression and purification technologies (section 6) offer significant improvements in operating efficiencies, reduced system complexity, and economies associated with capital and operational costs. To exploit these advantages, material science challenges relating to minimizing the hysteresis and slope of the plateau pressure in PCIs, improving cyclic durability, and enhancing thermal properties need to be addressed. Also accurate measurements performed at high hydrogen pressures of more than 100 MPa are needed to be able to design novel 90 MPa hydride based hydrogen compressors. Higher energy efficiency can be achieved by tuning hydrogen storage performance specifically to minimise the hysteresis and slope of the plateau in hydride materials. To deliver cyclic durability, the mechanisms that lead to structural degradation must first be identified enabling compositional tuning to be used to suppress them. Enhancing thermal management will require more reliable methods for measuring the thermal properties of hydrogen materials under operational conditions relevant for H_2 compressors and over multiple cycles. Computer simulations capable of accommodating microstructural factors should also be conducted, assessing the influence that hydride microstructures, interfaces and impurities have on the heat transport mechanisms. Figure 6 provides an overview of technological developments.

- Liquid hydrogen carriers (section 7) store hydrogen through chemical reactions under near-ambient temperatures and pressures, and can take advantage of the current liquid handling infrastructure. Key current challenges include: system cost, especially capital equipment costs; round-trip efficiency, currently around 40-60%; and catalyst reactivity for hydrogenation and dehydrogenation reactions. Future research has been moving from materials development to pilot demonstrations, with system level analysis needed to optimise overall cost and efficiency, integrating hydrogenation and dehydrogenation of the liquid carriers with upstream and downstream processes. An schematic of example integrated upstream and downstream processes are shown in Figure 7.

- Metal hydride materials have also found application in thermal energy storage (section 8), with prototypes now under development incorporating thermal energy storage materials, gas storage and heat transfer. Hydrogen-based materials can be selected to operate under different temperature ranges, up to 1000 °C for CaH_2, for instance. Certain engineering aspects are still to be optimised for the use of hydrogen-based materials in thermal energy storage systems, including large-scale material durability upon cycling, heat transfer from powder beds to the heat engine (minimising corrosion), and kinetic reaction modelling. Advances have been made in the modelling of heat transfer methods, though wider system models for larger-scale prototypes are still required. Figure 8 shows the maximum operating temperature for a range of thermal energy storage materials, as a function of their gravimetric energy densities.

- Hydrogen can interact with intermetallic compounds electrochemically, allowing the use of metal hydrides as negative electrodes in Ni-MH and Li-ion batteries (section 9). Currently, layered hybrid Mg-based intermetallics show the best performance as battery anodes for Ni-MH batteries, and composites of MgH_2 with TiH_2 show

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promising performance as anodes for Li-ion batteries. Future research challenges include finding efficient synthesis routes to prepare superlattice alloys, reducing the cost and the use of critical raw materials (such as Co, Ni and rare earth metals), and improving anode corrosion resistance (e.g. through the use of protective layers. An application-based timeline showing developments of metal hydride batteries from 1997 to 2024 is given in Figure 9.

- In addition to their use as negative electrodes, hydrogen-based materials are also beneficial as solid-state electrolytes for use in solid-state batteries (section 10). In particular, boron-based complex hydrides are becoming an excellent platform for the rational design of electrolytes with extremely high cationic conductivities. Unique to hydridoborates, their structure, interphases and dynamics enhance the cationic conductivity in the solid state. Current challenges include improvement of the divalent cationic conductivity at low temperatures (room temperature and below), improvement of the electrochemical stability to allow the use of high voltage cathodes, and scalable fabrication methods needed to reduce costs. Recent research has shown that forming complexes with neutral organic molecules can enhance cationic conductivity, and has focussed on metal *closo*-(carba)borates, which have higher electrochemical stabilities. Figure 10 demonstrates the record-high conductivity of divalent metal hydridoborates with magnesium and calcium.

- Experimental methods for characterization (section 11) are key to understanding and developing hydrogen-based materials for energy storage. By employing advanced techniques, these materials' structures, properties, and performance can be analysed. Current challenges in the field include: ensuring rigorous and accurate characterization, due to a lack of standardised reference materials and data formats; advancing in-situ and operando experiments, essential for studying hydrogen storage under real conditions; and integrating techniques from other fields, developing sample cells which can handle elevated temperatures and/or pressures. Recent advances comprise the development of standardized experimental protocols, exciting new instrumental tools (such as total scattering with synchrotron radiation and neutrons) and using combinations of techniques, such as scattering and spectroscopy with theoretical calculations to accelerate discoveries in the field. A schematic summarizing current and future challenges and directions in the characterization of hydrogen storage materials is displayed in Figure 11.

- Computational modelling and simulation (section 12) has become a crucial approach for designing, discovering and probing hydrogen-based materials. Models can complement experimental data to clarify results and suggest new experiments. Four challenges have been identified as a future focus for research efforts: method and model development to improve predictive power and accuracy, including often-neglected thermodynamic contributions such as solid mechanics and anharmonicity; extending models beyond idealized descriptions of single crystal materials, navigating compositional and structural complexity in materials such as high entropy alloys; predicting kinetics across scales, incorporating factors such as chemical bond activation, mass and heat transport, and phase nucleation and growth; and predicting real-world operation of materials and systems, incorporating hard-to-predict real-world properties such as materials lifetime and activation kinetics, and improving the understanding of trade-offs among performance, capacity, and durability. Recent developments include, among others, hierarchical approaches incorporating multiple levels of theory, and utilising machine learning for complex compositions. Figure 12 shows the variety of processes that need to be modelled for kinetics predictions, and Figure 13 gives examples of different work addressing the four identified challenges.

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2. Nanoporous materials for hydrogen storage

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Status

Hydrogen storage using nanoporous materials is a promising solution for clean energy systems, offering high capacity and efficiency. However, its development is complex, requiring material composition, structure, and performance optimization. Hydrogen uptake depends on factors such as surface area, pore volume, pore size distribution, and chemical functionality,[1] demanding a balance between gravimetric and volumetric capacity for practical feasibility. Balancing these attributes to enhance hydrogen storage while maintaining practical feasibility is an ongoing scientific endeavor. At the material level, optimizing the Brunauer–Emmett–Teller (BET) surface area remains essential, with Chahine's Rule hydrogen uptake increases linearly with surface area up to ~4,000 m²/g at around -200 °C.[2] Beyond this threshold, simply increasing surface area is insufficient; pore volume, pore geometry, and chemical functionality become critical parameters for enhancing storage performance. This reflects the fact that hydrogen storage in nanoporous materials at cryogenic conditions is governed primarily by physisorption rather than chemisorption. Accordingly, storage performance depends not only on accessible surface area, but also on pore confinement, where overlapping adsorption potentials from opposing pore walls and chemically specific sites, such as open metal sites or polar functional groups, can enhance H_2 binding. However, stronger adsorption is not always advantageous, because excessively high adsorption enthalpy may hinder hydrogen release and reduce usable capacity under practical operating conditions. The following steps focus on achieving a careful balance between gravimetric and volumetric uptake.[3,4] Lightweight porous frameworks maximize gravimetric capacity, while denser architectures improve volumetric efficiency. In contrast to activated carbons (ACs), whose pore texture is less readily tunable, metal-organic frameworks (MOFs) and covalent organic frameworks (COFs), with tunable pore structures, offer significantly higher surface areas and enable precise adjustment of pore size, shape, and chemistry for real-world applications. Future research must focus on usable

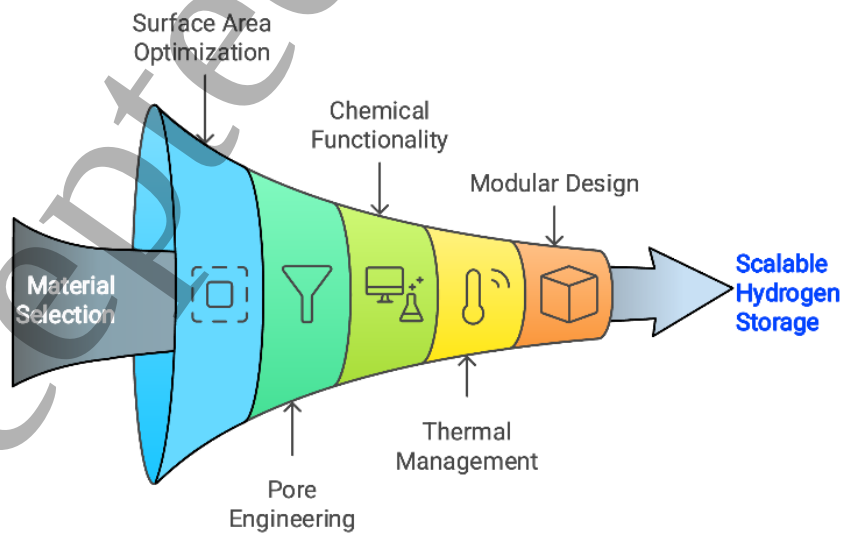


Figure 2: A schematic of the optimisation steps required for nanoporous materials for hydrogen storage.

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capacity[5]—the amount of hydrogen practically stored and released under operational conditions.[6,7] This requires integrating advanced materials with engineering solutions, such as thermal management, modular storage designs, and system-level analytics, ensuring scalability and cost-effectiveness. Additionally, nanoporous materials are being explored to reduce LH_2 boil-off losses during transport. Despite advanced insulation, LH_2 at -253 °C inevitably vaporizes. Pore-engineered surfaces may help stabilize hydrogen at cryogenic temperatures,[8] mitigating losses and strengthening hydrogen supply chains. Related cryogenic adsorption/desorption concepts are also being explored for thermally driven physisorption-based hydrogen compression. In this approach, hydrogen is adsorbed at low temperature and released upon heating, generating a pressure swing without relying solely on mechanical compression.[9–11] This emerging concept further broadens the engineering relevance of nanoporous hydrogen adsorbents beyond storage and boil-off mitigation. By bridging fundamental science with engineering, these advancements could drive more efficient and sustainable hydrogen infrastructure.

Current and future challenges

Cryogenic hydrogen storage in nanoporous adsorbents is advancing toward technical implementation, but key challenges remain, including volumetric capacity, thermal conductivity, kinetics, green synthesis, and LH_2 boil-off management.

Challenge 1: Volumetric capacity

Optimizing surface area maximizes *gravimetric* uptake (weight percent), but the low bulk density of high-surface-area materials limits the surface area per volume, i.e., the volumetric capacity. A balance between gravimetric and volumetric uptake is a critical factor and interpenetrated MOF structures are one route for improving volumetric surface area.[12] From experimental data on many MOFs, a phenomenological relation has been developed between gravimetric and volumetric uptake.[13] Here the volumetric capacity using the crystal density (theoretical maximum) is approximately a factor of two higher than applying the packing density of the MOF powders. The challenge is closing this gap to the theoretical limit by shaping MOFs into pellets and monoliths and thus reducing the interparticle void space of powders.

Challenge 2: Thermal conductivity

Nanoporous materials like activated carbons and MOFs inherently have very low thermal conductivity, which hinders heat management during H_2 charging and discharging. Heat must be removed efficiently when hydrogen adsorbs (exothermic) and be added during desorption (endothermic), but porous adsorbents act as thermal insulators. Typical activated carbons have bulk thermal conductivities lower than 0.4 W m^{-1} K^{-1}, whereas a crystalline graphite plate can reach ~2000 W m^{-1} K^{-1} along the in-plane direction.[14] MOF powders show thermal conductivities below 1.5 W m^{-1} K^{-1} leading to poor heat transfer in a hydrogen storage bed.[15] During fast refueling, the heat released from H_2 adsorption can create thermal gradients, slowing down further adsorption and reducing storage efficiency. Likewise, on discharge, the material cools, and hydrogen desorbs more slowly if heat input is insufficient.

Challenge 3: Charging and discharging kinetics

Adsorption/desorption kinetics dictate how fast a hydrogen storage system can be filled or emptied. Fortunately, physisorption of H_2 in most high-surface-area carbons and large-pore MOFs is inherently fast, and diffusion through open micropores (> ~1 nm) is not rate-limiting even at cryogenic temperatures. However, ultramicroporous materials (pore apertures < ~0.7 nm) can exhibit diffusion limitations, gate-opening or molecular sieving effects slowing down the rates of uptake and release.[16] Then, higher temperatures are required for faster transport, and the interplay between thermodynamics and kinetics can result in an optimal temperature window for adsorption.[17] The increased heat of adsorption in narrow pores shifts the optimal operation temperature to higher values but is associated with a decrease in usable capacity.[1,7]

Challenge 4: Green synthesis

For nanoporous materials to be viable at industrial scale, their synthesis must be cost-effective, scalable, and environmentally friendly. Traditional solvothermal MOF syntheses often require high temperatures, lengthy reaction times (days), and toxic organic solvents. These energy-intensive conditions and the ban of dimethylfumarate (DMF) by the EU bring the urgent need to move towards "green" synthesis methods for the sustainable production of MOFs. Room-temperature aqueous synthesis enables the fabrication of MOFs like MIL-100 in water, allowing the incorporation of a wide range of *p*-, *d*-, and *f*-block elements with oxidation states from +I to +V.[18] Mechanochemical synthesis, which involves solvent-free grinding or

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extrusion, has emerged as a rapid, scalable method for producing MOFs such as HKUST-1 and ZIF-8 with minimal waste and short reaction times.[19,20]

Challenge 5: Boil off for LH2 transportation

Storing and transporting LH_2 (~20 K, –253 °C) poses boil-off challenges due to inevitable heat ingress.[21] Even with advanced insulation, zero boil-off is unattainable, leading to hydrogen loss and safety concerns. Large LH_2 tanks use vacuum-insulated double walls and multilayer insulation to reduce heat flux, but boil-off gas still escapes, wasting stored hydrogen and liquefaction energy.

Advances in science and technology to meet challenges

Challenge 1: Enhancing Volumetric Capacity

Optimizing the volumetric hydrogen storage capacity of a tank filled with MOF materials remains the key challenge. For a long time, the approach has focused on shaping nanoporous powders into monoliths to increase the packing density. Compacting MOF powders into mechanically stable monoliths can significantly improve volumetric H_2 storage, however, this can also reduce the porosity. Recently, ZIF-8 has been directly synthesized as peletts by continuous mechanochemical and reactive extrusion basically without the loss of surface area or H_2 uptake.[19,22] Another very promising approach is sol-gel derived monoliths, with HKUST-1 demonstrating volumetric capacities close to the single crystal limit.[23,24] MOFs hybridization with carbon materials also enhances the volumetric capacities for hydrogen storage and release by increasing the tapped density of the resulting hybrids, while reducing their water affinity and improving their thermal conductivity.[25,26]

Challenge 2: Improving Thermal Conductivity and Tank Design

The poor thermal conductivity of nanoporous materials limits their efficiency in hydrogen storage applications, as local heating or cooling slows down the refueling or discharge, respectively. Recent strategies focus on enhancing heat dissipation in adsorbent-based hydrogen storage through hybrid materials and optimized tank designs. Incorporating highly conductive additives, such as expanded natural graphite (ENG), into MOFs or activated carbons significantly improves thermal conductivity while preserving adsorption capacity, e.g., the addition of 10 wt.% ENG to MOF-5 pellets increases thermal conductivity five times without compromising porosity.[27] Moreover, structured heat exchangers, such as honeycomb designs,[28] enable more uniform temperature control during rapid hydrogen charging and discharging, further improving system efficiency.[15]

Challenge 3: Improving Kinetics in Hydrogen Adsorption/Desorption

Ultramicroporous materials often suffer from diffusion-limited hydrogen uptake, especially at cryogenic temperatures where gas diffusivity is low. To overcome slow adsorption/desorption kinetics, researchers have explored new material structures and activation methods.[29] One approach is to introduce hierarchical pore structures that combine ultramicro pores with larger mesopores or macropores, creating multi-scale pathways for H_2 transport. Such hierarchical porosity can accelerate H_2 uptake by facilitating a stepwise diffusion process: hydrogen quickly fills mesopores and then migrates into micropores, reducing bottlenecks. Experimental studies on MOFs or carbons with bimodal pore size distributions consistently show faster equilibration than purely microporous analogs.

Challenge 4: Upscaling and Recycling in Green Synthesis

Industrial-scale MOF production for hydrogen storage remains a challenge, however, several companies started up-scaling MOF production.[30] Cost-effectiveness has been recently addressed in a MOF database of ~3,600 structures (https://mofdb-bam.de/),[31] prioritizing affordable linkers and metals such as Fe, Al, and Cu while maintaining high volumetric H_2 capacity. Additionally, waste-derived precursors have been used for MOF production, e.g., terephthalic acid from PET plastic bottles to synthesize MIL-47, MIL-53, and MIL-101(Cr), or nickel and chromium recovered from industrial waste.[32] Mechanochemical synthesis, particularly twin-screw extrusion,[19] has emerged as a scalable, solvent-free alternative to conventional methods. Multi-kilogram batches of MOFs such as HKUST-1 and ZIF-8 can be produced with yields exceeding 90% and surface areas and H_2 uptakes comparable to solvent syntheses.[22]

Challenge 5: Minimizing Boil-Off Loss in Liquid Hydrogen Transport

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Reducing boil-off loss is essential for efficient LH_2 handling. Integrating nanoporous adsorbents such as MOFs into cryogenic tanks can capture evaporated H_2 and limit pressure buildup. DUT-6 cryo-adsorbents retain ~95% of LH_2's volumetric capacity while significantly extending dormancy.[33] Enhanced hydrogen-framework interactions at 20–77 K, mainly due to stronger interactions within the nanopores under 2 nm,[34] stabilize the vapor phase and absorb heat, offering a scalable solution to minimize hydrogen loss.[35]

Concluding remarks

Cryogenic hydrogen storage using nanoporous materials has advanced significantly, yet key challenges remain for practical implementation. Addressing these requires a combination of materials optimization, thermal management, and scalable synthesis. Enhancing volumetric efficiency is crucial, requiring densification strategies that maximize hydrogen uptake while preserving porosity. Hierarchical pore engineering and monolithic MOF synthesis offer promising solutions. Thermal management must also improve, with conductive hybrid materials and optimized tank designs enabling faster refueling and discharge. Industrial adoption depends on scalable, green synthesis, moving from solvent-intensive processes to mechanochemical and aqueous-based methods for cost-effective, sustainable production. Additionally, cryogenic 20 K adsorbents for LH_2 boil-off mitigation could significantly reduce hydrogen losses during transport. The future of nanoporous hydrogen storage lies in the integration of material innovation with practical engineering, ensuring a transition from laboratory research to commercial deployment in hydrogen infrastructure.

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3. Magnesium-based hydrides for energy storage

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Status

Magnesium (Mg) has been investigated as a hydrogen (H) storage material by many research groups worldwide, due to its abundance in the earth's crust, non-toxicity, moderate cost and low density. The dihydride MgH_2 has appealing gravimetric and volumetric capacities of 7.6 wt% and 110 g/L, respectively.[36] The research activity on MgH_2 became particularly fervent at the beginning of this century when it was shown that the sluggish H sorption kinetics typical of microcrystalline Mg can be dramatically improved by microstructural refinement, which enhances H diffusion and heterogeneous nucleation, coupled with nanoscale dispersion of transition metals and metal oxides that catalyse H_2 dissociation/recombination at the surface.[37] However, the strong Mg-H binding energy remains an obstacle against H storage applications at close-to-ambient conditions of pressure and temperature. In fact, in order to match a H_2 release pressure of 1 bar, the desorption temperature T_d must be higher than the equilibrium value $\Delta H^0/\Delta S^0 \approx 565\ K$, with $\Delta H^0 \approx 74\,\mathrm{kJ/mol H_2}$ and $\Delta S^0 \approx 130\,\mathrm{J/(mol H_2 \cdot K)}$ being the standard enthalpy and entropy of hydride decomposition, respectively.[38] Several approaches aimed at destabilizing the thermodynamics of the Mg-H system by materials engineering, including alloying, interfacial energetics, and nano-confinement, have resulted in small, insignificant changes of T_d, but have helped in reaching higher H_2 desorption rates.[38–40] Mg-based ternary hydrides, such as Mg_2NiH_4, Mg_2FeH_6, and Mg_2CoH_5, have also been studied extensively. However, the reduction in T_d is relatively modest (T_d is even higher for the Fe-containing hydride) and is counteracted by significantly increased weight and cost.[36,37] Mg-based compounds with long period stacking order (LPSO) contain Mg nanolayers in the crystal structure. By decreasing the H absorption temperature, the formation of the orthorhombic γ-MgH_2 polymorph was found to be favoured over the more stable tetragonal α-MgH_2.[41] However, the unique LPSO nanostructure is generally not retained upon hydrogen sorption cycles.[42] Destabilization by formation of intermediate phases such as Mg_2Si during reactions was proposed,[43] but T_d remains high because of kinetic limitations, which also make it challenging to re-hydride the intermediate compound. On the other hand, Mg-based composites that embed catalytic phases such as TiH_2 or Nb_2O_5 along with thermal conductors such as graphite can exhibit outstanding H sorption kinetics coupled with good thermal conductivity and resistance against sintering, while maintaining a high gravimetric capacity in the 5-6 wt% range.[44,45] This has led to a renewed industrial interest in the production and commercialization of Mg-based hydrogen storage systems.[46,47]

Current and future challenges

The adoption of Mg-based solutions for hydrogen energy storage hinges on overcoming several materials-based science-driven challenges, in particular: i) affording H_2 release at mild temperatures while maintaining high gravimetric H density, ii) developing safe, cost-effective synthesis and processing methods, and iii) ensuring the long-term cyclability, as described below.

Reduction of the hydrogen desorption temperature

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The reduction of the operational H_2 release temperature can be addressed by minimizing the kinetic barriers for H_2 desorption and/or by destabilizing the Mg-H bond. The former goal can be achieved through the use of catalytic additives and their efficient dispersion; ongoing research aims at using small amounts of catalysts, typically a few wt%, with mainly earth-abundant constituents. Conversely, changing the Mg-H thermodynamics requires altering the chemical and/or structural environment of H in the Mg-based matrix, which may be achieved through extensive alloying, nano-sizing, nano-confinement or by introducing a high density of structural defects, such as interfaces. Since grain boundaries can be unstable during cycling, heterophasic interfaces between MgH_2 and immiscible phases may offer greater prospects. While some experimental evidence of hydride destabilization exists,[48,49] significant progress is still needed to make a real impact. Furthermore, materials engineering is necessary to achieve a good thermal conductivity that ensures heat exchange during cycling, and facilitates the use of external heat stores or waste heat.

Development of low-cost, scalable synthesis and processing routes

Lab-scale synthesis of Mg-based hydrides often employs high-energy ball milling, which effectively achieves fast sorption kinetics. The application of ball milling to large-scale processing of metallic powders for hydrogen storage has been demonstrated recently in the activation of TiFeMn alloy using an industrial-sized mill with a 100 L drum.[50] However, ball milling is demanding in terms of processing time and poses significant manpower requirements. Additionally, handling the pyrophoric MgH_2 powders produced by ball milling presents severe safety concerns. Therefore, the development of alternative synthesis and processing methods, and/or the development of additives to enable handling in air, is crucial for a widespread adoption of Mg-based hydrides.

Ensuring long-term cycling stability for sustainable storage applications

Mg-based materials undergo significant morphological and microstructural changes during repeated H sorption cycles at elevated temperatures because of the ongoing phase-structural transformations. These changes, including grain and particle growth,[51] catalyst segregation, and oxidation due to impurities in the hydrogen stream, typically lead to a loss of reversible storage capacity and decreased reaction rates. Therefore, creating stable, poisoning-resistant microstructures is essential for sustainable H storage applications.

Advances in science and technology to meet challenges

Figure 3 illustrates recent research work carried out to address the aforementioned challenges, as summarized in the subsections below.

Reduction of the hydrogen desorption temperature

Altering the average chemical environment of H requires extensive alloying without the formation of secondary hydrogen-inert phases. In this respect, Mg-based amorphous alloys offer a vast playground for compositional tuning (Figure 3a): for instance, the addition of elements with low H affinity such as Cu to amorphous Mg-Ce-Ni alloys can significantly decrease T_d.[52] Furthermore, their normally poor absorption kinetics can be strongly improved by surface decoration with hydride-forming crystallites that act as hydrogen pumps.[53] Another approach exploits the high density of heterophasic interfaces that characterize nanocomposite materials (Figure 3b,c). In order to destabilize the hydride, it is necessary that H absorption increases the interface free energy or induces elastic strain. These effects have first been showcased in Mg-based multilayers,[54–56] MgH_2 nanoparticles confined in a porous scaffold or compact matrix (Figure 3d),[48,49] and more recently in biphasic MgH_2-TiH_2 nanoparticles.[57] However, their impact is moderate, for two reasons: i) the specific interface area decreases upon cycling due to coarsening processes, and ii) the associated ΔH change is often coupled to a partially compensating change of ΔS.[58] In spite of the small thermodynamic changes,[57] nanoscale mixing of MgH_2 and TiH_2 leads to outstanding sorption kinetics,[59] while maintaining a gravimetric capacity suitable for H storage tanks.[60] This identifies TiH_2 as an appealing catalyst for H sorption in Mg (Figure 3e), especially considering its reasonable cost in comparison to other transition metal oxides such as Nb oxides. Additional advantages of nanocomposite powders such as MgH_2/TiH_2 or MgH_2/Mg_2NiH_4 produced by ball milling (Figure 3f) are their augmented resistance to coarsening and stability upon cycling compared to nanostructured MgH_2 with small amounts of catalysts. A significant improvement of H sorption kinetics was also achieved using oxygen-stabilized intermetallic compounds such as $Ti_4Fe_2O_x$ and $Zr_3V_3O_{0.6}$,[61] as well as the liquid alkoxide, titanium isopropoxide,[62] all finely dispersed within MgH_2 by means of ball milling.[60] These advances in the materials science of Mg-based composites have effectively overcome the sluggish hydrogen absorption characteristic of coarse-grained,

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non-catalyzed Mg, arising from surface MgO layers, limited H_2 dissociation on Mg, and slow hydrogen diffusion through the forming hydride.

Development of safe, low-cost, scalable synthesis and processing routes

Alternative methods to ball milling based on severe plastic deformation have been proposed for improving the sorption kinetics of hydride-forming alloys.[63,64] Among these, drop-forging of Mg-based alloys offers promising storage properties while providing a safe and efficient route toward large-scale manufacturing.[65] *In situ* neutron diffraction combined with kinetic measurements was applied to uncover the sequence of phase transitions in a Mg-Mg_2Ni composite processed at room temperature.[66] The basal fiber texture of Mg, the presence of structural defects, and the occurrence of microcracks formed upon forging were identified, but their intimate connection with the faster hydrogen uptake kinetics needs further research. To be able to scale-up production, a quantitative description of the microstructural changes induced in Mg-Ni composites as a function of applied plastic deformation energy is required. Accurate measurements of the mechanical and thermal stresses are needed to enable the formulation of behavioral laws and their integration into a theoretical model.

Another approach combines surface catalysis, second-phase dispersion, and powder compaction methods to produce Mg-Ni alloy pellets that can absorb 6.4 wt% hydrogen. A recently established collaboration enabled the realization of large-scale production with about 100 tons of Mg-Ni alloy pellets being manufactured annually.[47] This development required addressing the oxidation issues during the powder production process and optimizing the compaction parameters.

Ensuring long-term cycling stability for sustainable storage applications

The mixing of MgH_2 particles with expanded natural graphite (Figure 3g), followed by uniaxial compaction, was initially developed to produce disk-shaped H storage media with a good thermal conductivity, which is necessary for the thermal management during ab/ desorption cycles.[44] An additional advantage conveyed by carbon-based additives is the stabilization of microstructure and consequently of H sorption during cycling. A study of MgH_2-TiH_2 composites showed that the introduction of just 5 wt% graphite is sufficient to achieve an intergranular distribution of carbon that prevents the grain growth of both MgH_2 and TiH_2;[45] as a result, the H storage capacity remains stable upon cycling, in contrast with the same composite without graphite. An excellent stability over 3000 cycles was also achieved in the aforementioned Mg-Ni pellets by employing grain refinement casting methods, such as fast cooling with nucleation-promoting agents, which yield a microstructure where Mg domains are well separated by Mg_2Ni. Due to the accelerated kinetics achieved via microstructural refinement and catalyst dispersion, hydrogen absorption in the cycled material can become fast even below 400 K;[67] however, cycling remains constrained to temperatures above the thermodynamically dictated T_d, as previously discussed.

Concluding remarks

The on-going interest in MgH_2 as a hydrogen storage and transport material stems from the moderately high hydrogen capacity, good reversibility and the light, abundant nature of the magnesium. While significant advances have been made in improving the kinetics of hydrogen absorption and desorption through the use of additives/catalysts as well as structural enhancements such as ball-milling and severe plastic deformation, moderating the temperature required to release hydrogen has proven more difficult. The high enthalpy of formation of pure MgH_2 necessitates substantial energy for desorption as well as requiring efficient heat management for both the material and the tank system. Advances have been made in material thermal conduction through the addition of carbon materials, which have also helped to prevent agglomeration during cycling and improve lifetime. However, intermetallic alloys of Mg with lower enthalpy have typically failed to produce suitable materials due to lower capacity or poorer cycling. Nano-sizing and nano-confinement in porous materials have been shown to reduce the enthalpy, but by relatively small amounts, and there are additional costs of processing and materials. Future work to address these challenges will involve laboratory-based research to investigate new material combinations and additives, and engineering solutions to tank design and thermal management.

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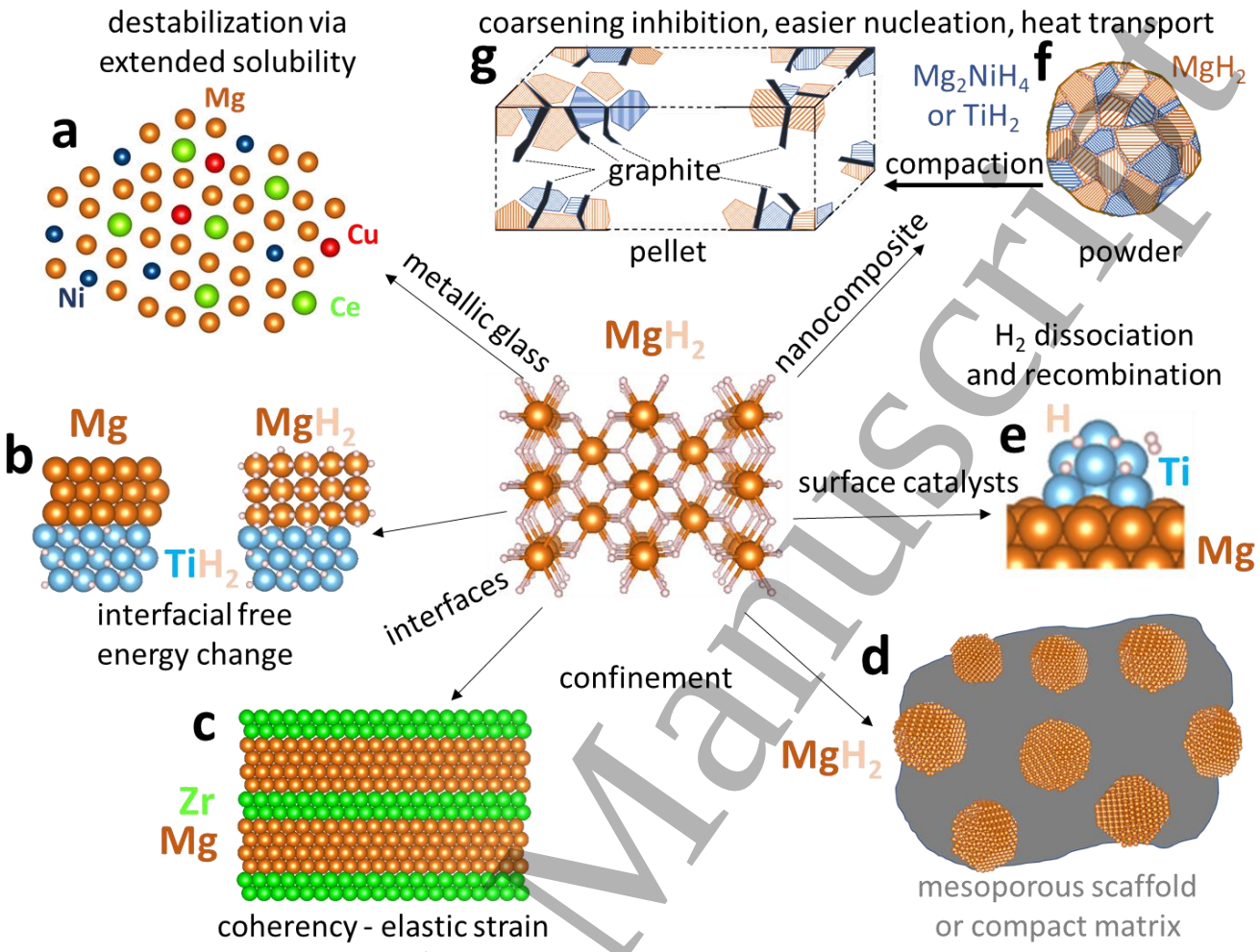


Figure 3: schematic illustration of strategies devised to improve thermodynamic and kinetic properties of Mg-based hydrides compared to MgH_2 (crystal structure shown at the centre). ***a****: Mg-based metallic glasses with destabilizing elements such as Cu.* ***b, c****: nanostructures with hetero-interfaces where the interface free energy increases upon hydride formation or the coherency of interfaces induces elastic strains that destabilize the Mg-H bond.* ***d****: confined MgH_2 nanoparticles.* ***e****: dispersion of catalysts at the surface.* ***f, g****: biphasic microstructures showing better resistance to coarsening and easier nucleation, either in form of powders (ball milling) or compact pellets (powder compaction, drop forging). Including dispersed graphite can enhance the thermal conductivity of the material within the hydrogen storage system. See text for more detailed explanation and references.*

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4. Intermetallic hydrides for energy storage

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Status

Metal hydrides have been extensively developed and studied for many decades for reversible hydrogen storage. Binary hydrides, formed from a single metal and hydrogen, are typically very stable and thus requiring a high temperature for reversibility. However, the present commercial applications of hydrogen storage in solid compounds are based on intermetallic compounds.[68] Their crystal structures can either be ordered or solid solutions with hydrogen atoms occupying interstitial positions between the metal atoms in the lattice. Hydrogen absorption in intermetallic compounds is typically exothermic and the corresponding desorption endothermic, the latter requiring added heat. These compounds typically consist of both hydride forming (e.g. Ti, Zr, La) and non-hydride forming (at ambient hydrogen pressures) elements (e.g. Fe, Ni, Mn), and the thermodynamic properties and the total hydrogen content can be varied and optimized by varying the relationship between the different metals. The hydrogen absorption and desorption kinetics are very fast in many intermetallic compounds, with equilibrium hydrogen pressures useful for hydrogen storage applications. The volumetric hydrogen storage capacity can be high in intermetallic hydrides (e.g. 158 g/L in TiVCrNbH8)[69] and since operating pressures are conveniently low, 1-10 bar H2 at ambient conditions, these compounds are of significant interest for stationary and mobile applications. Approaches range from: optimization of cost-efficient established hydrides such as TiFe-based hydrides for use at ambient conditions and low hydrogen pressures; detailed understanding of crystal structures and hydrogen storage properties of different intermetallic hydrides; to newer multi-principal-element alloys, also called high-entropy alloys.[70] The latter are promising alloys for hydrogen storage, even though the stability of the high hydrogen capacity cubic high-entropy alloys is high, and temperatures exceeding 250-300 °C are required to completely release hydrogen.

The typical focus of applied oriented research activities is in selecting alloy compositions for three major applications: (a) hydrogen storage systems operating together with PEM fuel cells; (b) advanced anodes of the Ni-MH batteries; (c) materials for the efficient compression of hydrogen gas to pressures exceeding 700 bar H_2. AB, AB_5 and Laves type AB_2 alloys are often linked with H storage systems. AB_5 and AB_2 alloys are multipurpose metal hydrides that are also well suited as MH anodes (together with Mg-containing layered intermetallics with REM and Ni) and MH compression devices while working at different pressure ranges (0.1-10 bar: AB_5; 10-1000 bar: AB_2). Examples of recent work are given in the references.[38,71–77]

Current and future challenges

Key challenges related to intermetallic hydrides:

- *Understanding the hysteresis of hydrogen absorption and desorption, and the slope of plateau pressure in Pressure-Composition-Isotherms (PCIs).*
  Desirable negligible hysteresis of hydrogen absorption and desorption would eliminate the energy losses during the reversible storage of hydrogen, Figure 4a. This is very important for metal hydride compression and storage. The slope of the plateau pressure (Figure 4a) in the two-phase region is associated with the attractive elastically-mediated hydrogen-hydrogen interaction.[78] Extreme stiffness of the metal matrix may decrease this attractive interaction, and consequently decrease the enthalpy of hydride formation or even inhibit hydrogen absorption.[79,80] The variation of the exothermic enthalpies of hydrogen solution, ΔH^s, as a function of hydrogen content, is informative of the H-H interaction. An increase of $|\Delta H^s|$ with hydrogen content indicates an attractive H-H interaction,[81] while a decrease

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of $|\Delta H^s|$ indicates a very weak or even repulsive H-H interaction.[82] It has been demonstrated that a significant decrease of the elastic H-H interaction in $ZrMo_2$-H_2 results in a corresponding drastic increase of the solid solubility region and even to an unexpected decrease of the heat of hydride formation with respect to other members in the $Zr(Mo_xFe_{1-x})_2$ system.[80]

- *Material cyclability, including resistance towards amorphization and degradation upon cycling.*
  The cycle life of metal hydrides is critical for many applications where thousands of cycles are required. Loss of capacity has cost implications as additional material would need to be designed in. Ideally starting materials should have good capacity and kinetics, Figure 4b. Also, the intermetallic hydride should resist amorphization and degradation from contaminants in the hydrogen gas reducing capacity with cycles, Figure 4c. In addition, inconsistencies in material performance can be caused by production scale up. For example, industrially produced $TiFe_{0.85}Mn_{0.05}$ showed impure H_2 did not influence the cyclability,[83] yet some promising lab-scale alloys have showed a decreased performance when scaled-up.[84]

- *Experimental challenge to determine thermodynamic properties.*
  Enthalpy is typically derived from PCIs, using the Van't Hoff relationship $\ln\left(\frac{p}{p_0}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{T}$, rather than direct measurements by calorimetry. The equation assumes reversibility and temperature independence of the change in enthalpy ΔH and entropy ΔS. Variations between enthalpy of formation and decomposition are commonly reported in PCIs, for example up to 20%.[85] This combined with the challenges of volume and temperature calibration, maintaining isothermal samples and sensitivity of Sieverts apparatus to measure PCIs, mean that care must be taken in interpreting thermodynamic data for applications.

- *Understanding the first hydrogenation step.*
  For many metal hydrides, the first hydrogenation, also called activation, is a difficult and lengthy process leading to a cost increase of the metal hydride. Easy activation of H_2 absorption and fast kinetics of hydrogen absorption and desorption are needed for commercially suitable metal hydrides. There is, in general, limited basic knowledge about the activation processes in intermetallic hydrides. A segregation of pure metal species (with favourable, non-activated intersection of hydrogen physisorption and chemisorption curves)[86] on the surface or the subsurface of intermetallic compounds facilitates the corresponding hydrogen absorption.[87,88] It has been proposed that secondary phases and variation in composition at the interface matrix / secondary phase, for instance in TiFe with element substitution, may have a key role in improving the activation.[89]

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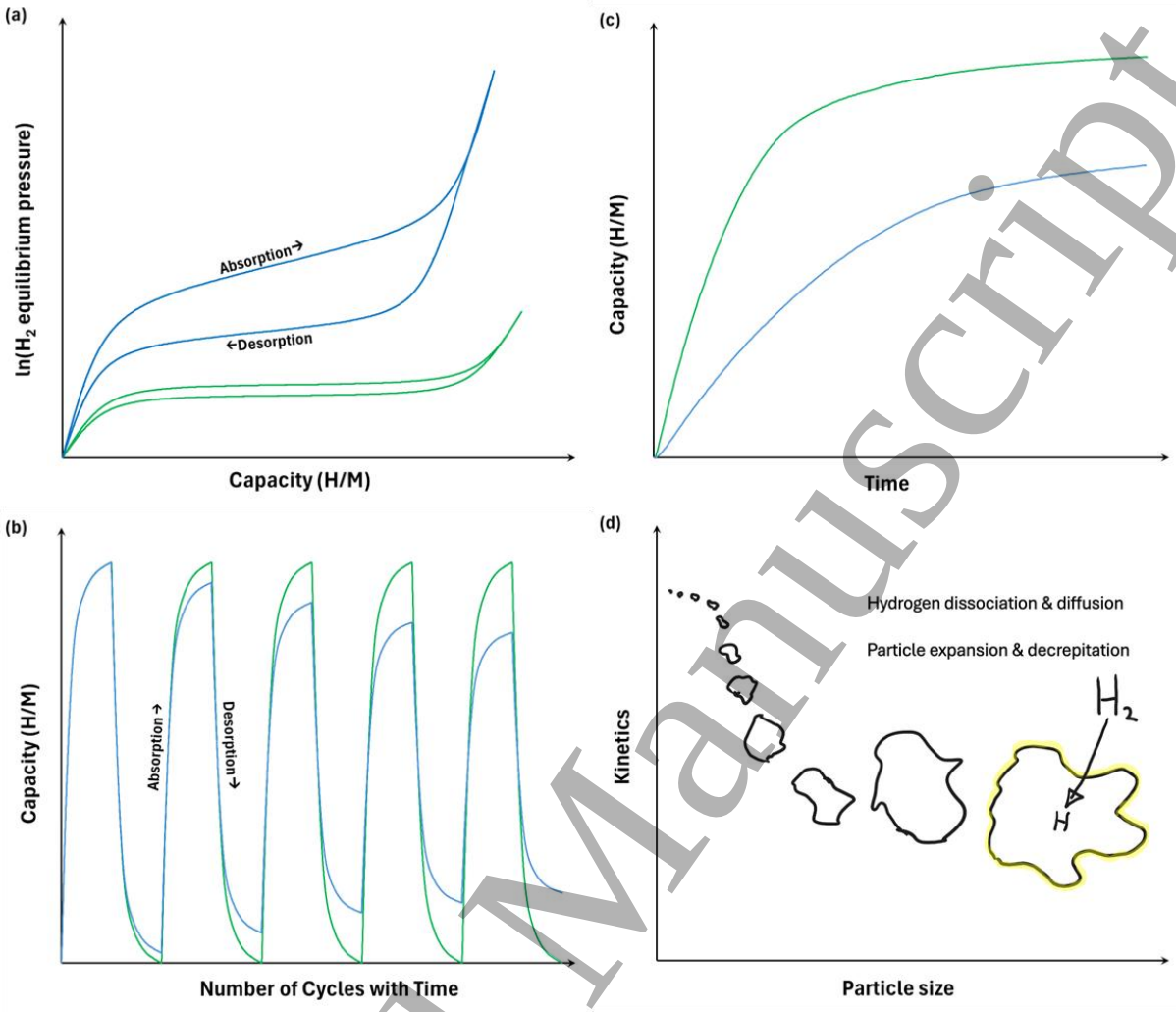


Figure 4: Illustrative sketch showing idealized improvements (green lines) compared to suboptimal performance (blues lines) in terms of (a) sloping plateau, hysteresis and capacity; (b) cycling behaviour; (c) kinetics and capacity; and (d) the challenges of activation of powder samples influenced by the surface chemistry to allow dissociation of hydrogen at the surface then diffusion through the bulk. As the material hydrides, expansion of the crystal structure causes decrepitation i.e. reduction of powder size enhancing kinetics due to limitation of diffusion.

Advances in science and technology to meet challenges

- *Understanding the hysteresis of hydrogen absorption and desorption, and the slope of plateau pressure in PCIs).* Hysteresis and slope, illustrated in Figure 4a, depends on many factors. External factors may play a role in the magnitude of hysteresis. For example, the geometry of the sample holder and the thermal conductivity of that sample holder. In addition, the method used to measure the PCI curve may have an impact. Since cycling can influence hysteresis, quantities such as the equilibrium time, the equilibrium values of the pressures of hydrogen absorption and desorption make it difficult to compare hysteresis measured from different laboratories. A detailed consideration of these factors into an overall study would give a deeper understanding of the mechanisms involved in the materials performances. For example, a better understanding of the H-H interaction is needed for tailoring the slope of the plateau pressure.

- *Material cyclability, including resistance towards amorphization and degradation upon cycling.* Since cycling is time consuming, it is necessary to carefully select the materials subjected to such testing. It is advisable to study cycling only on promising alloys and not as a standard characterization method for all alloys. With the goal of enabling a cost-effective technology, it is important to investigate the effect of impurities on the cycling behaviour

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of intermetallics, Figure 4c and their capacity, Figure 4b. Moreover, the reproducibility of their performance needs to be tested at scale in addition to the lab, since scale processing methods such as melting conditions, cooling profiles, post treatments, milling and compaction can influence material properties.[84]

- *Experimental challenge to determine thermodynamic properties.*
  The Van't Hoff derived enthalpies from PCIs show $|\Delta H^f| < |\Delta H^d|$ for formation and decomposition. Careful twin cell calorimetry combined with Sieverts experiments have shown $|\Delta H^f| = |\Delta H^d|$ for AB, AB_2 and AB_5 intermetallics (e.g. ZrNi-H_2,[85] $Zr(Fe_{0.75}Cr_{0.25})_2$-H_2,[90] $CaNi_5H_x$).[91] The magnitude of these calorimetrically derived enthalpies is between $|\Delta H^f|$ and $|\Delta H^d|$ generated by van't Hoff methods. Direct calorimetry measurements are consistent irrespective of cycle number and can identify the boundary between single and two-phase regions.[90] If direct calorimetry measurements are not possible, laboratories do have options such as using $p_{plateau} = (p^f . p^d)^{1/2}$ in their Van't Hoff plots, giving a closer match to the enthalpy determined by direct calorimetry.[92] Aligning and sharing good practice would improve databases used for the prediction of metal hydride thermal store performances, the prediction of pressures reached by metal hydride compressors, and machine learning approaches used to predict new materials.[93]

- *Understanding the first hydrogenation step.*
  The first hydrogenation mechanism is still not well understood. There are some indications that it may obey an Arrhenius law, but more investigations are needed to understand the effect of particle size, presence of oxide on the surface and microstructure.[94] The reduction of particle size can lead to improved capacity and kinetics, Figure 4b,d.

- An interrelation between the structure and chemical composition of multielement alloys and their hydrogen storage performance needs to be established, in order to develop alloys with large capacity exceeding 3 wt.%. A major challenge is developing materials with reversible capacity below 100 °C. Here, novel multicomponent alloys containing magnesium are of particular interest as has been recently shown through studies on LaMgSn as a hydrogen storage material.[95]

Concluding remarks

Intermetallic hydrides have potential applications ranging from hydrogen storage, efficient compression of hydrogen gas and advanced anodes of batteries. Here we present five challenges to the advancement of science and technology utilising these promising materials as part of the roadmap. These are: (a) a deeper knowledge of the H-H interactions to enable a better understanding of hysteresis of hydrogen absorption/desorption and slope of the plateau pressure with varying hydrogen composition, critical to efficient applications; (b) the influence of processing parameters including scale up and impurities on cycling behaviour; (c) more accurate and consistent measurements of thermodynamic quantities and cross referencing to alternative techniques, since this has repercussions on practical stores and their thermal management; (d) understanding the mechanism of the first hydrogenation step of intermetallic hydrides, which is important in alloy design especially if activation does not require elevated temperatures; (e) further enlightenment on the interrelation between the structure and chemical composition of multielement alloys to push towards higher capacity intermetallic hydrides of commercial interest. The excitement and potential of intermetallic hydrides for hydrogen storage and related applications remains. This is driving current and future work in understanding, modelling, consistency in measurement and improved performance to deliver low cost, high-capacity intermetallic hydrides with flatter plateau pressures, low hysteresis and fast kinetics for the application operating conditions.

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5. Complex hydrides for hydrogen storage

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Status

Solid state hydrogen storage has received growing interest since the oil crisis of the 1970s.[96,97] The initial focus was metallic hydrides, which have excellent thermodynamic properties but are too heavy with too little gravimetric hydrogen content for most applications.[38,98] Later, the lighter metal magnesium and its alloys came into focus. However, despite greater gravimetric capacities, hydrogen release and uptake occurred at temperatures too high for most applications.[36] Combining the benefits of high gravimetric capacities and low hydrogen release temperatures, complex metal hydrides present a promising solution.[96]

Until the late 1990s, the kinetic barrier associated with the reversible hydrogen release and uptake of complex hydrides at practical conditions was thought to be insurmountable. However, Bogdonovic's seminal discovery was that the kinetics of the reversible dehydrogenation of $NaAlH_4$ can be enhanced with the addition of a few mol% Ti, such that it can be achieved at 150 ˚C.[99] This finding initiated a paradigm shift for the research activities in hydrogen storage systems containing complex ions. Group I and II compounds of complex ions such as $[AlH_4]^-$, $[BH_4]^-$, and $[NH_2]^-$, commonly referred to as complex hydrides: denoted here as alanates, borohydrides, and amides (IUPAC tetrahydroaluminates, tetrahydroborates, and azanides). Pioneering work by Chen in 2002 motivated extensive studies on the reversible hydrogen storage based on amide complex hydrides,[100] while early efforts by Züttel and Orimo prompted investigation of lithium borohydride ($LiBH_4$).[101] During dehydrogenation, complex hydride systems can also release other undesired gases if not carefully managed. For example, the amide-imide system proceeds via an intermediate and can sometimes lose NH_3 during release and uptake of hydrogen. Similarly, lithium borohydride may release diborane when decomposed in vacuum or reacted with silicon dioxide.[102] Diborane can then condense to higher borates, *e.g.* the *closo*-borates $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, which often leads to side products or reacts with an ionic hydride to form a solid.[103] Finally, it should be noted the release and uptake of hydrogen by complex hydrides proceeds by significantly more complicated mechanisms than metallic and ionic hydrides, and often remains not fully understood. A summary schematic showing typical classes of complex hydrides for hydrogen storage, some key challenges and recent advances is shown in figure 5.

Current and future challenges

The high volumetric (ρ_V) and gravimetry (ρ_m) hydrogen capacity of complex hydrides have long suggested their utilization as hydrogen storage materials.[96,97,103] However, developmental efforts are confronted by the daunting challenges of: improving the kinetics of their reversible dehydrogenation, designing high performance and low-cost systems, and circumventing often unfavorable thermodynamics. As previously introduced, $NaAlH_4$ is among the few complex hydrides that are within in the narrow thermodynamic realm that allows reversible dehydrogenation at moderate pressure and temperature, becoming the first complex hydride to be widely studied as a hydrogen storage material.[104,105] However, efforts to develop onboard systems based on this material have not been able to achieve adequate hydrogen cycling capacities or kinetics. Additionally, system gravimetric hydrogen capacities, rates of heat rejection on recharging, and cost targets have not been met.

The high gravimetric H_2 density of 14.7 wt % of magnesium borohydride ($Mg(BH_4)_2$), alongside its favorable thermodynamic parameters ($\Delta H° = 38.6$ kJ/(mol H_2) and $\Delta S = 111.5$ J/(K·mol H_2),[106,107] make it a tantalizing candidate for

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hydrogen storage applications.[108] The direct hydrogenation of magnesium diboride, MgB_2 to $Mg(BH_4)_2$ has been achieved together with overall hydrogen cycling of 11 wt% hydrogen.[109] This stands as the highest hydrogen gravimetric capacity that has been achieved with any material to date. However, the hydrogenation was found to require 900 bar of hydrogen pressure and heating to 400 ˚C.[109] Table 1 summarizes the progress that has been made toward the development of $Mg(BH_4)_2$ as a practical hydrogen storage material. Improved hydrogenation kinetics have been achieved upon mechanical milling of MgB_2 with tetrahydrofuran (THF) or graphene which have recently been shown to result in carbon substitution into the boride layers of the material.[110–112] Additionally, transition metals and their halide complexes been found to improve the dehydrogenation kinetics of $Mg(BH_4)_2$.[113,114] The more limited, but reversible dehydrogenation $Mg(BH_4)_2$ to $Mg(B_3H_8)_2$ (theoretical capacity of 2.5 wt%) has been achieved at the moderate temperature of 200 ˚C.[114–116] Dehydrogenation at this temperature following addition of sub-stoichiometric amounts of THF has been observed to change the product selectivity to $Mg(B_{10}H_{10})$ and thereby elevating the amount of H_2 to 5.7 wt%.[116] The practical viability of $Mg(BH_4)_2$ as a hydrogen storage material awaits improvements in hydrogen cycling capacity and kinetics at moderate conditions.

Table 1: Amount of hydrogen release, products, and revisability observed upon dehydrogenation of $Mg(BH_4)_2$ at varied temperatures with and without additives.

Temp	Additive	Product(s)	$\rho_{gravimetric}$ (wt%)		$\rho_{Volumetric}$ (gH_2/L)		Reversibility	Ref
			theory	exp	theory	exp		
530 ˚C	none	MgB_2	14.9	12.6 cycled	117	97 cycled	950 bar H_2, 400 ˚C	[106]
530 ˚C	carbon doping	MgB_2	14.9	7..2 cycled	117	56 cycled	400 bar H_2, 300 ˚C	[110–112]
395 ˚C	none	Mg $Mg(B_{12}H_{12})$	11.0	11.0	86	86	Mg to MgH_2 only	[117]
310 ˚C	none	MgH_2 $Mg(B_{12}H_{12})$	8.0	8.0	62	62	not observed	[117]
200 ˚C	none	$Mg(B_3H_8)_2$ MgH_2	2.5	2.3 cycled	20	18 cycled	120 bar H_2, 250˚C	[114–116]
200-285 ˚C	E.g.: $TiCl_3$, $NbCl_5$, CaF2, ZnF_2, TiF_3, NbF_5; $ScCl_3$, TiO_2, CoF_3, $CoCl_2$, Co_2B, $NiCl_2$	$Mg(B_3H_8)_2$ $Mg(B_{12}H_{12})$ MgH_2	4.5	up to 4.0	35	31	Partial absorption at 120 bar H_2, 285 ˚C with Co-additives:	[113, 118]
200 ˚C	THF H_2 back pressure	$Mg(B_{10}H_{10})_2$ trace $Mg(B_{12}H_{12})$ MgH_2	8.1	5.7	63	45	not observed	[116]

Efforts to develop a partial onboard hydrogen storage system based on MNH_2 (M = Li, Na) amides and amide/ binary hydride composites have also been hampered by sluggish kinetics and insufficient hydrogen cycling capacities. However, they have found application in an auxiliary power unit.[119] Interest in the development of hydrogen storage systems beyond those for vehicular applications has resulted in renewed research on amide based systems.[120] Hydrogen carrier systems based on the hydrolysis of lithium and sodium borohydride have long been of interest for niche military applications. However, thermodynamics dictate that the resulting borates cannot be directly hydrogenated back to the borohydrides. Efforts to develop these systems for onboard vehicular applications were abandoned due to the costs associated with the chemical processes for regenerating the borates back into the borohydrides. Recently, however, borohydride hydrolysis technology has again become

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of interest in the context of long range, bulk hydrogen transfer. This development has led to a renewed effort for the development of a lower cost method for the conversion of borates to borohydrides.[121]

Advances in science and technology to meet challenges

A range of derivatives of complex hydrides with extreme hydrogen densities and a potential for solid state hydrogen storage have been recently discovered.[103] One compound, ammonium tetrahydridoborate, NH_4BH_4, is isoelectronic to natural gas with a very high hydrogen density (~25 wt% H_2), but is metastable.[122,123] However, it was discovered that the physical and chemical properties can be modified by a reaction with more stable metal borohydrides, $M(BH_4)_x$, to form $(NH_4)_yM(BH_4)_{x+y}$.[124–126] The ammonium metal borohydrides suppress the aggressive decomposition of NH_4BH_4 and possibly alter the decomposition pathway. However, the thermal stability decreases with increasing ratios of NH_4BH_4 in the compounds owing to increasing numbers of di-hydrogen bonds in the solid state, which facilitate low temperature hydrogen elimination.

A porous magnesium borohydride framework was shown to contain small pores and a unique partially negatively-charged non-flat interior, able to reversibly store small guest molecules such as nitrogen, hydrogen and dichloromethane.[127] Recently, this material was studied for hydrogen and nitrogen uptake using neutron powder diffraction, volumetric gas adsorption, inelastic neutron scattering, and first-principles calculations.[128] Molecular hydrogen is packed extremely dense with about twice the density of liquid hydrogen, i.e. $Mg(BH_4)_2{\cdot}2.33H_2$, 144 g H_2/L of pore volume, determined independently by three experimental techniques. A penta-dihydrogen cluster was discovered where H_2 molecules in one position have rotational freedom, whereas others have a well-defined orientation and a directional interaction with the framework. Thus, densely packed hydrogen can be stabilized in small-pore materials at ambient pressures.[128] Larger molecules, such as ethane and noble gasses, are able to enter the pores reversibly, despite very different kinetics.[129,130] Porous $Mg(BH_4)_2$ can be seen as the first member of a new class of framework materials, adding to the emerging group of novel nanoporous solids, such as flexible metal-organic frameworks (MOFs). The similarity of these frameworks to MOFs provides a route to novel hybrid materials. Combined use of the BH_4^- ions with other directional ligands may produce new porous materials with high hydrogen storage density, demonstrated by γ-$Mg(BH_4)_2$.

Another promising approach to enhance kinetics and tailor thermodynamics of complex hydrides is the concept of reactive hydride composites.[131] It was first introduced by Chen et al.,[100,132] combining amides with hydrides such as $LiNH_2$ and LiH or $Mg(NH_2)_2$ and LiH. Later this concept was extended by Vajo et al.[43] and Barkhordarian et al.[133] to borohydride-hydride systems such as $LiBH_4$–MgH_2 mixtures with measured reversible hydrogen storage capacities of more than 10 wt%, and rehydrogenation pressures below 50 bar. These composites have in common that they show significantly improved dehydrogenation and rehydrogenation kinetics as well as lowered reaction enthalpies compared to single phase complex hydrides. Further improvement could be demonstrated by use of transition metal additives acting as nucleation sites for the required phase transformations.[134,135] Despite the enormous success in using this concept, hydrogenation and dehydrogenation temperatures for such 2-component reactive hydride systems remained at temperatures of 170 °C or higher. However, by combining two complex hydrides and one light weight hydride Wang et al. demonstrated that both hydrogenation and dehydrogenation is possible at temperatures below 100 °C,[136,137] offering a new strategy to design high-capacity hydrogen storage materials with ambient working temperatures. To further optimize such systems with complex reaction mechanisms, the development and usage of a wide variety of *in-situ* characterisation tools as well as computational methods is required to gain the necessary understanding to further fine-tune such systems.[138,139]

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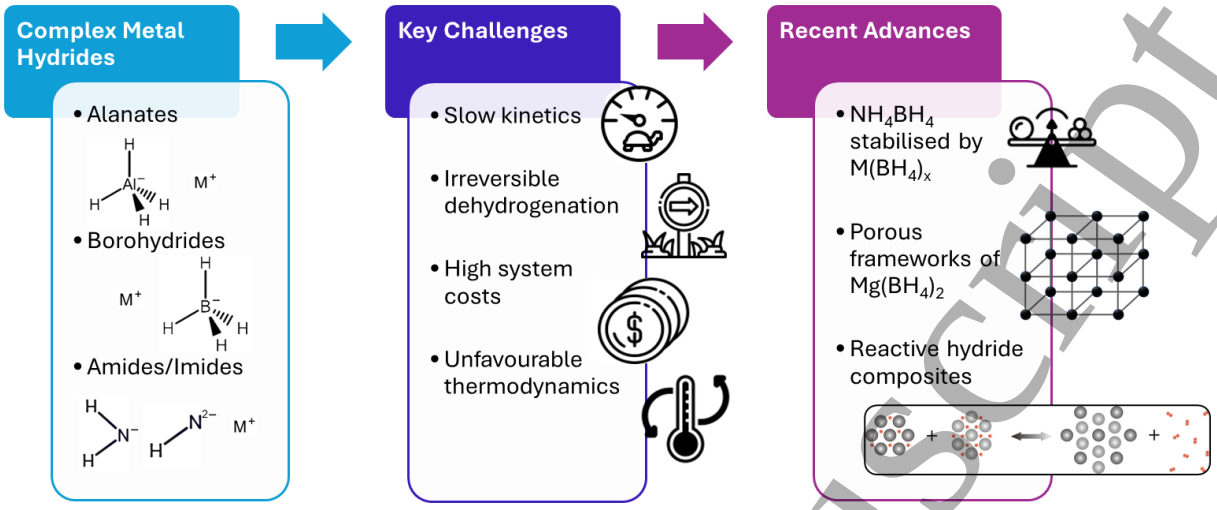


Figure 5: A summary schematic showing complex hydrides for hydrogen storage, key challenges and recent advances.

Concluding remarks

After the finding in 1997 that Ti-enhanced $NaAlH_4$ was reversible at moderate temperature and pressure,[99] there has been significant worldwide research activities related to complex hydrides for hydrogen storage. Many different complex hydrides with high gravimetric hydrogen capacities have been explored, based on aluminium (alanates), boron (metal hydroborates) and nitrogen (amides/imides). Key challenges for the materials have been related to sluggish kinetics, unfavourable thermodynamics for hydrogen release and uptake and high system cost. Recent advancements to overcome these hurdles include tuning the hydrogen storage properties of ammonium metal borohydrides, combining complex and light weight hydrides into reactive hydride composites, as well as the optimization of hydrogen storage in porous $Mg(BH_4)_2$ systems.

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6. Materials-based hydrogen compression and purification

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Status

Hydrogen is one of the most promising secondary energy vectors to help realize a decarbonized society. Its storage and compression, however, still pose technological challenges. For example, hydrogen compression for mobile application needs more than 4 kWh/kg H_2 of electrical energy. Energy consumption of purification in pressure-swing-adsorption is mainly determined by the electrical power of the compressors. Increasing efficiency and lowering costs are therefore key. Here, we will discuss an alternative hydrogen compression and hydrogen purification technique using hydrogen sorbing materials. Solid-state hydrides have been applied for hydrogen storage due to their higher volumetric hydrogen storage density,[98] but they can also be considered for hydrogen compression and purification because of their thermodynamic stability and selective absorption reaction with hydrogen.[140–142]

Hydrogen compression can be categorized into mechanical compression and non-mechanical compression (such as electrochemical compression),[143] but it can be obtained also using adsorption or absorption-based materials.[140–142] Hydrogen compression using hydrogen sorbing materials offers several advantages, including the absence of moving parts, leading to less maintenance, noise and vibration, as well as a small footprint and no hydrogen contamination. Techno-economic analyses for metal hydride compressors indicate that operating costs can be significantly reduced when waste heat is available nearby,[144] as hydrogen is compressed by reversible absorption and desorption reactions induced by a temperature swing.

Hydrogen purification techniques can be physical, such as pressure swing adsorption (PSA), thermal (cryogenic method) or chemical, including metal hydride separation.[145,146] Depending on the scale, a suitable selection of the purification technique is required. PSA has been used in large-scale hydrogen production applications but is not always suitable in small applications. Since hydrogen purification by absorbing materials is based on the selective absorption and desorption reaction with only hydrogen, scale is not an issue. It has the advantages of a simple device layout, simple and safe operation and high recovery ratio of hydrogen.[146] Two main methods have been developed: flow-through purification and periodic evacuation of impurities,[147] depending on the purity of hydrogen. Since this is also a thermochemical process, low energy consumption is expected if waste heat is available. In addition, this system is suitable for daily start and stop operation, and 99.999% purity can be expected.[147,148]

Materials-based hydrogen compression technology has seen business and demonstration developments,[149–151] and materials-based hydrogen purification of H_2 from CO_2 and NH_3 has also been demonstrated at large scale.[147,148,152]

Current and future challenges

Hydrogen compression and purification using hydrogen storage materials have several issues that need to be solved from a materials science viewpoint: 1) tuning of hydrogen storage performance leading to higher energy efficiency, 2) long-time utilization including impurity tolerance, 3) thermal management.

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Energy efficient hydrogen compression and purification

Since the processes are driven by heat, an increase in the energy efficiency of the compression or purification processes can be obtained by minimizing hysteresis and the slope of the plateau in hydride materials, keeping high volumetric hydrogen density. To achieve higher outlet pressures at lower heating temperatures, the hysteresis in the PCI must be reduced. Sloping plateaus due to compositional inhomogenity or operational temperatures above the critical temperature require increasing inlet pressures to stay above the equilibrium pressure during hydrogen charging, while, during hydrogen release, outlet pressures gradually decrease along with equilibrium pressures. Therefore, the factors governing these properties must be identified and controlled. Additionally, deviations of experimental data from Van't Hoff predictions tend to be larger with increasing working pressure ranges. Therefore, hydrogenation properties need to be evaluated experimentally up to target pressures, instead of extrapolating the data measured at lower pressures. Further, dynamic compression or purification experiments supplying hydrogen under hydrogen flow conditions need to be carried out to confirm their performance under operational conditions. Finally, optimization of the external heat management (for example, using heat pumps) needs further investigation.[153]

Degradation upon cycling and impurity tolerance

Hydrogen compression and purification rely on repeated hydrogen absorption and desorption reactions, making cyclic durability crucial. Even with pure hydrogen, cycing can induce defects, amorphization or decomposition leading to poor durability (intrinsic effect). Suppression of such structural degradation can be achieved through compositional tuning, but its mechanism needs to be identified. This is the main mechanism available to make compression alloys resistant against degradation, since repeated cycling is the main challenge there. When hydrogen gas contains impurities, hydrogen storage performance (capacity and kinetics) is often degraded (extrinsic effect).[154,155] This can be due to the formation of secondary phase on the surface such as oxides, or adsorption of impurity gases including those formed during absorption such as methane and carbon monoxide. There are three potential strategies to improve degradation from impurity gas species: compositional tuning,[156] surface modification,[157–160] and gas circulation.[161] To solve extrinsic degradation, the mechanisms behind the interaction of impurity gases with hydrogen and surfaces of the hydrogen sorbing material need to be identified. Following that, a suitable compositional tuning can be found to reduce the interaction with the impurity gas, and methods to modify the surface to make stable and effective gas barrier layers can be established. For large-scale applications, not only do suitable composite materials for gas barrier layers need to be developed, but also scalable synthesis processes to manufacture them.

Thermal management

Because the processes are thermally driven, thermal management is critical to hydrogen compression and purification using metal hydrides. Poor thermal management slows down the sorption reactions leading to a decreased system efficiency. Since both adsorption-based materials and absorption-based materials are produced in powder forms, their thermal conductivities are typically low. To improve system efficiency, thermal conductivity, thermal diffusivity and heat capacity are critical. In addition, these properties need to be evaluated under operational conditions. For this, reliable methods are needed to measure under pressures relevant for H_2 compressors (up to 100 MPa H_2), and over multiple cycles.[162] Materials with higher thermal conductivity and the development of simulation techniques to identify key factors affecting thermal transport during hydrogenation and dehydrogenation reactions are needed.[163]

Advances in science and technology to meet challenges

Recent research work carried out to address the afore-mentioned challenges are summarized in the subsections below.

Energy efficient hydrogen compression and purification

Direct measurement of pressure-composition isotherms up to 100 MPa and candidate compounds for hydrogen compression up to 80 MPa have been reported.[164–166] Since some of these compounds show a critical temperature below 100°C, as described in the previous part, further material tuning is needed in order to reduce the hysteresis of the PCI curves. In this respect, machine learning, as well as the use of machine learning interatomic potentials (MLIP), offer an efficient approach to identify potential compositions and alloys using existing materials databases. It can speed up the materials design by selecting suitable candidates prior to synthesis and characterisation. Flattening of the plateaus from a slope of 2 in the lnP vs. concentration isotherm to zero increases the thermal efficiency by 12.1 %.[167] Nonetheless, alloys selection must also consider materials cost, which significantly impact the overall cost of the system.[168] It has been shown that a 50% reduction of

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materials cost can lower the initial cost of the system by approximately one third.[169] Additionally, raw materials availability must also be considered as limited natural resources and volatile supply chains can become bottlenecks for scalability and commercialization.

Degradation upon cycling and impurity tolerance

For hydrogen purification, extrinsic degradation causing capacity loss and slowing kinetics are serious issues. AB_5 type compounds typically show relatively good impurity resistance. Recently, however, AB_2 compounds have been investigated because of their flexibility in working pressure range by tuning chemical compositions, where substitution of elements can impact antipoisoning behavior. Surface modification has also shown excellent performance.[157–160] For instance, confined composites improve the kinetics under mixed gas conditions,[159] and coated nanoparticles retain excellent hydrogenation properties even after exposure to air.[158] However, the long-lifetime stability of these composites still need to be addressed. Furthermore, gas circulation can be beneficial for limiting high local impurity gas concentration near the surface after hydrogen absorption and preventing the impeding blanket effect observed for ZrCo.[161] To understand the degradation mechanisms, in-situ measurements and first-principle calculations for surface analysis, such as ambient XPS techniques, are especially helpful. With this in mind, a durability of 10,000 cycles (depending on the requirements of the application) should be achievable.

Thermal management

The thermal conductivity and heat capacity of materials significantly affect reaction kinetics and efficiency. Heat transport in metal hydrides is affected by various factors, including hydrogen-to-metal ratio,[170] hydrogen pressure,[171] temperature,[172,173] particle size,[44,174] and porosity.[175] Therefore, it is important to understand how the heat transport properties change with these factors through *in-situ* measurements, along with PCI measurements. Experimental results and the associated thermal conduction mechanisms can be analyzed by computer simulations. Recently, the mesoscale modeling framework has effectively verified key microstructural factors and thermal conduction pathways affecting the effective thermal conductivity of composites under varying porosity, additive content, and gaseous conditions.[176] Future investigations should also examine the influence of hydride microstructure, interfaces, and impurities on the heat transport mechanisms, in particular at pressures relevant for compression.[162,163,177] These approaches can also be utilized to quantify the effects of several types of additives (e.g., metals,[178] expanded natural graphite,[175,176] and graphene-based materials)[179] on enhancing the heat transport properties of hydrides.

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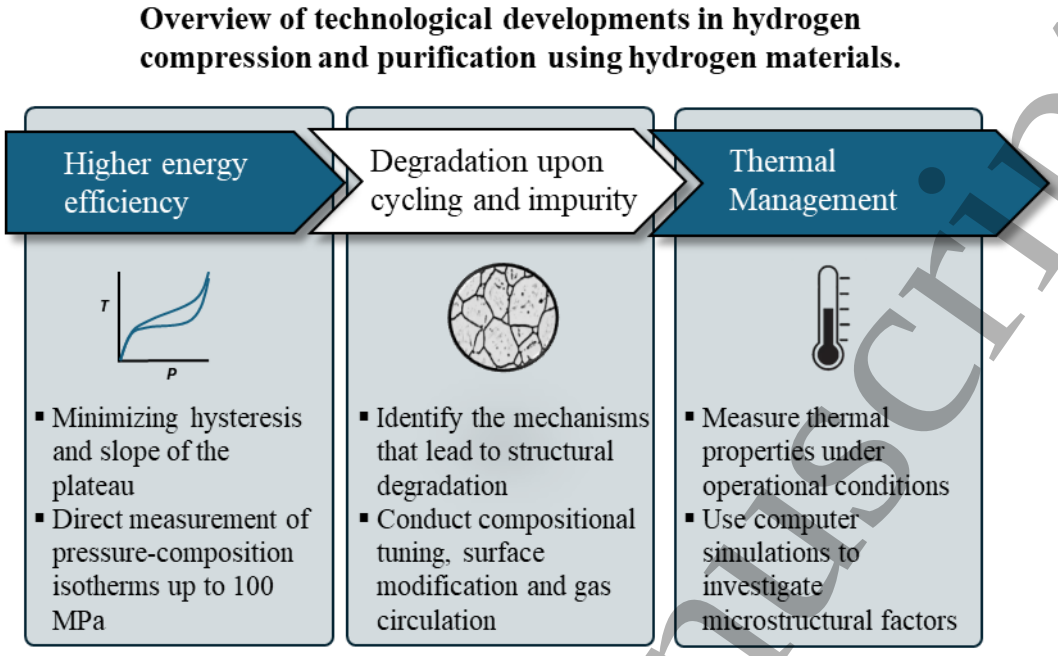


Figure 6: An overview of future technological developments required for hydrogen compression and purification using hydrogen materials.

Concluding remarks

The development of improved, cost-efficient and reliable hydrogen compression and purification technologies is an urgent need for the implementation of a hydrogen economy. The use of hydrogen absorption and adsorption reactions for hydrogen compression has significant advantages such as less moving parts, lower noise levels, higher reliability and lower maintenance costs. However, materials properties such as reaction enthalpies and plateau pressures have to be tuned properly, plateau slopes and hysteresis must be reduced significantly to achieve the desired efficiencies, as well as optimisation of ab- and adsorption pressures at uptake temperatures and desorption pressures at the envisioned release temperatures. Furthermore, in such thermochemical systems the heat transfer has to be significantly improved either by compaction, the use of additives, or the design of the internal vessel structure. Computer simulations such as multi physics simulations and machine learning are essential tools to improve vessel designs and to accelerate material discovery. Accurate measurements at hydrogen release temperatures and pressures of up to 100 MPa are needed to select the best suited materials for targeted temperatures and pressures. Finally, long-lifetime and cycling measurements need to be demonstrated for new alloys, and large scale demonstrators need to be developed and tested. Alternative concepts based on cryogenic adsorption/desorption are also being explored for thermally driven physisorption-based hydrogen compression, as described in chapter 2.

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7. Hydrogen storage in liquid hydrogen carriers

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Status

Liquid hydrogen carriers (LHCs) are chemicals that store hydrogen through chemical reactions, requiring a catalyst to make the hydrogenation and dehydrogenation reactions more efficient.[180–183] While some LHCs require higher temperatures to release H_2, it is notable that all LHCs can store and transport H_2 under near-ambient temperatures and pressures, can take advantage of current liquid handling infrastructure, and are well suited for large scale and long-duration storage given the wide scale availability of the inexpensive materials.[184] This broad class of materials includes ammonia, cyclic hydrocarbons, alcohols, and aqueous salts.[185–189]

Several companies are in the early stages of marketing LHCs for H_2 storage, transport and power generation with a wide range of pilot and demonstration projects underway. Chiyoda in Japan has demonstrated using methylcyclohexane (MCH) to transport H_2 by international shipping from Brunei to Japan.[190] Hydrogenious has partnered with Bosch on a demonstration to provide heat and power to a hospital in Erkelenz Germany using benzyl toluene (BT). Amogy, in the US, describes using ammonia cracking to produce hydrogen to power a fuel cell marine vessel. Companies like DENS, in the Netherlands are advertising formic acid (FA) power units to replace diesel generators and Hydro X in Israel advertises using aqueous formate salts for long-term stationary storage of hydrogen.

It remains unclear how close to market readiness these applications are as many challenges are being addressed both in commercial settings and research laboratories. Systems analysis approaches provide valuable insight to best match various LHCs with the wide variety of potential end uses. Further research into increasing the round-trip efficiency of storing hydrogen in LHCs, determining the levelized cost of hydrogen (LCOH) for a wide variety of use case, and a comparison of the reduction of carbon emissions through life-cycle analysis of LHCs compared to the physical storage of H_2 as a compressed gas or cryo-liquid will help to transition LHCs from pilot scale demonstrations to large scale applications.

Current and future challenges

Currently, the key challenges for LHCs are system cost, round-trip efficiency, and catalyst reactivity.[191] LHC use for storage and/or transport should be competitive with conventional compressed gas or liquid hydrogen in all these ways to provide the greatest advantage. Identification of use cases that benefit most from LHCs still relies heavily on full context. No single LHC has emerged as a clear frontrunner, as these underlying drivers are highly variable with length of time, volume of storage, and transport distance.

While LHCs can alleviate high costs of hydrogen usage associated with compression, liquefaction, and high-pressure or cryogenic materials, they present their own cost contributions that must be considered. The capital cost of the LHC, catalysts, reactors, and other equipment needed may be significant. Operating costs are associated with the need to supply heat to drive reactions, complexity of operations in converting between hydrogen-rich and hydrogen-lean LHCs and ensuring safety and potential toxicity are adequately addressed. Catalyst reactivity, selectivity, and stability challenges can add further costs where catalyst or LHC replenishment or additional purification/separation steps and equipment are needed.

Similarly, potential round-trip efficiency improvements of using LHCs over conventional compressed gas or liquid hydrogen usage are offset by efficiency losses where energy inputs are needed to produce and/or purify the LHC and to supply heat to drive reactions. Currently, the energy efficiency of LHCs such as toluene/MCH, ammonia, and methanol are estimated at ~42-47% compared to 59% for compressed hydrogen gas under similar usage scenarios.[191]

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A key future challenge for LHC usage, if realized at projected large scales, will be managing sustainability. Ammonia and methanol are commodities, used to produce fertilizers and other products, with fully commercialized production processes with a high reliance on fossil fuels. Rapid adoption of renewable processes will be needed to meet growing demand for these and other LHCs. Considering the importance of nitrogen to the global ecosystem, care must be taken to ensure a new environmental crisis does not emerge from NH_3 and NO_x emissions in a quest to avoid the impacts of CO_2.[192] Petroleum-derived carriers such as MCH or other potential carriers that are produced at smaller scales presently may become more scarce and costly to source if petroleum refining declines in the future. Lastly, long-term effects of environmental release and human exposure to LHCs must be considered to ensure potential adverse effects do not outweigh the benefits of hydrogen use.

Advances in science and technology to meet challenges

Although current demonstrations of LHC systems are costly at their pilot scales, it is likely that costs will reduce dramatically at the larger scales to which LHCs are best suited. In the near term there are several science and technology challenges that need to be addressed on the development of more stable, highly selective catalysts and finding creative approaches to increase the round-trip efficiency of storing and releasing hydrogen.

Science challenges

- Catalyst reactivity is defined by rates of reaction, stability of the catalyst under operating conditions and product selectivity. In many cases, precious metal nanoparticles, for example Pt, Pd, Ag, Ru on oxide or carbon supports are reported to yield high reactivity for release of hydrogen from LHCs. To reduce the cost associated with precious metal catalysts some work has investigated the use of single atom catalysts, but they are not generally stable under the highly reducing conditions found in both hydrogenation and dehydrogenation reactions.
- Dehydrogenation of cyclic hydrocarbons requires higher temperatures to overcome the enthalpic barrier for hydrogen release. A scientific challenge is to maintain selectivity at the higher operating temperatures or to develop LHCs with lower enthalpic barriers for H_2 release. This has led to an interest in LHC molecules that have lower enthalpic barriers for release of H_2.[193–195]
- Hydrogenation of LHCs requires high pressures to obtain the necessary rates of hydrogenation at elevated temperatures from heat accumulation. Developing catalysts with higher reactivity at lower onset temperatures is crucial. This would allow for a wider operating temperature range, enabling lower-pressure hydrogenation processes. Lower temperatures will favour catalyst stability. The high temperatures in both hydrogenation and dehydrogenation can lead to catalyst sintering, C-C bond scission of the cyclic hydrocarbons and coking that deactivates the catalyst.[196] Higher H_2 pressures can decrease coking by caping dangling bonds of surface C with hydrogen, retarding growth of C-C bonds. However, this is not feasible for dehydrogenation reactions that are limited to low pressures. Sulfiding is also reported to minimize coking and increase catalyst lifetime but leads to potential problems with impurities in the H_2 stream.
- Palladium on carbon is reported as one of the best catalysts for the release of hydrogen from aqueous formate salts and formic acid,[197] however, these catalysts do not appear to be stable as the activity drops significantly over time and there is little insight into how the catalyst changes during the reaction.[198] Understanding the deactivation pathways could lead to novel approaches to maintain stability.
- Ru-based catalysts perform well for both ammonia synthesis and decomposition under mild condition, but they are expensive. N and H will cover the surface of early and late transition metals, respectively, thus preventing them from being functional at lower temperatures.[199] Multi-component non-noble metal catalysts which have dynamic and electron-rich reactive sites hold good prospects.[200] A composition-structure-reactivity relationship should also be explored.

Technology challenges

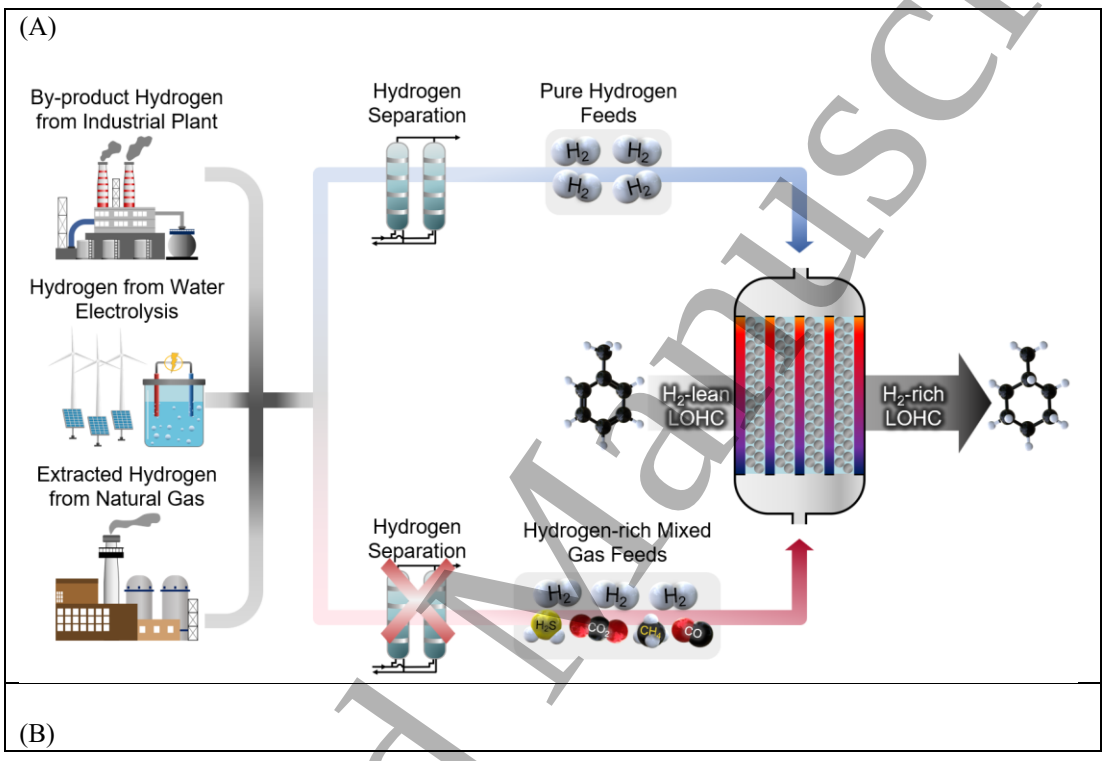
Current hydrogen round-trip efficiencies for liquid hydrogen carriers (LHCs), LOHCs and NH_3, are conservatively estimated at 60 – 62%. This indicates significant hydrogen consumption during storage, transport, and reconversion processes. The endothermic nature of LOHC and NH_3 dehydrogenation requires substantial energy to extract hydrogen from these carriers. Additionally, the use of highly pure hydrogen in storage and conversion to LHCs is necessary to minimize side reactions and catalyst deactivation, leading to energy-intensive separation and purification processes.

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To achieve a round-trip efficiency of 75%, suggested by IEA in 2019, several measures can be implemented: In the upstream hydrogen value chain (production and conversion to LHCs), directly storing unpurified hydrogen (mixed hydrogen) from multiple sources into LHCs has significant potential to lower the levelized cost of hydrogen (Figure 7A).[201] In the downstream processes (hydrogen reconversion and utilization), two strategies can be employed to reduce energy demand for dehydrogenation: a) Improving the thermal efficiency of components, including heat exchangers for internal waste heat recovery and preheaters. b) Integrating the dehydrogenation system with downstream hydrogen utilization systems such as fuel cells and gas turbines (Figure 7B).[202] These combined strategies aim to optimize the entire hydrogen value chain, from production to utilization, potentially enabling the achievement of the 70% round-trip efficiency target by 2030 and enhancing the viability of LHCs for large-scale energy storage.



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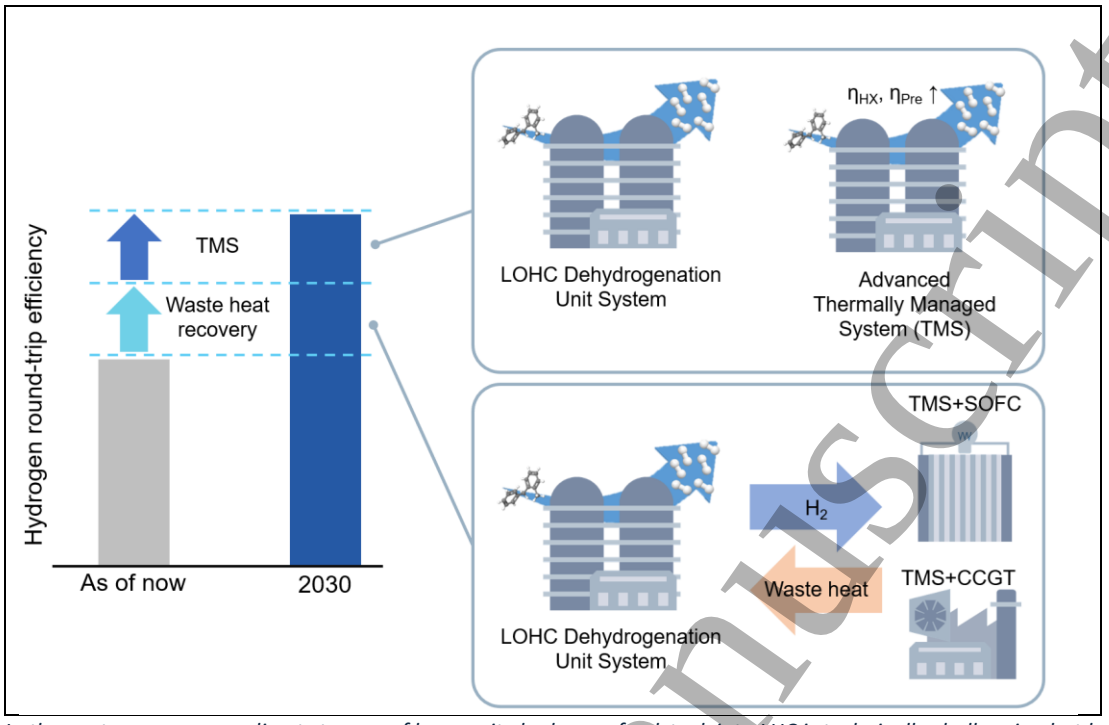


Figure 7: (a) In the upstream process, direct storage of low-purity hydrogen feedstock into LHC is technically challenging but beneficial for improving hydrogen round-trip efficiency (adapted from reference [201] under CC BY-NC 4.0). (b) In the downstream process: advanced thermally managed system (TMS), waste heat recuperation from solid oxide fuel cell (SOFC), and combined cycle gas turbine (CCGT) will significantly reduce energy consumption in the dehydrogenation process and improve hydrogen round-trip efficiency (adapted from reference [202] under CC BY-NC 4.0).

Concluding remarks

Priorities for LHC research are moving from materials development to pilot demonstrations, driven by impending government targets for decarbonization. Analysis from the systems level is needed to ensure overall cost and efficiency is competitive, and to identify the components that will provide the largest benefits for any given LHC. Consideration of life-cycle, community impact, and environmental justice will also become increasingly important as LHCs move closer to commercial deployment.[203] It is essential that these are addressed at an early stage of development to avoid costly corrections later on. The challenges and corresponding advances reviewed in this report are defining the use-cases which can be best fulfilled by LHCs, and making them more cost-competitive with alternative storage systems. The most pressing research needs for LHCs are catalysts that provide better activity, stability, and selectivity, and integrating hydrogenation/dehydrogenation of LHCs with upstream and downstream processes to improve round-trip efficiency.

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8. Metal hydride materials for thermal energy storage

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Status

The applications for thermal energy storage (TES) systems and the desire for their implementation into industrial processes, grid stabilisation and large scale energy storage continues to grow.[162,204–209] TES systems, or thermal batteries, are complete systems that require multiple components including the TES material, gas storage (for solid-gas thermochemical energy storage), heat transfer 'fluid' (HTF), and heat engine to produce electricity (if required).[210] There are many thermochemical materials for TES developed that cover low to high temperatures, several having high durability and reasonable cost, with Figure 1 illustrating the range of materials, their operating temperatures and gravimetric energy densities. The hydrides tend to operate in three broad temperature ranges. For high temperature ranges 700 – 1000 °C, CaH_2 remains the metal hydride with the highest gravimetric energy density of 5131 kJ.kg^{-1} and operates at temperatures of ≈ 947 °C. It has a 1 bar H_2 equilibrium pressure, but the sluggish reaction kinetics makes this material difficult to implement without modification.[211,212] Improving the kinetics of this material has been achieved, albeit at the detriment of its operating temperature and energy capacity, by the addition of reactive additives, such as Al and Zn.[213–215] That being said, $CaAl_2$ can operate at ~700 °C with a energy density of 874 kJ.kg^{-1}.[214]

In the mid-range of 500 – 700 °C, materials such as Mg_2FeH_6 have been demonstrated to be ideal candidates with multiple TES prototypes being built.[216–220] Another class of material that operates at ~ 577 °C and has gained attention in recent years are miscibility gap alloys, which have a relatively low energy density of ~ 423 kJ.kg^{-1}, but are easy to manufacture and have less engineering considerations since gas storage is not required due to their reliance on latent heat.[221,222] In the low temperature range for TES, MgH_2 has an excellent gravimetric energy density of 2811 kJ.kg^{-1}, a 1 bar H_2 operating pressure at 282 °C and can operate up to 450 °C, where the dissociation pressure is ≈ 40 bar.[36,223]

Determination and optimisation of heat transfer from the TES material to the heat engine (or thermal process) has continued to progress over recent years via the development of prototypes and computational modelling.[162,216,220,224–237] Heat transfer to and from solid metal hydride powder beds is more challenging than from liquid-based TES materials due to the poor thermal conductivity of the powder bed and difficulties in employing a HTF at high temperature.[170,219] Recent investigations include prototypes using superheated steam, heat transfer using highly conductive metals, and computational studies on the optimisation of heat transfer, with helical coils increasing the residence time of the heat transfer fluid and enhancing heat transfer from the powder bed.[225,226,232] Other studies include conductive additives into the powder bed including exfoliated natural graphite and copper fins.[162,227]

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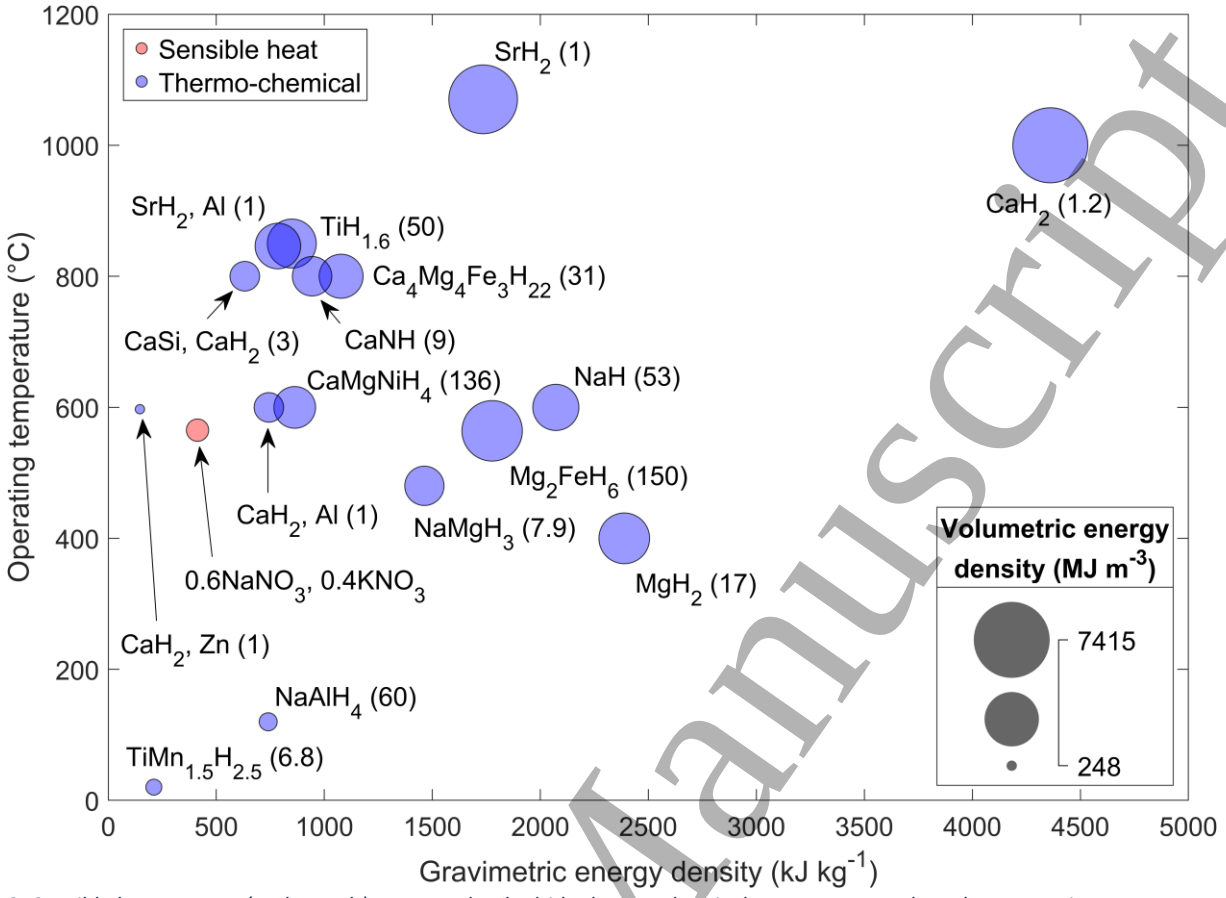


Figure 8: Sensible heat storage (molten salt) compared to hydride thermo-chemical energy storage, based on operating temperature, gravimetric and volumetric energy density, with target temperatures around 400 °C, 600 °C, 800 °C, and above. Two low temperature metal hydrides (< 200 °C) are also shown. The figure indicates the required equilibrium pressure (in bar) in brackets after the chemical formulae at example operating temperatures, which vary based on chosen operating pressures. Practical energy densities, assumed to be 85% of theoretical values, are shown - though in some systems, actual densities may differ due to reactor design factors such as packing density and heat transfer design.[210,238]

Current and future challenges

TES systems, or thermal batteries, have progressed considerably in recent years due to the optimisation of various TES materials, but other engineering aspects are yet to be optimised:

- Metal hydride materials that have been identified as strong candidates require full system-level optimisation to ensure durability and performance of the thermal battery in a real-world setting. Some materials such as MgH_2, Mg_2FeH_6 and intermetallic hydrides such as Ti-Mn alloys have been shown to cycle hundreds, if not thousands of times, but many others have not. Strong candidates should be cycled extensively on at least a 1 kg scale to ensure that there are no surprises during implementation.[162]
- A metal hydride (MH) system must be paired with a hydrogen store to enable operation. Concentrated solar power (CSP) requires rapid cycle times, typically operating on a daily cycle, which limits viable hydrogen storage to overground pressurised vessels. Current technology does not support underground storage solutions for such frequent cycling. In contrast, other TES applications, which can accommodate much longer cycles, may be more suited to underground storage options.
- A high temperature metal hydride (HTMH) can be combined with low temperature metal hydride (LTMH) instead of a compressed hydrogen store. To be competitive, the combined material cost must be below, or near the molten salt material cost benchmark.[216,235]
- Heat transfer from powder beds to the heat engine (or thermal process) continues to be a challenge, especially at elevated temperatures, where corrosion and material containment become problematic or expensive. Solutions to the heat transfer problem involve reducing the thermal resistance of powders (improving conductive heat transfer), to including other heat transfer mechanisms such as radiative and convective to assist conduction. Corrosion could be solved by using

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coatings or corrosion resistant alloys. At the same time, these coatings must be resistant to thermal gradients to avoid shearing and must not crack under thermal or gas pressure fluctuations. Optimisation of these aspects will allow an increase in plant efficiency, which would reduce costs.

- To allow multi-physics modelling and design of TES systems, either as a module or a whole system, kinetic reaction models for gas-solid materials must be individually established. There is only a small portion of thermochemical materials where this data is available, including MgH_2,[239] but the specific operating conditions of the system can lead to kinetic models being applicable to only certain systems often with relatively poor fits. This is because reaction mechanisms during solid-gas absorption and desorption reactions tend to be fitted via nucleation and growth, power law and exponential reaction rates, which must be experimentally determined in addition to their thermodynamics and activation energies. These empirical reaction rates are often not transferrable to other systems. This has serious implications for predicting behaviour when scaling up TES.
- One challenge that industry is facing is the transition from fossil fuels to renewable energy. Alumina refining and steel manufacturing, for example, are extremely energy intensive and require high temperatures up to, and above, 1000 °C. Modelling, and adapting TES systems to suit such industrial processes will need to be undertaken in partnership with industry and academia.

Advances in science and technology to meet challenges

The challenge of modelling for hydride TES behaviour has progressed to a more universal Site Availability Model which has shown to be applicable to a wide range of practical operating pressures and temperatures for MgH_2.[240] For example, the model can explain the reduction in capacity if high overpressures are used in the MgH_2 through clustering, interface and strain effects. However, this approach, along with the required kinetic data measurements, must be expanded for other promising materials. Once these materials-based models have been established, TES systems can be designed according to the operating conditions required.

Research on TES materials and complete systems continues to thrive, although to date, there doesn't appear to be literature devoted to full systems. A fully automated prototype containing 900 g of Mg_2FeH_6 was cycled using superheated water as the heat transfer fluid.[220] The material showed 13% degradation but did illustrate that heat storage efficiency suffered due to the small scale (high surface area to volume) of the vessel. As such, larger prototypes are likely to improve this efficiency. In a separate study, storage of the hydrogen desorbed from Mg_2FeH_6 was demonstrated using a low temperature metal hydride pair ($TiMn_{1.5}$) instead of compressed storage.[216] A 5 kg Mg_2FeH_6 heat storage prototype was operated with a molten salt as the heat transport medium. The system was constructed as a tube bundle reactor (consisting of 13 individual tube bundles for holding the heat storage material) and was able to store and release ≈ 1.5 kWh of heat at temperatures in the range of 450 – 500 °C. During the experimental operation of the system, the need for efficient thermal insulation was identified to ensure stable working conditions and minimal heat losses.[217] A 150 g prototype containing $NaMgH_3$ was also developed with incorporated exfoliated natural graphite to increase thermal conductivity.[224] This system also used superheated water as a heat transfer fluid, since the operating temperature was 450 °C. As a demonstration object, which already has a technically relevant order of magnitude, a heat storage system for the absorption of 250 kWh of heat at a temperature of ≈ 370 °C was realized. The associated storage tank contains 350 kg of Mg powder (5.5 wt.% Fe powder as a catalyst) and employs pillow plate heat exchangers for efficient heat transfer. The heat was transported by a heat transfer oil.[162]

Concluding remarks

The technology readiness level of thermal energy storage and "thermal batteries" has continued to increase with prototypes being developed that include all aspects of the system including the TES material, gas storage and heat transfer. Materials have also been developed that operate at low to high temperatures enabling the integration of these systems into multiple industrial scenarios, while the durability, cost and thermal conductivity of these materials continue to be optimised.

Modelling of TES systems and various heat transfer methods continue, although most research appears to be devoted to small scale prototypes rather than large scale developments. One reason for this is that each plant would hold individual concerns, but that shouldn't prevent the study of hypothetical large-scale facilities. For instance, the installation of TES into an iron-ore processing plant would potentially use the raw heat produced from the reaction and not require a heat engine to produce electricity, whereas grid stabilisation would require a heat engine. In addition, one aspect impeding progress of the publication of TES integration into existing industrial sites is potentially the protection of existing and developing intellectual property (IP).

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9. Metal hydrides for electrochemical energy storage

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Status

Metal hydrides (MH) used as negative electrodes in alkaline Ni-MH batteries are undoubtedly the major commercial application of the Hydrogen Storage Alloys (HSAs). Compared to lithium-ion batteries, Ni-MH batteries are less prone to thermal runaways as the batteries comfortably operate at high temperatures, while the electrolyte is highly stable over the entire performance.[241,242] Ni-MH batteries retain 30% of the market for Hybrid Electric Vehicles (HEVs) thanks to their favourable performance, cost, lifetime, and high safety. Various advanced Ni-MH batteries have been developed to meet application needs, particularly based on the improvements of MH anodes. The baseline is that materials for prospective MH anodes formed by rare earth metals (RE), Zr, Ti, Ni and other transition metals must have high reversible H storage capacity at ambient pressure, high-rate capability, good corrosion resistance in alkaline solutions and low cost.

Current and future challenges

Electrode materials for Ni-MH Batteries

Improvement of Ni-MH batteries requires advances in the performance of both positive and negative electrodes. For the positive electrode, a significant gain in discharge capacity can be achieved by replacing a conventionally used β-$Ni(OH)_2$ with an α-$Ni(OH)_2$. When β-$Ni(OH)_2$ oxidizes to β-NiOOH (Ni^{3+}), a discharge capacity of 289 mAh/g is achieved during a one-electron transformation. If an α/γ Ni hydroxide-oxyhydroxide redox couple is used instead, where nickel's oxidation state can reach 3.67 upon charging, a much higher capacity of 482 mAh/g can be achieved. In that situation, Ni-MH batteries would reach the capacity of Li-ion batteries, but with a safer chemistry. Experimentally, achieved capacities are as high as 410 mAh/g.[243,244] To realize a stable electrode performance at high current densities using an α/γ electrode transformation, three measures are applied in parallel: a) doping of hydroxide by various metal ions (e.g., Al^{3+}) to stabilize α-$Ni(OH)_2$; b) surface coating of the spherical particles with highly conductive CoOOH to improve electronic conductivity; c) using composites with carbon additives as electrodes to ensure low resistance at high current densities.

As negative electrodes, three main groups of MH alloys are utilized:

1. Superlattice Mg-containing alloys based on RE and Ni (AB_3, A_2B_7, A_5B_{19}).[245] A significant reduction of the molar mass due to a replacement of the RE by magnesium causes H storage and electrochemical capacity enhancements, and improved battery performance (30% higher capacity compared to AB_5 alloys). These compounds are used as anode electrodes in the commercial Eneloop batteries by Sanyo [246] provide excellent capacity retention (85% after one year) and show impressive performance at high current densities. When optimised, variations of the Mg content, selection of the specific RE and type of the layered compounds $AB_3/A_2B_7/A_5B_{19}$ or their mixtures allow the best electrochemical performances to be reached.[247–254]
2. Zr-based AB_2 Laves type alloys.[255–259] These alloys show discharge capacities between 400 and 450 mAh/g.[258,259] The basic multielement AB_2-type alloys typically contain Ti, Zr, V, Ni, Cr, Co, Mn, Al and Fe. Substitution of Zr by Ti plays a major role in defining the stability of the hydrides, which affects the maximum discharge capacities and cycle stability of the anodes. Discharge capacity around 460 mAh/g has been reached for the $Zr_{0.85}Ti_{0.15}M_2$ alloy.[257,259] For a

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multielement anode by Ovonic, $V_5Ti_9Zr_{26.2}Ni_{38}Cr_{3.5}Co_{1.5}Mn_{15.6}Al_{0.4}Sn_{0.8}$, an energy storage density of 100 Wh/kg was achieved and a specific power of 1057 Wh/kg, showing an excellent stability over 1000 cycles.[255]

3. AB_5 alloys of RE and Ni.[254] These alloys show relatively modest capacities of 320-350 mAh/g for state-of-the-art commercial formulations such as $La_{0.62}Ce_{0.27}Pr_{0.03}Nd_{0.08}Ni_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$ (optimized mischmetal based alloy $MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7}$), and are broadly commercially applied. Current research focuses on minimizing the content of expensive Co in the alloys and on materials suitable for application at subzero temperatures.

By increasing the content of the *A*-type hydride-forming elements, higher gravimetric H storage capacities can be envisaged. These include BCC-type V-based alloys from the ternary V-Ti-Ni system,[260] and Mg-based materials such as Mg-Ni amorphous alloys. For MgNi alloys, initial capacities can be as high as 1000 mAh/g.[261,262] Unfortunately, these alloys quickly degrade in highly aggressive alkaline electrolytes. The surface of the hydrogen storage alloy is important for the functionality of the electrode. A protective layer should be formed to stop corrosion developing into the bulk of the alloy, which must also have catalytic properties to promote the formation and breaking of the oxygen-hydrogen bond in the water molecules that shuttle hydrogen between the electrodes during charge-discharge. The formation of reactive nickel containing clusters have proven to be very efficient in this respect.

Many binary, intermetallic and complex hydrides can also be used as negative electrodes of Li-ion batteries demonstrating the highest energy densities among the rechargeable battery systems.[263] Instead of a conventional intercalation/deintercalation reaction, metal hydrides undergo a conversion reaction with lithium ions $MH_x + xLi^+ + xe^- \leftrightarrow M + xLiH$. MgH_2 has been focussed on due to its high energy density and high specific gravimetric/volumetric capacity (2036 mAh/g, 2944 mAh/cm^3), low electrode potential (0.55 V vs. Li^+/Li) and absence of Li-plating. Its specific capacity is five times better than that of graphite, which is presently used as a commertial anode material. Unfortunately, low H diffusion rates,[261] large volume changes in the electrodes during their charge-discharge and low electronic conductivity, cause fast fading of the discharge capacity because of unsatisfactory reversibility of the reaction. Advances have been made through the use of $LiBH_4$ as an electrolyte, application of composites (e.g., MgH_2:TiH_2), nanostructuring by ball milling and by using porous conducting scaffolds.[264] This resulted in increased cycle life, improved initial reversible capacities and in lower polarisation. Despite these advances, the application of hydrides as negative electrodes of the Li-ion batteries has not reaches a maturity required for the commercial applications.

Advances in science and technology to meet challenges

When comparing gravimetric and volumetric energy storage densities and the price per kWh of the battery capacity, commercial Ni-MH batteries are currently inferior to the rivalling Li-ion technology. However, Ni-MH batteries remain competitive in their contributions to the market of secondary batteries for hybrid vehicles and in consumer electronics. Limited access to the available natural resources creates a problem in the availability of RE ores, since 95% of their globally availability is in China. Recycling of REs has appeared as a growing mitigating mechanism.[265–267]

Increasing the low output voltage of Ni-MH batteries, causing low energy densities, requires changing the aqueous electrolyte to an ionic liquid or solid electrolyte, which have larger electrochemical windows of operation.[264,268–272] This has been recently validated by coupling MH anodes (AB_5 type) with protonic ionic liquid, which expanded the operating voltage to exceed 2 V.[273] Such ionic liquids will allow the replacement of presently used $Ni(OH)_2$ with cathodes that have higher potentials. Kawasaki Motor Company demonstrated a solid proton conductor with a high proton conductivity, combining a high-capacity Si anode and a high-voltage MnO_2-based cathode, demonstrating a novel ultra-high-energy and high-safety battery.[274]

Much attention has been paid to the use of MH anodes in Li-ion batteries. Reversibility of the reaction at operating temperatures above 100 °C and cycle life stability have proven to be satisfactory. However, a remaining challenge remains in achieving operation at ambient temperature. Positive results were obtained by applying novel strategies to improve performance of the batteries, including the use of a mechanical buffer component inside the electrode, and the use of a hydride-based solid electrolyte to facilitate H diffusion within the electrode composite. Multi-phase composites, where each component has its own dedicated role in contributing to the capacity, H and Li transport, electronic conductivity and volume accommodation, can show synergy in their functionality, resulting in improved performance. This has opened up a prospective path to be followed in the future.

Concluding remarks

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Ni-MH batteries are major contributors to the market of consumer electronics and HEVs, and stand as competitors to the Li-ion battery due to their suitability for use in broad temperature ranges, both subzero (-30 to -40 °C) and at severe heat conditions (>60 to 80 °C). This advantage is due to the superior features of the chemistries of MH batteries compared to alternatives. Such favourable performances rely on the potential to optimise the composition of the MH anodes, allowing adaptation to extreme climate conditions, by varying phase equilibria in the alloy-hydrogen systems.

An application-based timeline for the development of MH batteries is shown in Figure 9. It covers a period from 1997, when the first Toyota Prius hybrid vehicle was commercially available, until 2024, when Panasonic Energy presented MH battery systems developed for railway applications. Also shown are Panasonic's prismatic cells from 2021, which featured improved performance at high current densities. The recently developed advanced MH battery modules and their packs for the railway vehicles (Figure 9) show several advantages over traditional systems, including a scalable design, improved efficiency and performance and reduced space.

Despite the fact that superlattice Mg-containing A_mB_n HSAs and their AB_5 predecessors have been commercialized for decades, further improvement of these materials is ongoing and focuses on the development of efficient synthesis routes to prepare the superlattice alloys. These routes would allow the synthesis of phase-pure alloys, with operating temperatures optimised for the best electrochemical performance. In addition to applications at various climate conditions, work is also focused on the elimination of cobalt, the reduction of critical raw materials (e.g., RE, nickel), and cost reduction of the battery electrodes. These are complemented by work to improve the cycle and calendar life of the batteries, focusing on enhanced corrosion resistance of the battery anodes by alloy development and by reducing the corrosion activity of the currently used KOH electrolyte. The use of proton-conducting ionic liquids as a replacement to aqueous electrolytes is a promising path for future developments, as this will both increase the operating voltage of the batteries and improve corrosion resistance.

For MH used as anodes of Li-ion batteries, a limited reversibility of the conversion reaction prevents their use in commercial applications, though improvements have been achieved using nanostructuring, optimised electrode formulation and operation temperatures. The transfer of these results to novel battery chemistries, such as Na-ion batteries, is an added value to the outcome of the performed research.

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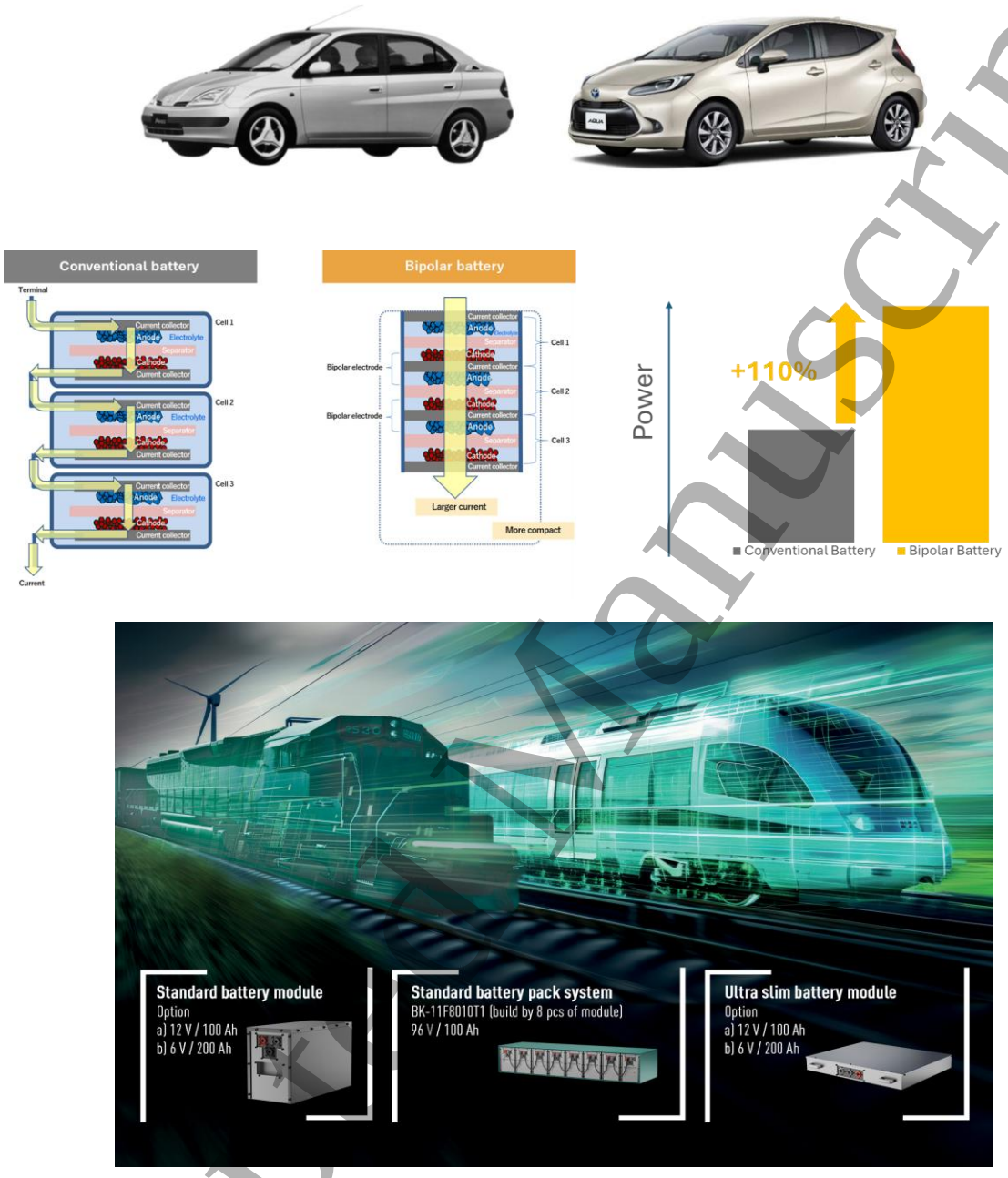


Figure 9: Top: Toyota Prius (left) was the first HEV with a Ni-MH battery, in 1997. The first version had a 1.8kWh - 500W/kg battery pack with cylindrical D-size cells. Later on this was replaced with prismatic cells in a 1.4kWh - 1300W/kg battery pack. Toyota 2nd generation Aqua (right) contains a new bipolar battery from 2021. Middle: the new bipolar design which further increases power rating. Bottom: Ni-MH modules for railway applications in 2024 (Panasonic Energy presents new nickel metal hydride battery system for railway vehicles at Innotrans fair). All batteries are based on Panasonic developments. Top and middle images courtesy of Toyota Global Newsroom and Dr. Katsuhiro Hirose, International Institute for Carbon Neutral Research Kyushu University (https://www.toyota-global.com/company/history_of_toyota/75years/vehicle_lineage/car/id60012360/index.html, https://global.toyota/en/newsroom/toyota/35584064.html).

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10. Metal hydridoborates as electrolytes for solid state batteries

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Status

Rechargeable batteries are an obvious solution for storing electricity generated from wind and solar energy. Metallic hydrides have made a significant impact in the electrochemical storage of energy as discussed in chapter 9 in this roadmap paper.[275] Ionic hydrides such as BaH_2 and LaH_3 are now also being investigated as hydride (H^-) conductors where a superionic state can be reached upon phase change or lattice deformation.[276,277] These H^- conductors can also become electrolytes for a new type of all-solid state hydride batteries.

During the past two decades lithium-ion batteries (LIB) have had a huge impact on our everyday life, but they are now approaching their performance limits. Solid-state batteries are expected to have several advantages, including increased safety owing to replacement of the flammable organic liquid electrolyte with solid inorganic materials. Furthermore, the inclusion of abundant divalent metals, such as magnesium (Mg^{2+}) or calcium (Ca^{2+}), may further increase their energy density and lower the price. Their drawback is that fast divalent cationic conductivity in the solid state is very challenging to achieve at ambient conditions.[278] However, the discovery of numerous metal hydridoborates with record-high cationic conductivity have inspired new research within solid state batteries.[279,280]

Lithium tetrahydridoborate was recognised as a fast lithium ionic conducting material in 2007, but only at $T > \sim 110$ °C, owing to a polymorphic transition forming the disordered high temperature polymorph, *h*-$LiBH_4$,[281] which can be stabilised at room temperature by anion substitution.[282–284] It was realized that the structural disorder was in fact dynamic disorder, i.e. rotation or vibration of anions, and that these entropy effects in the solid-state are mainly associated with larger composite anions. It was also suggested that the anion rotations can directly promote or facilitate cationic migration, sometimes referred to as the "paddle wheel" mechanism.[285,286]

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Many metal hydridoborates have useful solubility windows in non-aqueous solvents, that can be utilised in liquid and polymeric batteries.[287] Liquid magnesium electrolytes were successfully synthesized from $Mg(BH_4)_2$ or $Mg(CB_{11}H_{12})_2$ dissolved in ether, demonstrating convincing plating/stripping, low overpotentials and a significant step forward for divalent batteries.[288–290] Similarly, the analogous compound $Ca(CB_{11}H_{12})_2$ has also been confirmed to be an effective calcium electrolyte, highlighting its potential for application in calcium-based energy storage systems.[291]

The discovery of very fast solid-state magnesium and calcium cationic conductivities at moderate temperatures by metal hydridoborates, initiated by diethylamine and aminoborane derivatives of magnesium tetrahydridoborate, $Mg(BH_4)_2$, raised significant interest.[292–295] A new mechanism for cation conductivity was discovered for $Mg(BH_4)_2{\cdot}NH_3$, that explains the very high conductivity, $\sigma(Mg^{2+}) = 3.3{\cdot}10^{-4}$ S/cm at 80 °C, about 8 orders of magnitude higher than that of $Mg(BH_4)_2$.[296] Density functional theory calculations (DFT) revealed that the exchange of the neutral molecule (NH_3) between lattice and interstitial Mg^{2+} in $Mg(BH_4)_2{\cdot}NH_3$ is facilitated by a highly flexible structure. This mechanism is denoted ligand-assisted cationic conductivity and is also observed for $LiBH_4{\cdot}0.5NH_3$.[297] This is primarily due to a network of di-hydrogen bonds and the flexible coordination of BH_4^- complexes to Mg^{2+}.[296]

Advantages. Metal hydridoborates can provide several essential properties that are required for an ideal solid-state electrolyte. Derivatives of metal hydridoborates are usually stable in dry air, and are not pyrophoric. However, they are hygroscopic and will slowly absorb water, and may also react with water from the atmosphere. Hydridoborates consist of light elements and have low material densities, similar to liquid organic electrolytes (~1.1 g cm^{-3}), which contributes to a high battery cell energy density. They are soft, compactable materials, which facilitates good electrode-electrolyte contact, even upon cold pressing. A significant advantage of metal hydridoborates as electrolytes is their ionic and polar covalent bonding, which provides extremely low electronic conductivity (typically, $\sigma_e < 10^{-11}$ S cm^{-1} at room temperature). Additional advantages include their relativity weak ion pairing interaction which promotes high ion conductivity and low reduction potentials that contribute to their electrochemical stabilities.

Current and future challenges

A significant challenge to the development of new types of solid-state batteries is the further improvement of the divalent cationic conductivity at low temperatures (RT and below). An improved ion conducting electrolyte is key to enhancing battery performance while the electrolyte stability towards the anode and cathode defines the battery chemistry. Therefore, the electrochemical stability of metal hydridoborates must also be improved significantly to allow the use of high voltage cathodes. In addition, metal hydridoborates are currently produced in small quantities, and scalable fabrication methods need to be developed to reduce costs.

Cationic conductivity. Fast cationic conductivity of monovalent cations, such as Li^+, Na^+, K^+ or Ag^+, has been demonstrated for metal hydridoborates.[298–300] Unfortunately, high conductivity is usually observed only for high temperature polymorphs with significant anionic disorder and empty cation positions. This is illustrated by the very different Na^+ conductivities of the high and low temperature polymorphs of sodium decahydrido-*closo*-1-carbadecaborates, $NaCB_9H_{10}$, with $\sigma(Na^+) = 3.10^{-3}$ and 4.10^{-5} S cm^{-1}, respectively, at 296 K.[301] Anion substitution with halides or nano-confinement have been shown to stabilise the disordered polymorph *h*–$LiBH_4$, revealing good compatibility between hydridoborates and halides and oxides.[302–305] This is also illustrated by the antiperovskite-type Na_3OBH_4, $\sigma(Na^+) = 4.4$ mS cm^{-1} at RT, and the argyrodite type composite material $Li_{5.3}PS_4(BH_4)_{2.3}$, $\sigma(Li^+) = 11$ mS cm^{-1} at RT.[306,307] These techniques have been more successful than anion modification to control charge density and polarisation, e.g. through functionalisation of $B_{12}H_{12}^{2-}$ to $B_{12}X_{12}^{2-}$, where X = OH, Cl, Br, I, or modifications into $B_{11}H_{11}Pb^{2-}$, $B_{11}H_{11}Sn^{2-}$ or $B_{12}H_{11}NH_3^-$.[308,309] However, these approaches become more challenging to utilise for divalent cations, such as Mg^{2+} or Ca^{2+}.

Electrochemical stability. Attempts to use $LiBH_4$ with a relatively high voltage cathode $LiCoO_2$ operated at 120 °C were unsuccessful, but the stability and reversibility were much improved by coating with Li_3PO_4.[310] However, it was suggested that $LiBH_4$ electrochemically oxidised to form an interphase of the more stable *closo*-hydridoborate $Li_2B_{12}H_{12}$ towards the cathode, allowing stable charge and discharge of battery cells.[311] Thus, a significant focus on reactions between electrolyte and electrodes is necessary to further investigate interphase formation.

Materials cost. Reduction of the electrolyte cost is essential. The use of abundant metals, such as sodium, magnesium and calcium, is advantageous; however, the production of hydridoborate anions needs to be simplified and scalable.

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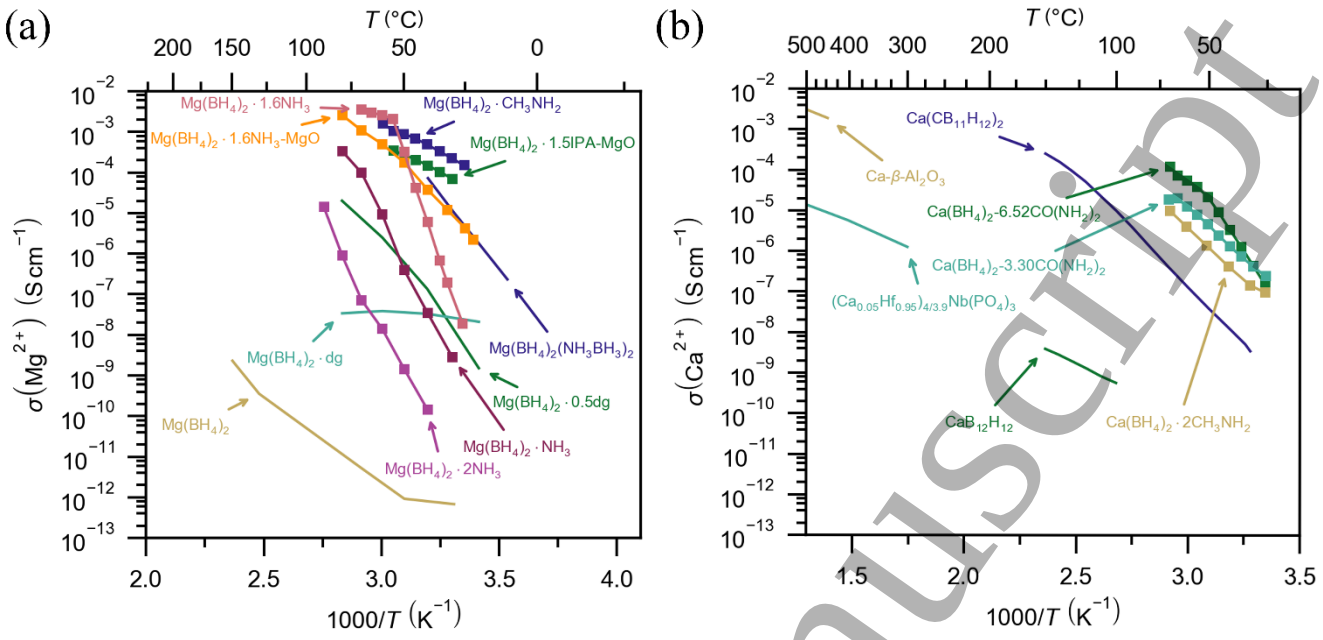


Figure 10: Record-high conductivity of divalent metal hydridoborates: (a) Magnesium ionic (Mg^{2+}) conductivity of magnesium tetrahydridoborate derivatives and (b) Calcium ionic (Ca^{2+}) conductivity of calcium tetrahydridoborate derivatives and selected inorganic calcium electrolytes.

Advances in science and technology to meet challenges

Cationic conductivity. Recent research has revealed several phenomena that can enhance the cationic conductivity of metal hydridoborates. Lithium, magnesium and calcium hydridoborates readily complex with neutral organic molecules, which further expands the diversity in structure and composition. New types of metal tetrahydridoborates coordinated by organic molecules have demonstrated record-high conductivities, *e.g.* $LiBH_4{\cdot}CH_3NH_2$, $Mg(BH_4)_2{\cdot}CH_3NH_2$, and $Ca(BH_4)_2{\cdot}2CH_3NH_2$.[298,312–314] Neutral molecules can create weak dihydrogen bonds and dispersion interactions and induce structural flexibility. Further fundamental understanding of the nature of these interactions, as well as their impacts on ion conduction mechanisms in the bulk materials and across functional interfaces, should provide a rational guide to inducing yet higher cationic conductivity.[286,315] Furthermore, the conductivity, as well as the thermal and mechanical stability, have been further improved by incorporating nano-particles of inert, insulating materials. For instance, MgO and Al_2O_3, which have stabilised eutectic molten composites, *e.g.* $Mg(BH_4)_2{\cdot}NH_3$–$Mg(BH_4)_2{\cdot}2NH_3$–MgO, exhibit an impressive conductivity of $\sigma(Mg^{2+}) = 2.0$ mS/cm at 55 °C. Nano-particles also prevented recrystallization upon cooling and decreased the activation energy to $E_A = 1.1$ eV for the nanocomposite.[316,317] Urea derivatives of calcium tetrahydridoborate have impressive conductivity, e.g. $\sigma(Ca^{2+}) = 1.23 \times 10^{-4}$ S cm^{-1} for $Ca(BH_4)_2$–$6.52CO(NH_2)_2$ at 70 °C and a very high ionic transport number of $T_{ion} = 0.997$.[318]

Electrochemical stability. Metal hydridoborates are often slightly reducing and therefore have a good stability toward metallic anodes, but are also stable toward low potential cathodes. More research is crucial to better understand the formation of solid interfaces between electrolytes and the electrodes. There is now increasing focus on metal *closo*-(carba)borates, which have higher oxidation stabilities. A sodium anode-free all-solid-state battery, using the electrolyte $Na_2B_{10}H_{10}$–$Na_2B_{12}H_{12}$, was successfully charged and discharged over several hundred cycles potentially leading to reduced weight, volume and cost.[319] A polymorph of sodium decahydrido-*closo*-1-carbadecaborate ($NaCB_9H_{10}$) was found to have very high ionic conductivity $\sigma(Na^+) = 13$ mS cm^{-1} at 23 °C, and a low activation energy of $E_a = 0.18$ eV. A battery cell, $Na|NaCB_9H_{10}|NaTi_2(PO_4)_3$, was successfully operated with an oxidative stability of 3.1 V vs. Na^+/Na.[301] The use of double layer electrolytes with a metal hydridoborate and a catholyte with higher stability towards a high-voltage cathode may be possible, due to good compatibility of metal hydridoborates with oxides and halides.

Materials cost. A variety of synthesis routes for hydridoborates have been described,[275,279,287] and a range of new synthetic approaches for synthesis of *closo*-(carba)borates, such as $CB_9H_{10}^-$ and $CB_{11}H_{12}^-$, have been recently identified.[320–322] The synthesis of $Na_2B_{10}H_{10}$–$Na_2B_{12}H_{12}$ has been achieved by co-crystallisation.[323] However, there is still a need to further simplify the synthetic methods to become industrially scalable and cheaper.

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Concluding remarks

The ideal electrolyte for solid state batteries has not yet been identified but metal hydridoborates clearly form a promising class of materials.[278,279,324,325] In particular, significant progress has been recently demonstrated for divalent metal electrolytes. Nevertheless, there is still a lack of detailed understanding of structure-composition-property relationships necessary for targeted materials design. The continued use of advanced theoretical simulation and analysis will be critical for deciphering migration mechanisms and impacts of structural and chemical modification on ionic transport and chemo-mechanical response. Future computational studies should also consider impedance contributions from defects, interfaces, microstructure, and mixing to improve connections to materials processing and real-world battery behaviour.

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11. Experimental methods for characterization

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Status

Researchers are developing efficient and safe hydrogen storage materials for a sustainable energy future. They use characterization techniques to investigate the structure, properties, and performance of these materials. Combining experimental and computational methods allows a comprehensive understanding of hydrogen storage mechanisms with the overall goal of optimizing the properties. Characterization methods are classified based on length scale and the material components they analyze, including solids and gases. Among others, the most commonly used techniques include gas sorption measurements that determine pressure-concentration-temperature (P–C–T) isotherms and other sorption techniques that provide key insights into hydrogen absorption and desorption behavior.[28] Thermal desorption spectroscopy (TDS) determines the activation energy for hydrogen release and offers valuable kinetic information.[326] Differential scanning calorimetry (DSC) measures heat flow during phase transitions and hydrogen sorption/desorption processes.[327] Transmission electron microscopy (TEM) enables atomic-scale visualization of material structures, defects, and grain boundaries while scanning electron microscopy (SEM) examines surface morphology and particle structures.[328–330] X-ray and neutron diffraction techniques determine crystal structures of hydrogen storage materials and catalysts at Ångstrom length scales.[331–333] Small-angle X-ray and neutron scattering (SAXS/SANS) provide insights into material structures at the nanometer to micrometer level.[334] Infrared (IR) and Raman spectroscopy probe vibrational properties and chemical bonding in materials, while nuclear magnetic resonance (NMR) and neutron spectroscopy analyze the local environment of solid hydrides or hydrogen in liquid carriers.

Most of these techniques are used ex-situ, before and after hydrogen uptake and release. However, evaluating the performance of hydrogen storage materials operando in real-world applications such as large storage tanks, where techniques such as neutron imaging and tomography visualize the distribution of hydrogen in a device, would provide important insights into the transport and storage processes. By combining several techniques, researchers can gain a comprehensive understanding of hydrogen storage materials, including their fundamental properties, performance limitations, and potential for improvement. This knowledge is essential for the development of advanced materials with high hydrogen storage capacities, rapid kinetics, and long-term stability.

Current and future challenges

Hydrogen storage encounters multiple challenges, ranging from material synthesis, recyclability, safety, and overall device performance. Overcoming these obstacles requires a comprehensive understanding of the fundamental mechanisms governing hydrogen storage, which can be achieved through advanced characterization techniques. Current and future challenges for characterization can be grouped into the following three broad aspects, as summarized in Figure 11.

1) Ensuring Rigorous and Accurate Characterization

Characterizing hydrogen storage materials is complex and involves multiple techniques. The lack of standardised reference materials and data formats makes it difficult to compare results from different laboratories. Rigorous instrument calibration is required for accurate, consistent measurements, including certified reference materials and well-established procedures. Guidelines for sample preparation, measurement conditions and data processing must be defined.[335] Publishers and funding agencies should establish data sharing policies and promote effective data management and curation practices to facilitate data reuse and ensure attribution. This is vital for preserving and accessing data, especially for machine learning to speed up materials development. Computational modelling and simulation of hydrogen storage materials and processes depend on the

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quality of the input parameters and assumptions. Computational and multiscale models must be validated against experimental data. This requires collaboration between experimentalists and theoreticians as well as open-access databases to share experimental data and computational results.

2) Advancing In-Situ and Operando Characterization

In-situ and operando techniques are essential for studying hydrogen storage under real conditions. Real-time observation of structural and chemical changes requires advanced instrumentation, yet differing time scales across methods complicate data correlation. The corrosiveness of hydrogen and of the hydrogen carrier ammonia challenges long-term experiments, necessitating gas-tight, high-temperature-pressure resistant sample cells. Precise temperature and pressure control are crucial for reproducibility. Most operando studies use small sample cells, but full-scale tank characterization would offer more realistic insight into the storage materials. Safety concerns limit in-house in situ and operando structural characterization experiments to ~100 bar, requiring innovative small-volume cell designs. Synchrotron and neutron sources are powerful tools but require competitive beamtime access, therefore collaborative experiments could improve efficiency. Integrating multiple techniques demands synchronization, while managing large datasets requires advanced analysis tools.

3) Integrating Techniques from Other Fields to Analyse Hydrogen Storage Materials

There are several techniques that are not widely applied to hydrogen storage materials. In-situ TEM is useful for studying the interaction of hydrogen with solid-state materials. However, the processes proceed at elevated temperatures and/or pressures, which require special sample cells.[329] As surfaces and interfaces may affect catalysis and storage properties, they should be studied by scanning probe microscopy (SPM) and X-ray photoelectron spectroscopy (XPS).[336,337] Inelastic neutron scattering (INS) and quasi-elastic neutron scattering (QENS) measure the dynamic behaviour of hydrogen in solids and the hydrogen-material interactions at the atomic scale.[338,339] These methods are not routinely used due to the limited availability of neutron facilities and complex data analysis and the community would benefit from more rapid access to large-scale facilities and dedicated computational support at those facilities to ease data interpretation as implemented at ORNL for INS experiments.[340] While computational techniques make the analysis of the INS data tractable, we are much further away from having automated data treatment and on-the-fly modeling of QENS H_2 diffusional data. At the atomic level, X-ray absorption spectroscopy (XAS), total scattering (TS) and pair distribution function analysis (PDF) provide detailed insights into the local structure of materials, enabling a comprehensive understanding of hydrogen-solid interactions.[341,342] Both methods require synchrotron radiation or a neutron source, and data analysis is not straightforward, which seems to discourage researchers from using these methods for hydrogen storage materials. Machine learning and artificial intelligence can be utilized to analyze large

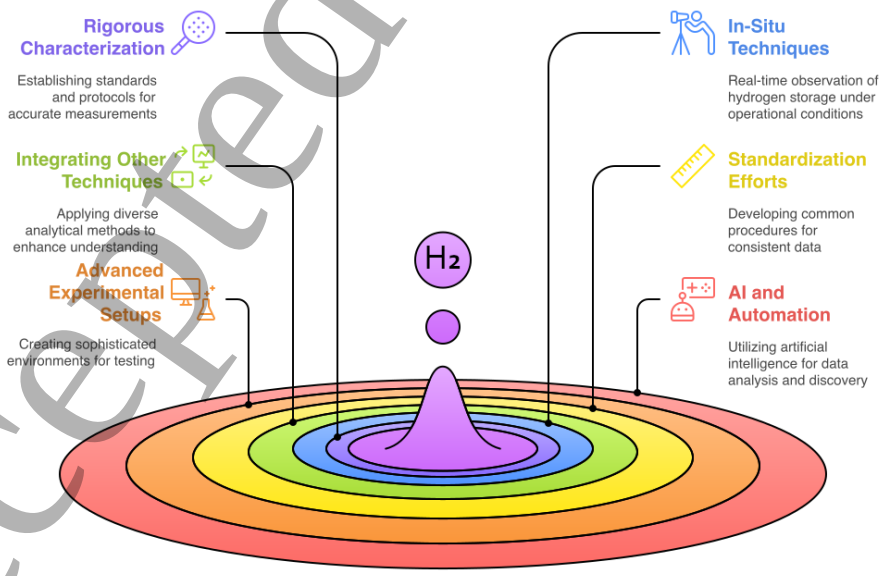


Figure 11: A schematic summarizing current and future challenges and directions in the characterization of hydrogen storage materials.

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datasets obtained from operando characterization experiments, identify trends and hidden correlations, and accelerate the discovery of new materials.[343–345]

Advances in science and technology to meet challenges

Following the key challenges identified in the previous section, progress based on recent work will be discussed. Despite the numerous appeals from experts for the correct and reproducible use of characterization techniques and data evaluation, there has been minimal progress. However, there are some initiatives for improvement. The accurate determination of hydrogen sorption properties has been addressed by Broom and Hirscher, who defined measurement procedures and guidelines for reporting experimental data.[346] For XPS, a broad initiative of experts is attempting to establish common procedures for measurement and data treatment.[347,348] A round-robin initiated for SAXS shows how different results from different labs can be compared and offers solutions.[349] While no common standardisation procedures for powder diffraction have yet been developed for hydrogen storage materials, several round-robin tests on phase quantification demonstrate the need for such procedures.[350,351]

The situation is different for the development of in situ/operando experiments for hydrogen storage. In the last ten years, progress has been made in the field of operando X-ray and neutron diffraction experiments on hydrogen storage materials. The enhancements enabled the study of structural changes during the uptake and release of H_2 in solid carriers,[74] as well as of solid catalysts during hydrogen release from ammonia.[352–354] Conducting high-pressure experiments at or above 100 bar H_2 is challenging for in-house diffraction studies. However, small sample cells, combined with X-ray transparent materials, enable the monitoring of the hydrogen uptake into solids up to 100-200 bar.[355] Additives or catalysts are important to enhance kinetics and reversibility. A deep understanding of their structure and function calls for a combination of complementary advanced methods such as synchrotron radiation X-ray diffraction and absorption and Raman spectroscopy.[356] Recently, tools have been developed to study the properties of metal hydrides at the local scale using TS with synchrotron radiation and neutrons and implementing data analysis with reversible Monte Carlo Methods.[77,357]

Concluding remarks

Standardization of experimental protocols, the development of sophisticated operando environments, and systematic catalyst studies are crucial for advancing the understanding of hydrogen storage materials on different length scales. These approaches collectively enhance reproducibility, improve the understanding of reaction mechanisms on different length scales, and facilitate the design of highly efficient catalysts to improve reaction kinetics. Future work may also integrate automation, theoretical calculations, AI-driven data analysis, and multi-technique characterization to further accelerate discoveries in this field. This will enable the development of efficient and safe hydrogen storage materials, a critical step towards a sustainable energy future.

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12. Computational methods

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Status

Computational modeling has become indispensible for discovering, interrogating, and designing hydrogen-based materials. Models increasingly act alongside experiments to provide complementary data, suggest new experiments, and clarify results, building on hardware and algorithmic advances. Predictive models derived from first principles or physical governing equations can extrapolate into difficult-to-probe physical regimes and deconvolute key multiphysics factors governing hydrogen-materials interactions. Models can operate in the atomistic or continuum domain, which offer complementary tradeoffs in model complexity and accessible time/length scales to probe different physicochemical phenomena. Machine learning (ML) has emerged a companion tool for accelerating predictions and accessing higher-dimensionality complexity based on training data from simulations and/or experiments.

At the atomic scale, density functional theory (DFT) has long been the workhorse for probing bonding and electronic structure, as well as for predicting bulk thermodynamics of formation and reaction for hydrogen-based materials. More limited has been the application of methods to study critically important materials kinetics, which often involve simultaneous transport, chemical reactivity, and/or phase evolution processes. At the continuum scale, multiphysics and engineering models have mostly been applied to design scalable tanks rather than materials, although limited studies of materials microstructures are also emerging.

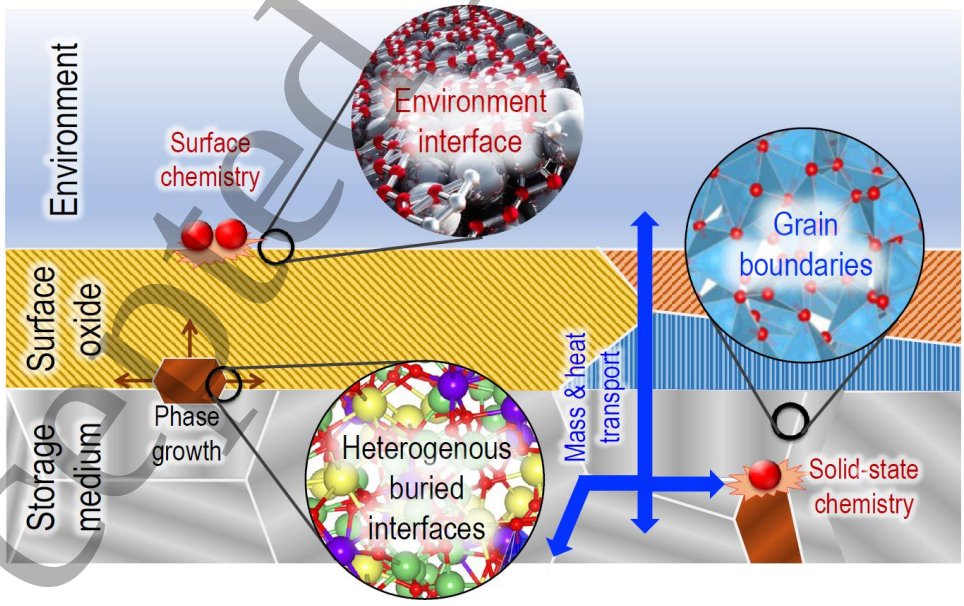


Figure 12: Predicting kinetics of hydrogen reactions involves modelling a variety of processes occurring at exposed and buried interfaces.

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Current and future challenges

It is imperative to move beyond the idealized and homogenized models that have dominated hydrogen-based materials simulations, and to adopt approaches capable of probing more complex multiscale phenomena. Equally important is to improve integration among experiments, simulation, and data-driven approaches. Below, we outline four key challenges in improving fidelity, reliability, and utility of computational models of hydrogen-based energy storage materials (Figure 12).

Challenge 1: Improving accuracy in predictive models and capabilities

No single flavor of theory can fully address the variety of bonding interactions with hydrogen. Moreover, current models frequently employ idealized descriptions based on bulk, single-crystal materials that are of limited utility for predicting practical hydrogen storage systems.[179] Atomic-scale structural inhomogeneities and chemical substituents at surfaces and interfaces severely affect interactions with hydrogen, as do microstructural factors such as porosity, grain structure, and phase morphology.[138,358] Predictions of often-neglected thermodynamic contributions, such as solid mechanics and anharmonicity, as well as nuclear quantum effects, are also needed to account for fast dynamics and volume expansion during hydrogen reactions.

Challenge 2: Navigating compositional and structural complexity

Emerging materials classes such as high-entropy alloys introduce a high degree of atomic compositional variability, and interfaces, inhomogeneities, and microstructural features add similarly large structural diversity. Such factors can critically determine energy storage capacity, durability, and performance but are difficult to navigate using current tools. Approaches that can address high-dimensional feature sets, incorporate them into existing models, and translate them into intentional design strategies are sorely needed.

Challenge 3: Predicting kinetics across scales

Although thermodynamics provide a starting point for reaction predictions, kinetics often dictate actual performance. Prominent kinetic factors include chemical bond activation, mass and heat transport, and phase nucleation and growth (Figure 12). These intrinsically coupled, multiscale processes are dictated by a driving force and materials response, both of which can evolve dynamically. Novel multiphysics prediction and integration approaches are required to span vast ranges of time and length scales and properly capture hydrogen-materials interactions.

Challenge 4: Predicting real-world operation of materials and systems

Predicted metrics like theoretical capacity and thermodynamic stability must connect to actual performance under scaled storage scenarios. Incorporating hard-to-predict, real-world properties such as materials lifetime and activation kinetics, as well as improving experiment-theory integration, can bridge gaps between laboratory and deployment scales. Likewise, improved understanding of tradeoffs among performance, capacity, and durability can enable models that consider materials impacts on system or tank design. Such understanding can enable fit-for-purpose energy storage solutions by co-designing materials and energy storage systems concurrently.

Advances in science and technology to meet challenges

Challenge 1: Improving accuracy in predictive models and capabilities

Method accuracy for atomic-scale hydrogen interactions. A hierarchical approach incorporating multiple levels of theory appears best suited to properly capture these interactions. Advanced Quantum Monte Carlo or quantum-chemical methods can provide benchmarks to downselect application-tailored DFT functionals, which in turn can provide training data for surrogate interatomic potentials based on deep neural networks to suitably balance accuracy and scalability.[359] Interatomic potentials may also be used to capture nuclear quantum effects on hydrogen diffusion using path integral simulation approaches.[360,361]

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Incorporating surfaces, interfaces, and multiple phases. Explicit atomistic modeling of these features is a priority, particularly for nanoscale materials, additives, and composites.[362–364] Approaches that can be scaled easily are critical,[365] as are predictions of spectroscopic fingerprints that can be directly compared against measurements to identify relevant chemical motifs. Recent studies have incorporated effects of surfaces, interfaces, and grain boundaries into continuum thermodynamic models to predict size-dependent stability and changes to reaction pathways. Advanced multiscale methods have also rigorously incorporated effects of metal hydride interphases in chemomechanical models.[366]

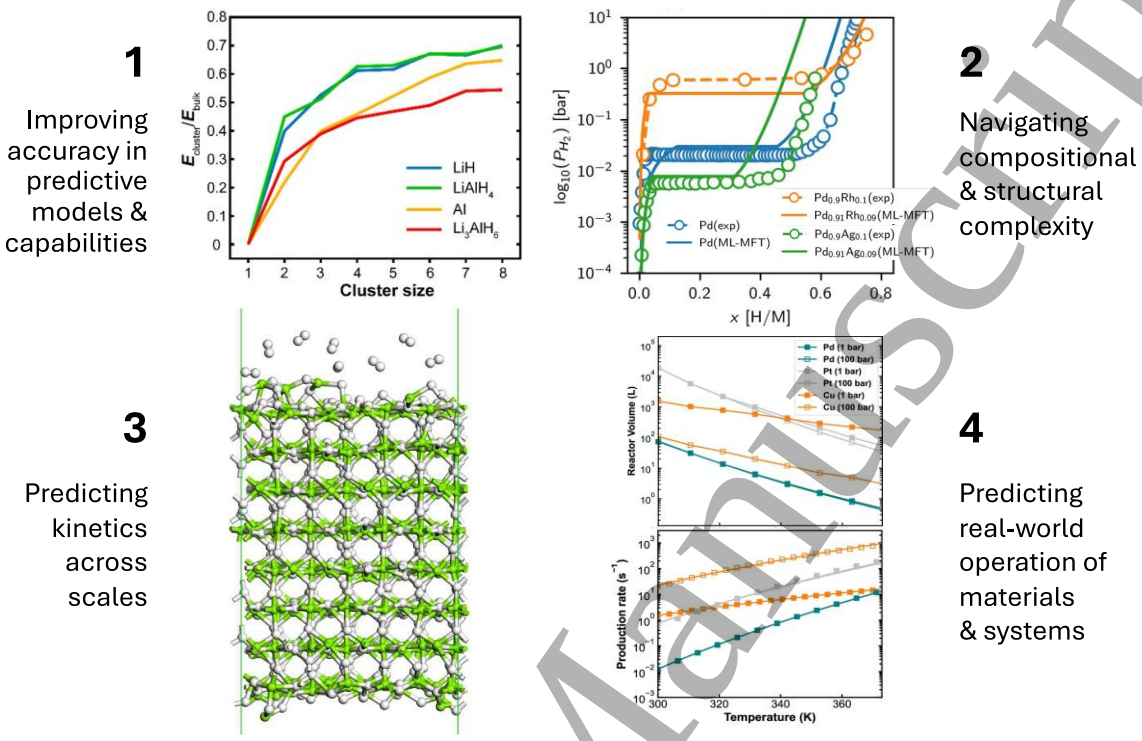


Figure 13: Examples of work addressing the four identified challenges: (1) Size-dependent thermodynamics of metal hydride nanoparticles and clusters from DFT, demonstrating changes in relative stability (Reprinted with permission from Ref. [362], Copyright 2021 American Chemical Society). (2) Pressure-composition isotherm predictions of metal hydride alloys using an accelerated DFT-trained machine learning model (Adapted with permission from Ref. [372], Copyright 2024 American Chemical Society). (3) Machine learning molecular dynamics simulation of MgH_2 dehydriding (Reproduced from Ref. [359] under CC BY 4.0). (4) Simulated H_2 production rate from formic acid on metal catalysts using DFT-based microkinetics (bottom) and corresponding prediction of required reactor scale (Adapted with permission from Ref. [385], Copyright 2025 American Chemical Society).

Additional thermodynamic contributions. CALPHAD methods have been widely applied to estimate thermodynamic properties,[367] but building a multicomponent database for hydrogen-based materials requires consistent models suitable across different applications. Proper configurational sampling of hydrogen at intermediate compositions is also difficult for realizing accurate enthalpy predictions.[368] There is also a need to include additional factors beyond enthalpy into thermodynamic models, such as thermal free-energy contributions that can incorporate anharmonicity (particularly for complex metal hydrides), as well as effects of volume expansion and mechanical stress upon hydrogen incorporation.[369] For electrochemical charge-transfer reactions, application of an explicit voltage bias can produce results that differ significantly from standard assumptions of constant charge

Challenge 2: Navigating compositional and structural complexity

Machine learning (ML) for complex compositions. High-entropy alloys can tailor hydrogen interactions but feature an immense compositional space. Compositional ML models can predict interstitial metal hydride thermodynamics from experimental databases based only on composition,[93,370,371] but accuracy suffers in regions of low data density. Physics-derived ML approaches may be better suited, as in recent studies in which DFT or numerical simulation results were used to

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train an ML surrogate within an efficient graph neural network representation to successfully predict key performance and stability metrics for hydrides.[372,373]

Tools for structural and microstructural diversity. In principle, similar ML tools could incorporate the effects of atomic structural and microstructural diversity in amorphous, porous, and polygranular/polyphasic materials, although to date this has not been done. For atomically disordered regions, graph neural network approaches show great promise for characterizing and predicting properties of atomic structures, exemplified in recent work on Ti-based materials in hydrogen.[365,374]

Databases and accelerated sampling. Computational databases of microstructures and atomic structures that can be applied universally is another priority. These could be used within multiphysics models to predict sensitivity of performance metrics to ranges of properties within the feature databases and to direct improvement strategies towards the most impactful features.

Challenge 3: Predicting kinetics across scales

Energy landscape sampling. Methods are needed that can move beyond bulk thermodynamics to predict the full energy landscape of coupled solid-state chemical and structural transitions. This is particularly crucial for complex metal hydride reactions, as shown in a recent study of $Mg(BH_4)_2$.[375] One suitable approach is metadynamics,[376] which is being used to derive energy landscapes and reaction barriers in nanoscale metal hydrides.[120]

Multiscale transport modeling. For diffusion barriers, the common nudged elastic band (NEB) approach is limited to a zero-temperature, dilute-carrier description, whereas finite-temperature molecular dynamics (MD) can explicitly incorporate correlated dynamics and anharmonicity.[275,377] MD has been crucial for understanding initial stages of MgH_2 dehydrogenation,[359] and for identifying factors motivating ion diffusion in complex hydrides for solid-state electrolytes.[286] Emerging ML-derived interatomic potentials can enable more efficient energy landscape sampling with longer MD simulations and quantum accuracy, while also enabling implicit or explicit incorporation of nuclear quantum effects in simulations of hydrogen diffusion.[360,361] Microstructural models can incorporate these diffusivities to study mass transport in polyphasic and polycrystalline microstructures,[378] drawing upon methods developed for solid electrolytes that can translate to hydrogen-based materials.[38,365] Similar multiscale approaches can also be employed to predict heat transport.[176]

Nucleation and phase evolution modeling. Methods to incorporate atomistically derived (particularly first-principles) parameters into nonequilibrium continuum formalisms are needed to study phase formation and evolution. Nucleation barrier predictions can begin with cluster models,[379] but could be more powerfully coupled to classical or non-classical nucleation models to extend scales. For microstructure evolution, the phase-field method is well suited for simulating the metal-to-hydride transition and can in principle be parameterized from atomistic calculations;[163] here, a priority is to identify atomic-scale details to preserve in reduced-order models for parameterization, which could be aided by advanced sampling or ML.

Challenge 4: Predicting real-world operation of materials and systems

Materials durability. Lifetime predictions beyond thermodynamic stability remain difficult, but proxies for failure propensity can be computed, such as concentrated local stresses that can induce fracture during hydriding, or current density gradients that can break down a battery cell. Microstructure evolution simulations can also predict orphaned phases and unwanted phase segregation. Such proxies could aid the development of accelerated stress testing protocols for rapid durability assessment.

Activation. Penetration of hydrogen into a metal and subsequent hydride phase nucleation determine activation conditions, which can limit efficiency in certain interstitial metal hydrides such as TiFe. Here, it is critical to model the formation and evolution of the protective surface oxide chemistry,[38,380] which can then be incorporated into transport and permeation simulations, as recently demonstrated.[374]

Performance at scale. Model verification can benefit from automated extraction of macroscale metrics like usable capacity and rate performance, which can be directly compared to hydrogen tests under real-world conditions. At the same time, multiphysics predictions of full deployment scales can identify emergent limitations that may go unnoticed in the laboratory.[381] For example, composite models that incorporate tradeoffs between thermal conductivity and porosity can optimize compositions to ensure sufficient heat management at full-scale operation.

Co-design of materials and systems. Models that couple materials properties and systems designs is another emerging priority. One example is recent work on Li_3N nanoconfinement, which reduced theoretical storage capacity but enhanced thermal conductivity, leading to counterintuitive predictions of higher practical system-level capacity.[382] Enhanced systems models can incorporate material property evolution and interdependency during hydrogen cycling, whereas materials models can incorporate system-level stressors such as desired rates, scales, and usable capacities that affect performance-durability tradeoffs. Automated sensitivity analysis and surrogate models can enable custom optimization across material, device, and system scales for desired operation scenarios.[383–385]

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Concluding remarks

In summary, research in the development and application of scalable computing tools for hydrogen-materials interactions is well underway, with a promising future ahead. The movement away from simple bulk thermodynamic predictions of bulk reactions, which have dominated the field for decades, towards more complex calculations that incorporate kinetics of more realistic materials is welcome and promises to better bridge the divide between theory and application. In the coming years, exciting advancements in machine learning/data science, multiscale integration, and automated workflows will continue to push computation forward as a fast, reliable predictive tool for optimal design of hydrogen materials across a variety of energy storage applications.

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13. Conclusions

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Hydrogen-based materials form an exciting family of multifunctional materials with a wide range of extraordinary properties for a wide range of applications from hydrogen storage even to superconductivity. This roadmap addresses still existing key challenges for the wider implementation of such materials for energy storage related applications.

In it we discuss five different classes of hydrogen-based materials for energy storage: nanoporous materials, magnesium-based hydrides, intermetallic hydrides, complex hydrides, and liquid hydrogen carriers. The interaction of hydrogen with these material classes ranges from weak van der Waals forces (physisorption) to strong chemical bonds (chemisorption). The technology readiness level (TRL) of these hydrogen-based materials covers the entire spectrum from laboratory scale to mature technologies. Curiosity-driven research seeks new nanoscale materials or catalytic reactants for improved properties (TRL = 1-3). In contrast, for upscaled prototypes, high-purity materials are replaced by recycled or waste materials to reduce costs and increase competitiveness (TRL = 4-5).

One major focus of this roadmap is on hydrogen storage for mobile and stationary applications. The different materials cover a wide range of potential operating temperatures, from cryogenic to high temperatures, ensuring that a suitable material can be found for every application. While liquid hydrogen carriers have started to move to pilot demonstrations, defining their best use-cases and improving cost-competitiveness, research is still continuing to improve the material performance, especially catalyst performance and cyclability. Over the past two decades, nanoporous materials with large surface areas, such as MOFs, have shown promising results as mobile, lightweight hydrogen storage solutions. Small-scale prototypes of cryogenic tanks have been tested for later use in heavy-duty vehicles or trains (TRL = 3-4). Intermetallic hydrides, on the other hand, have been investigated for decades, and large hydrogen storage systems for stationary applications are in use in energy-autonomous buildings and maritime applications (TRL = 4-11). While these materials show extraordinary high volumetric storage densities, the gravimetric storage densities so far are rather limited (< 3 wt.%). Complex hydrides, light weight hydrides and Reactive Hydride Composites for hydrogen storage applications (TRL = 2-4), on the other hand, show much higher reversible gravimetric storage densities of more than 10 wt.%, while often suffering from slow kinetics and/or requiring elevated operation temperatures above 100 °C. Besides the operation temperature, reaction kinetics, operation temperature, volumetric and gravimetric hydrogen storage density, must meet numerous other requirements, such as reaction heat, cyclability and recyclability, material handling, heat conductivity, scalability, etc. All these different aspects have to be addressed and fine-tuned for each application area. To achieve this, many new approaches have been developed, but not all issues have been fully resolved yet. In addition, in many cases, there is still a lack of testing and integration of these materials into prototypes and systems, as well as a lack of optimisation of heat management systems.

In addition to these hydrogen storage related activities, this roadmap discusses other applications of hydrogen-based materials, including hydrogen purification and thermochemical compression, thermal energy storage in hydrides, as well as electrochemical energy storage. Hydride-based compressors are commercially available for medium pressure range (200-400 bar) and their operation without moving parts increases reliability and reduces maintenance costs (TRL = 8-9). Materials for pressures up to 1000 bar are currently being developed and investigated for use in H_2 refuelling stations (TRL =3-5). The identification of materials with the required plateau pressures, flat plateaus and low hysteresis are key issues to be addressed. For thermal energy storage, high-temperature hydrides are being investigated in small laboratory setups and a first larger prototype facility under test operation with Mg hydride (TRL = 3-5). In most hybrid electric vehicles, electrochemical energy storage continues to be based on metal hydride batteries, which are continuously being improved (TRL = 3-11). Novel metal hydridoborates, on the other hand, are among those materials with the highest solid state Li+, Na+, Mg2+, Ca2+ ion conductivities and show promising potentials for applications in a new class of all solid-state batteries (TRL = 1-3). In addition, H- ion conductors are developed enabling the design of a new class of hydride based all solid-state batteries, fuel cells or electrolysers.

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For all the above mentioned applications, the development, synthesis and characterisation of new hydrogen-based materials is the key to implementation. In recent years, the development of experimental methods has progressed rapidly, and new characterisation methods under operando environments are crucial for understanding hydrogen storage materials on various length scales. In parallel, computational methods are evolving rapidly - from atomic scale through density functional theory (DFT) to predicting kinetics across multiple scales. Machine learning, data science and multi-scale integration enable the use of computational methods as a fast, predictive tool for optimised design of hydrogen-based materials for energy storage.

In an economy based on renewable energies, the decisive challenge for success lies in efficient energy storage and conversion. Research into hydrogen-based materials will develop and provide materials in the coming years that can compete with or even surpass conventional systems.

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No new data were generated in this study.

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