



UCLouvain

**Process intensification of hydrogen production from
alkaline water electrolysis using 3-D electrodes**

Fernando Saraiva Rocha da Silva

Composition of the jury

Prof. Joris Proost (advisor)	Université catholique de Louvain
Prof. Alexandru Vlad	Université catholique de Louvain
Prof. Juray de Wilde	Université catholique de Louvain
Prof. Hervé Jeanmart (president)	Université catholique de Louvain
Prof. Shigenori Mitsushima	Yokohama National University
Prof. Jens Oluf Jensen	Technical University of Denmark

Louvain-la-Neuve, January 12, 2024.

“TUAHIR: O que faz andar a estrada? É o sonho. Enquanto a gente sonhar a estrada permanecerá viva. É para isso que servem os caminhos, para nos fazerem parentes do futuro.”

Extract from *Terra Sonâmbula*, Mia Couto, 1992

To my grandmother, vó Manu (in memoriam). Her strength, affection,
and wisdom illuminated my life. *Como era lindo o seu olhar.*

Abstract

Green hydrogen, produced from water electrolysis using renewable electricity, can decarbonize certain sectors such as the cement, steel, and fertilizer industries; long-haul shipping, aviation and cargo road transportation; and store and transport renewable energy. Given the urgent need to limit anthropogenic greenhouse gas emissions, hydrogen technologies must be deployed on a large scale shortly. This Ph.D. thesis focuses on investigating two process intensification strategies for enhancing scalability of alkaline water electrolysis, the most mature and cost-effective method for green hydrogen production. The first strategy explores the utilization of flow-designed 3-D electrodes under the effect of forced electrolyte flow. Throughout a combined experimental and computation fluid dynamics simulation approach, we have demonstrated that engineering the 3-D electrode macro-porous geometry towards enhanced bubble removal can lead to substantial performance improvements (reaching up to $2 \text{ A}\cdot\text{cm}^{-2}$ at 2 V). The second strategy investigates the application of pulsed electric power in alkaline water electrolysis. A comprehensive review of existing literature identified specific scenarios where pulsed power can be advantageous, particularly under low power input conditions. Then, we experimentally confirmed the literature results and highlighted the importance of considering capacitive effects in the pulse performance analysis. Overall, the findings presented here offer promising routes for accelerating the implementation of green hydrogen technologies on a large scale, contributing to the global efforts for mitigating climate change and transitioning towards a sustainable, low-carbon future.

Acknowledgments

I extend my deepest gratitude to Prof. Proost, my supervisor, whose encouragement and commitment to excellence were fundamental to the realization of this thesis. I am indebted to the esteemed jury members: Profs. De Wilde, Jensen, Mitsushima, and Vlad, whose invaluable insights and meticulous revisions significantly elevated the quality of this work. I am also thankful for the peer-reviewers who read and provided feedback on my papers.

The contributions from members of my institute were instrumental. The expertise and dedication of technicians, especially Frédéric and Ronny, were pivotal in the success of this research. I am equally appreciative of my lab colleagues Antoine, Cristhian, Grégoire, Kevin, Maxime, Nathan, Quentin, Raul, Renaud, and Remy for their indispensable collaboration and insights and a special acknowledgment to Christos for his invaluable CFD simulations. I acknowledge your collective role as co-thinkers in this endeavor. Acknowledgment extends to Catherine and Rania for their indispensable administrative support and Grzegorz for his uCT analysis and discussions.

External contributions were invaluable. My sincere thanks to David from Sirris for his 3-D printing, Jonathan for implementing TPMS in Migflow, and DLR researchers Asif and Sanaz for their contribution to thermal spray coating.

Completing a Ph.D. thesis is not only a personal triumph but also a collective endeavor. I am deeply grateful for the unwavering support of my family. I am grateful to my father, whose shared dreams fueled my

aspirations, my mother for her unconditional love, and my sister for being an unshakable support in my life. My sincere appreciation to my uncles, aunts, and cousins. Vó Vera, your love has been a guiding light. This thesis is dedicated to vó Manu, whose memory and inspiration will forever guide me.

This work would not be possible without the support of my friends. Special thanks to my friends in Brazil: Felipe, João, Lucas, Lys, and Thales. To my friends in Belgium: Filippo, Ian, Jacyara, Maria, Max, Neill, Romain, Sueli, Virna, and Yann, your friendship has been invaluable. I also thank the families of Rodrigues, Mulligan, Bombardi, and Faria. Genuine gratitude to those who stood against hate and denialism in Brazil.

A heartfelt and special thanks to Paloma, whose relentless support during challenging times has been invaluable.

Lastly, I express my profound gratitude to the scientific colleagues who developed the SARS-CoV-2 vaccine, which undoubtedly saved countless lives, including my father, and provided us with a means to combat the pandemic.

I gratefully acknowledge financial support from the European Commission through the H2020 Project "NexTAEC" (Materials for Next Generation Alkaline Electrolyzers), under contract n° 862509. I also acknowledge financial support from the catholic University of Louvain (UCLouvain).

Scientific outputs

International peer-reviewed articles

1. **Rocha F**, Delmelle R, Georgiadis C, Proost J. Electrochemical Performance Enhancement of 3D Printed Electrodes Tailored for Enhanced Gas Evacuation during Alkaline Water Electrolysis. *Advanced Energy Materials* (impact factor: 27.8) 2022;13:2203087.
2. **Rocha F**, Delmelle R, Georgiadis C, Proost J. Effect of pore size and electrolyte flow rate on the bubble removal efficiency of 3D pure Ni foam electrodes during alkaline water electrolysis. *Journal of Environmental Chemical Engineering* (impact factor 7.7) 2022;10:107648.
3. **Rocha F**, de Radiguès Q, Thunis G, Proost J. Pulsed water electrolysis: A review. *Electrochimica Acta* (impact factor: 7.4) 2021; 377:138052.
4. **Rocha F**, Proost J. Discriminating between the effect of pulse width and duty cycle on the hydrogen generation performance of 3-D electrodes during pulsed water electrolysis. *International Journal of Hydrogen Energy* (impact factor: 7.2) 2021;46:28925–35.
5. **Rocha F**, Georgiadis C, Van Droogenbroek K, Delmelle R, Pyka G, Kerckhofs G, Egert F, Razmjooei F, Ansar SA, Shigenori S, Proost J. PEM-like alkaline water electrolysis using flow-engineered 3-D electrodes. Submitted.

International conference proceedings

1. **Rocha F**, Georgiadis C, Pyka G, Razmjooei F, Ansar SA, Proost J. PEM-like alkaline water electrolysis using flow-engineered 3-D electrodes. 4th International Conference on Electrolysis; Sun City, 2023.
2. **Rocha F**, Wauthy N, Delmelle R, Georgiadis C, Proost J. Electrochemical Performance of 3-D Printed Electrode Geometries in View of Enhanced Gas Evacuation during Alkaline Water Electrolysis. 23rd World Hydrogen Energy Conference, Istanbul, 2022.
3. Delmelle R, **Rocha F**, Georgiadis C, Proost J. Upscaling High-Performance 3-D Electrodes for Alkaline Water Electrolysis Towards Near-Industrial Conditions. 23rd World Hydrogen Energy Conference, Istanbul, 2022.
4. Georgiadis C, **Rocha F**, Lambrechts J, Proost J. Investigation of Electrolyte Forced Flow for Alkaline Water Electrolysis Using Computational Fluid Dynamics. 23rd World Hydrogen Energy Conference, Istanbul, 2022.

Table of content

Abstract.....	i
Acknowledgments	iii
Scientific outputs.....	v
List of figures.....	xi
List of tables	xxiv
List of acronyms and abbreviations.....	xxv
List of symbols.....	xxix
Chapter 1: Introduction	1
Chapter 2: Fundamentals	15
2.1 Thermodynamics of water electrolysis.....	16
2.2 Kinetics of water electrolysis.....	21
2.2.1 Hydrogen evolution reaction (HER)	23
2.2.2 Oxygen evolution reaction (OER)	24
2.3 Ohmic resistances	26
2.4 Bubble effect.....	27
2.5 Efficiencies	29
2.6 3-D electrodes	31
2.7 Pulsed electrolysis.....	37
Chapter 3: State of the art	43

3.1	Alkaline electrolyzer	43
3.1.1	<i>Electrolyte</i>	43
3.1.2	<i>Separator</i>	45
3.1.3	<i>Electrocatalysts</i>	50
3.1.4	<i>Cell and electrode design</i>	55
3.1.5	<i>Stacks</i>	65
3.2	Pulsed water electrolysis.....	67
3.2.1	<i>Voltage pulses</i>	68
3.2.2	<i>Current pulses</i>	83
3.2.3	<i>Pulses with a redox mediator</i>	89
3.2.4	<i>Pulses for other electrochemical applications</i>	95
Chapter 4:	Objectives	97
Chapter 5:	Materials and methods	99
5.1	Electrochemical measurements	99
5.2	Three-dimensional foams	106
5.3	Raney Ni coating and activation.....	108
5.4	Three-dimensional printed electrodes.....	112
5.5	X-ray micro-computed tomography	118
5.6	Computational fluid dynamics simulations	118
5.7	Characterization techniques.....	121
5.7.1	<i>ECSA measurement</i>	121
5.7.2	<i>Electrochemical impedance spectroscopy</i>	124
5.7.3	<i>Porosity measurement</i>	124
5.7.4	<i>Polarization curve fitting</i>	125

5.7.5	<i>Other techniques.....</i>	126
Chapter 6: Electrochemical characterization of 3-D foam-shaped electrodes 127		
6.1	Effect of pore size on electrochemically active surface area 129	
6.2	Effect of pore size on the electrochemical performance	132
6.3	Effect of pore size on bubble entrapment.....	137
6.4	Conclusion	139
Chapter 7: PEM-like alkaline water electrolysis using flow-engineered 3-D electrodes 141		
7.1	Forced upstream electrolyte flow	149
7.2	Laterally-graded bi-layer cell configuration.....	155
7.3	Ni-Al-(Mo) coating and activation	162
7.4	Perspectives and strategies for future electrolyzer developments.....	165
7.5	Conclusion	169
Chapter 8: Performance of 3-D printed electrodes 171		
8.1	Geometrical and Structural Characterization of 3-D printed TPMS electrodes.....	172
8.2	Electrochemical performance of 3-D printed TPMS electrodes 175	

8.3	Simulation of electrolyte flow inside 3-D printed TPMS electrodes	180
8.4	Electrochemical performance of 3-D printed TPMS electrodes as a function of electrolyte flow	183
8.5	Conclusion	185
Chapter 9: Experimental validation of pulsed water electrolysis		
187		
9.1	Voltage pulses with a duty cycle of 50%	188
9.2	Voltage pulses with a higher duty cycle	194
9.3	Current pulses with a duty cycle of 50%	198
9.4	Current pulses with duty cycles other than 50%	201
9.5	Literature overview	204
9.6	Conclusion	205
Chapter 10: Conclusions and perspectives		209
References		215

List of figures

Fig. 1. a) Yearly anthropogenic GHG emissions over the past years, and b) variation in mean global temperature compared to the value at 1850. Adapted from ref. [2].	2
Fig. 2. Global energy flows in the IEA Net Zero Emissions by 2050 scenario. From ref. [10].	4
Fig. 3. Global hydrogen and hydrogen-based fuel use in 2050 according to the IEA NZE by 2050 scenario [11]. Onsite indicates that hydrogen was produced within the industrial facility where it is consumed, while merchant indicates that it was produced by one company to sell to another. Refineries include both onsite and merchant.	6
Fig. 4. Total Cost of Ownership of electrolytic H ₂ , delivered at 35 bar, as a function of power input. Operational expenditure (opex) includes the use of electricity, water, and nitrogen (for purge), assuming a renewable electricity price of 40 and 45 €·MWh ⁻¹ , respectively. From ref. [43].	13
Fig. 5. Pourbaix diagram for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) at a) 25°C and different pressures, and b) 1 bar and different temperatures. Constructed based on thermodynamic data from ref. [50].	18
Fig. 6. Equilibrium and thermoneutral cell voltage as a function of a) pressure and b) temperature. A detailed explanation of the estimation method can be found in refs. [52,53].	20
Fig. 7. Exchange current densities for HER in alkaline media as a function of the energy of adsorption. Adapted from ref. [59].	23

Fig. 8. OER overpotential for metal oxides as a function of the difference in free Gibbs energy between $^*\text{O}$ and $^*\text{OH}$. From ref. [64].	25
Fig. 9. Schematic of a) potential distribution, and b) current distribution along a zero-gap flow-by electrolyzer with 3-D electrodes.	36
Fig. 10. Schematic representation of a) voltage pulse with an on-voltage at which a reaction occurs and an off-voltage at which no reaction occurs b) current pulse with a null total current during off-time.	39
Fig. 11. a) Specific conductivities as a function of mass fraction for sodium and potassium hydroxides [90], b) Specific conductivity for potassium hydroxide as a function of concentration and temperature [91].	44
Fig. 12. HTO as a function of current density for a) different temperatures and separator thicknesses and b) different pressures. Adapted from ref. [96].	46
Fig. 13. Schematic showing different materials for electrolyzer separators. From ref. [88].	48
Fig. 14. Pourbaix diagram for the Ni-water system. The pH region of interest for AWE is highlighted in gray. Red, blue, and green lines represent Ni molarities of 10^{-4} , 10^{-6} , and 10^{-8} , respectively. Adapted from ref. [109].	51
Fig. 15. Schematic showing the Raney Ni coating using the plasma spray process. Adapted from ref. [111].	53

Fig. 16. Schematic showing the evolution of cell designs showing a) traditional gap cell, b) zero gap-cell with 2-D electrodes, and c) zero-gap cell with 3-D electrodes.	57
Fig. 17. Schematic of the metal production using deposition on a precursor foam. From ref. [81].	59
Fig. 18. Schematic of the laser beam melting process. From ref [81].	63
Fig. 19. Schematic of bubble removal strategies. From ref. [45].....	64
Fig. 20. Schematic of a common electrolyzer stack. From ref. [45]..	66
Fig. 21. Behavior of semiconductor switch a) Power loss elements b) Command signal. Adapted from [166].	71
Fig. 22. a) Experimental setup for pulse width modulation [166] b) Current versus frequency plot for aluminum electrodes in 0.1 M KOH c) Equivalent circuit for a water electrolysis cell From [168] d) Relaxation time [170].	74
Fig. 23. Oxygen and hydrogen bubbles being produced simultaneously on a different nickel electrode immersed in a KOH solution with an electrode distance of 2 mm, $E_{on} = 4.0$ V, and $E_{off} = 0$ V. Adapted from [174].	81
Fig. 24. HHV efficiency as a function of electric power input (right) and schematics of the proposed mechanism at low-loads (left). For pulsed current, current flows in all the electrodes. Current by-pass the middle electrodes for DC, and only the first and last electrodes are active. Adapted from ref. [188].....	86

- Fig. 25. Schematic view of the pulsed current supply used in [197] for two-step water electrolysis with a $\text{MnO}(\text{OH})/\text{MnO}_2$ intermediate electrode, a metal hydride (lanthanum) for hydrogen evolution reaction, and a $\text{Ni}(\text{OH})_2$ electrode for the oxygen evolution reaction. If the switch is connected to the metal hydride electrode, HER occurs; if it is connected to the nickel electrode, OER occurs. 92
- Fig. 26. Pulse width-cell voltage profile at a current density of 0.1 A.cm^{-2} for (black) oxygen evolution reaction at a nickel electrode and the reduction of the intermediate MnO_2 electrode, thermodynamic cell voltage = 0.828 V ; (red) hydrogen evolution reaction in metal hydride electrode and the oxidation of the $\text{MnO}(\text{OH})$ electrode, thermodynamic cell voltage = 0.402 V ; (blue) and overall reaction i.g. sum of the two previous cell voltages, thermodynamic cell voltage = 1.229 V (blue). Adapted from [197]. 94
- Fig. 27. Experimental setup in: a) Schematic b) Photo documentation. c) Photo documentation of a demounted cell. 100
- Fig. 28. Temperature difference between the reservoir and the cell as a function of electrolyte flow rate. At natural convection (zero forced flow), the temperature at the cell is close to room temperature. 102
- Fig. 29. Schematic illustration of the representation of an experimental data set as a) a normal distribution and b) a cumulative normal distribution. 105
- Fig. 30. Scanning electron micrographs taken at the same magnification for porous nickel foams with specified pore sizes of a) $3000 \mu\text{m}$, b) $1200 \mu\text{m}$, c) $800 \mu\text{m}$, d) $580 \mu\text{m}$, and e) $450 \mu\text{m}$ 107

Fig. 31. Scanning electron micrographs of Ni foams before and after coating taken with a field emission gun scanning electron microscope (Zeiss Ultra 55). Electron high tension of 15 kV, working distance of 10 mm, type II secondary electrons.....	108
Fig. 32. Ionic concentrations in solution as analyzed by Inductively Coupled Plasma analysis for activation of a) NiAlMo coated foam (cathode) and b) NiAl coated foam (anode). For the in-situ electrochemical activation, the same electrolysis cell presented in the Materials section was used and samples were collected at the reservoir level.....	110
Fig. 33. Polarization curve at 70°C and 30wt% KOH from the first current scan performed on spray-coated and chemically activated Raney nickel foams in dark blue, and subsequent ones in light blue. In purple, the first current scan of another spray-coated and chemically activated Raney Ni foam. The scan rate was $0.025 \text{ A} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$	111
Fig. 34. Examples of TPMS geometries. They all contain a lattice size L of 8 mm and a t parameter of 0.26. Arrows indicate the direction of forced electrolyte flow.....	113
Fig. 35. Gyroidal electrode geometries with different structural parameters: a) L = 1 and 6 mm at t = 0.6; b) t = 0 and 0.8 at L = 4 mm.	113
Fig. 36. a) Surface area as a function of lattice size L for t = 0; b) porosity as a function of t, the latter relation being independent of L.	115

Fig. 37. Photo documentation of SLM 3-D printed electrodes a) Gyroid with an $L = 4$ mm and a $t = 0$ c) Gyroid with an $L = 4$ mm and a $t = 1.2$ e) Schwarz with an $L = 2$ mm and a $t = 0.18$ g) Schwarz with an $L = 4$ mm and a $t = 0.18$. FEGSEM micrographs of 3-D printed electrodes b) Gyroid with an $L = 4$ mm and a $t = 0$ d) Gyroid with an $L = 4$ mm and a $t = 1.2$ f) Schwarz with an $L = 2$ mm and a $t = 0.18$ h) Schwarz with an $L = 4$ mm and a $t = 0.18$. The dimension of the electrodes is $2 \cdot 2 \cdot 0.8$ cm.....	117
Fig. 38. Evolution of pressure drop versus velocity a) $450 \mu\text{m}$ foam compared to experimental data from ref. [216] for a $423 \mu\text{m}$ foam (60 pores per inch) with a porosity of 0.918; b) $3000 \mu\text{m}$ foam compared to experimental data from ref. [217] for a $2540 \mu\text{m}$ foam (10 pores per inch) with a porosity of 0.85.....	120
Fig. 39. Cyclic voltammetry for a $2 \cdot 2 \text{ cm}^2$ Ni foam with characteristic pore size of $450 \mu\text{m}$. Experimental conditions of 1 M KOH, room temperature. The red rectangle indicates the potential range used for capacitance measurements.....	121
Fig. 40. a) Cyclic voltammetry from -0.6 V vs Ag AgCl sat. to -0.4 V vs Ag AgCl sat. at scan rates between 50 mV/s and 400 mV/s for one $2 \times 2 \text{ cm}^2$ layer of nickel foam with a pore size of $450 \mu\text{m}$; b) Resulting capacitive current as a function of scan rate. Experiments were performed at 1 M KOH, room temperature.....	123
Fig. 41. Probability plot for pore size distribution of foam electrodes	127
Fig. 42. Specified and measured foam surface area per cell as a function of measured average pore size.....	130

- Fig. 43. Cell voltage as a function of a) geometrical current density during natural convection; b) geometric current density for a flow rate of 1.1 L/min; c) electrochemical current density at natural convection; d) electrochemical current density at a flow rate of 1.1 l·min⁻¹. Lines represent the results of CV scans at 100 mA/s, while the additional symbols in b) represent the mean cell voltage during a 5 minutes galvanostatic stay..... 131
- Fig. 44. Cell voltage for the different foams and flow regimes at a) 0.1 A·cm⁻² and c) 0.5 A·cm⁻². Overvoltage reduction caused by a forced electrolytic flow (1.1 L·min⁻¹) at b) 0.1 A·cm⁻² and d) 0.5 A·cm⁻².. 133
- Fig. 45. a) Illustration of the method for calculating the available surface fraction for a foam electrode; b) Fraction of available surface area as a function of measured average pore size at 1 A under natural convection and 1.1 l·min⁻¹. Solid red lines are merely a guide to the eye..... 136
- Fig. 46. Evolution of cell voltage for three series of galvanostatic pulses of 5 minutes at a geometric current density of 0.5 A·cm⁻² followed by 5 minutes at zero current; a) natural convection b) 1.1 l·min⁻¹. Experiments were performed at 30 wt% KOH and room temperature. 138
- Fig. 47. Graphical abstract of chapter 5 showing the main improvements demonstrated in this work : (1) the use of a high forced upstream electrolyte flow, as opposed to the use of serpentine flow fields in most of the literature reports; (2) the integration of 3-D electrodes in a zero-gap cell using a laterally graded bi-layer configuration consisting of a fine 450 µm foam in contact with a coarse

3000 μm foam, the combination being flow-engineered to enhance gas removal; (3) the application of a Raney Ni coating on the fine foam, resulting in catalytically highly active electrodes free of Pt group metals. 141

Fig. 48. Representative polarization curves at 70°C and 30wt% KOH for 2 electrolyte upstream flow velocities for pure Ni bi-layers (a) and bi-layers with a catalytic Raney Ni coating (b). Lines are measured from cyclic voltammetry, while bullet points from selected galvanostatic experiments have been superimposed. Hatched zones represent the range of literature data, for which all polarization curves are shown in Fig. 49. 145

Fig. 49. Polarization curves from literature for Pt group metals (PGM)-free electrodes in alkaline medium using a Zirfon gas separator for a) pure Ni and b) Raney Ni electrodes. Zirfon resistance was estimated individually for each reference in Table 6 considering a MacMullin number of 2.82 (as in ref. [48]), and represented above with an average value of $R_{\text{Zirfon}} = 105 \pm 5 \text{ m}\Omega/\text{cm}^2$. Similarly, values the equilibrium cell voltage were calculated for each reference according to Eq.(76), resulting in the average value for $E_{\text{eq}} = 1.19 \pm 0.02 \text{ V}$ represented above. 146

Fig. 50. Cumulative normal probability plots comparing our own data to relevant data from the literature using Ni-based electrodes and a Zirfon diaphragm for a) Tafel slopes and b) Ohmic resistance minus Zirfon resistance. Raw data are compiled in Table 6 and obtained by fitting all polarization curves by Eq. (23)..... 148

Fig. 51. Graphical representation of a) our own flow-engineered cell with the bi-layer configuration consisting of a catalytic 450 μm foam and a porous transport foam of 3000 μm ; b) serpentine flow field along with a 450 μm foam. Flow streamlines for an inlet velocity of $1.5 \text{ m}\cdot\text{s}^{-1}$ for c) our own cell and d) serpentine flow field; e) cumulative distribution function at the outlet, representing the fraction of tracers exiting the electrolyzer that have spent a time t or less in the electrolyzer; f) residence time distribution function $E(t)$. The product $E(t)\cdot dt$ represents the fraction of tracers exiting the electrolyzer that have spent a time between (t) and $(t + dt)$ in the electrolyzer. The mean residence time was 0.26 s and 0.60 s for the bi-layer configuration and for the serpentine, respectively. 152

Fig. 52. TOP: Cole-Cole plot for an electrochemical cell containing pure Ni bi-layer electrodes at 70°C , 30 wt% KOH, and an electrolyte flow rate of $0.35 \text{ L}\cdot\text{min}^{-1}$ (left) and b) $1.2 \text{ L}\cdot\text{min}^{-1}$ (right); BOTTOM: EIS-measured Ohmic resistance derived from the high frequency region of the Cole-Cole plot; the dashed horizontal lines represent the value obtained from curve fitting of the polarization curves using Eq. (23). 154

Fig. 53. a) Pore-resolved bi-layer geometry and simulation domain (left), velocity streamlines emanating from the catalyst (middle), and from the porous transport foam (right); b) Averaged lateral (in the direction normal to the diaphragm) velocity of x-z plans as a function of distance for single-phase and 2-phase simulations, the latter with different gas fractions α . The upstream electrolyte inlet velocity was set at 0.22 m/s . The fine 450 μm pore size catalytic foam is indicated by the dashed region. 157

- Fig. 54. Velocity vectors scaled by magnitude for the single-phase (left) and 2-phase (right) simulations, the latter with a gas fraction of 40%. The electrolyte upstream inlet velocity was set at 0.22 m/s, as in Fig. 53. The bottom figures are details at the entrance section of the bi-layer region. The fine catalytic foam is on the left, with a thickness of 1.6 mm. The top figures cover the entire cell width of 5.6 mm. 159
- Fig. 55. Comparison of mass transfer in the lateral (y-) direction for different porous transport foam porosities. 161
- Fig. 56. Comparison of mass transfer in the lateral (y-) direction for different porous transport foam (PTF) thicknesses. The catalytic foam thickness was set at 1.6 mm and the PTF thickness was varied between 1.6 and 4.8 mm. 161
- Fig. 57. a) X-ray micro-computed tomography of a coated and activated 450 μm foam showing pure Ni in blue and coating in purple; b) Coating volume per substrate surface area as a function of thickness for the coated 450 μm Ni foam, c) Specific surface area per slice of 0.65 μm thickness for the 450 μm pure Ni foam as a function of scanning depth. 163
- Fig. 58. a) Polarization curves for different water electrolysis technologies including the ones reported in this work; b) Cell-voltage as a function of current density in amperes per euro. Data for PEM, classic and improved alkaline have been reproduced from DeNora [248]. The cost of our own bi-layer foams was estimated based on Alantum projections (90 $\text{€}\cdot\text{m}^{-2}$ for each layer) and the cost of plasma spray coating was set at 314 $\text{€}\cdot\text{m}^{-2}$ as specified in ref. [249]. 166

Fig. 59. Polarization curves for Raney-Ni bi-layer foams with different separators. Tafel slopes are within the range for Raney-Ni: $54.5 \pm 0.3 \text{ mV} \cdot \text{dec}^{-1}$ and $119.1 \pm 0.5 \text{ mV} \cdot \text{dec}^{-1}$ for the experiment using Zirfon and Dapozol, respectively.	168
Fig. 60. a) Measured porosity as a function of expected porosity b) Electrochemical active surface area as a function of theoretical surface area.	174
Fig. 61. Evolution of cell voltage vs. current for structures with an ECSA of 100 cm^2 at natural convection (a) and forced flow (b), and for structures with an ECSA of 175 cm^2 at natural convection (c) and at forced flow (d).	176
Fig. 62. Evolution of the cell voltage vs. electrochemical current density for structures with an ECSA of 100 cm^2 at natural convection (a) and forced flow (b), and for structures with an ECSA of 175 cm^2 at natural convection (c) and at forced flow (d).	177
Fig. 63. Electrochemical current density as a function of surface area at a constant voltage of 2.6 V	179
Fig. 64. Velocity streamlines for structures with the same theoretical surface area (32 cm^2) and porosity (61%): a) Schwarz $L = 4$ and $t = 0.18$; b) Gyroid $L = 3.94$ and $t = 0.34$; c) Fischer-Koch $L = 6.5$ and $t = 0.25$	180
Fig. 65. Resulting pressure drop as a function of vertical velocity..	181
Fig. 66. Flow sensitivity at projected current density of $0.4 \text{ A} \cdot \text{cm}^{-2}$ for: a) Structures with a measured ECSA around 100 cm^2 (Gyroid $L = 4 \text{ mm}$, $t = 1.2$; Fischer-Koch $L = 8 \text{ mm}$, $t = 0.7$; Schwarz $L = 4 \text{ mm}$, $t =$	

0.26); b) Structures with a measured ECSA around 175 cm^2 (Gyroid $L = 4 \text{ mm}$, $t = 0$; Fischer-Koch $L = 4 \text{ mm}$, $t = 0$; Schwarz $L = 2 \text{ mm}$, $t = 0.18$). Overvoltage is the difference between the cell voltage and the sum of the equilibrium cell voltage – 1.23 V - and the ohmic contribution of the separator – 0.8 V 184

Fig. 67. Time evolution of the on-current at 2.0 V (a) and off-current at 1.2 V (b) during the first voltage pulse for different pulse widths. Duty cycle of 50%, natural convection. The time resolution was 1% of the pulse period, except for the pulse with a period of 1 ms , where the resolution was 10% of pulse period..... 189

Fig. 68. Average current of the first voltage pulse as a function of pulse width. Duty cycle of 50%, both natural convection and forced flow. 190

Fig. 69. Time evolution of the on- and off-current during the first 60 ms for a pulse width of 1 and 10 ms. Duty cycle of 50%, natural convection. 191

Fig. 70. (a) Average current after 10 s of experiment as a function of voltage pulse width. For a pulse width of 10 s and 100 s, the second applied pulse was used to calculate the average; (b) Pulse width dependence of the ratio between on-charge and total charge during one voltage pulse period. Duty cycle of 50%, both natural convection and forced flow..... 193

Fig. 71. Average current (left ordinate) and hydrogen production rate (right ordinate) as a function of voltage pulse period for an off-time of (a) 1 ms and (b) 10 ms . Both natural convection and forced flow... 195

Fig. 72. Faraday efficiency for voltage pulses with an off-time of a) 1 ms and b) 10 ms.	197
Fig. 73. Time evolution of the cell voltage for current pulses between 0 and $0.075 \text{ A}\cdot\text{cm}^{-2}$ for pulse widths of a) 0.01 and 0.1 s, and b) 1 and 10 s. The DC behavior at $0.075 \text{ A}\cdot\text{cm}^{-2}$ is shown for comparison. Duty cycle of 50%, natural convection.	199
Fig. 74. (a) Average cell voltage during 10 min of experiment as a function of the current pulse width. Duty cycle of 50%, both natural convection and forced flow; (b) Time evolution profile of the cell voltage during a typical pulsed current experiment, showing that the DC behavior measured at the end of each experiment was the same as the one at the beginning.	200
Fig. 75. Average cell voltage as a function of current pulse period for an off-time of (a) 10 ms and (b) 100 ms. Both natural convection and forced flow.	202
Fig. 76. Duty cycle dependence of the average cell on-voltage for current pulses with different pulse periods. Peak current of $0.075 \text{ A}\cdot\text{cm}^{-2}$, forced flow.	203

List of tables

Table 1. Summary of voltage pulse methods	69
Table 2: Summary of current pulse methods.....	88
Table 3. Inductively coupled plasma (ICP) analysis of Raney nickel electrodes	109
Table 4. Geometrical electrode characteristics.....	128
Table 5. Details of cell setups for alkaline water electrolysis with Zirfon separator and PGM free electrodes.....	143
Table 6. Electro-kinetic parameters and Ohmic resistance obtained from curve fitting all polarization curves by Eq. (23).....	147
Table 7. Structural and geometrical characteristics of selected 3-D printed triply periodic minimal surface (TPMS) electrodes.....	173

List of acronyms and abbreviations

AC	Alternating Current
AWE	Alkaline Water Electrolysis
BET	Brunauer, Emmett and Teller
capex	capital expenditure
μCT	micro-Computed Tomography
CFD	Computational Fluid Dynamics
CV	Cyclic Voltammetry
DC	Direct Current
DIW	Direct Ink Writing
DLP	Digital Light Processing
EBM	Electron Beam Melting
ECPB	Electron-Coupled-Proton Buffer
ECSA	Electrochemically Active Surface Area
EDL	Electrical Double Layer
EPDM	Ethylene Propylene Diene Monomer
FEGSEM	Field Emission Gun Scanning Electron Microscope
GHG	Greenhouse Gases
HER	Hydrogen Evolution Reaction
HHV	Higher Heating Value

HTO	Hydrogen To Oxygen
ICP	Inductively Coupled Plasma
IEA	International Energy Agency
LBM	Laser Beam Melting
LDH	Layered Double Hydroxide
LHV	Lower Heating Value
NZE	Net Zero Emissions
OCP	Open Circuit Potential
OER	Oxygen Evolution Reaction
OES	Optical Emission Spectrometer
opex	operational expenditure
OTH	Oxygen To Hydrogen
PBI	polybenzimidazole
PEM	Proton Exchange Membrane
PFSA	perfluorosulfonic acid
PGM	Platinum Group Metals
PTF	Porous Transport Foam
PTFE	polytetrafluoroethylene
PU	polyurethane
PV	photovoltaic
PWM	Pulse Width Modulation

redox	reduction–oxidation
RLC	Resistive-inductive-capacitive
RTD	Residence Time Distribution
SHE	Standard Hydrogen Electrode
SLM	Selective Laser Melting
SMR	Steam Methane Reforming
SOE	Solid Oxide water Electrolysis
TPMS	Triply Periodic Minimal Surfaces
ZCS	Zero Current Switch
ZVS	Zero Voltage Switch
2-D	Two-dimensional
3-D	Three-dimensional

List of symbols

Subscripts/superscripts	Meaning
$\circ$	standard state
<i>a</i>	anodic
<i>air</i>	air
<i>c</i>	(a) cathodic (b) capacitive
<i>cell</i>	cell
<i>e</i>	electrolyte
<i>eff</i>	effective
<i>electric</i>	electric
<i>energetic</i>	energetic
<i>eq</i>	equilibrium
<i>f</i>	(a) faradaic (b) forward
<i>faraday</i>	faraday
<i>i/j</i>	characteristic of compound i/j
<i>L</i>	inductive
<i>l</i>	limiting
<i>m</i>	metal
<i>n</i>	normal

<i>s</i>	separator
<i>sol</i>	solution
<i>strut</i>	strut
<i>tn</i>	thermo-neutral
<i>voltage</i>	voltage
<i>wb</i>	without bubbles
<i>zirfon</i>	zirfon
Ω	ohmic

Roman symbols	Meaning	Usual units
<i>a</i>	activity	none
<i>A</i>	surface area	cm ²
<i>a_v</i>	electrochemically active volumetric surface area	m ² ·m ⁻³
<i>b</i>	Tafel slope	V·dec ⁻¹
<i>c</i>	specific capacitance	F·cm ⁻²
<i>C</i> [*]	bulk concentration	mol·cm ⁻³
<i>C_D</i>	double-layer capaciance	F
<i>D</i>	(a) diffusion coefficient	m ² ·s ⁻¹
	(b) pore diameter	m
<i>E</i>	potential vs. a reference	V

E_{act}	activation energy	$\text{J}\cdot\text{mol}^{-1}$
f	fugacity of compound i	none
F	(a) Faraday constant	$\sim 96,485 \text{ C}\cdot\text{mol}^{-1}$
	(b) drag coefficient	m^{-1}
f_g	fraction of the total product forming gas bubbles	none
G	Gibbs free energy	J
H	enthalpy	J
i	current	A
j	current density	$\text{A}\cdot\text{cm}^{-2}$
j_0	exchange current density	$\text{A}\cdot\text{cm}^{-2}$
k	(a) ionic conductivity	$\text{S}\cdot\text{m}^{-1}$
	(b) rate constant	s^{-1}
K	Darcian permeability	m^2
l	interelectrode distance	m
L	(a) TPMS lattice size	m
	(b) electrode thickness	m
m	molality	$\text{mol}\cdot\text{kg}^{-1}$
M	molarity	$\text{mol}\cdot\text{l}^{-1}$
$\dot{m}$	production rate	$\text{mol}\cdot\text{s}^{-1}$
m_d	sample dried mass	g

m_t	mass transfer coefficient	$\text{cm}\cdot\text{s}^{-1}$
m_w	sample submerged mass	g
n	amount of substance	mol
N_m	MacMullin number	none
P	pressure	Pa bar
P_s	solution vapor pressure	Pa bar
P_w	vapor pressure of pure water	bar
P_{el}	electric power	W
Q	volumetric flow	$\text{cm}^3\cdot\text{s}^{-1}$
R	(a) universal gas constant	$\sim 8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
	(b) resistance	Ω
R_r	bubble departure radius	m
Re	Reynolds number	none
S	entropy	$\text{J}\cdot\text{K}^{-1}$
Sc	Schmidt number	none
S_v	Specific surface area	$\text{m}^2\cdot\text{m}^{-3}$
Sh	Sherwood number	none
T	temperature	K

t	(a) time	s
	(b) TPMS parameter	none
t_p	pulse period	s
t_r	residence time	s
ν	(a) stoichiometric number	none
	(b) scan rate	$V \cdot s^{-1}$
V	volume	m^3
ν_d	fluid superficial velocity	$m \cdot s^{-1}$
V_m	Solid volume fraction	none
x	separator thickness	M
	porosity	none
x, y, z	cartesian coordinates	none
X_a	conversion	none
z	stoichiometric electron number	none
Z	impedance	Ω

Greek symbols	Meaning	Usual units
α	charge transfer coefficient	none
ϵ	volumetric gas fraction.	none
η	(a) efficiency	none
	(b) overpotential	V
θ_b	bubble coverage	none

μ	chemical potential	$\text{J}\cdot\text{mol}^{-1}$
μ_e	electrochemical potential	$\text{J}\cdot\text{mol}^{-1}$
μ_f	fluid dynamic viscosity	$\text{Pa}\cdot\text{s}$
ρ	density	$\text{kg}\cdot\text{m}^{-3}$
σ	electronic conductivity	$\text{S}\cdot\text{m}^{-1}$
ϕ	electric potential	V

Chapter 1: Introduction

It is widely known that the global temperature is rising, and the scientific consensus firmly attributes global warming to anthropogenic activities [1]. Between 2011 and 2020, the Earth's average temperature was approximately 1.1°C higher than the average temperature recorded between 1850 and 1900. The best estimate predicts that 97% of this increase (i.e., 1.07°C) was caused by human activities, principally through the emission of greenhouse gases, dominated by the rise in the atmospheric concentration of carbon dioxide (47% increase since 1750), methane (156%), and nitrous oxide (23%), partially masked by aerosol cooling. This increase is unprecedented and compares to the natural multi-millennial changes between glacial and interglacial periods over at least the past 800,000 years. Despite the scientific knowledge about global warming, global greenhouse gas emission continues to increase, causing a rapid increase in Earth's average temperature, as shown in Fig. 1 [2].

Human-caused climate change negatively impacts nature and society. There is an increase in the frequency of extreme weather events such as heatwaves, heavy precipitation, droughts, and tropical cyclones, which increases human mortality and morbidity. Furthermore, there is a change in precipitation patterns, the melting of ice-covered surfaces, and the rise in sea levels. As a consequence of all these effects, food and water security has been compromised, and there was an increase in human and animal diseases [2]. Climate change adversely affects economies, particularly damaging agriculture and causing human mortality. Considering recent estimates for the social cost of carbon

(\$185·tCO₂⁻¹) [3] and the current greenhouse gas emissions from Fig. 1, roughly 10 trillion dollars are lost per year due to damages caused by climate change. These adverse effects disproportionately affect vulnerable communities, which have contributed the least to climate change. Least developed countries and small island developing states, who have much lower per capita greenhouse gases (GHG) emissions than the global average, have high vulnerability to climate hazards.

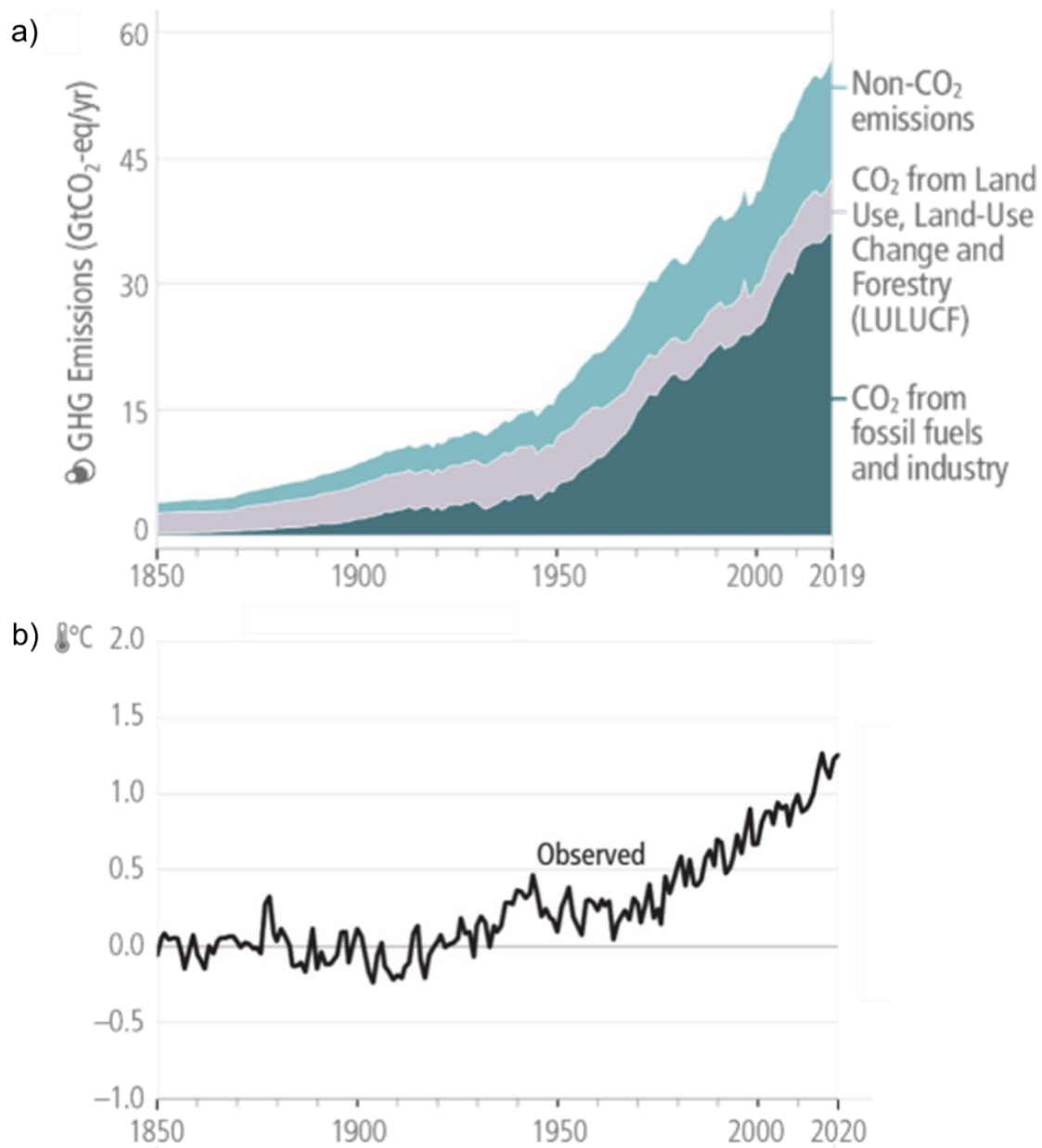


Fig. 1. a) Yearly anthropogenic GHG emissions over the past years, and b) variation in mean global temperature compared to the value at 1850. Adapted from ref. [2].

Inside countries, vulnerability is higher for Indigenous Peoples and in regions of low- income. Approximately 3.3 to 3.6 billion people live in a context of high vulnerability [2]. Moreover, if no action is taken to mitigate global warming, 16% of species are predicted to be extinct [4]. For example, large-scale coral reef dissolution may occur if the temperature rise reaches 2.5°C [5]. Extinction risk is the highest in South America with 23% of species threatened of extinction [4]. Finally, it is worth noticing that ecosystem and human vulnerability are interdependent [2].

To address these threats, the international community has united under climate agreements like the United Nations Framework Convention on Climate Change (1992) [6], Kyoto Protocol (1997) [7], and Paris Agreement (2015) [8]. These agreements aim to enhance national commitments to combat global warming, increase public awareness, and accelerate efforts. Essential to achieving the objectives outlined in these agreements is the attainment of net zero anthropogenic CO₂ emissions. This goal requires implementing measures that include transitioning to zero or low-emission fuels. The urgency for alternative energy sources grows as environmental risks linked to global warming become more pronounced [2].

To guide the necessary actions, various normative scenarios have been developed to control global temperatures. One particularly noteworthy scenario is the International Energy Agency (IEA) Net Zero Emissions (NZE) by 2050 scenario, which aligns closely with the goals outlined in the Paris Agreement [9]. This scenario presents a viable pathway towards achieving net zero emissions by 2050, in line with the long-term temperature targets set forth in the agreement.

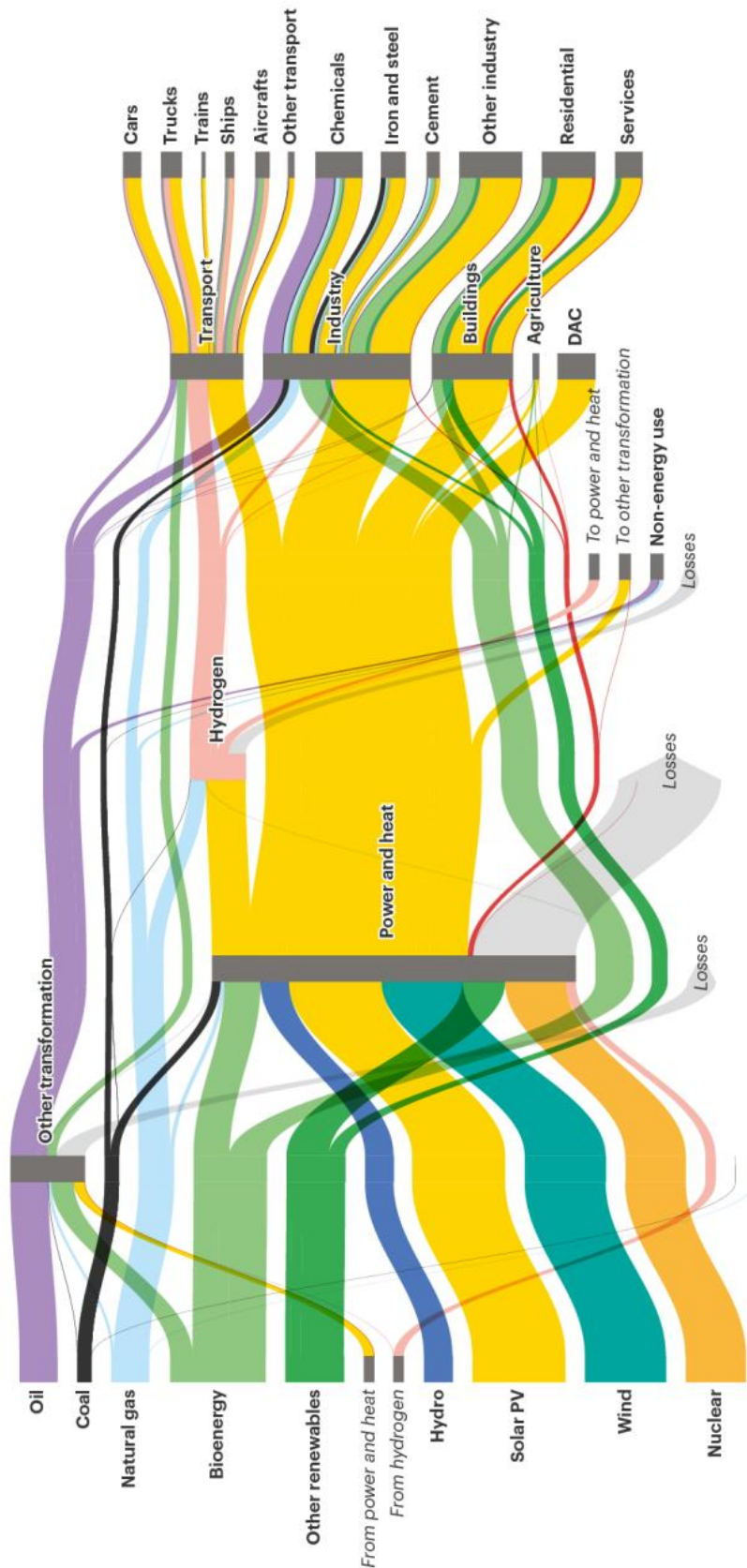


Fig. 2. Global energy flows in the IEA Net Zero Emissions by 2050 scenario. From ref. [10].

The strategies present in the IEA roadmap include, by order of impact, electrification (27% of total emissions reduction); carbon capture utilization and storage (18%); behavioral change and avoided demand (16%); wind and solar (12%); hydrogen and hydrogen-based fuels (11%); switching from coal and oil to natural gas, nuclear, hydropower, geothermal, concentrating solar power or marine (7%); energy efficiency (6%); and bioenergy (3%) [11].

As shown in Fig. 2, hydrogen plays a pivotal role as an energy carrier in this scenario, accounting for 13% of the global final energy demand in 2050. This is because there are energy needs where the main energy carrier, electricity, cannot easily or economically replace fossil fuels. For some of these needs, like aviation, sustainable bioenergy can be used, but limitations on supply make it necessary to use a mix of solutions, with hydrogen and hydrogen-based fuels being one of them [11]. Additionally, since many renewable energy sources generate energy intermittently, there is a need for long-term seasonal energy storage and load balancing, and hydrogen offers a solution to address these needs [12,13]. Furthermore, hydrogen is flexible: it can, for example, be converted to electricity through fuel cells [14] or gas turbines [15] and to heat through burners [16]. It can also be converted to other fuels, like ammonia through the Haber-Bosch process [17] and kerosene through the Fischer-Tropsch reaction [18].

In the IEA NZE by 2050 scenario, about 40% of the hydrogen produced in 2050 will be used for transport, either in the form of hydrogen or in the form of hydrogen-based fuels, as shown in Fig. 3. Hydrogen and ammonia are expected to control the shipping sector [11], mainly for fuel cell-powered long-range ships [19]. About a quarter of road

transport will be driven by hydrogen, especially for long-haul heavy-duty trucks [11]. For these vehicles, fuel cells are considered more appealing with respect to electric batteries, which cannot guarantee long distances without stopping and recharging [20]. About a third of the aviation sector will be propelled by hydrogen-based synthetic fuels, like synthetic kerosene [11], as electric planes (battery or fuel-cell-driven) are unable to fly long distances [21].

Hydrogen will also be important to the industry. It is expected that 20% of iron and steel production will come from hydrogen-based direct reduced iron facilities [11], where coal is replaced by hydrogen as the reducing agent [22]. Furthermore, it is projected that hydrogen will provide heat to the industry, especially high-temperature heat. As an

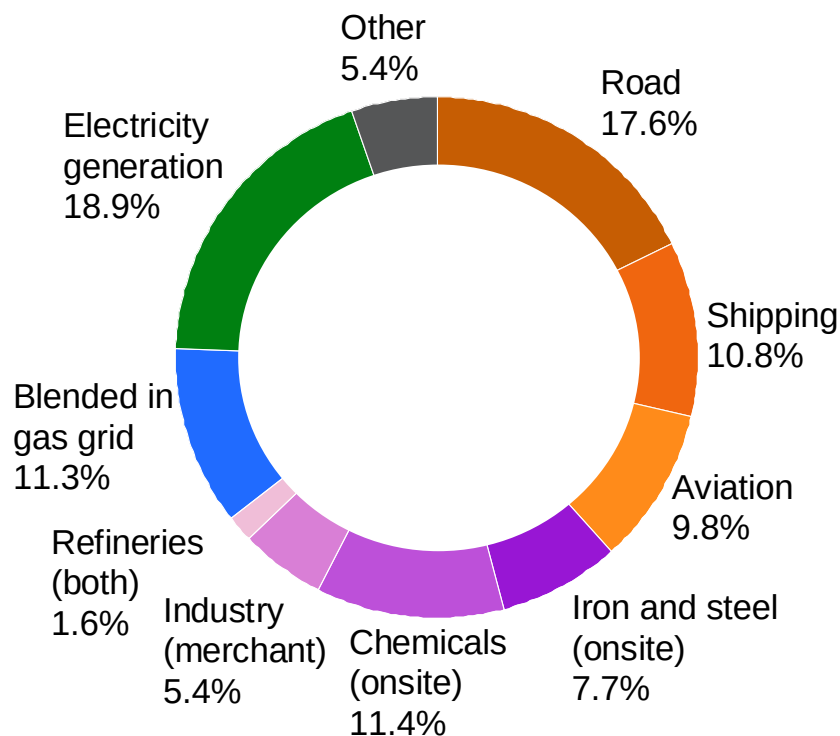


Fig. 3. Global hydrogen and hydrogen-based fuel use in 2050 according to the IEA NZE by 2050 scenario [11]. Onsite indicates that hydrogen was produced within the industrial facility where it is consumed, while merchant indicates that it was produced by one company to sell to another. Refineries include both onsite and merchant.

example, it will provide around 10% of the thermal energy necessary in the cement industry. Moreover, it will be used to produce chemicals like ammonia and methanol [11].

About one-fifth of the global hydrogen in 2050 will be used to produce electricity, helping to balance seasonal fluctuations in electricity demand and offer, as hydrogen storage facilities have several orders of magnitude more capacity than battery storage projects. Hydrogen will also be used to increase electricity system flexibility through retrofitting existing gas-fired capacity to co-fire with hydrogen, together with some retrofitting of coal-fired power plants to co-fire with ammonia. It can also increase flexibility by being produced in regions and, at times, with surplus renewables-based capacity and from dedicated off-grid renewable power [11].

Hydrogen will also be blended in the existing gas network (15% in volume), and building gas boilers will be able to run on hydrogen [11]. Hydrogen is an appealing green alternative to provide heating and electricity to large commercial buildings, building complexes, and district energy networks [23].

In order to meet the growing demand for hydrogen as an energy carrier, different production methods have been developed, each with its own advantages and considerations. These methods are often classified and distinguished by different colors, which will be explained in the following paragraphs.

One classification is based on naturally occurring hydrogen (white hydrogen [24]), which is continuously generated underground [25]. It is present as free gas, adsorbed in inclusions, or dissolved [26].

Contrary to gas giants such as Jupiter and Saturn, which are mainly composed of hydrogen and helium, Earth's gravity is not high enough to hold such a light substance [27]; thus, reserves are not abundant. The estimated annual amount of natural hydrogen available at the Earth's surface is about 23 Mt [26], which could fulfill only 4% of the projected demand by 2050. Nevertheless, the exploration of white hydrogen is still in its early stages [25]. Fortunately, hydrogen is the most abundant element in the universe, and hydrogen atoms exist abundantly in chemical compounds [32], such as hydrocarbons and water. Consequently, molecular hydrogen can be generated through chemical reactions, leading to the other hydrogen classification colors.

Conventional methods for hydrogen production involve the use of fossil fuels without carbon capture (gray hydrogen) [28]. In 2021, almost all the produced hydrogen was gray: about 60% derived from natural gas through a process called steam methane reforming (SMR), 20% from coal, and the other 20% as a by-product of naphtha reforming in refineries. These processes result in the emission of approximately 900 Mt of carbon dioxide per year [29] (approximately 2.5% of total emissions, as from Fig. 1).

To reduce CO₂ emissions, the concept of coupling a unity of carbon capture utilization and storage to the fossil fuel-based hydrogen plant has emerged (blue hydrogen). Regrettably, this approach is relatively new and currently implemented in only very few facilities [30]. In the IEA NZE by 2050 scenario, it is projected that this method will account for approximately 40% of the total hydrogen production.

Fortunately, hydrogen production is not limited to fossil fuels, as it can also be derived from water in a carbon-free method called water electrolysis. This well-established technology is based on the application of a direct current to an aqueous solution to dissociate water into hydrogen and oxygen gas. Besides being carbon-free, electrolytic hydrogen has the advantage of reaching a high hydrogen purity that can reach up to 99.999 vol% [31]. Moreover, the produced oxygen can be economically used as well [32]. The classification of hydrogen, in this case, depends on the energy source used to generate the electricity applied in the electrolyzer, which is the electrochemical cell where water electrolysis occurs. If the electricity is sourced from the grid, the resulting hydrogen is classified as yellow. If it comes from renewable sources, it is referred to as green hydrogen, and if it comes from nuclear power plants, it is known as purple hydrogen [28]. According to the IEA scenario, green hydrogen will be the main production method in the net-zero society.

Concerns about water depletion arising from the conversion of water into hydrogen and oxygen might emerge, particularly regarding large-scale implementation of green hydrogen. However, achieving the predicted 11% reduction in GHG emissions, as outlined in the IEA NZE scenario with green hydrogen, would lead to less than a 1.1% increase in water withdrawal. At a production rate of 300 Mt of hydrogen per year, the required stoichiometric water volume stands around 2.7 billion m³ annually, a mere 0.07% of the world's current annual freshwater withdrawal (3,976 billion m³) [33]. If one adds to this the water required for the manufacturing and operation of green energy power plants combined with electrolyzers, one has 0.3% of the total water withdrawn

if the power source is wind turbines and 1.1% if it is solar panels [33]. Ref. [33] shows that, except from Trinidad and Tobago, hydrogen demand does not create water scarcity anywhere in the world if water scarcity is not already present.

There are three main water electrolysis technologies utilized for hydrogen production. The most mature and widely adopted method is alkaline water electrolysis (AWE), which currently holds a market share of approximately 70% [29]. This method utilizes an alkaline solution, typically potassium hydroxide (KOH), with a concentration of 5-7 M, operating within a temperature range of 70-90°C and pressures between 1-30 bar. It employs either a diaphragm or an anion exchange membrane, along with nickel-based electrodes [34]. AWE is known for its lower capital cost (€·kW⁻¹) compared to other methods [35], as it utilizes abundant and cost-effective materials [36].

The second technology is proton exchange membrane (PEM) electrolysis, accounting for around one-quarter of the current market share [29]. It utilizes perfluorosulfonic acid (PFSA) proton-exchange membranes as both the separator and the electrolyte (solid), operates at temperatures ranging from 50 to 80°C, and pressures up to 70 bar. Noble metals such as platinum (Pt) and iridium (Ir) serve as catalysts in this process [34]. However, it appears unlikely that the projected green hydrogen demand by 2050 can be met solely through PEM technology due to a significant imbalance in iridium supply and demand. The electrolyzer demand for iridium is projected to reach 32 tons per year (1 g of Ir per kWh output and 3,600 GW electrolyzer capacity) [11,37], far exceeding the current production rate of around 7 tons per year [38]. Furthermore, about 30% of the current Pt production would be needed

for electrolyzer production [37,39]. This imbalance poses a substantial obstacle to relying exclusively on PEM electrolysis and demands a drastic reduction in catalyst loading and a strong focus on recycling (Ir recycling rates higher than 90%) [38]. In contrast, alkaline electrolyzers offer a more sustainable alternative, requiring only 10% and 2% of current nickel and zircon production [37,39], respectively, to fulfill the green hydrogen demand by 2050. Moreover, PGMs (platinum group metals) are concentrated in one country. South Africa is responsible for about 92% and 71% of the global Ir and Pt production, respectively. As a consequence, the supply risk is much more elevated when compared to AWE materials. The supply risk for Ir and Pt is 3.2 and 1.8, respectively, while it is 0.5 for Ni and 0.8 for Zr. A value higher than 1 is considered high (critical) [40].

Lastly, there is solid oxide water electrolysis (SOE), which is still in the pilot demonstration stage. SOE utilizes Ytria-stabilized Zirconia as the separator and electrolyte, where O^{2-} acts as the electron carrier. This method operates at elevated temperatures between 700 and 850°C and atmospheric pressure. Perovskite-type anodes and Ni-based cathodes are employed as electrodes [34].

There are different challenges that green hydrogen technologies will face before being widely implemented. One of them is related to the rapid scale-up. In order to reach a net-zero society, the production of green hydrogen needs to increase radically from almost zero to approximately 300 Mt per year, according to the IEA NZE by 2050 scenario. In other terms, this demands an increase in the worldwide electrolyzer capacity by five orders of magnitude, going from the current 0.3 GW to 3,600 GW by 2050. To put it into perspective, this

represents a daily capacity increase of approximately 0.3 GW per day. Another challenge is related to the production cost, as it will guide the regional choice between blue and green hydrogen. If green hydrogen cannot be cost-competitive with blue hydrogen, it will not be produced [11].

Nowadays, the production cost of green hydrogen is about 2-3 times higher than that of blue hydrogen. This cost disparity is primarily influenced by the time-dependent costs of natural gas and electricity, with the cost of renewable electricity being the primary cost component for green hydrogen and natural cost being the primary cost component for blue hydrogen [34]. Over time, the cost of natural gas tends to increase as its reserves become scarcer [41], while the cost of renewable electricity tends to decrease as new technologies reach the market and economies of scale are achieved [42]. As a result, there is a long-term trend towards increased competitiveness of green hydrogen in comparison to blue hydrogen.

Nevertheless, simply reducing the cost of electricity is not enough to ensure the competitiveness of green hydrogen. It is also crucial to address its second largest cost component, which is the electrolyzer [34]. Scaling up green hydrogen plants is one approach to increase production rate and reduce costs, as shown in Fig. 4. Increasing the capacity of multi-stack systems to 50-100 MW and extending the power input that can be taken up by a single-stack electrolyzer to a few MW are potential strategies to reach cost parity with blue hydrogen [43], which has a levelized cost of about $2 \text{ €} \cdot \text{kg}^{-1}$ (green line in Fig. 4) [44]. Furthermore, this aligns with the scale of basic units of renewable electricity generation.

As shown in Fig. 4, the hydrogen cost reduction is much more pronounced for single stacks compared to multi-stacks as the power input increases. Therefore, there is significant interest in extending the power input of single stacks. This can be achieved by increasing the number of cells per stack and/or intensifying single-cell hydrogen production [43]. It is essential to notice that there is a limitation on the

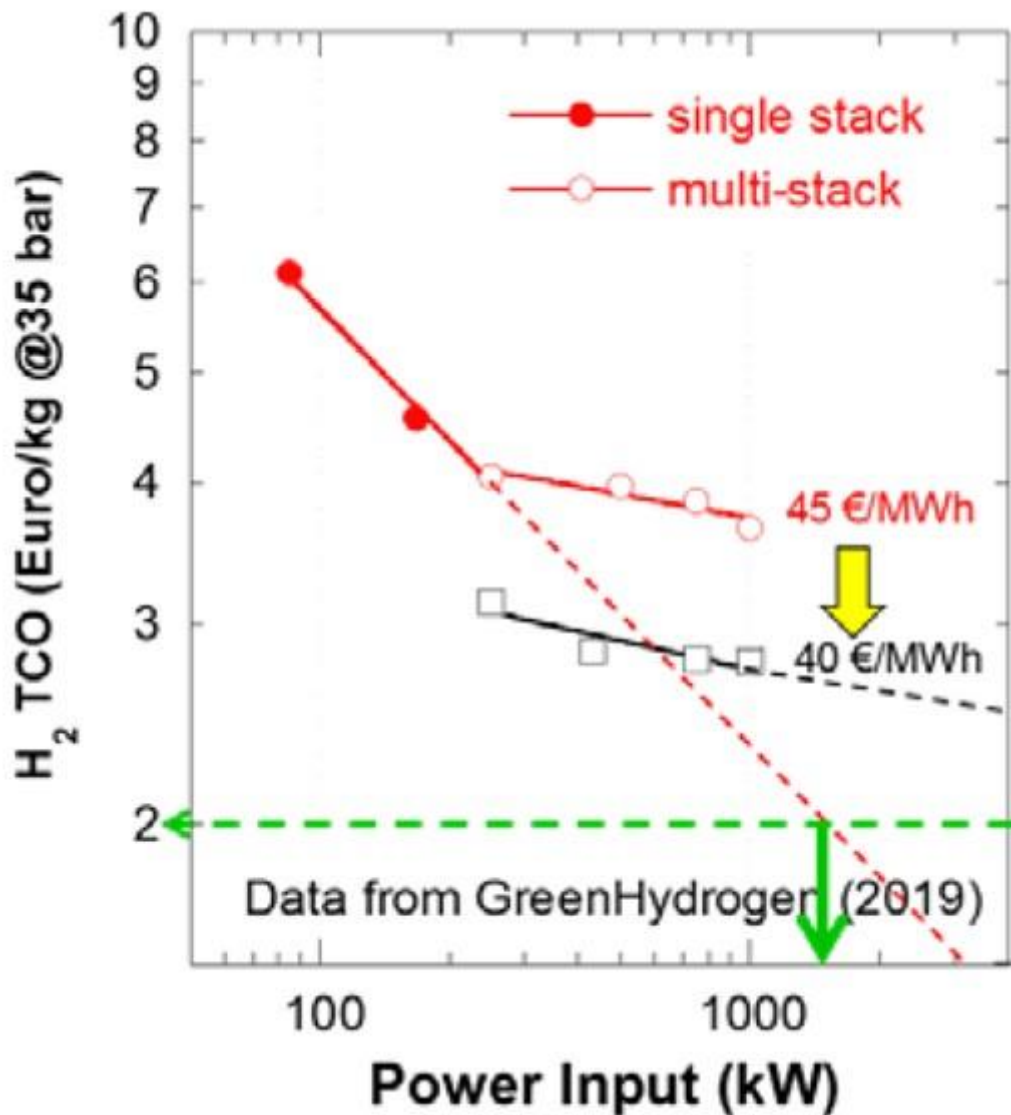


Fig. 4. Total Cost of Ownership of electrolytic H_2 , delivered at 35 bar, as a function of power input. Operational expenditure (opex) includes the use of electricity, water, and nitrogen (for purge), assuming a renewable electricity price of 40 and 45 $\text{€} \cdot \text{MWh}^{-1}$, respectively. From ref. [43].

number of cells that can be stacked, as beyond a certain threshold, stacking more cells becomes challenging due to the increased shunt current, which negatively impacts overall efficiency [45]. Consequently, once this limit is reached, the primary avenue to enhance the power input of a stack is to intensify the hydrogen production process within individual cells, and this Ph.D. thesis is focused on that.

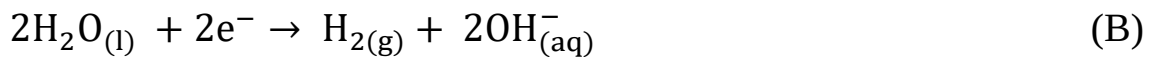
In this chapter, the research topic, context, and significance were presented. Ch. 2 discusses the fundamental concepts of water electrolysis, covering thermodynamics, kinetics, ohmic resistances, bubble effect, efficiencies, and the theoretical aspects behind 3-D electrodes and pulsed electrolysis. Ch. 3 reviews existing knowledge and research related to alkaline electrolyzers and pulsed water electrolysis. Ch. 4 will explain the research objectives. Ch. 5 presents a detailed description of the materials and methods used in the research. The experimental work is divided per intensification strategy. Chs. 6 and 7 study 3-D flow-by foam-shaped electrodes. Ch. 8 discusses the effect of the geometry of 3-D printed electrodes on bubble removal. Then, Ch. 9 studies the integration of this type of electrode with a pulsed power supply. Conclusions and perspectives are outlined in Ch. 10, and the references are presented at the end of this work.

Chapter 2: Fundamentals

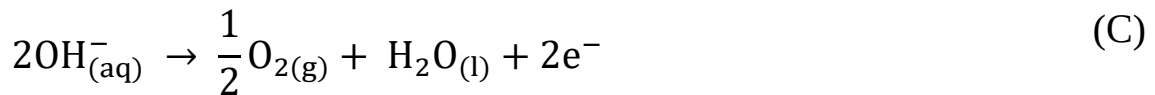
Water electrolysis was discovered in 1789 by Van Troostwijk and Deiman, who used an electrostatic generator to decompose water into hydrogen and oxygen. Soon after, in 1800, Carlisle and Nicholson utilized Volta's newly invented voltaic pile to split water molecules [46]. Since then, this process has been extensively studied and utilized for various applications. The overall reaction is expressed as follows:



and if the medium is alkaline, this reaction can be decoupled in a cathodic reaction (where reduction occurs):



and an anodic one:



where oxidation takes place.

Understanding the principles of water electrolysis is essential for optimizing the performance and efficiency of electrolysis systems. This chapter will provide an overview of the fundamentals of water electrolysis, with a focus on the thermodynamics, kinetics, and mass transport resistances of the process. The chapter is divided into seven sections: the first section will cover the thermodynamics of water electrolysis, including the voltage requirements and how it varies with pressure and temperature; the second section will cover the kinetics of water electrolysis, including the reaction mechanisms in alkaline media

and the most suitable catalysts; the third section will cover transport resistances, including the transport of electrons and ions; the fourth section covers the effect of bubbles in gas evolving electrodes; the fifth will explain how to estimate efficiency; the sixth section, the fundamentals of 3-D electrodes, including mass transfer, flow resistance, and potential distribution; the seventh chapter explain the theory of pulsed electrolysis. By the end of this chapter, the reader will have a fundamental understanding of the key principles underlying the water electrolysis process, which can be applied to the design and optimization of electrolysis systems for hydrogen production.

2.1 Thermodynamics of water electrolysis

The electrochemical potential of a compound, μ_{ei} ($\text{J}\cdot\text{mol}^{-1}$), is defined as the sum of the chemical potential and a molar-charge/field interaction term [47]:

$$\mu_{ei} = \mu_i + z \cdot F \cdot \phi \quad (1)$$

with z the stoichiometric electron number, F the Faraday constant ($\sim 96,485 \text{ C}\cdot\text{mol}^{-1}$), and ϕ the electric potential of the phase in question (V). The chemical potential (μ_i) is defined as the differential of a mixture's Gibbs free energy (J) relative to the amount of the compound [47]:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,n_j} \quad (2)$$

The general formula for electrochemical equilibria was proposed in 1889 by Walther Nernst [48], and it gives the equilibrium potential (V) of a given electrochemical reaction [49]:

$$\Delta\phi_{eq} = \frac{\sum v_i \cdot \mu_i}{z \cdot F} = \frac{-\Delta G}{z \cdot F} \quad (3)$$

This relation can be easily derived from the definition of equilibria, $\sum v_i \cdot \mu_{ei} = 0$. The electrochemical potential can also be defined as a function of a standard (1 bar) potential [49]:

$$\Delta\phi_{eq} = \Delta\phi_{eq}^\circ + \frac{R \cdot T}{z \cdot F} \cdot \sum v_i \cdot \ln(a_i) \quad (4)$$

where R is the universal gas constant ($8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), T is the temperature (K), a is the activity or the fugacity (dimensionless), depending on the state, and [49]:

$$\Delta\phi_{eq}^\circ = \frac{-\Delta G^\circ}{z \cdot F} \quad (5)$$

Standard Gibbs free energy can be calculated as a function of the temperature [50]:

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (6)$$

with H the enthalpy (J), S the entropy ($\text{J} \cdot \text{K}^{-1}$). Eq. (4) shows a difference in electric potential between two electrodes, but it is convenient to decouple the two reactions and define a potential, E , for each one. Consequently, the potential of the standard hydrogen electrode (SHE) was set at zero for all temperatures [50]:

$$Pt_{(s)} | H_{2(g)} | H_{(aq)}^+ \quad E^\circ = 0 \text{ V}$$

with hydrogen ion activity and hydrogen gas fugacity at 1. Therefore, one has for the cathode:

$$E_c = E_{H_2O/H_2}^\circ - \frac{R \cdot T}{2 \cdot F} \ln \frac{(f_{H_2}) \cdot (a_{OH^-})^2}{(a_{H_2O})^2} \quad (7)$$

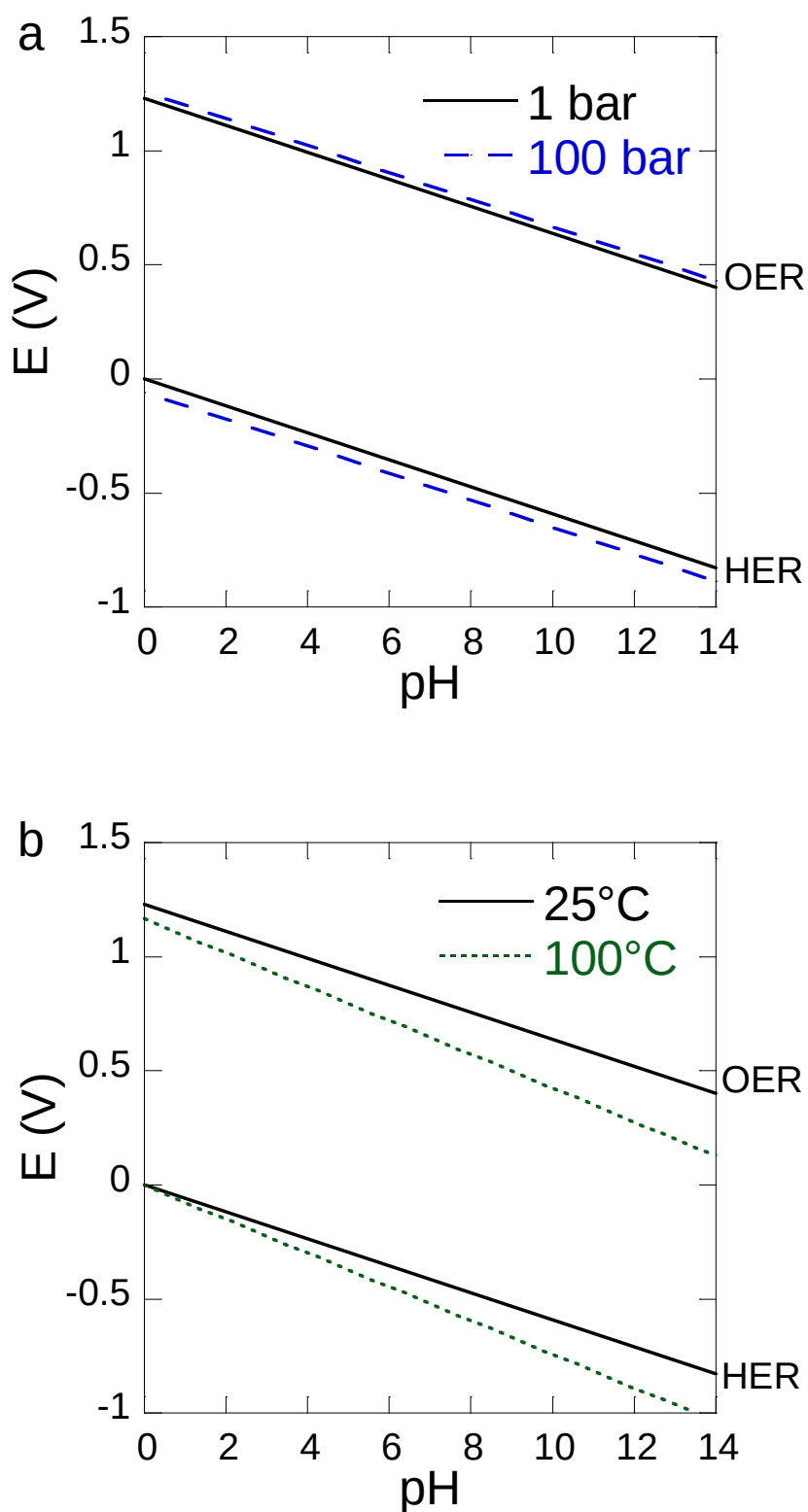


Fig. 5. Pourbaix diagram for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) at a) 25°C and different pressures, and b) 1 bar and different temperatures. Constructed based on thermodynamic data from ref. [50].

and for the anode:

$$E_a = E_{OH^-/O_2}^\circ + \frac{R \cdot T}{2 \cdot F} \ln \frac{(f_{O_2})^{1/2} \cdot (a_{H_2O})}{(a_{OH^-})^2} \quad (8)$$

with the potential in volts.

The cell voltage at equilibrium is given by the difference between the anode and the cathode:

$$\Delta E_{eq} = \Delta E_{eq}^\circ + \frac{R \cdot T}{z \cdot F} \ln \frac{(f_{H_2}) \cdot (f_{O_2})^{1/2}}{(a_{H_2O})} \quad (9)$$

Marcel Pourbaix (1904-1998) proposed to represent this equilibrium graphically in a plot known as the potential-pH diagram or Pourbaix diagram [49], as shown in Fig. 5. This figure clearly shows that equilibrium cell voltage does not depend on pH. Eq. (3) shows that the equilibrium cell voltage depends on the variation of Gibbs free energy. Its value determines the minimum thermodynamic voltage necessary to split water, but it gives no information on the heat being produced or consumed during the process. What gives this information is the so-called thermoneutral voltage [51]:

$$\Delta E_{tn} = \frac{-\Delta H}{z \cdot F} = \Delta E_{eq} + \frac{T \cdot \Delta S}{z \cdot F} \quad (10)$$

Below this voltage, the reaction is endothermic, and above it, exothermic.

As shown in Fig. 6, the equilibrium cell voltage increases with pressure and decreases with temperature. The thermoneutral voltage, on the other hand, decreases with pressure and increases with temperature.

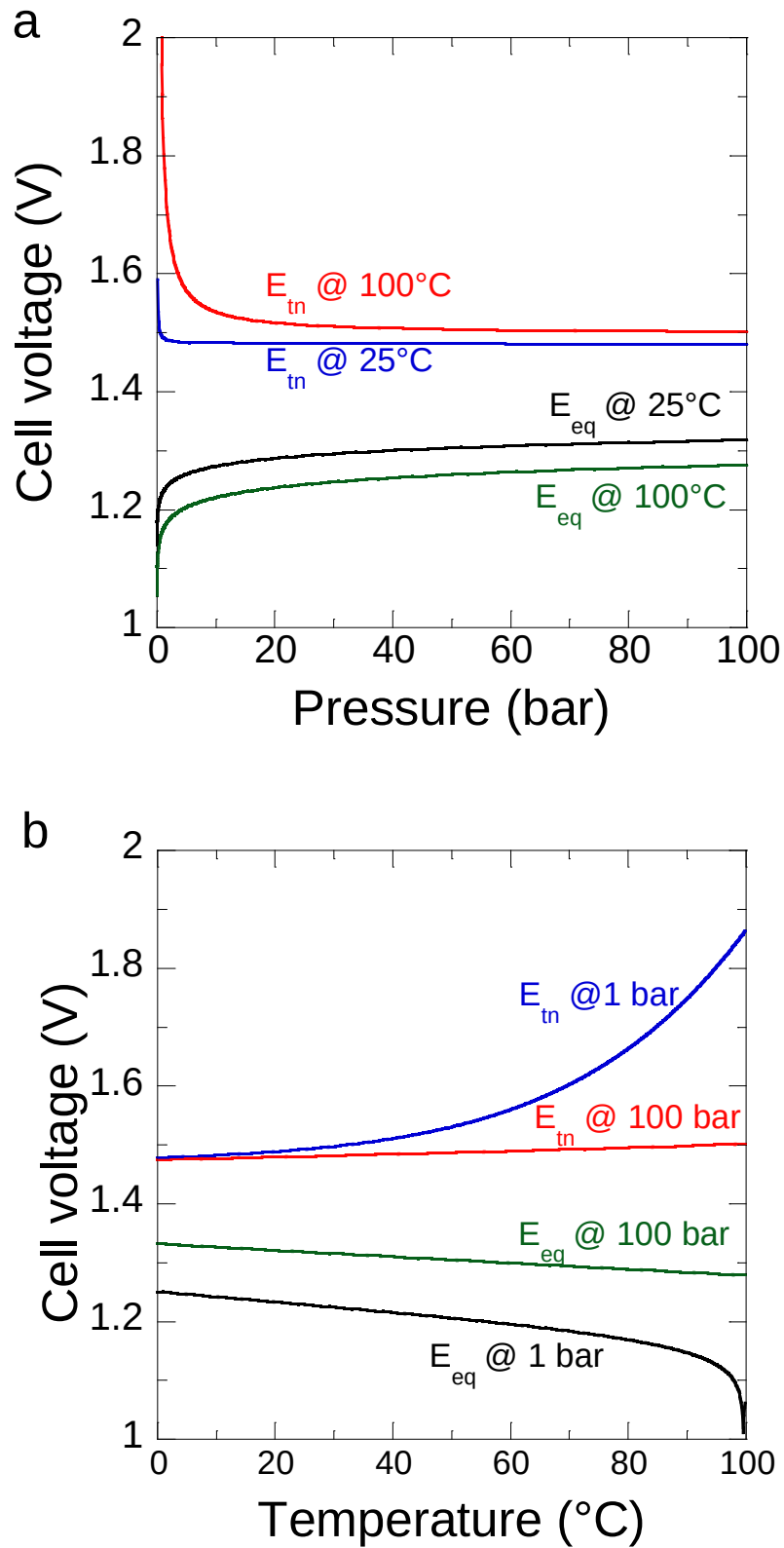
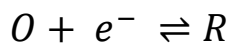


Fig. 6. Equilibrium and thermoneutral cell voltage as a function of a) pressure and b) temperature. A detailed explanation of the estimation method can be found in refs. [52,53].

2.2 Kinetics of water electrolysis

A general reduction-oxidation (redox) reaction involving one electron transfer can be represented as:



with O the oxidized and R the reduced form. Its kinetics is given by the so-called Butler-Volmer equation [54]:

$$\frac{j}{j_0} = \exp(\alpha_a \cdot f \cdot \eta) - \exp(-\alpha_c \cdot f \cdot \eta) \quad (11)$$

This equation shows the ratio between the current density, j ($\text{A}\cdot\text{cm}^{-2}$), and the exchange current density, j_0 ($\text{A}\cdot\text{cm}^{-2}$). The latter is the magnitude of both cathodic and anodic current when the electrode-electrolyte potential is at its equilibrium value (when the total current is null), and it is temperature dependent, following the Arrhenius equation:

$$j_0 = A \cdot \exp\left(\frac{-E_{act}}{R \cdot T}\right) \quad (12)$$

with A a pre-exponential factor and E_{act} the activation energy ($\text{J}\cdot\text{mol}^{-1}$). α_a and α_c are the transfer coefficients for the anodic and cathodic reaction, respectively. The η in Eq. (11) is the overpotential (V), which is the difference between the instantaneous electrode-electrolyte potential difference and its equilibrium value, and [54]:

$$f = \frac{F}{R \cdot T} \quad (13)$$

Eq. (11), as written, is found in engineering textbooks (e.g., ref. [55]) and is compatible with multi-electron transfer processes [54]. It should be used only when the applied current is maintained at a sufficiently

low level to ensure that the surface concentrations remain relatively unchanged compared to the bulk values. Otherwise, the effect of mass transfer should be considered [56]:

$$\frac{j}{j_0} = \left(1 - \frac{j}{j_{l,a}}\right) \cdot \exp(\alpha_a \cdot f \cdot \eta) - \left(1 - \frac{j}{j_{l,c}}\right) \cdot \exp(-\alpha_c \cdot f \cdot \eta) \quad (14)$$

with $j_{l,a}$ ($\text{A} \cdot \text{cm}^{-2}$) and $j_{l,c}$ ($\text{A} \cdot \text{cm}^{-2}$) the limiting current density for the anodic and cathodic reaction, respectively, such as [57]:

$$j_l = z \cdot F \cdot m_t \cdot C^* \quad (15)$$

with m_t the reactant mass transfer coefficient ($\text{cm} \cdot \text{s}^{-1}$), given by the ratio between the diffusion coefficient and the thickness of the diffusion layer, and C^* is the reactant concentration at the bulk ($\text{mol} \cdot \text{cm}^{-3}$) [57].

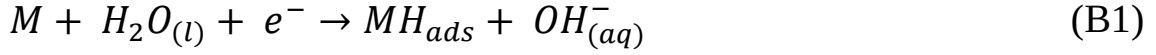
From a practical point of view, what is measured is current, and the current density is estimated by dividing the measured current by the active surface area. Nevertheless, gas bubbles are produced during water electrolysis; thus, part of the electrode surface can be covered by these bubbles, reducing the surface area. Considering this bubble effect, Eq. (14) can be expressed as a function of the measured current, i , and the bubble coverage, θ_b [58]:

$$\frac{i}{A \cdot (1 - \theta_b)} = j_0 \cdot \left[\left(1 - \frac{i}{A \cdot (1 - \theta_b) \cdot j_{l,a}}\right) \cdot \exp(\alpha_a \cdot f \cdot \eta) - \left(1 - \frac{i}{A \cdot (1 - \theta_b) \cdot j_{l,c}}\right) \cdot \exp(-\alpha_c \cdot f \cdot \eta) \right] \quad (16)$$

For Eqs. (11), (14), and (16), when the overpotential is large and positive (anode), the second term can be neglected. When, on the other hand, it is large and negative (cathode), it is the first term that can be neglected.

2.2.1 Hydrogen evolution reaction (HER)

In alkaline media, hydrogen is produced following reaction A. The first step of this reaction is the Volmer reaction [60]:



with MH_{ads} representing a hydrogen atom adsorbed in the electrode. The subsequent step is either the Tafel reaction [60]:



or the Heyrovsky reaction [60]:

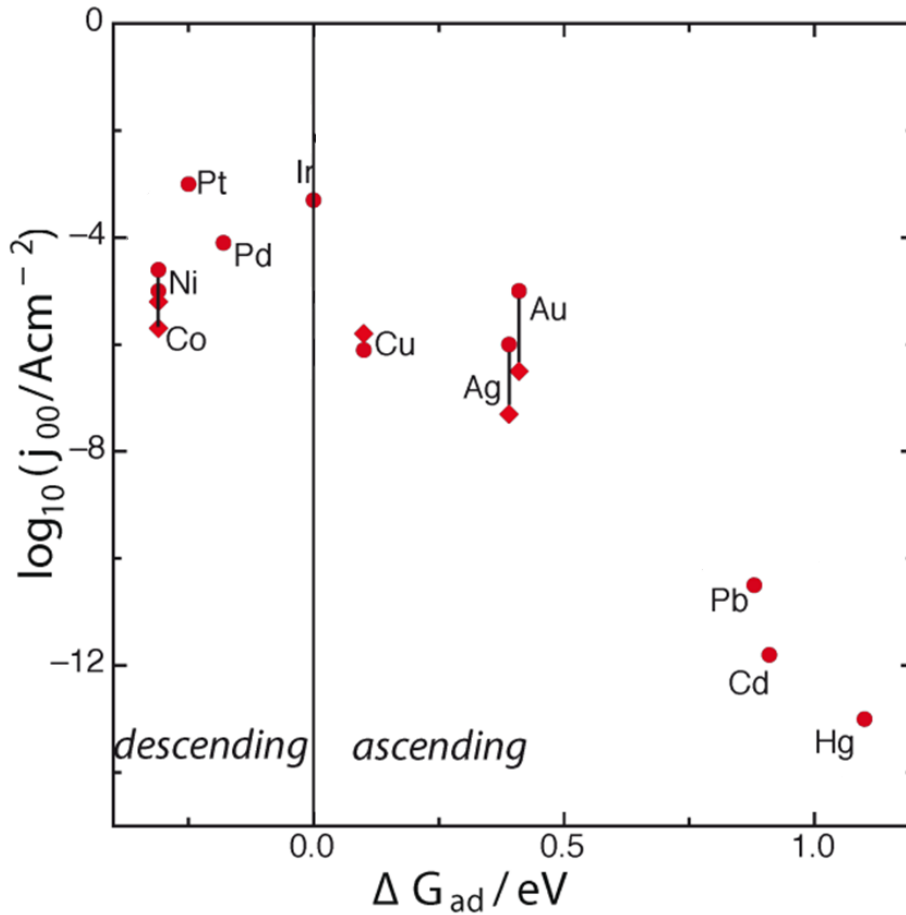
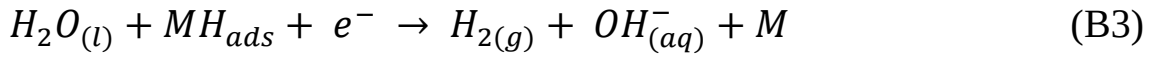


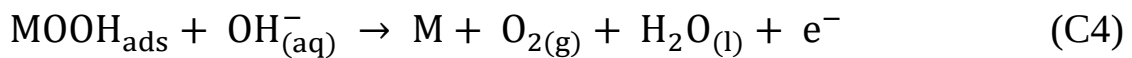
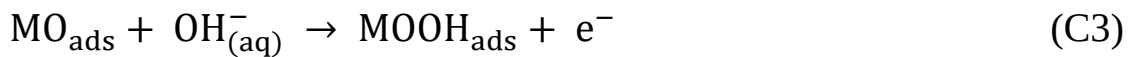
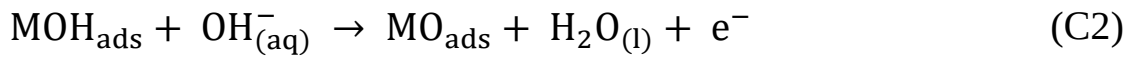
Fig. 7. Exchange current densities for HER in alkaline media as a function of the energy of adsorption. Adapted from ref. [59].

with the strength of the M-H bond being essential for the HER kinetics [61]. According to the Sabatier principle, ideally, the free energy of the reaction intermediate (MH_{ads}) with respect to reactants should be close to zero, $\Delta G_{ad} = 0$. If the bond is too weak ($\Delta G_{ad} > 0$), the Volmer step is thermodynamically unfavorable. On the other hand, a strong bond ($\Delta G_{ad} < 0$) disfavors the second step (Tafel/Heyrovsky) [62]. Fig. 7 summarizes this reasoning, showing that, in practice, the metals with the highest exchange current densities are the ones with a ΔG_{ad} near zero. The Tafel slope for this reaction is known to be between 30 and 120 $mV \cdot dec^{-1}$, depending on the rate-determining step and on the overpotential [61].

As shown in reaction B (step 1), the source of protons in an alkaline medium is water. In an acidic medium, however, it is solvated protons. Since the formation of hydrogen intermediates from water is slower than when they are formed from solvated protons, alkaline HER has a slower kinetics than acidic HER [61].

2.2.2 Oxygen evolution reaction (OER)

This reaction is commonly assumed to consist of four electron/proton transfer steps [63]:



The total change in energy free energy of this reaction is 4.92 eV. Since it comprises four steps, in an ideal catalyst, each step should present a difference in free energy of one-fourth of this value, i.e., 1.23 eV. Nevertheless, the difference in the free energy between $^*\text{OH}$ and $^*\text{OOH}$ is fixed at 3.2 ± 0.2 eV. Consequently, the best possible catalyst would have a difference in free energy between $^*\text{OH}$ and $^*\text{O}$ of 1.6 eV (half of the fixed 3.2 eV) [65]. As a consequence, the catalyst activity for the OER is represented as a function of this parameter [66], as shown in Fig. 8. This figure also shows that due to this fixed free energy difference, even for the best possible catalyst, there is already a minimum overpotential of 0.3 mV. As a consequence, the kinetics of this reaction is slower than the one of the HER [63].

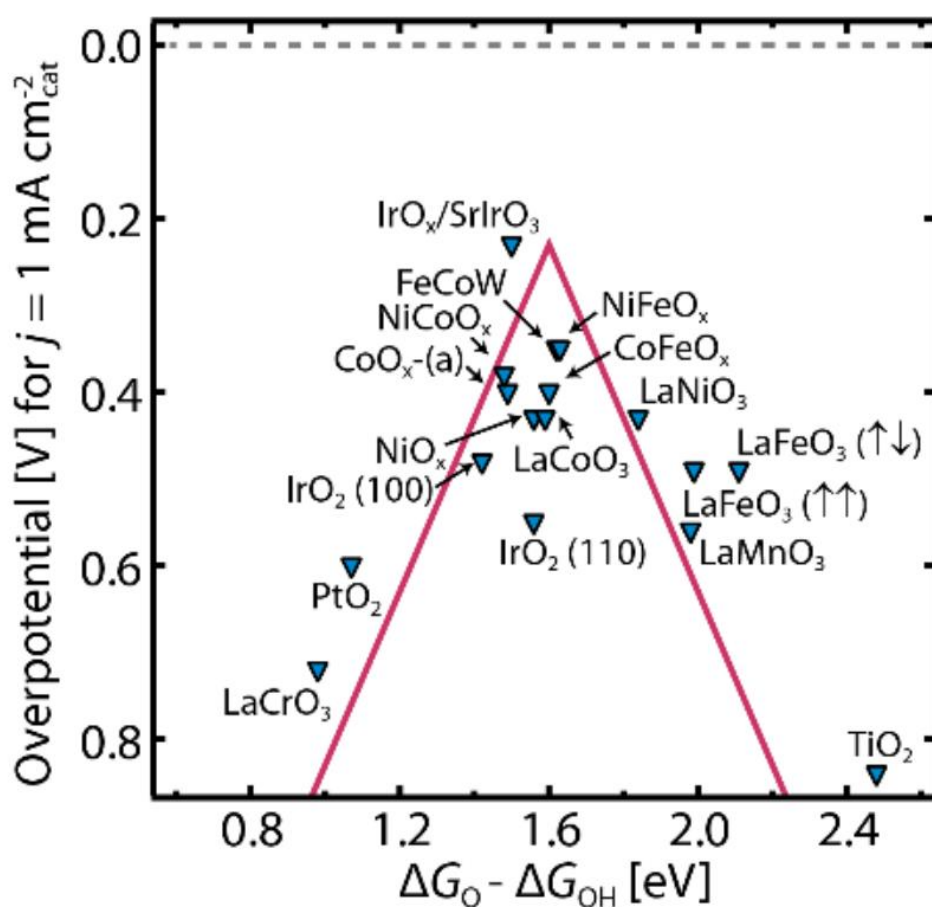


Fig. 8. OER overpotential for metal oxides as a function of the difference in free Gibbs energy between $^*\text{O}$ and $^*\text{OH}$. From ref. [64].

2.3 Ohmic resistances

Apart from the thermodynamic and kinetic contributions to the cell voltage, electrical resistances present in an electrolyzer also contribute to the final cell voltage. They increase the voltage following Ohm's law [67]:

$$\Delta E = i \cdot R_{\Omega} \quad (17)$$

with i the current (A) and R_{Ω} the resistance (Ω).

The first ohmic contribution arises from the electrical circuit, including the resistance of wires, connectors, and electrodes. It can be reduced by reducing cable length, increasing cross-sectional area, or both [67]. As electrolytic cells are made by stacking different components, there is also ohmic resistance related to the electrical contact between each component. It can be reduced by increasing the bolt torque [68].

The second one is related to the mass transfer of ions and includes the electrolyte and the separator resistance. The electrolyte resistance depends on the solution conductivity and distance between the electrodes [56]:

$$R_e = \frac{l}{A \cdot k_{eff}} \quad (18)$$

with l the interelectrode distance (m), k_{eff} the effective electrolyte conductivity ($S \cdot m^{-1}$), and A the cross-sectional area (m^2). As hydrogen bubbles are formed at the cathode and oxygen at the anode, they increase the electrolyte path, hence, causing a decrease in electrolyte conductivity, following the Bruggemann equation [69]:

$$k_{eff} = k_{wb} \cdot (1 - \epsilon)^{1.5} \quad (19)$$

with k_{wb} the conductivity without bubbles ($S \cdot m^{-1}$) and ϵ , the volumetric gas fraction. As a consequence, equation (18) can be rewritten as:

$$R_e = \frac{l}{A \cdot k \cdot (1 - \epsilon)^{1.5}} \quad (20)$$

The separator resistance is estimated in a similar way as for the electrolyte [67]:

$$R_s = \frac{x}{A \cdot k_s} \quad (21)$$

with x the separator thickness (m) and k_s its conductivity ($S \cdot m^{-1}$), normally specified by the fabricant.

To sum up, the cell voltage of an electrolyzer can be estimated as:

$$\Delta E_{cell} = \Delta E_{eq} + \sum \eta + \left[R_{electric} + \frac{(R_e + R_s)}{A} \right] \cdot i \quad (22)$$

This equation can be simplified to [70]:

$$\Delta E_{cell} = \Delta E_{eq} + b \cdot \log \left(\frac{j}{j_0} \right) + R_\Omega \cdot j \quad (23)$$

with b the sum of the Tafel slopes for the cathodic and anodic reaction, j the current density, j_0 the nonlinear average of the exchange current densities for the cathodic and anodic reaction.

2.4 Bubble effect

As shown previously, in gas evolving electrodes such as the ones from water electrolysis, gas bubbles cover the electrode surface, decreasing the available surface area and increasing the total current at constant potential (Eq. (16)). Bubbles also raise the electrolyte resistance (Eq.

(20)). Furthermore, the presence of bubbles disturbs current distribution, making it non-uniform [45]. It is quite complex to estimate bubble coverage. However, there are several quantities describing it [71]:

$$\theta_b = \frac{3 \cdot t_r}{8 \cdot R_r} \cdot f_g \cdot \eta_{faraday} \cdot \frac{j \cdot R \cdot T}{z \cdot F \cdot (P - P_s)} \quad (24)$$

with R_r the bubble departure radius (m), t_r the residence time (s), f_g the fraction of the total product forming gas bubbles, $\eta_{faraday}$ the Faraday efficiency (i.e., the fraction of the current used in the desired reaction), P the total pressure (Pa), and P_s the solution vapor pressure (Pa). This equation considers that bubbles are perfectly spherical, which is a good approximation for most of the aqueous electrolyte solutions.

The bubble departure radius clearly depends on the balance of interfacial tensions, which depends on the electrode potential. As the potential (and consequently the current) increases, the bubble departure radius decreases. An increase in temperature directly increases bubble coverage, being a variant in Eq. (24), but also indirectly increases it through the increase in vapor pressure [71]. The effect of pressure comes from experimental observations which demonstrated a reduction in bubble departure radius and a raise in the number of bubbles with the increase in pressure. The former effect was dominant and the result of an increased pressure was a decrease in bubble coverage [72,73]. One possible explanation for this observed effect is a reduction in the oversaturation factor (i.e., hydrogen concentration divided by solubility), which reduces the driving force for nucleation [74], and consequently, reduces coalescence. The fraction of the total product forming gas bubbles is dependent on the bubble coverage. The

residence time is given by a complex function containing nearly all the quantities from Eq. (24) [71].

The bubble coverage is also strongly affected by forced electrolyte flow. Increasing electrolyte velocity can help to substantially decrease bubble coverage, reaching only a few percent of the one in a stagnant electrolyte. Moreover, it also increases the limiting current by reducing the thickness of the diffusion layer. Macroconvection also reduces bubble fraction and, consequently, reduces electrolyte resistance [75].

2.5 Efficiencies

There are different manners of comparing the performance of water electrolysis techniques. A simple way is to compare the polarization curves. In a voltage vs. current plot, the curve located at the far right is from the most performing system, i.e., higher currents at fixed voltage and lower voltages at fixed current. Another way to compare different techniques is by efficiency. At the same production rate, the one with the best efficiency is the greatest. Voltage efficiency is defined as [76]:

$$\eta_{voltage} = \frac{\Delta E_{eq}}{\Delta E_{cell}} \quad (25)$$

with ΔE_{eq} the theoretical voltage value (1.23 V for water electrolysis at standard conditions) and ΔE_{cell} the cell voltage. Alternatively, efficiency can be calculated considering the thermo-neutral voltage (1.48 V at standard conditions):

$$\eta_{tn} = \frac{\Delta E_{tn}}{\Delta E_{cell}} \quad (26)$$

Another way to define efficiency is by considering the energy input and output, defined as follows [77]:

$$\eta_{energetic} = \frac{\dot{n} \cdot (-\Delta H)}{P_{el}} \quad (27)$$

where $\dot{n}$ is the molar hydrogen production rate ($\text{mol} \cdot \text{s}^{-1}$), ΔH is the heating value for hydrogen (lower or higher, in $\text{J} \cdot \text{mol}^{-1}$), and P_{el} is the consumed electric power (W). The lower heating value (LHV) is the enthalpic variation of the hydrogen combustion reaction when the only product is water vapor, and its magnitude at standard conditions is approximately $-242 \text{ kJ} \cdot \text{mol}^{-1}$ [78]. The higher heating value (HHV), on the other hand, corresponds to the variation in enthalpy of the hydrogen combustion reaction when liquid water is the only product, and its magnitude at standard conditions is approximately $-286 \text{ kJ} \cdot \text{mol}^{-1}$ [78]. Using the Faraday law of electrolysis, one has an energetic efficiency equal to:

$$\eta_{energetic} = \frac{-\Delta H}{z \cdot F} \cdot \frac{i_{H_2}}{i_t} \cdot \frac{1}{\Delta E_{cell}} = \frac{-\Delta H}{z \cdot F} \cdot \eta_{faraday} \cdot \frac{1}{\Delta E_{cell}} \quad (28)$$

with i_{H_2} the current used for hydrogen production, and i_t the total current. The first term is a constant and equals to the thermo-neutral voltage. The second term is defined as Faraday efficiency ($\eta_{faraday}$), and it is commonly 100% in practical water electrolysis applications, unless a parasitic reaction takes place. Therefore, considering no parasitic reaction, the energetic efficiency depends only on the cell voltage, as in the case of voltage efficiency. The operational range for commercial alkaline electrolyzer is considered to be between 1.8 V and 2.4 V [79]. For values outside this range, the heat balance is difficult to

be kept, as it heats too much or too little. Consequently, the thermo-neutral (HHV) efficiency lays between 62% and 82% and the voltage (LHV) efficiency, between 51 and 68%.

2.6 3-D electrodes

Three-dimensional electrodes offer a very high surface area, causing an enhancement in the rate of electrolysis. They are often used under the effect of a forced electrolyte flow. The fluid dynamics inside those electrodes is often defined by (i) non-uniform fluid distribution; (ii) changes in porosity due to the build-up of solid products (e.g., metal); and (iii) two-phase flow due to the presence of gases (typically H₂, O₂ or entrained air) [80].

Resistance to flow of a fluid through a porous medium at steady state and a given unidirectional average velocity is governed by Dupuit–Forchheimer modification of Darcy’s law [81]:

$$-\frac{\partial P}{\partial x} = \mu_f \cdot v_d \cdot K^{-1} + \rho_f \cdot F \cdot v_d^2 \quad (1 - D) \quad (29)$$

where P is the local pressure in the fluid (Pa), x is distance along the direction of macroscopic fluid flow (m), μ_f is the fluid dynamic viscosity (Pa·s), v_d is the superficial fluid velocity (m·s⁻¹), and ρ_f is the fluid density (kg·m⁻³). The characterizing parameters are the Darcian permeability, K (m²), and the form coefficient, F (m⁻¹). This equation is valid for isotropic materials such as foams. For anisotropic materials like lattice structures, the equation that fits the best is given by [81]:

$$-\nabla P = \mu_f \cdot v_d \cdot K^{-1} + \rho_f \cdot F \cdot \|v_d\| \cdot v_d \quad (3 - D) \quad (30)$$

The first term on the right-hand side of both equations represents the viscous losses and the second represents the porous electrode drag. The transition from a linear (Darcy) regime to a quadratic (Forchheimer) regime takes place around a certain Reynolds number [81]:

$$Re = \frac{\rho_f \cdot v_d \cdot L}{\mu_f} \quad (31)$$

with L the characteristic length (m). In opposition to a flow in a pipe, it is complex to define L in a porous electrode. Considering the wall effects caused by a highly permeable electrode structure such as foams, Eq. (29) can be expressed in the simplified form of the Brinkman equation [81]:

$$-\frac{\partial P}{\partial x} = -\mu_f \cdot \frac{\partial^2 v_d}{\partial y^2} + \mu_f \cdot v_d \cdot K^{-1} + \rho_f \cdot C \cdot \|v_d\| \cdot v_d \quad (32)$$

Besides the expressions that describe the flow resistance inside a porous electrode, another important expression is the one related to mass transport. Similarly to the Reynolds number, mass transfer is also described by a dimensionless numbers. The first one is the Sherwood number [80]:

$$Sh = \frac{m_t \cdot L}{D} \quad (33)$$

with m_t is the mass transfer coefficient ($\text{m} \cdot \text{s}^{-1}$), and D is the diffusion coefficient ($\text{m}^2 \cdot \text{s}^{-1}$). The second, known as Schmidt number defined the physical properties of the solution [80]:

$$Sc = \frac{\mu_f}{D} \quad (34)$$

They are correlated according to the following expression [80]:

$$Sh = a \cdot Re^b \cdot Sc^c \quad (35)$$

with c normally considered to be 1/3. Expanding the dimensionless numbers yields [80]:

$$\frac{m_t \cdot L}{D} = a \cdot \left(\frac{\rho_f \cdot v_d \cdot L}{\mu_f} \right)^b \cdot \left(\frac{\mu_f}{D} \right)^c \quad (36)$$

which shows that m_t is proportional to v_d to the power of b . It also implies that the limiting current follows the same proportionality, as it is directly proportional to the mass transfer coefficient, as shown in Eq. (15). For mass-controlled reactions, the conversion inside a flow-through or flow-by porous electrode can be approximated to the one of a plug flow reactor [80]:

$$X_A = 1 - \exp\left(\frac{-m_t \cdot A}{Q}\right) \quad (37)$$

with A the electrode surface area (m^2) and Q the volumetric flow ($\text{cm}^3 \cdot \text{s}^{-1}$) [80].

Contrary to 2-D electrodes, in 3-D ones there is a current and potential distribution along the thickness of the electrode. For the case of high concentration and well-mixed electroactive species, such as alkaline water electrolysis, Ohm's law apply [82]:

$$j_m = -\sigma \cdot \frac{d\Phi_m}{dx}, \quad j_m(0) = j, \quad j_m(L) = -0 \quad (38)$$

$$j_{sol} = -k \cdot \frac{d\Phi_s}{dx}, \quad j_s(0) = 0, \quad j_{sol}(L) = j \quad (39)$$

with the indexes m and sol indicating metal and solution, respectively; σ is the electronic conductivity of the electrode ($\text{S} \cdot \text{cm}^{-1}$), and k is the

ionic conductivity of the solution ($\text{S}\cdot\text{cm}^{-1}$). The ionic current follows Butler-Volmer equation - Eq. (11). For sufficiently a high overvoltage, the equation can be simplified to [82]:

$$j_n = j_0 \cdot \exp(\alpha \cdot f \cdot \eta) \quad (40)$$

with j_n the normal the current density normal to the surface area. The ionic current density increases with x according to:

$$\frac{dj_{sol}}{dx} = a_v \cdot j_0 \cdot \exp(\alpha \cdot f \cdot \eta(x)) \quad (41)$$

with a_v the electrochemically active volumetric surface area, ($\text{m}^2\cdot\text{m}^{-3}$) of total electrode plus electrolyte volume. The overpotential is given by [83]:

$$\eta = \phi_m - \phi_{sol} \quad (42)$$

and by the assumption of electroneutrality [55]:

$$\frac{dj_m}{dx} + \frac{dj_{sol}}{dx} = 0 \quad (43)$$

Applying the boundary conditions [83]:

$$j_m + j_{sol} = j \quad (44)$$

with j the applied current density. Differentiating Eq. (41), replacing the derivatives of potential by using Eqs. (38) and (39), and eliminating j_m by using Eq. (44):

$$\frac{d^2 j_{sol}}{dx^2} = a \cdot f \cdot j_0 \cdot \left(\frac{j_{sol}}{k} + \frac{1 - j_{sol}}{\sigma} \right) \quad (45)$$

Applying the boundary conditions yields the following solution:

$$j_{sol}(x) = j \cdot \left(\gamma + \frac{\gamma \cdot \sinh(g(x - L)) + (1 - \gamma) \cdot \sinh(g(x))}{\sinh(g(L))} \right) \quad (46)$$

with:

$$\sinh(x) = \frac{e^x + e^{-x}}{2} \quad (47)$$

$$g = \sqrt{a_v \cdot f \cdot j_0 \cdot \left(\frac{1}{k} + \frac{1}{\sigma} \right)}$$

$$\gamma = \frac{\sigma^{-1}}{k^{-1} + \sigma^{-1}}$$

Where L is the electrode thickness. The resulting potential and current distribution are qualitatively shown in Fig. 9. The current distribution is shown for two cases: (i) high electronic and ionic conductivities and (ii) high electronic conductivity and low ionic conductivity. For the first, the current has a linear profile. Those two cases were chosen because they are representative of alkaline water electrolysis. Details about the characterizing equations and the current potential distribution are described elsewhere (ref. [83]).

If the electrode is sufficiently thick, the solution potential can drop to a value at which the driving force (η) becomes so small that the reaction become negligible from a certain distance of the separator. Furthermore, in sufficiently thick electrodes the reaction rate can be controlled by different factors, going from mass transfer control near the separator to electron transfer control near the current distributor [80]. In other words, there is a maximum effective electrode thickness.

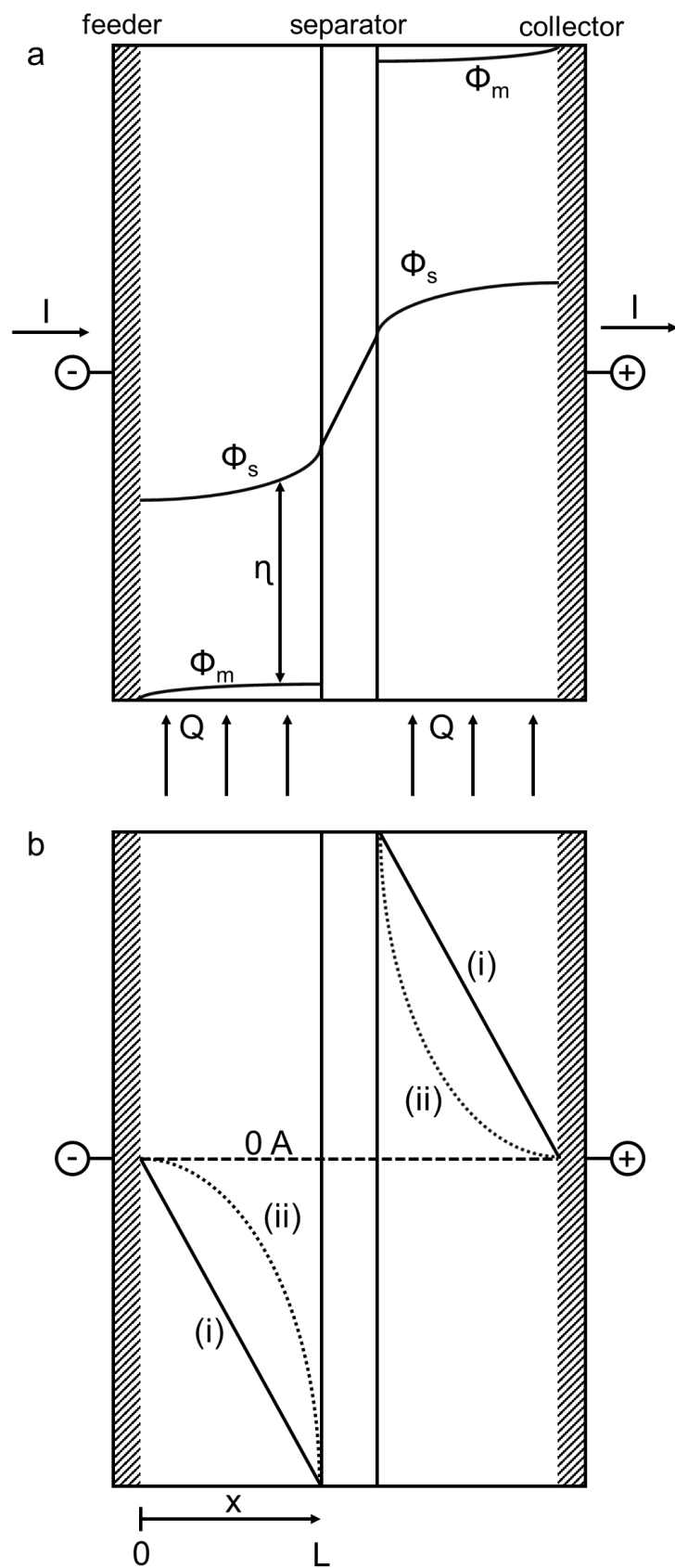


Fig. 9. Schematic of a) potential distribution, and b) current distribution along a zero-gap flow-by electrolyzer with 3-D electrodes.

2.7 Pulsed electrolysis

Conventionally, water electrolysis occurs either at a fixed and constant current or at a fixed and constant voltage. For the sake of simplicity, this conventional operation mode will be defined here as DC electrolysis in reference to the term direct current. Pulsed electrolysis, on the other hand, implies the application of a pulsed power supply.

Two kinds of pulses operation are considered in this thesis: voltage and current. In the first, voltage is changed from a base value (off-voltage) to a peak value (on-voltage). The pulse period is the sum of on-time (t_{on}) and off-time (t_{off}). The ratio between the on-time and pulse period is defined as the duty cycle, and the frequency is the inverse of the pulse period. The pulse amplitude is the difference between off-voltage and on-voltage. The resulting current will be the sum of a faradaic current (if the peak current is in a potential range at which water electrolysis occurs) and a capacitive current for the charging/discharging of the double layer.

When a voltage pulse is imposed, the capacitive current can be estimated as the charge/discharge of an ideally polarized electrode [56]:

$$i_c(t) = \frac{\Delta E}{R_e} \cdot \exp(-t \cdot R_e^{-1} \cdot C_D^{-1}) \quad (48)$$

with ΔE the amplitude of the voltage pulse (V), R_e the electrolyte resistance (Ω), C_D the double layer capacitance (F), and t the time (s). Notice that the capacitive current decays exponentially with time.

On the other hand, the faradaic current can be estimated considering a semi-infinite linear diffusion at a planar electrode. For a quasi-

reversible, one-step, one-electron case ($O + e^- \rightarrow R$), the current time-behavior is given as [56]:

$$j_f(t) = F \cdot (k_f \cdot C_O^* - k_b \cdot C_R^*) \cdot \exp(H^2 \cdot t) \operatorname{erfc}(H \cdot \sqrt{t}) \quad (49)$$

with:

$$k_f = k^0 \cdot \exp[-\alpha \cdot f \cdot (E - E^0)] \quad (50)$$

$$k_b = k^0 \cdot \exp[(1 - \alpha) \cdot f \cdot (E - E^0)] \quad (51)$$

$$H = \frac{k_f}{\sqrt{D_O}} + \frac{k_b}{\sqrt{D_R}} \quad (52)$$

with erfc the error function complement of x , defined as:

$$\operatorname{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x e^{-y^2} dy \quad (53)$$

with k^0 the standard rate constant (s^{-1}), α the transfer coefficient, k_f and k_b the rate constant for the forward (reduction) and backward (oxidation) reactions (s^{-1}), respectively, C_O^* and C_R^* the concentration of the reactant O and the product R in the bulk ($\text{mol} \cdot \text{cm}^{-3}$), respectively; t the time (s), D_O and D_R the mass transfer coefficients for specimens O and R, respectively ($\text{m} \cdot \text{s}^{-1}$). The graphical representation of a voltage pulse with a peak voltage at which water electrolysis occurs and a base voltage at which no reaction is possible is shown in Fig. 10. The capacitive current was estimated using Eq. (48) and the faradaic current using Eq. (49). It can be seen that when a voltage pulse is applied, the total current starts mainly capacitive and after the complete charge of the electrical double layer - EDL, it becomes mainly faradaic. The EDL is discharged when the voltage returns to the base value, giving a pure capacitive current.

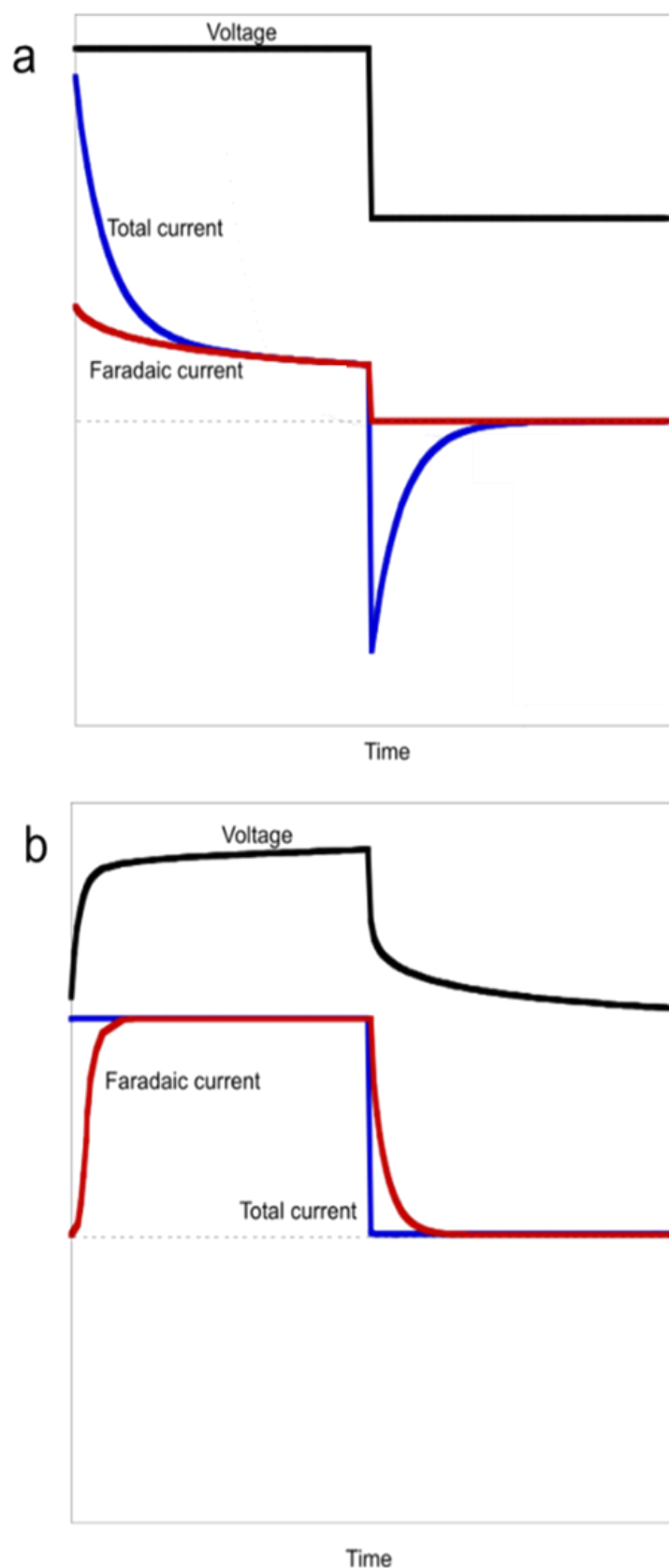


Fig. 10. Schematic representation of a) voltage pulse with an on-voltage at which a reaction occurs and an off-voltage at which no reaction occurs b) current pulse with a null total current during off-time.

In the case of current pulses, the voltage-time behavior at the beginning of a pulse can be estimated considering again the ideally polarized electrode [56]:

$$\Delta E(t) = i_c \cdot (R_e + t \cdot C_D^{-1}) \quad (54)$$

As the double layer is charged and the voltage reaches the reversible cell voltage, faradaic processes start to occur. Then, considering a quasireversible one-step one-electron reaction, the potential-time behavior is given by [56]:

$$-\eta = \frac{R \cdot T}{F} \cdot i \cdot \left[\frac{2 \cdot \sqrt{t}}{F \cdot A \cdot \sqrt{\pi}} \left(\frac{1}{C_O^* \sqrt{D_O}} + \frac{1}{C_R^* \sqrt{D_R}} \right) + \frac{1}{i_0} \right] \quad (55)$$

with η the overpotential and i_0 the exchange current. Additionally, when the current is off (0 A), the potential-time decay for a quasireversible reaction can be estimated as [56]:

$$\eta(t) = \frac{\eta_{(t=0)}}{\varepsilon - \beta} \cdot [\varepsilon \cdot \exp(\beta^2 \cdot t) \cdot \operatorname{erfc}(\beta \cdot \sqrt{t}) - \beta \cdot \exp(\varepsilon^2 \cdot t) \cdot \operatorname{erfc}(\varepsilon \cdot \sqrt{t})] \quad (56)$$

with ε and β related to the relaxation times. Notice that the voltage relaxes to the reversible cell voltage. Olmstead [84] proposed a method to differentiate the capacitive current from the faradaic current when current pulses are applied to an electrochemical system. In this case, the ratio of the capacitive to total current density, $h(y)$, is calculated as the numerical solution of the following equation:

$$\frac{1 - \exp \left[\frac{-1}{\Psi} \int_0^y h(x) dx \right]}{1 + \exp \left[b - \frac{1}{\Psi} \int_0^y h(x) dx \right]} = \sqrt{y} - \frac{1}{2} \int_0^y \frac{h(x) dx}{\sqrt{y-x}} \sqrt{\frac{D_O}{D_R}} \quad (57)$$

with:

$$\exp(b) = \frac{C_O^*}{C_R^*} \quad (58)$$

and

$$\psi = \left(\frac{R \cdot T}{z \cdot F} \right) \cdot \left(\frac{4 \cdot i \cdot C_d}{\eta \cdot F \cdot C_O^* \sqrt{\pi \cdot D_O}} \right) \quad (59)$$

with i the total current (A). Notice that when ψ is zero, no capacitive effect is expected. For the off-time, considering a total current of zero, the faradaic and capacitive currents can be estimated as follows [85]:

$$i_c = C_D \cdot \frac{d\eta}{dt} \quad (60)$$

$$i_f = -i_c \quad (61)$$

The graphical representation of these equations for a current pulse with an off-current of 0 A is shown in Fig. 10.b. In the beginning, the voltage increases linearly with time due to the charge of the EDL as predicted by Eq. (54). Then, it increases with the square-root of time, following Eq. (55) for the faradaic reaction. As in the voltage pulse case, the current starts mainly capacitive and then becomes faradaic, as from Eq. (57). During the off-period, the EDL is discharged by faradaic processes, promoting a voltage decay.

Chapter 3: State of the art

As shown in Ch. 1, there are two commercially available water electrolysis technologies: alkaline and PEM [86]. The former presents the lowest capital cost per kilowatt of electricity [87] but suffers from the lowest hydrogen production rate per electrode area [88]. PEM electrolysis can achieve much higher production rates but depends on scarce and expensive electrocatalytic materials, such as iridium and platinum [88]. The ideal electrolyzer should combine the advantages of both systems, presenting high production rates while using inexpensive and abundant electrode materials [89].

The present thesis will focus on the process intensification of AWE. Therefore, this chapter will start by providing an overview of alkaline water electrolysis's main components and characteristics. As it will be seen, in AWE, the electrolyte solution is typically potassium hydroxide; the separator is often a diaphragm; and the electrodes are usually made of nickel, iron, cobalt, or their combinations. Then, the state of the art of pulsed water electrolysis will be presented, including voltage and current pulses and pulses with a redox mediator.

3.1 Alkaline electrolyzer

3.1.1 Electrolyte

In electrochemistry, an electrolyte implies any substance that conducts electricity via the movement of ions. This substance can be a covalent compound that reacts with a medium to produce ions, an ionic compound that dissociates into its constituent cations and anions when dissolved, or an ionic compound in a molten state. The term electrolyte

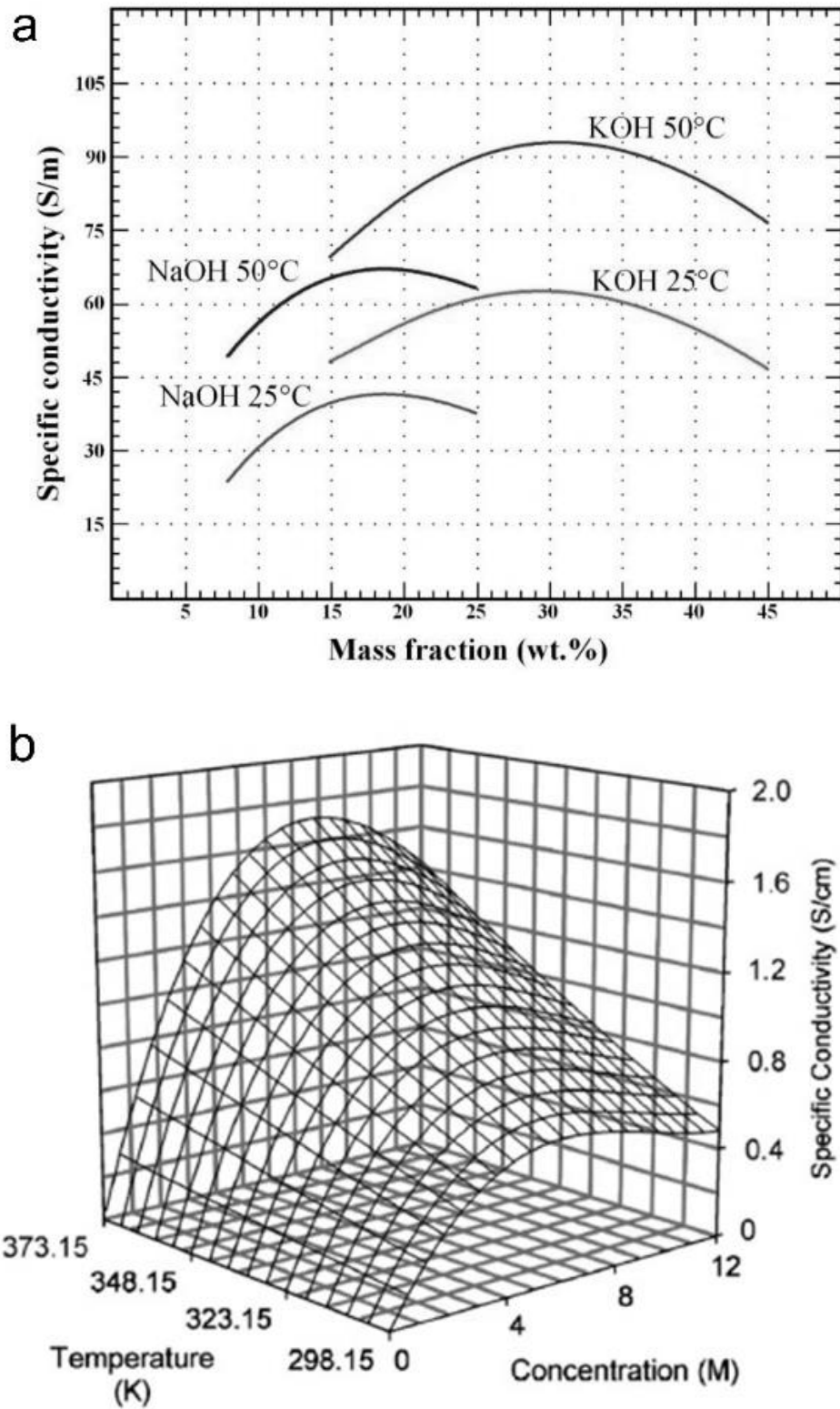


Fig. 11. a) Specific conductivities as a function of mass fraction for sodium and potassium hydroxides [90], b) Specific conductivity for potassium hydroxide as a function of concentration and temperature [91].

was first introduced by Michael Faraday (1791-1867), and it originates from the junction of the ancient Greek words *electro* (ἤλεκτρο) and *lytos* (λυτός), meaning able to be untied or loosened [92]. The prefix *electro* comes from a misconception that ions were produced by electrolysis. It was Svante Arrhenius who proposed the dissociation of salts into cations and anions when dissolved, and now we know that typically, electrolytes are formed by the dissociation of salts into ions, which are then solvated by solvent molecules [92]. The most used electrolyte for alkaline water electrolysis is potassium hydroxide (KOH) [93]. Compared with its main alternative, sodium hydroxide (NaOH), it presents a much higher maximum electrical conductivity (about 50% higher), as shown in Fig. 11.a. It is worth noticing that the conductivity of KOH is optimal for concentrations between 25 and 30 wt%, while for NaOH is optimal between 15 and 25 wt%. The maximum conductivity for KOH is at 100°C and 7.5 M, as shown in Fig. 11.b. However, at this temperature, the water vaporization becomes too important. Generally, industrial electrolyzers work at 70-90°C [94] and 25-30 wt% KOH [76].

3.1.2 Separator

A separator between the cathode and the anode is necessary to avoid gas mixing [95] and to avoid a short circuit in the case of zero-gap electrolyzers. The mixing of hydrogen into an oxygen-rich environment is known as HTO, and the mixing of oxygen into a hydrogen-rich environment is known as OTH. They are given in percentages. The HTO is the critical factor defining the minimum load of an electrolyzer, as the lower the load, the higher the HTO. The mixture is explosive for

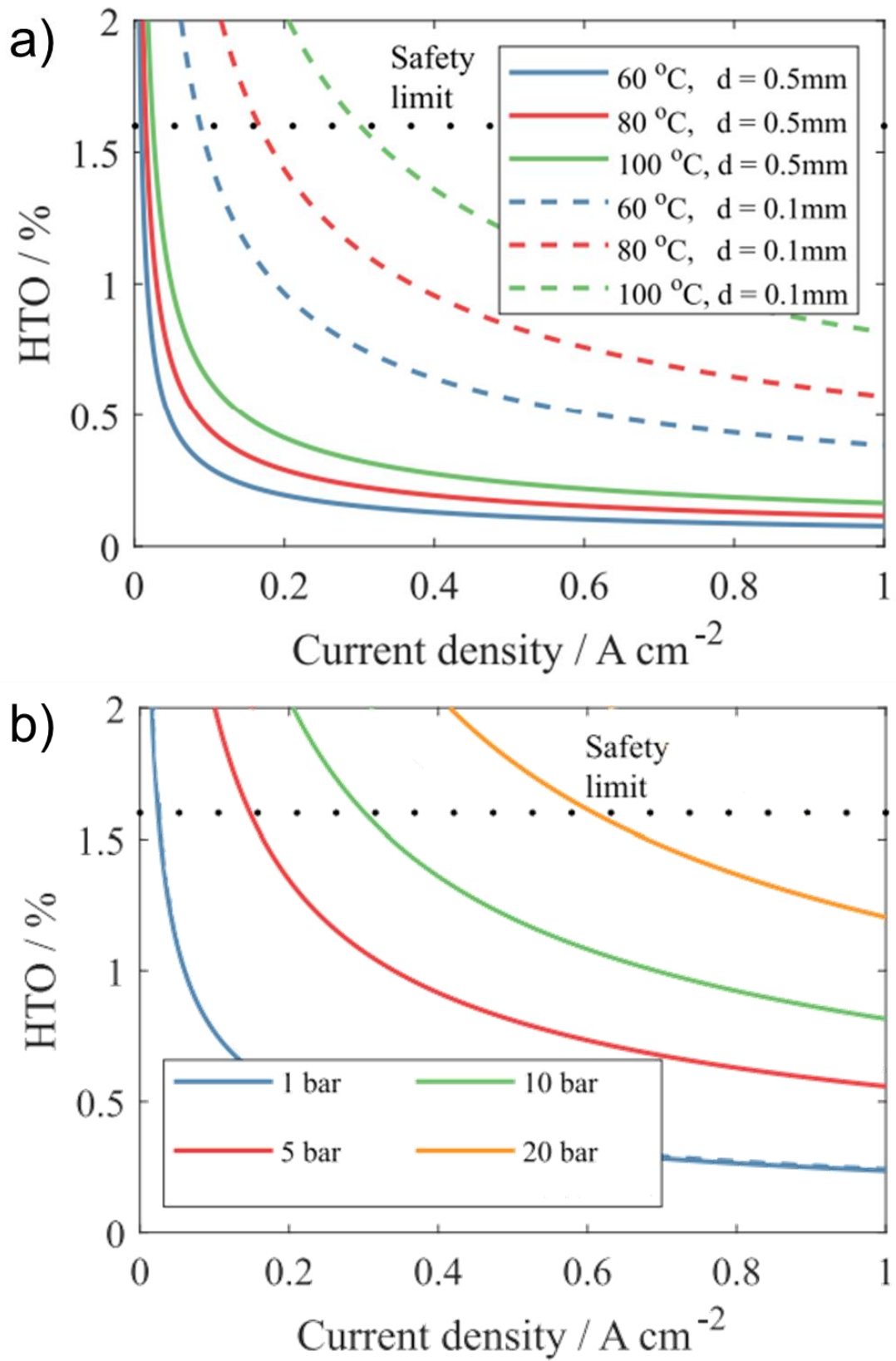


Fig. 12. HTO as a function of current density for a) different temperatures and separator thicknesses and b) different pressures. Adapted from ref. [96].

an HTO higher than 4%. Consequently, a maximum value of 2% was agreed upon International Standards. Often, an alarm is set for an HTO of 1.6%, and the system is shut off if it reaches 2% [96].

Several factors influence HTO, as shown in Fig. 12. The HTO increases significantly at low current densities and increases with the temperature and pressure. Furthermore, thinner separators present a lower ohmic resistance but a higher HTO [96].

An advantage of alkaline separators with respect to the proton exchange membranes used in acidic electrolysis is the lower hydrogen permeability, which is one order of magnitude lower [97]. There are three different kinds of separators for AWE: diaphragm, anion exchange membrane, and ion solvating membrane [98]. They are schematically shown in Fig. 13.

A diaphragm is a porous separator containing pathways where the electrolyte enters. Its conductivity depends on the electrolyte conductivity [88]. At first, asbestos-based diaphragms were the most common separator found in electrolyzers [95]. However, this material was banned in more than 50 countries when scientists discovered that asbestos exposure was harmful to human health, leading to several diseases, including cancer [99]. As a replacement, zirconium dioxide (ZrO_2) based separators emerged, and, until now, they are the most used ones. The state-of-the-art separator is marketed under the name of ZironTM Perl UTP 500 [95]. It is composed of a polysulfone network (15 wt%) with ZrO_2 as an inorganic filler (85 wt%), presents a thickness in the order of 500 μm [100] and an ohmic resistance of about $0.1 \Omega \cdot \text{cm}^2$ at the benchmark conditions of 30 wt% KOH and 80°C (conductivity

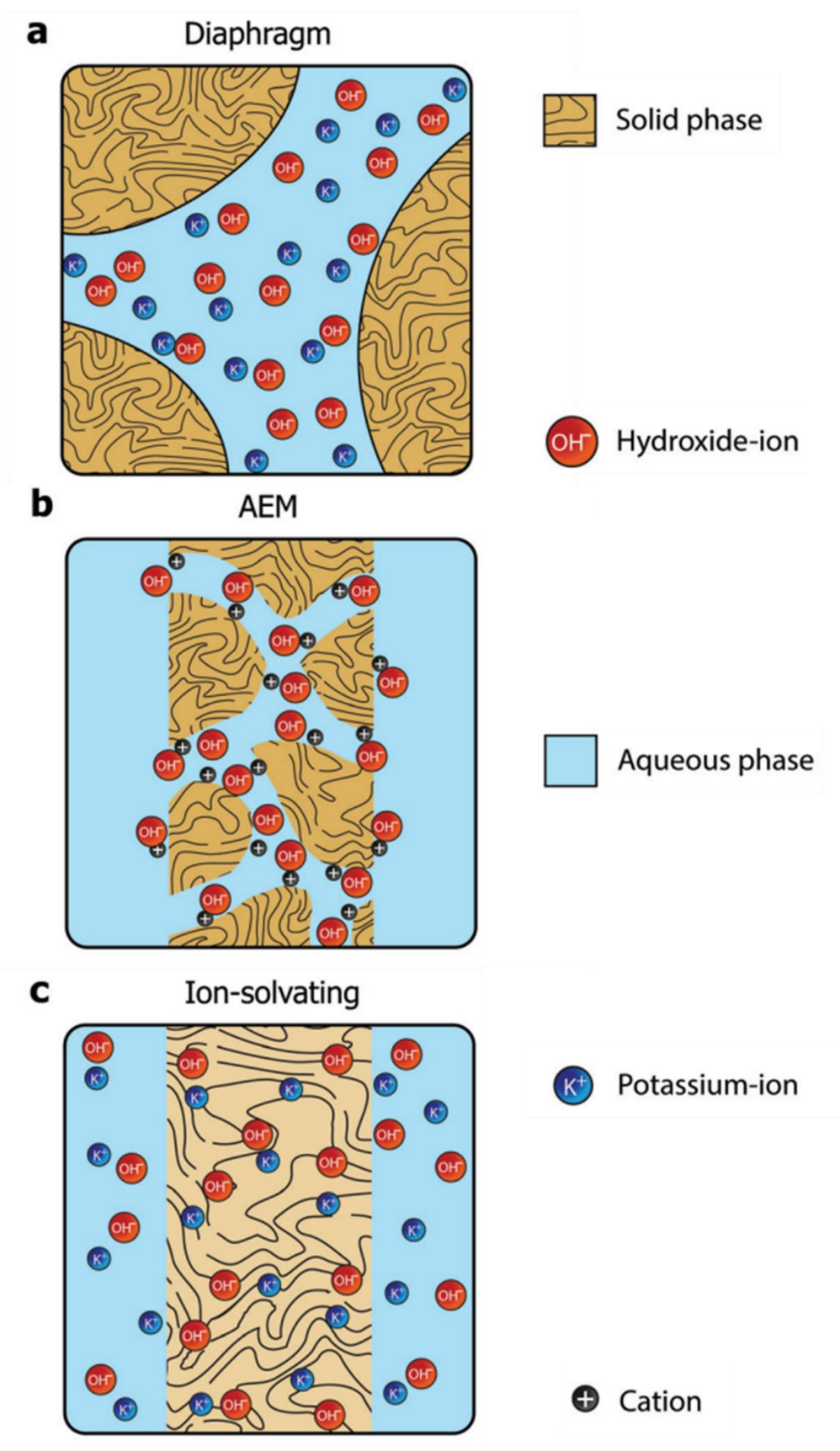


Fig. 13. Schematic showing different materials for electrolyzer separators. From ref. [88].

of $500 \text{ mS}\cdot\text{cm}^{-1}$) [70]. As a comparison, the conductivity of a proton exchange membrane used in acidic water electrolysis at the same temperature is about $200 \text{ mS}\cdot\text{cm}^{-1}$, but as the thickness of the proton exchange membrane is lower, the resulting resistance is about $0.03\text{-}0.13 \text{ }\Omega\cdot\text{cm}^2$ [101]. A recent study achieved to further decrease diaphragm ohmic resistance by the reduction of the diaphragm thickness, the polysulfone content at the diaphragm surface, and the number of large pores [102].

As an alternative to diaphragms, anion-exchange membranes are being studied. Until now, none satisfies the performance and stability requirements to replace diaphragms in electrolyzers, but these membranes can be a better option when working in less corrosive environments such as dilute solutions or even demineralized water. They present high ionic conductivity at dilute electrolytes and offer a good barrier for gas despite their lower thickness [95]. These membranes possess a polymer backbone with positively-charged functional groups (usually quaternary ammonium) to facilitate anionic transport. The reported conductivity is between 5 and $20 \text{ mS}\cdot\text{cm}^{-1}$, with some new studies showing $200 \text{ mS}\cdot\text{cm}^{-1}$ [103]. As a comparison, the conductivity of Zirfon is approximately $9 \text{ mS}\cdot\text{cm}^{-1}$ at 25°C and 0.1 M [70].

Additionally, there are ion-solvating membranes, which absorb the electrolyte and swell, forming a dense (non-porous) physic barrier against gas mixing. Based on polybenzimidazole (PBI), some have reached a performance comparable to the one of Zirfon. Nevertheless, long-term stability is still an issue [95].

Finally, membrane-less electrolysis is emerging as an alternative to the use of separators. In this case, the gas separation is obtained by fluid-dynamic forces, as explained in more detail by ref. [104].

3.1.3 Electrocatalysts

The ideal electrocatalyst should possess good catalytic activity, high stability, and low cost [105]. In this section, the main materials investigated for HER and OER are going to be briefly reviewed.

Electrocatalysts for HER

Platinum-group metals are the most active materials towards HER, as shown previously in Fig. 7. However, their scarcity and high cost make them unsuitable for industrial applications. Consequently, non-precious metal-based catalysts are the only viable option for the construction of large-scale alkaline electrolyzers.

The overpotential at $10 \text{ mA} \cdot \text{cm}^{-2} - \eta_{10}$ - for PGMs is around 45-90 mV, while for PGM-free materials, it is between 90 and 240 mV [106]. The most investigated non-precious materials for alkaline HER are iron, nickel, cobalt, and their alloys [105]. Among them, Ni is the most studied material because it is the most resistant to corrosion in hot and concentrated alkaline solutions [105], and it is also the cheapest and most abundant [106]. Ni stability at the hydrogen evolution region in alkaline media is shown in Fig. 14.

The most popular nickel alloy is Ni-Mo, as Mo increases the electrocatalytic activity and the corrosion resistance [105]. The increase in activity is commonly explained by the enhancement of the surface area and the synergism from combining a metal from the left-half of the

transition series with one from the right-half (Brewer intermetallic bonding theory) [105]. Ref. [107], for instance, reported a low energy barrier for the Volmer step (reaction B1) when using Ni_4Mo electrodes. The energy barrier was not only lower than the ones of pure Ni and pure Mo, but it was even lower than Pt. A comprehensive review on the use of Ni-Mo alloys as catalysts for the HER can be found in ref. [108]. Molybdenum is also a popular alloying metal for Fe and Co alloys [105].

In the case of metalloids, phosphorous is one of the most investigated for doping with alloys. Ni-Al alloys are also widely studied, as they are

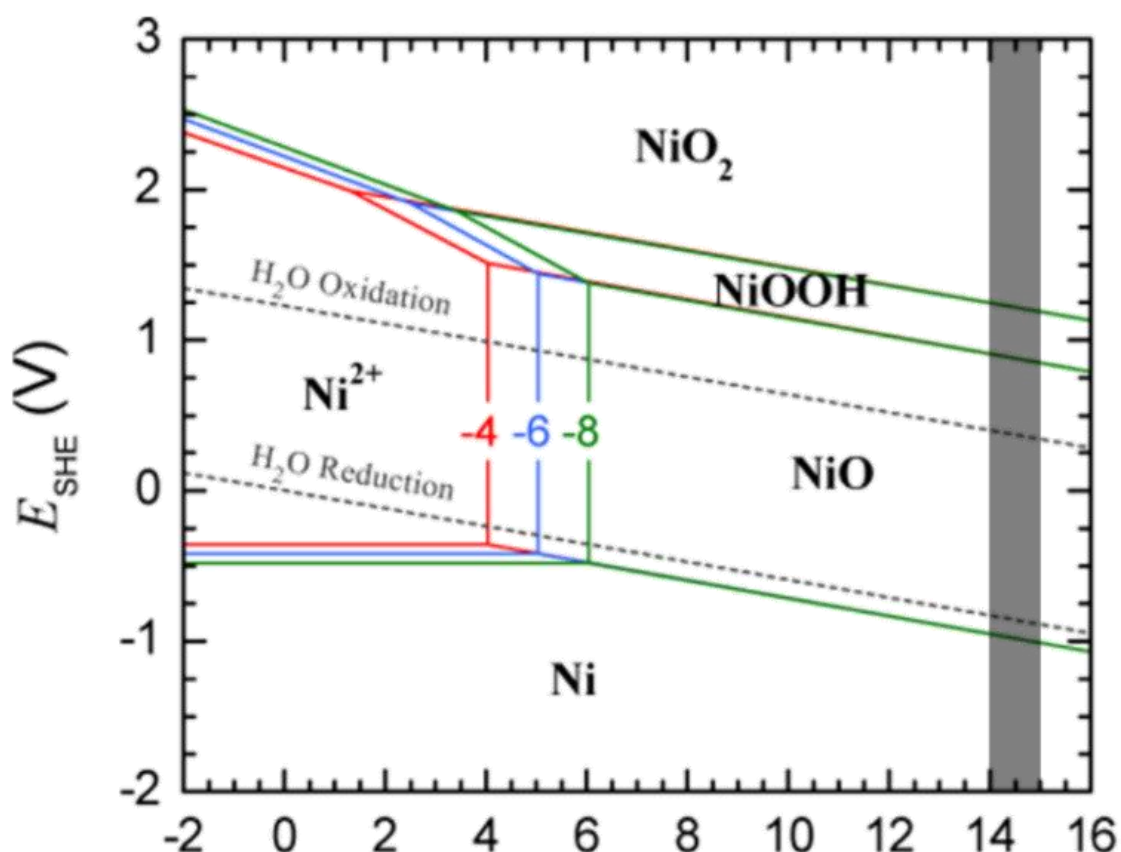
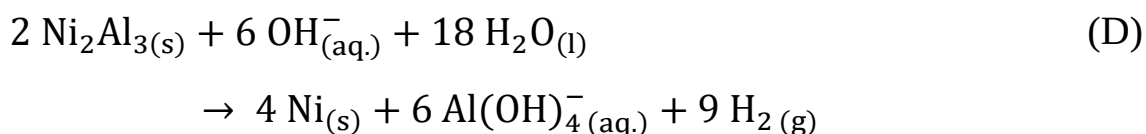


Fig. 14. Pourbaix diagram for the Ni-water system. The pH region of interest for AWE is highlighted in gray. Red, blue, and green lines represent Ni molarities of 10^{-4} , 10^{-6} , and 10^{-8} , respectively. Adapted from ref. [109].

used to produces a very porous structure with high surface area, known as Raney Ni. [105].

Raney Ni is a highly active form of nickel widely used as a catalyst in various chemical reactions, particularly hydrogenation reactions. It is named after its inventor, who developed the catalyst in the 1920s [110]. Its first deployments in large-scale electrolyzers date to the late 1970s [46]. Its preparation starts with the formation of a Ni-Al alloy, commonly by adding molten Al to Ni, followed by rapid quenching in water [110]. For the preparation of AWE electrodes, Raney Ni has been applied to the surface of substrates by different methods, including chemical vapor deposition, electrodeposition, and plasma spray. The latter is suitable for large-scale electrode production due to its rapid prototyping and ability to cover large surface areas. This process can be done in vacuum or atmospheric conditions. During plasma spraying, a fine metal powder is introduced through injection nozzles into a plasma jet, leading to the acceleration and heating of metal particles. Subsequently, the semi-molten or entirely molten particles hit the relatively cold surface of the substrate, where they undergo solidification, as illustrated in Fig. 15 [111]. Depending on the Ni weight percentage, this process yields the intermetallic Ni_2Al_3 , NiAl_3 , or some frozen eutectic, as determined by the phase diagram [110].

Subsequently, there is the activation process, at which the Al is leached out in an alkaline solution. Taking Ni_2Al_3 as an example, the leaching process can be described by the following reaction:



The resulting structure is very porous and has an enhanced surface area with a sponge-like form. For this reason, it is also called skeletal nickel. The activation temperature should be chosen carefully, as high temperatures increase leaching rates but decrease the resulting surface area due to an increased crystallite size. The phases present in the alloy are also critical in the resulting Ni structure, as each phase has its leaching rate and influence on the resulting pore size and volume. An additional metal, such as Mo, is often introduced to enhance activity or selectivity [110].

In the case of electrodeposition, Raney Ni is formed by the co-deposition of Ni with either Zn [112] or Sn [113]. As for aluminum, its highly negative reduction potential (-1.67 V vs. SHE) makes electrodeposition in aqueous solutions impractical due to the significant hydrogen evolution reaction occurring prior to any Al metal or Al alloy

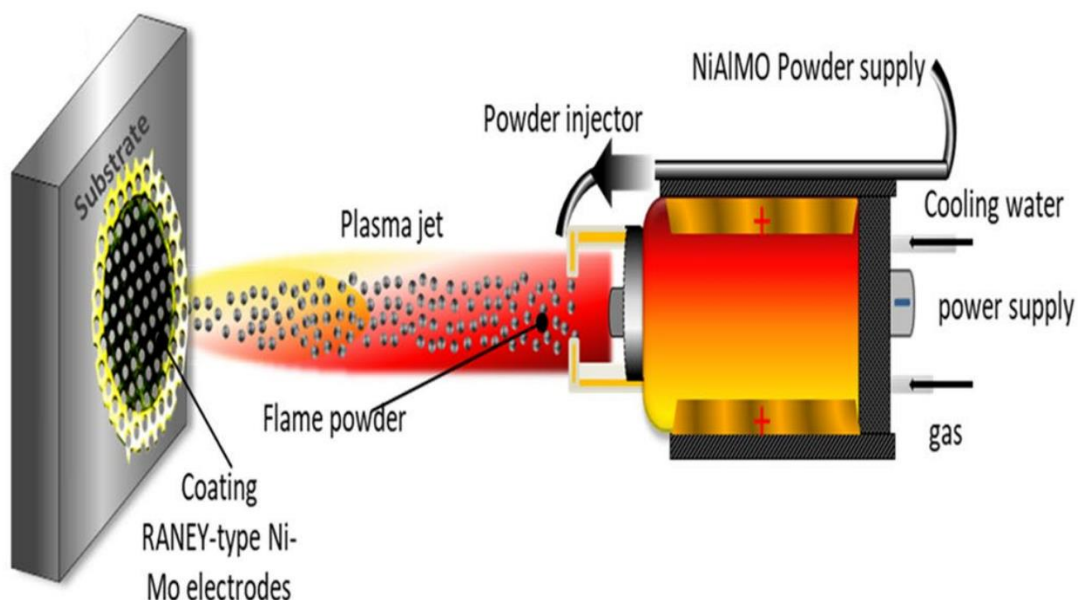


Fig. 15. Schematic showing the Raney Ni coating using the plasma spray process. Adapted from ref. [111].

reduction [114]. The co-deposition occurs in a slightly acid electrolyte and it is followed by Zn or Sn leaching in alkaline media [115].

When exposed to air, Raney Ni rapidly oxidizes, liberating heat that has the potential to ignite nearby combustible materials. As a consequence, it is recommended to store this metal in an alkaline solution or isopropanol [110].

Joining the efforts to enhance the electrode surface area, Schalenbach *et al.* [116] could increase the surface area of Ni meshes by three orders of magnitude by hot-dip galvanizing in zinc followed by de-alloying. The result was an improved AWE performance. Kim *et al.* [117] inserted a nickel powder in one side of a nickel foam and sintered it, creating an asymmetrical electrode with a pore size changing from 5 μm at the catalyst layer to 100 μm at the porous transport layer. Han *et al.* [118] achieved a 40-fold increase in the surface area using sputtering. Consequently, at a current density of $0.5 \text{ A}\cdot\text{cm}^{-2}$, 25 wt% KOH, 80°C, Zirfon separator, and Ni foam electrodes, the cell voltage was decreased from 2.2 V to 2.0 V. Kraglund *et al.* [88] reduced the cell voltage from 2.1 V to 1.7 V at $0.5 \text{ A}\cdot\text{cm}^{-2}$, 24 wt% KOH, 80°C, Zirfon diaphragm, by means of vacuum plasma spraying. The cathode was Ni foam, and the anode was a Ni perforated plate. It is worth noting that an increase in the electrochemically active surface area (ECSA) will also cause an increase in bubble generation and coverage, making it difficult to maintain the effective ECSA in the course of water electrolysis. It is then critical to promote efficient bubble removal [119].

Electrocatalysts for OER

In the case of the OER in alkaline media, PGMs are also the most active (as already shown in Fig. 8), presenting a mean η_{10} of 344 mV, and with RuO_2 being the one with the highest activity. For the same reasons as before, non-precious metals are more interesting for the scalability of AWE. The most studied catalysts in this category are Ni, Fe, Co, and their combination. The η_{10} for metal oxides is around 415 mV, with nickel oxides being the most active. It is worth noticing that the overpotential of the OER is higher than that of the HER. Besides the oxides, layered double hydroxides (LDH) of Ni and Fe seem to be very promising materials, achieving η_{10} lower than 280 mV. Phosphides and selenides are also causing a performance improvement, reducing the η_{10} to values near 300 mV [66]. Furthermore, the presence of iron ions in the electrolyte is known to cause an enhancement in the activity of the OER due to the formation of $\alpha\text{-FeOOH}$ at the electrode surface [120]. Raney Ni is another commonly used material [121].

3.1.4 Cell and electrode design

Initially, alkaline electrolyzers used gap-cells, where there was an important physical distance between the cathode and the anode (>2 mm) [122], with a cell separator (membrane or diaphragm) between them. The problem with this configuration is that at high current densities (usually higher than $0.45 \text{ A}\cdot\text{cm}^{-2}$ [123]), the produced gases form a non-conductive layer over the entire electrode surface, creating a screening effect and limiting the increase in current density. This effect also causes an increase in the gas cross-over across the cell separator, as it favors gas transport in both directions across the

diaphragm [123]. Therefore, this design has gradually been substituted by the zero-gap cell. In this more advanced design, the electrodes, perforated or porous, are in direct contact with the separator. As a consequence, the interelectrode distance is reduced to the thickness of the separator (<0.5 mm) rather than (>2 mm) in the traditional setup. Furthermore, it prevents the screening effect as bubbles can no longer be generated in between the electrodes. This leads to a significant reduction in the electrolyte ohmic resistance [122], and it has been widely accepted for improved cell design since the 1980s [124]. In the early developments, 2-D perforated plates were used as zero-gap electrodes [124,125], and more recently, 3-D electrodes are being studied as they increase the surface area [126]. The cell design is slightly altered as flow-field etched bipolar plates are no longer necessary due to electrolyte flow through the porous material, although they are often still employed [122].

The 3-D electrodes consist of macroporous structures that allow hydroxyl ions and gases to pass through. The result is the achievement of current densities of up to $25 \text{ A} \cdot \text{cm}^{-2}$ [127]. Various strategies leading to improvements in current density – notably optimization of electrode intrinsic activity, resistivity, surface area, bubble removal, and stability [119] – means a reduced capital expenditure (capex) [123] and enable to scale up the electrolyzers to the megawatt level. The different cell designs are shown in Fig. 16. It can be seen that for the traditional gap-cell, gas bubbles evolve from the surface of the 2-D current distributor plates only, with an important interelectrode gap. For zero-gap cells,

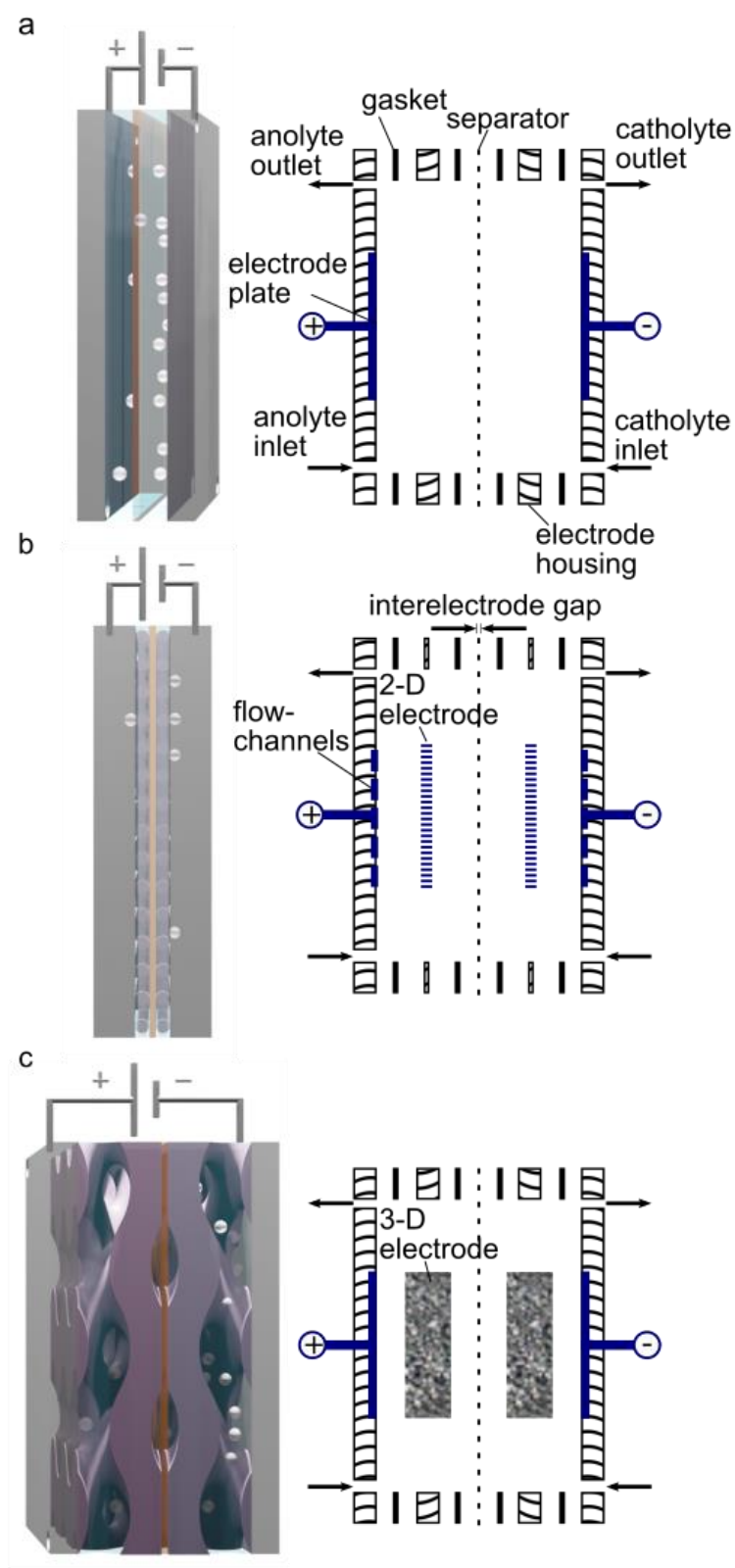


Fig. 16. Schematic showing the evolution of cell designs showing a) traditional gap cell, b) zero gap-cell with 2-D electrodes, and c) zero-gap cell with 3-D electrodes.

gases are forced to be released from the backside of the electrodes, allowing the active side of the electrode to be bubble-free and preventing screening effect. As a result, bubbles will have a smaller contribution to the Ohmic resistance [122]. When using 3-D electrodes, bubbles may additionally evolve from within the 3-D electrode, especially at the region close to the separator, as this is the region with the lowest voltage drop as a consequence of the lower interelectrode distance between the cathode and the anode, as already discussed in the previous chapter.

This thesis will study two porous electrodes: metallic foams and 3-D printed electrodes. Foams are suitable electrode materials because they are light and have high porosity and surface area [128]. The foams we are interested in are made of nickel, as it is an abundant and cheap material that resists corrosion in alkaline solutions and presents a high electroactivity for hydrogen and oxygen evolution (see Ch. 2). Ni foams are commonly produced by deposition on polymer foam [81]. This process uses a polymeric open-celled foam, usually polyurethane (PU), as a precursor for a metal deposition which can be electrolytic, chemical vapor, or physical vapor deposition. Subsequently, the polymer is removed by leaching or pyrolysis, as shown in Fig. 17. The resulting foam has a structure roughly similar to the precursor foam but with voids within the metallic struts left by the polymer after its removal [81].

For the electrolytic deposition, the polymeric foam must first become electrically conductive. This is achieved by pre-coating the foam with carbon or metal through sputtering or electroless plating [81].

In the process of physical vapor deposition, Ni is vaporized by the use of an electric arc. When in contact with the surface of the polymeric foam, the metal vapor cools down and solidifies. Chemical vapor deposition, on the other hand, uses nickel tetracarbonyl gas, which decomposes at relatively low temperatures. The reaction occurs using a

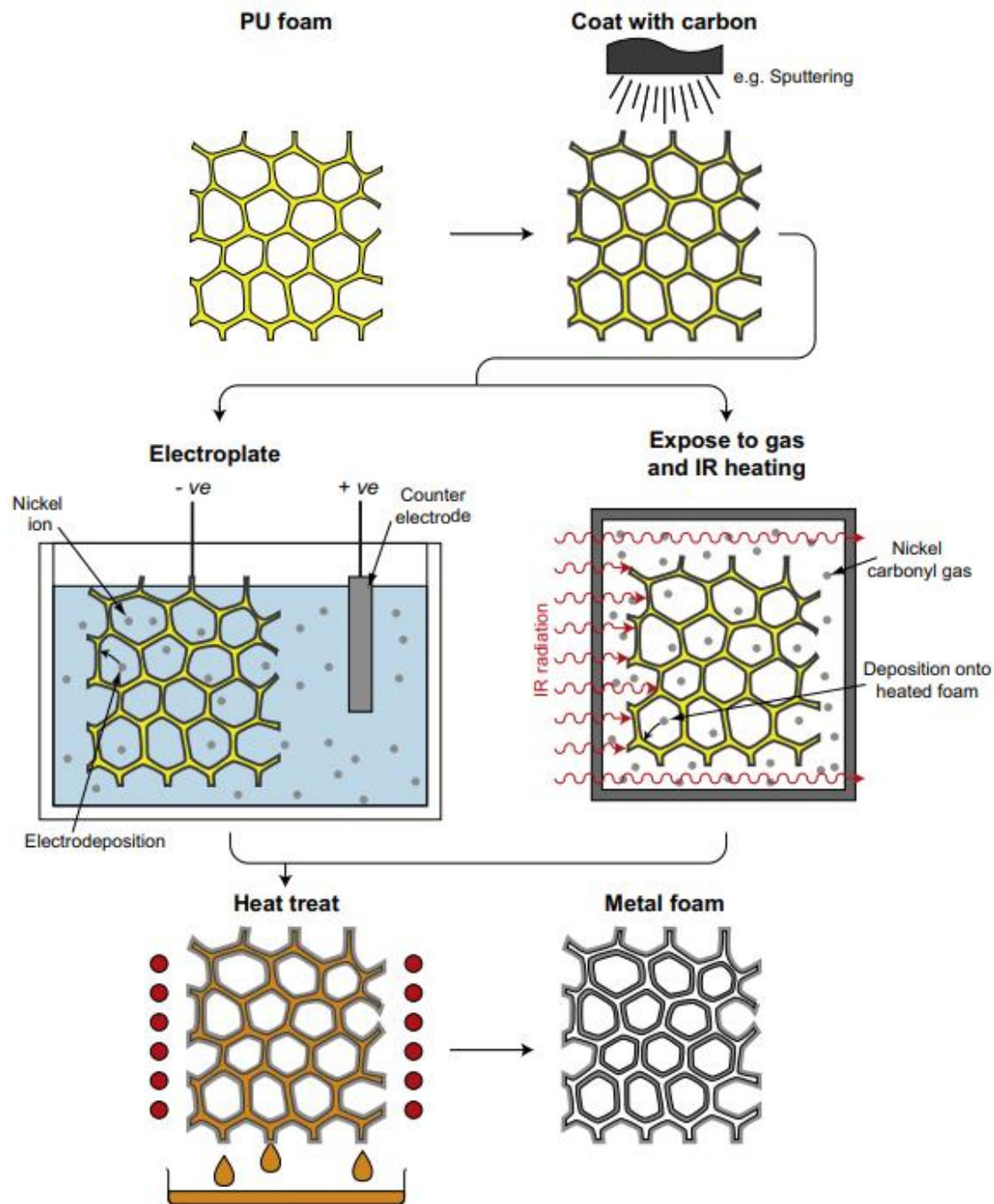


Fig. 17. Schematic of the metal production using deposition on a precursor foam. From ref. [81].

carbon-coated polymeric foam in a chamber with infrared radiation. The carbon absorbs the nickel tetracarbonyl liberating a localized heat that causes gas break-down and Ni deposition [81].

The specific surface area ($\text{m}^2 \cdot \text{m}^{-3}$) of the resulting metal foams can be described by the dodecahedron model proposed by ref. [129] as a function of the edge length and the width of the cell wall. More straightforwardly, it can be estimated considering a spherical pore shape [81]:

$$S_v = \frac{3}{D} \cdot (1 - V_m) \quad (62)$$

with D the pore diameter (m) and V_m the solid volume fraction.

Recently, 3-D printed structures have emerged as an alternative for Ni foams. For example, Kou *et al.* [130] observed a gas evacuation enhancement when replacing foams with periodic 3-D printed structures. This was a consequence of the reduction in bubble residence time and coalescence. Later on, Huang *et al.* [131] showed that the replacement of a Ni foam gas diffusion layer by a 3-D printed structure could significantly improve the electrolysis performance. The better performance was due to the periodic structure and higher aerophobicity surface, which could suppress bubble growth and decrease the bubble residence time. Furthermore, a better electric contact was observed between the 3-D printed gas diffusion layer and the bipolar plate.

The studies mentioned above both employed the direct ink writing (DIW) method for electrode printing. DIW, or robocasting, is an extrusion-driven approach that begins with formulating a unique ink possessing specific rheological attributes. Then, ink filaments are

extruded through a nozzle under controlled pressure onto a building platform. Print resolution is affected by variables such as nozzle diameter, pressure, and ink properties. Notably, the rheological characteristics of the ink, particularly its yield stress, significantly impact the printing quality [132]. After the printing, the sample goes through a heat treatment in an Ar/H₂ atmosphere to remove organic compounds and reduce and sinter metals [133]. For the printing of 3-D Ni electrodes, the ink is commonly composed of Ni or NiO particles, polymers, and volatile solvents [130,134].

Using another electrode printing approach, Xu *et al.* [134] showed that 3-D printed electrodes can enhance surface roughness, causing an increase in the electrode's hydrophilicity as compared to metal foams. Consequently, this effect leads to a reduction in bubble size and departure time. The authors also demonstrated that periodic electrode structures can significantly reduce bubble size by avoiding bubble collision and coalescence. In their study, electrodes were fabricated using digital light processing (DLP). To be short, this process uses light-sensitive resins (photopolymers) which are cured layer by layer by a UV digital light source. The light source is projected onto several hundred thousand micromirrors, forming a pixel matrix. The light reflected by the mirrors onto the building platform solidifies the resin layer at once, without scanning [135]. To prepare metallic structures, heat treatment to remove organics and sinter and reduce the metal is needed [134].

Another process used to produce 3-D electrodes is laser beam melting – LBM - also called selective laser melting (SLM) [136]. In this technique, a thin layer of powder is deposited over a substrate plate or

on the previously deposited layer, and a laser beam melts the powder particles selectively, as shown in Fig. 18. To avoid oxygen contamination, the process is done in a closed chamber containing an inert gas [137]. Alternatively to the laser beam, an electron beam can produce the highly directional heat source. In this case, the process is called electron beam melting – EBM. The resolution of the printing process depends on the dimension and power of the heating source and the size of the metal powder used [81].

An important issue when employing the zero-gap configuration is the entrapment of gas bubbles within the 3-D electrode structure, as such entrapment results in a reduced available surface area and hinders mass transport. Notably, the dominant factor influencing ohmic resistance at high current densities is often attributed to bubble coverage [119].

Implementing a forced electrolyte flow proves crucial to mitigate the accumulation of generated gases and ensure a continuous supply of electrolytes to the electrode surface. This strategy has been recognized to enhance the AWE performance for both the gap-cell [138,139] and zero gap cell designs [140,141]. In the traditional gap-cell setup context, the flow is particularly important for narrow gap sizes (e.g., below 4 mm) [142]. Furthermore, the role of flow becomes even more pronounced when working with foam electrodes subjected to high current densities, offering benefits not only for mass transport but also for heat distribution [122]. A positive effect caused by a forced electrolyte flow was reported when using Ni foams with a nominal pore diameter of 600 μm [140]. Flow can also help to stabilize the current or

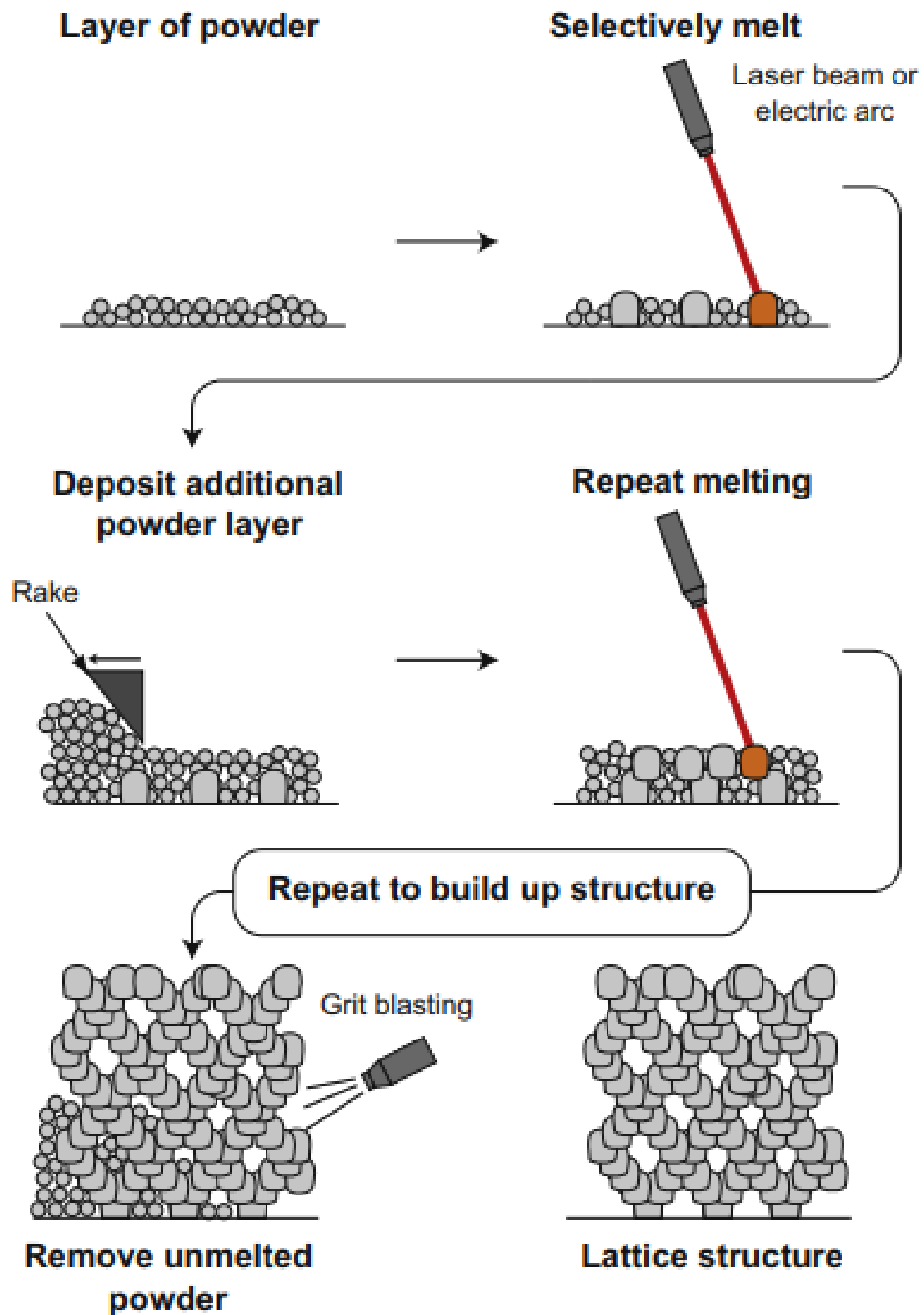


Fig. 18. Schematic of the laser beam melting process. From ref [81].

voltage response by reducing oscillations induced by bubble detachment. Without flow, the bubble departure size is considerable, and bubbles leave the surface synchronously, leading to periodic fluctuations in available surface area. In contrast, in the presence of a forced flow, the departure size is reduced, and bubbles leave the surface at distinct intervals, resulting in an averaged surface area over time [143].

Besides forced flow and the design of flow-sensitive electrodes, there are different strategies for bubble removal, such as (i) the fabrication of superaerophobic (superhydrophilic) electrode surfaces [144], which causes a reduction in bubble size and rapid separation from the surface; (ii) breathable electrodes to guide bubbles out of the electrode by capillary forces [145]; (iii) the creation of superaerophilic sacrificial sites for bubble formation [146]; (iv) the use of ultrasound [147]; (v) magnetic fields [148]; (vi) photothermal fields [149]; (vii) supergravity fields [150]; (viii) surfactants [151]; and (ix) pressure modulation [152]. Fig. 19 shows some of these strategies and more information about them can be found in refs. [45,153–155].

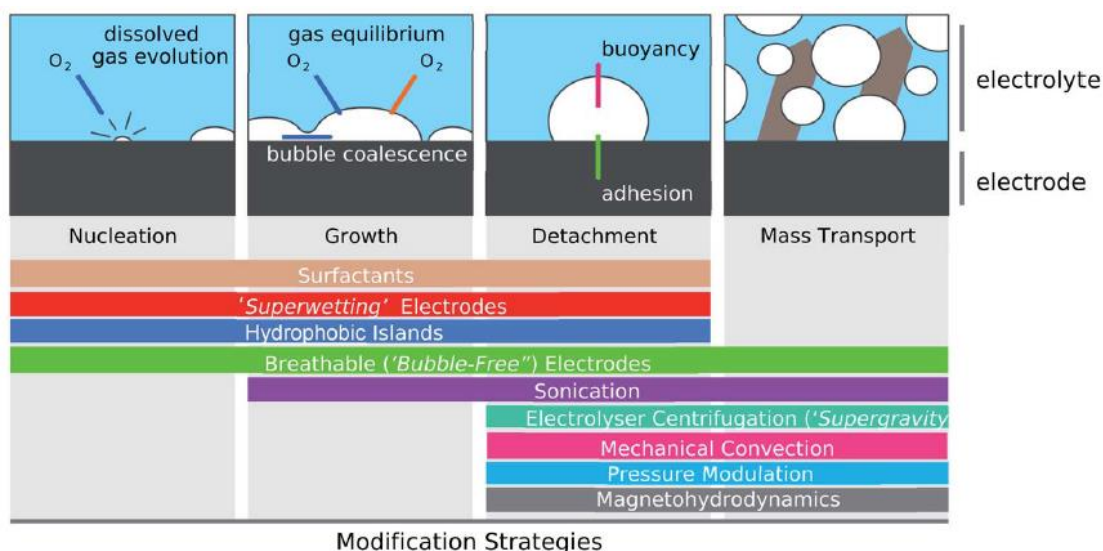


Fig. 19. Schematic of bubble removal strategies. From ref. [45].

Finally, a recently proposed breathable electrode design is worth mentioning. The concept developed by ref. [156] includes a porous separator that feeds the electrodes with electrolytes thanks to capillary-induced transport. The electrodes are not immersed in an electrolyte; consequently, the operation is intrinsically bubble-free. The authors claim to have achieved the impressive performance of 1.51 V at 0.5 A·cm⁻². One potential concern they may encounter relates to heat management, as maintaining a constant temperature for a gas is more demanding than maintaining a steady temperature for a liquid. To exemplify, the heat capacity of liquid water exceeds that of water vapor, oxygen, or hydrogen gas by more than twice [157].

All these different electrode designs and fabrication methods aim to maximize the surface area while still allowing for quick gas removal [127]. In the context of this thesis, our objective aligns with this pursuit as we delve into the investigation of various electrode geometries to enhance bubble removal, leveraging the influence of forced electrolyte flow.

3.1.5 Stacks

When stacking cells, two configurations are possible: unipolar, at which the cells are connected in parallel, and bipolar, at which cells are connected in series. In the case of unipolar electrolyzers, the voltage applied to the stack is the same as the cell voltage, but the stack current is the sum of the cells' current. Consequently, these electrolyzers must deal with huge currents and low voltages, which is the most inefficient and expensive form of power conversion. On the other hand, in a bipolar electrolyzer, the stack current equals the cell current, but the

voltage applied across the electrolyzer increases with each additional cell. Consequently, the system operates at low current at high voltage, which is far more efficient and cheaper. That is why industrial electrolyzers present the bipolar configuration, shown in Fig. 20 [45].

An issue present in stacks and not in single cells is the shunt current, also known as leakage current or current by-pass. It is an ionic current that passes through the manifold (electrolyte line) by-passing cells. In other words, instead of going to the subsequent cell, the current by-pass it, going to a cell which are further away. This happens because all cells are connected, and cells further away have a higher potential difference. This phenomenon limits the number of cells that can be stacked together, with shunt current being proportional to the cubic function of the number of cells [45]. As a consequence of this process, the first and last few cells produce more gases than the ones in the middle of the stack. [158]. To address this issue, the electrolyte path is often increased

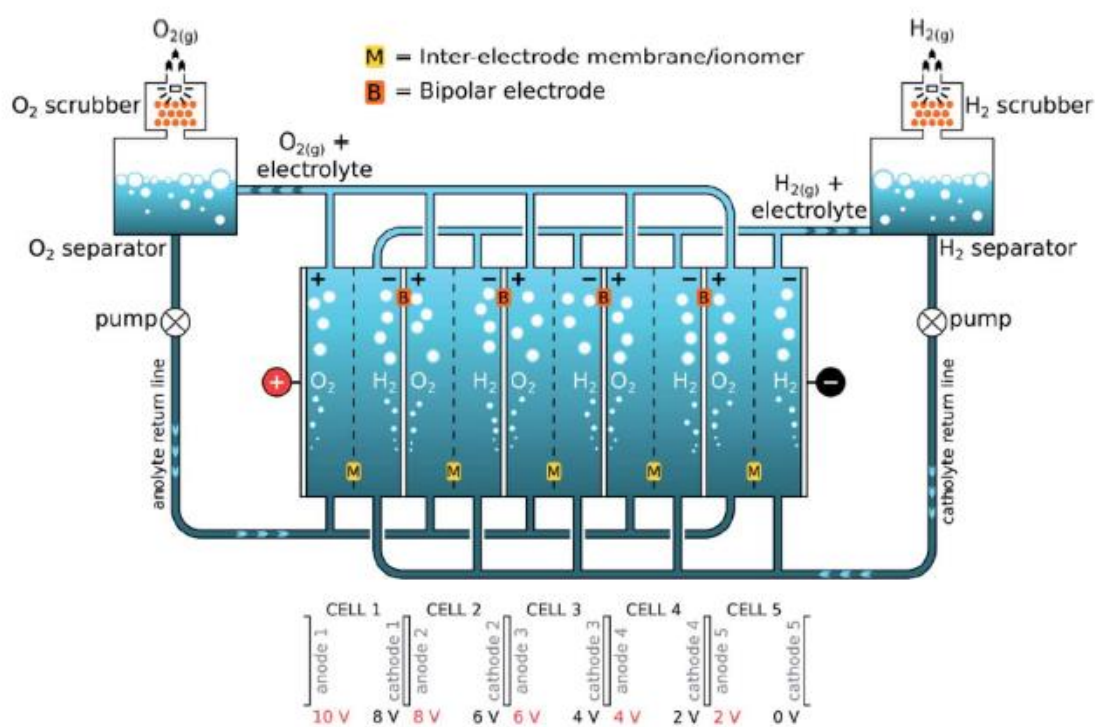


Fig. 20. Schematic of a common electrolyzer stack. From ref. [45].

in a way that increases its ohmic resistance [159]. This can be done using serpentine flow fields or decreasing the cell inlet diameter.

3.2 Pulsed water electrolysis

The replacement of a DC power by a pulsed one appears as a potential way to improve the performance of electrolyzers. Consequently, it will be a possible intensification strategy studied in this thesis. In this section, a selection of the most recent and peer-reviewed scientific papers on pulsed water electrolysis will be reviewed, focusing on the utilization of voltage and current pulses, as well as the use of redox mediators. The idea behind these pulsed operations is to get rid of bubbles and replenish the electrode surface with reactants during the off-period. Through an insightful discussion, it is going to be shown that generally, there is not enough evidence to support that pulsed power can improve the performance of water electrolysis, as the immediate increase in hydrogen production rate caused by removing bubbles and increasing the reactant's concentration at the electrode surface is hindered by the off-period when no hydrogen is produced. This observation will be further confirmed by our electrochemical characterization. There are two exceptions. The first one is the use of a redox mediator, as in this case, the operation is intrinsically pulsed but with continuous gas production, alternating between hydrogen and oxygen production, and the second is the application of current pulses in stacks at low-load conditions.

A review of pulsed electrolysis can be found in ref. [160], which also includes pulsed plasma and pulse modeling, and in ref. [161]. There are also reviews citing the impact of electric input fluctuation [162], the

effects of the applied voltage waveform [163], and the impact of pulsating power [164] in water electrolysis. Our own bibliographic review (ref. [165]) specifically includes a historical overview and a more fundamental insight into the mechanistic details of the processes and presents a larger number of analyzed articles. It also includes inductive pulses which will be not presented in this thesis as it is out of its scope.

3.2.1 Voltage pulses

Concomitantly with the work of the Latvian team, Mazloomi and Sulaiman conducted some research about Pulse Width Modulation (PWM) in water electrolysis [163,166–170]. PWM is based on a semiconductor switching element that promotes voltage pulses by cutting the circuit periodically. PWM is a way to control the amount of power delivered to an electrolysis cell. To illustrate, an increase in the duty cycle increases the power delivered, even if the voltage is constant. This section will present an overview of the key pulse width modulation techniques, and a critical summary is shown in Table 1.

This system is not ideal and presents some power dissipation. These losses can be due to switching or conduction losses. The latter is related to the nature of the switch, while the first has other influencing variables, such as the control system, switching method, and power electronics circuitry. A representation of these losses can be seen in Fig. 21. In their first publication [166], the authors studied the behavior of semiconductor switches (transistors) in an electrolysis cell, focusing on the losses. Among the studied transistors, a Metal Oxide Semiconductor

Table 1. Summary of voltage pulse methods

Group	Set-up	Contributions	Water electrolysis efficiency	Limitations	Ref
Mazloomi et al. (2013)	PWM. Aluminum plates as electrodes (surface areas between 2-16 cm ²) in 0.1-1 M KOH solutions at 25 °C. Frequencies between 1 Hz and 10 MHz.	Showed an increase in conductance up to 50% with the application of PWM relative to DC values	Not available	No detailed information about pulse amplitudes, process efficiency or hydrogen production rate.	[169]
(2013)	PWM. 8 cm ² Al plates in KOH solution (concentration not specified). On-voltages between 2-10 V and duty cycles between 10-90%	Showed that the PWM technique was more efficient at lower voltages and lower duty cycles	For 10% duty cycle, on voltage of 2 V, there was a hydrogen production rate of 1.04 ml.min ⁻¹ .cm ⁻² during on-time (against 0.88 ml/min.cm ² at DC)	Did not consider Al dissolution. No detailed information about materials or methods.	[170]
Martins et al. (2017)	PWM. Carbon, stainless steel and copper electrodes on H ₂ SO ₄ 0.25-1% (surface area of 8.8 cm ² for the cathode and 6.2 cm ² for the anode). On-voltages of 15 V, duty cycles between 10-90%, and frequencies between 1-16 kHz	Showed a non-linear behavior between duty cycle and production rate	On-time production of 1.3 ml/h.cm ² at 50% duty cycle	No analyses about efficiency. No comparison with DC.	[171]
Demir et al. (2018)	PWM. Cylindrical Pt electrodes (0.314 cm ²) in 10-15 wt% KOH solution at room temperature. On-voltages between 6-10 V, duty cycles between 10-50% and frequencies between 0.1 Hz and 1.2 MHz.	Showed that voltage pulsed presented much lower hydrogen production rates.	On-current of 2.3 A.cm ⁻² at 6 V, 50% duty cycle, and 1.2 MHz of frequency, and 15 wt% KOH. DC was 3 A.cm ⁻²	Studied only high cell voltages (6-10 V) compared to the reversible cell voltage (1.2 V). Power consumption was underestimated.	[172]

Table 1 (continued)

Group	Set-up	Contributions	Water efficiency	electrolysis	Limitations	Ref
Huang (2013)	PWM. Pt/carbon electrodes (5.3 cm ² each) separated by a membrane. Anolyte was 2.0 M (NH ₄) ₂ SO ₃ solution and catholyte was deionized water, all at 75°C. Pulse width of 10 ms and the duty cycles between 12.5% and 50%. On-voltages between 0.6-1.2 V.	Showed an increase in the on-current by the use of pulses.	On-current of 180 mA/cm ² at on-voltage of 1.2 V and 50% duty cycle (For the same current density, DC needed 1.26 V)	More understanding about the mechanisms of the process is needed. Did not study water electrolysis, but electrolysis of aqueous (NH ₄) ₂ SO ₃ solution ($E^{\circ}_{\text{cell}} = 0.11 \text{ V}$).	[173]	
Houring et al. (2014)	Nickel plates (1 cm ²) in KOH solution (5-40 wt%). Pulse period of 100 ms, duty cycles between 10-90%, on-voltages between 3.5-4.5 V, off-voltages between 0-4.5 V.	Observed an improvement of up to 40% in on-current with the application of voltage pulses. Showed a synergistic effect between voltage pulses and the application of a magnetic field. Showed that pulses help bubbles removal.	On-current of 3 A/cm ² at 4.5 V and 10% duty cycle (against 2.1 A/cm ² at DC)	Studied only one frequency.	[174]	
Al-Hasnawi (2015)	Pulse frequency between 2Hz - 1 MHz, on-voltages between 1.5-3 V, and square, sinus and triangular waveforms.	Showed that square voltage pulses presented the best hydrogen production rate.	0.5 ml/min at on-voltage of 2 V	None information about electrolyzer materials. No proper comparison with DC.	[175]	
de Radigués et al. (2019)	Nickel electrodes (20 cm ²) in 1 M KOH solution at 25°C. Frequencies between 2.5-250 Hz, 50% duty cycle, base voltage of 1.2 V and peak voltages between 1.3-3 V.	Showed that voltage pulses could increase the average current by more than two times (from 0.02 A/cm ² to 0.05 A/cm ²). Showed a synergistic effect between voltage pulses, forced electrolyte flow, and 3-D electrodes.	Average current of 2.17 mA/cm ² at a peak voltage of 2 V at a frequency of 250 Hz and porous electrodes (450 μm)	Studied only one pulse per condition. Did not collect the produced hydrogen.	[176]	

Field Effect Transistor (MOSFET) with soft switching methods such as zero voltage switch (ZVS) and zero current switch (ZCS) was the best. Furthermore, the authors also proposed a parallel connection of water electrolysis cells together with semi-conductor switches to provide a hydrogen production plant with a wide range of production rates.

After studying transistors, the authors published a review [167] on the influence of different variables on the efficiency of water electrolysis. They also stated that the equivalent circuit of a water electrolysis cell contains non-linear elements. Consequently, it was pointed out that applying other forms of voltage than DC may lead to a process improvement.

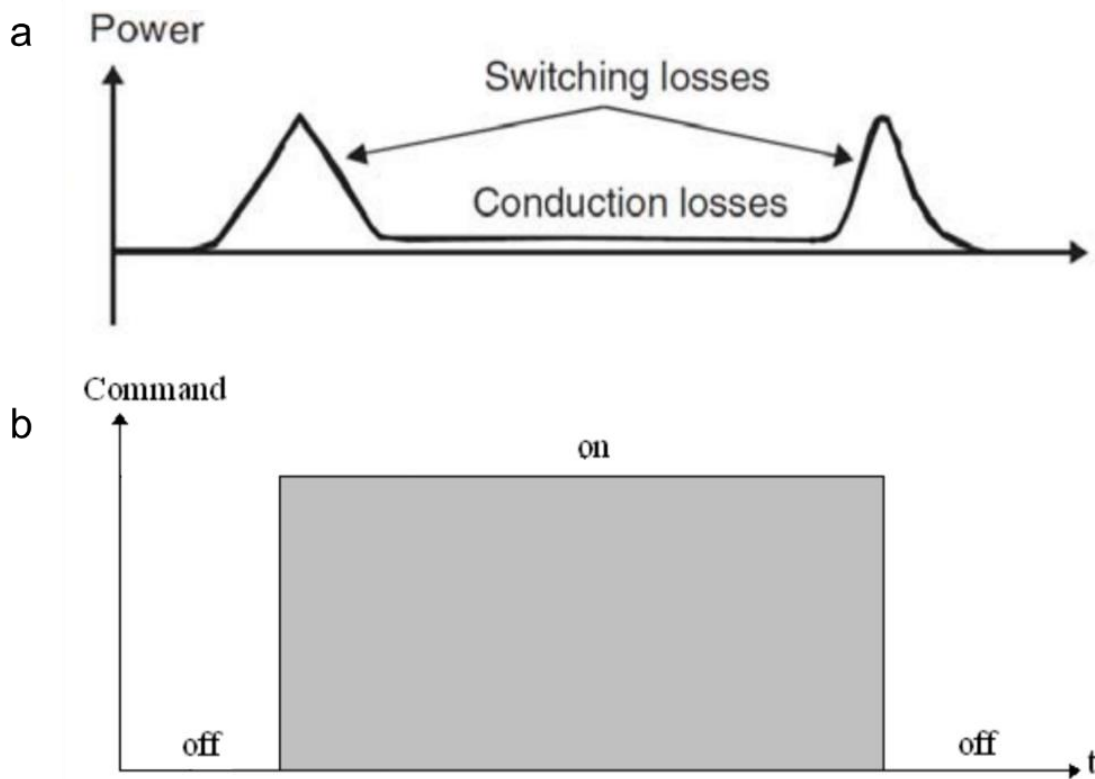


Fig. 21. Behavior of semiconductor switch a) Power loss elements b) Command signal. Adapted from [166].

Bearing in mind the last statement, Mazloomi *et al.* researched the electrical impedance of the water electrolysis cell [168]. Even though in this first experimental paper the authors applied current pulses and not voltage ones, we choose to include it in this section for a better understanding of the whole work. The authors applied current pulses by the use of PWM with a MOSFET transistor (as recommended in ref. [167]). This setup is seen in Fig. 22.a for different cells connected to an electrical grid. The electrodes were made of aluminum plates with a thickness of 0.5 mm and the electrolyte was potassium hydroxide with concentrations between 0.1 M and 2 M at 25°C. The choice of aluminum is unconventional since it leaches in an alkaline environment. Singh *et al.* reported a corrosion rate of $15.1 \text{ mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ for pure aluminum in a 1 M NaOH at 35°C [177]. At this rate, the aluminum plate used in the paper would be dissolved in only a few hours. This said, it may be inferred that the experiments presented by Mazloomi *et al.* had a short duration. Furthermore, the leaching of Al results in the production of gaseous hydrogen [178], which would then interfere with the results. Moreover, Al has not a high activity for HER, having an exchange current density for hydrogen evolution about a hundred times lower than the one for commonly used Ni electrodes (at 0.5 M H₂SO₄) [179]. The distance between electrode plates varied between 5 mm and 50 mm. At a fixed DC voltage given by the power supply, pulses of frequencies ranging from 20 Hz to 2 MHz were applied, and the current was measured. All pulses had a duty cycle of 50%. A typical plot of current versus frequency is shown in Fig. 22.b.

Some interesting aspects can be seen and they can be better understood supposing a second-order RLC (resistive-inductive-capacitive)

equivalent circuit shown in Fig. 22.c, where R_e is equal to the internal resistance of the electrolyte, C_D is the cell capacitance; L_{ext} and R_{ext} come mainly from the cabling and external connections of the system. The impedance of the capacitor and the inductor is given in Ω by:

$$Z_c = \frac{1}{2 \cdot \pi \cdot f \cdot C_D} \quad (63)$$

$$Z_L = 2 \cdot \pi \cdot f \cdot L \quad (64)$$

where f is the pulse frequency (Hz), C is the capacitance (F), and L is the inductance (H). At DC electrolysis, $f = 0$; consequently, the capacitor works as an open circuit and the inductor as a short circuit. The total impedance of the system described in Fig. 22.c is given by:

$$Z = Z_L + \frac{R \cdot Z_c}{R + Z_c} \quad (65)$$

with R the resistance (Ω). According to this equation, increasing the frequency decreases Z_c , and hence, the total impedance. Nevertheless, this decrease goes until a resonance frequency is reached, which was in the range of 0.4-700 kHz, depending on the interelectrode distance, size, electrolyte concentration, and DC magnitude. Notice that the 229 kHz previously reported by ref. [180] is within this range. For frequencies higher than that, the increase in Z_L becomes more important, increasing the total impedance. As the frequency tends to infinity, the inductor acts as an open circuit and blocks the current. This behavior was observed experimentally and it is shown in Fig. 22.b. Given that, the authors proposed that at the resonant frequency, the impedance is decreased and higher currents can be achieved at the same voltage.

After determining the natural frequency, the authors compared the voltage value needed to achieve the same current at DC electrolysis and at pulsed electrolysis at the resonant frequency. The results showed a decrease in the voltage value of up to 20% in the case of pulsed electrolysis at the same average current (from 5.34 V to 4.27 V). This decrease in voltage would mean a decrease in power and a more efficient process. Nevertheless, the process remains very inefficient, with the most-performing configuration presenting 3.95 V at 50 $\text{mA}\cdot\text{cm}^{-2}$ (while the DC process presented a voltage of 3.98 V at the same current density). In addition, the study did not consider the potential influence of galvanic dissolution of aluminum and the potential effects of varying the frequency of voltage pulses on this reaction. Thus, it is not clear whether the results are coming from water

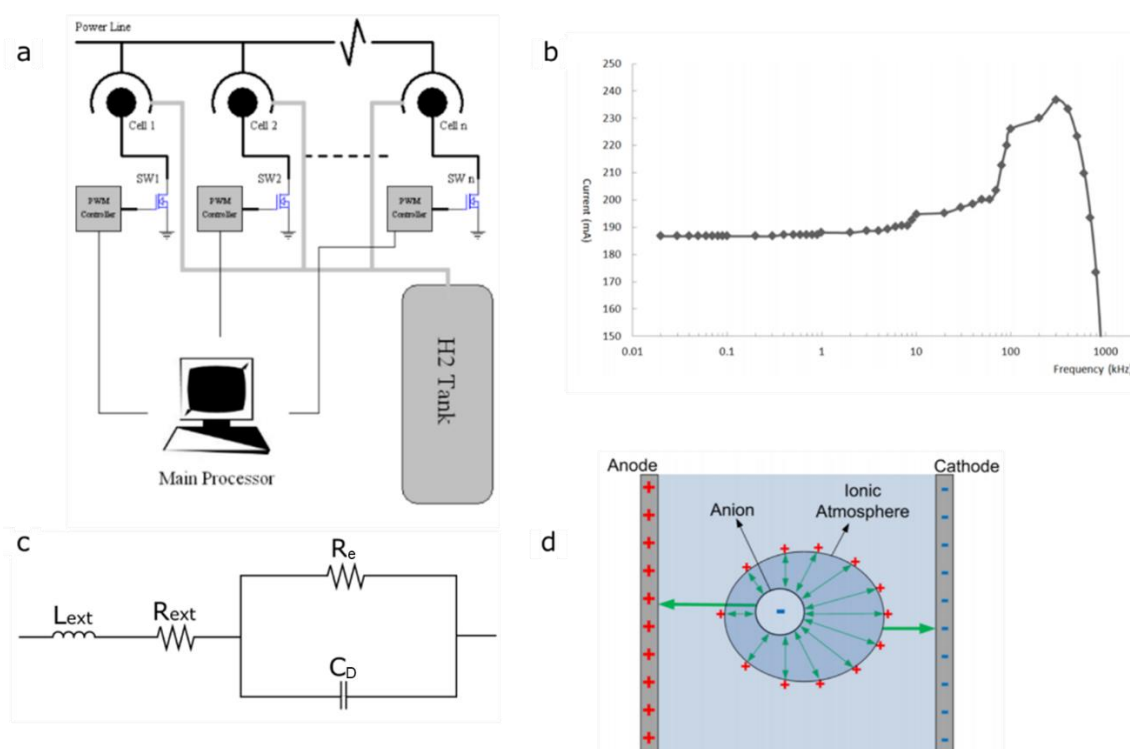


Fig. 22. a) Experimental setup for pulse width modulation [166] b) Current versus frequency plot for aluminum electrodes in 0.1 M KOH c) Equivalent circuit for a water electrolysis cell From [168] d) Relaxation time [170].

electrolysis or aluminum dissolution. Moreover, hydrogen gas was not collected; thus, it cannot be stated that the Faradaic efficiency was indeed 100%. Therefore, repeating their experiments with conventional nickel electrodes would be useful.

After that, the authors published a paper reviewing the influencing factors on water electrolysis efficiency [163]. Pulsed voltage was included as one of the factors that can enhance efficiency, giving as an example the work done by Shimizu *et al.* [181].

Later, Mazloomi and Sulaiman published another article detailing an electrochemical impedance spectroscopy analysis [169]. It was performed by applying DC sinusoidal voltage pulses (DC offset equal to alternating current (AC) pulse peak). The electrodes were again aluminum plates. The electrode size, distance, and KOH solution molarities were the variables. The results were similar to Fig. 22.b, with a peak in the resonant or natural frequency that was in the range between 0.8 MHz and 12.2 MHz, depending on the experimental conditions. Once more, the second-order RLC equivalent circuit shown in Fig. 22.c was proposed to be the best representation of a water electrolysis cell. Generally, the value for the resonance frequency increased by decreasing the distance between electrodes and increasing the molarity.

Finally, in their last paper about pulsed water electrolysis [170], Mazloomi's team performed an experiment similar to [169]: aluminum plates in potassium hydroxide solution. Once more, the aluminum dissolution in an alkaline solution was not considered. The pulses applied had a frequency of around 7 MHz, and the voltages varied

between 2 V and 10 V. According to their results, the pulsed process had better efficiency and a lower production rate. It is easy to understand the lower production rate as a consequence of the off-period at which no production is expected. This explains also the experimental observation that the lower the duty cycle, the lower the production rate. Nevertheless, efficiency depends only on the voltage, as in Eqs. (25) and (26). Since the on-voltage was constant, the efficiency should be the same. In the case of this study, the efficiency was estimated employing energetic efficiency, and the production rate was measured through hydrogen collection. Since the dissolution of aluminum in KOH produces hydrogen gas, it is expected that a percentage of the collected hydrogen was not coming from water electrolysis. As during the off-period hydrogen could be coming from Al dissolution without power consumption, the efficiency would appear to be better, when in reality another reaction was occurring. Hence, the production rate and efficiency are expected to be lower than the calculated ones. As the effect of pulses on the aluminum dissolution is unknown, it is difficult to validate the statement of better performance for pulsed water electrolysis. In any case, the authors claimed that the observed improvement in efficiency resulted from the fact that neither the EDL nor the diffusion layer had enough time to be fully formed. Furthermore, it was argued that immediately after a voltage application, ions are attracted to the electrode with the opposite side, but the ionic atmosphere around these ions takes some time to be rearranged. This delay, called relaxation time, is illustrated in Fig. 22.d. When the ion moves and the ionic atmosphere does not, an asymmetrical electric field is created, slowing the ion movement and consuming part of the energy

the electric field provides. They assumed a relaxation time in the order of several hundreds of nanoseconds. Since the pulse width was lower than the relaxation time, the energy for the rearrangement of the ionic atmosphere would not be consumed, being another factor that would explain the higher efficiency of the pulsed electrolysis.

As in the work of Mazloomi and collaborators, Martiningsih *et al.* [171] also studied PWM in water electrolysis using a MOSFET transistor. The frequency went from 1 kHz to 16 kHz, the duty cycle went from 10% to 90%, and the voltage was set at 15 V. Stainless steel electrodes were immersed in 1% sulfuric acid solution. For duty cycles between 10–50%, the production rate and duty cycle were directly proportional. At 70% duty cycle, a decrease in the production rate was observed when compared to the rate at 50% duty cycle. After this anomaly, the production continued to increase with the duty cycle in the interval of 70–90%. This raise was observed for pulses in the 4–12 kHz frequency range. No explanation of this phenomenon was given, and the error was not presented, so it is hard to say if this anomaly was statistically significant. No analysis was done regarding efficiency, and no comparison with conventional water electrolysis was done.

Demir *et al.* [172] also conducted experiments with pulses during alkaline water electrolysis. The authors used platinum electrodes in 10 wt% and 15 wt% KOH solution. The applied voltage values were 6 V, 8 V, and 10 V. Two duty cycles were used: 10% and 50%. The frequencies varied between 0.1 Hz–1200 kHz. The pulses were applied based on MOSFET transistors that cut the circuit during off-time. Using these voltage pulses, the authors claimed to have achieved an energy consumption per mole of hydrogen between 20–25% lower than the one

from DC electrolysis. Nevertheless, a careful look at the results shows that this conclusion was inaccurate. The way the average power consumption was calculated was as follows:

$$P_{el} = \sqrt{\frac{1}{t_p} \int_0^{t_p} \Delta E(t)^2 dt} \cdot \sqrt{\frac{1}{t_p} \int_0^{t_p} i(t)^2 dt} \quad (66)$$

with ΔE the cell voltage (V), i the current (A), and t_p the pulse period (s). However, this method of estimating power can bring different conclusions from those obtained using a more classical approach. For example, in the case of pulses of 6 V, 50% duty cycle, 1.2 MHz of frequency, and 15 wt% KOH, the authors claimed an improvement of 20–25% in efficiency when using pulses. For DC, there was a hydrogen production rate in the order of $0.108 \text{ ml}\cdot\text{s}^{-1}$, which gives a current density of approximately $3 \text{ A}\cdot\text{cm}^{-2}$, considering standard conditions of temperature and pressure. For pulsed voltage, the production rate was approximately $0.042 \text{ ml}\cdot\text{s}^{-1}$, giving a current density during the on-period of $2.3 \text{ A}\cdot\text{cm}^{-2}$. This result means that at a fixed cell-voltage of 6 V, DC electrolysis presented a higher current density, implying it had the best performance. If the consumed power was estimated as the integral with respect to time of the product of voltage and current and if the efficiency was calculated using Eq. (25), the efficiencies of the DC and the pulsed process would be the same and equal to 21%. This happens because their cell voltages were the same, and the efficiency depends only on this parameter. Since DC electrolysis presented a higher current density, it means that at a fixed production rate, DC would have a lower cell voltage and a higher efficiency. Furthermore, since the authors used cell voltages much higher than the reversible cell-

voltage, the LHV efficiencies were significantly low: 21%, 16%, and 13% for 6 V, 8 V, and 10 V, respectively.

An important contribution of this work was the observation of a relation between the hydrogen production rate and the frequency at a fixed duty cycle. Taking as an example pulses with 50% duty cycle, 8 V, and 15 wt% KOH, an increase in production rate was observed with frequency. This improvement was attributed to the relaxation time of the bubbles on the surface of the electrode (which enhanced diffusion of dissolved gases), and to the pumping effect created by the pulsed voltage on bubbles. The authors claimed that the method also improved the lifetime of electrodes since it reduced the contact with oxygen bubbles at the anode.

Still in the domain of electrolytic hydrogen production, Huang [173] studied the effect of pulses during the electrolysis of ammonium sulfite solutions (reversible cell-voltage equal to 0.108 V). As in water electrolysis, hydrogen was produced at the cathode. However, instead of oxygen, $\text{SO}_4^{2-}(\text{aq.})$ was produced at the anode from the oxidation of $\text{SO}_3^{2-}(\text{aq.})$. The author noticed that the rate of DC electrolysis was not constant at the microsecond scale. This observation indicated that the rate of electrolysis was controlled by the electrolyte transfer rate. Consequently, pulses were applied to try to improve this transfer. In their experiment, the pulse width was 10 ms, and the duty cycle was between 12.5% and 50%. On-voltage was changed between 0.6–1.2 V, and off-voltage was always zero. The result showed that pulsed electrolysis could achieve the same current as DC at lower voltages. For example, to reach a mean current density of $180 \text{ mA}\cdot\text{cm}^{-2}$, DC

electrolysis needed a cell voltage of 1.26 V, while pulsed electrolysis needed only 1.2 V. The improvement in electrolysis was attributed to mass transfer. Indeed, when the voltage was interrupted, the $\text{SO}_3^{2-}(\text{aq.})$ reactant migrated to the anode surface, and its concentration was allowed to build up before the next pulse was applied. Therefore, electrolysis always occurred at maximum reactant concentration on the electrode surface, minimizing the overpotential of the electrolysis.

Lin and Hourng [174] studied the effect of pulsed voltage and magnetic field in water electrolysis. Regarding the pulses, their width varied from 10–90 ms with duty cycles between 10–90%, on-voltages between 3.5–4.5 V, off-voltages between 0–4.5 V, and a frequency of 10 Hz. Nickel plates were immersed in a potassium hydroxide solution. It was argued that when the voltage was on, the reaction occurred and created a difference in concentration. During the off-time, diffusion replenished ions that were consumed in electrolysis. This argument justifies the results obtained: an increase in current density at on-time. The lower the duty cycle, base voltage, or both, the higher the on-current. Looking closely at the results, one can infer that the increase in the on-current was insufficient to compensate for the off-time. In other words, at a fixed on-voltage (thus efficiency), the average current was lower for the pulsed process. For example, for an off-voltage of 0 V, on-voltage of 4.0 V, period of 100 ms, and 10% duty cycle, the on-current density was $2.3 \text{ A}\cdot\text{cm}^{-2}$, representing an average current density of $0.23 \text{ A}\cdot\text{cm}^{-2}$. At 4 V, the DC process produced $1.65 \text{ A}\cdot\text{cm}^{-2}$, 7 times higher. Furthermore, as shown in Eq. (48), capacitive charging is expected at the beginning of a pulse. It is possible that part of the observed on-current was capacitive current due to EDL charging. If so, a discharge

would be observed during off-time and the capacitive current could be estimated. It is not clear if the authors considered this process in the analysis. With the help of a video camera, the authors observed that the pulses caused: (a) an increase in the concentration of gas in both electrodes, (b) a decrease in the thickness of the gas diffusion layer, (c) a faster bubble rise from the surface of the electrode. An example is shown in Fig. 23.

Al-Hasnawi [175] studied the effect of different pulse variables (amplitude, frequency, and waveform) on water electrolysis. Even if it is unclear what the experimental setup was, it is known that the pulses had a frequency between 2 Hz - 1 MHz, with amplitudes between 1.5–



Fig. 23. Oxygen and hydrogen bubbles being produced simultaneously on a different nickel electrode immersed in a KOH solution with an electrode distance of 2 mm, $E_{\text{on}} = 4.0$ V, and $E_{\text{off}} = 0$ V. Adapted from [174].

3 V, and the waveforms were square, sinus, and triangular. In this experiment, square waveforms were the only ones to present a significant hydrogen yield. Besides, the square waves presented the best efficiency. Nevertheless, the results presented for Faraday and energy efficiency were strangely very close, as if they were the same parameter. A higher frequency caused a decrease in production rate after 100 Hz, and efficiency increased until 10 Hz and then arrived at a plateau, starting to decrease only for frequencies higher than 10 kHz. It was unclear from the results if the efficiency was improved or not. At a fixed current of 0.05 A, it was observed a higher hydrogen production rate for pulsed operation ($0.35 \text{ mL} \cdot \text{min}^{-1}$ against $0.3 \text{ mL} \cdot \text{min}^{-1}$). This result implies that a side reaction was occurring at DC and that pulsed operation reduced its effects. However, it is not easy to judge without knowing the electrolyzer materials. Moreover, as statistical analyses were not performed, the observed difference may be an experimental error.

de Radiguès *et al.* [176] studied the application of pulsed voltage for hydrogen production. The authors used 3-D pure Ni foams, an anion exchange membrane, and 1 M KOH solution. The pulses had a duty cycle of 50%, frequencies varied from 2.5–250 Hz, and on-voltages were in the range of 1.3–3 V. A baseline voltage of 1.2 V was applied during off-time. Negative currents during off-time were observed due to transient electrical effects or to the inverse reaction taking place. The results showed that for a frequency of 250 Hz, pulses caused an increase in the average current from $0.02 \text{ A} \cdot \text{cm}^{-2}$ to $0.05 \text{ A} \cdot \text{cm}^{-2}$. Moreover, the authors concluded that there was a synergistic effect between 3-D electrodes, forced electrolyte flow, and pulsed voltage, which caused

the current to increase five times as compared to 2-D electrodes at DC operation and natural convection. Nevertheless, only one pulse of each kind was applied and it is not clear if the results come from faradaic or capacitive processes.

3.2.2 Current pulses

At the Bulgarian University of Chemical Technology and Metallurgy, researches have been conducted on the use of current pulses during water electrolysis. Their first paper [182] aimed to study the modification caused by pulses on surface films formed on AISI 316L stainless steel electrodes. The electrolyte was a 6 M KOH solution. The pulsed currents were applied with amplitudes of 12–250 mA, frequencies of 0.5–10 kHz, and duty cycles between 1 and 99%. The samples were analyzed after 24h of pulsed electrolysis by Electrochemical Impedance Spectroscopy, Cyclic Voltammetry, Scanning Electron Microscope, and X-ray photoelectron spectroscopic. At the cathodes, the formation of a layer of Cr(OH)_3 was observed, which decreased electronic conductivity. On the other hand, a decrease in the normalized Cr content was noticed at the anode, causing a decrease in electronic and ionic conductivity. This was attributed to Cr dissolution at the anode and its subsequent deposition at the cathode. They concluded that profound surface modifications occur during pulsed water electrolysis and are intimately related to the pulse duty cycle and frequency. These modifications were more significant at the cathode, and the number of observed crystals per surface area increased with the pulse duty cycle and frequency.

More recently, Yang *et al.* [127] investigated how porous nickel electrodes can improve hydrogen production in an alkaline water electrolysis cell. The authors showed that not only the surface area matters but also the structure of the electrodes, especially concerning bubble removal. To study the bubble behavior, pulses with a width of five minutes were applied, and it was noticed that at a constant current, the voltage increased with time due to bubble formation during the on-period. During the off-period, bubbles could be removed, as observed by the decrease in pressure. With fewer bubbles, the next pulse started at lower voltages, improving the overall efficiency of the process. This study shows the potential of using low-frequency pulses to improve bubble removal efficiency.

Siracusano *et al.* [183] studied current pulses for PEM electrolyzers. Pulses with frequencies between 0.5 mHz and 0.5 Hz, on-currents of 3 A·cm⁻², and off-currents of 0 A·cm⁻² were applied. The results show a higher degradation rate for pulsed operation, resulting in poorer performance after hours of operation. However, it was also found that keeping the current at zero for enough time can help to regenerate the catalyst and to allow entrapped gas to leave electrodes' micro-pores. In other words, it was not worth using pulsed current but it was beneficial to eventually let the current at zero for a certain amount of time. Refs. [184,185] also reported decreased PEM degradation losses upon current interruption.

Dobó *et al.* [186] studied the effect of current fluctuations during water electrolysis. The applied current varied around a mean value in different shapes: sinusoidal, triangular, saw-tooth, and square. The mean current density went from 0.1 A·cm⁻² to 0.5 A·cm⁻² (corresponding voltage

between 2.1–2.9 V), with frequencies ranging from 1 Hz to 10 kHz. Amplitude went from zero to twice the average value. The main conclusion was that any change from steady DC power caused a decrease in energetic efficiency. This decrease occurred because the current fluctuations increased the consumed power while the hydrogen production rate was the same.

Frensch *et al.* [187] studied different operation modes in for a PEM electrolyzer. The analyzed scenarios were constant current, constant voltage, and cycling operations. The latter consisted of current pulses switching between 0 and $2.0 \text{ A}\cdot\text{cm}^{-2}$ with a 50% duty cycle and relatively large pulse widths of 10, 60, and 100 s, chosen because they were close to a solar photovoltaic (PV) power profile. It was found that faster dynamic cycles improved the cell performance due to decreased total ohmic resistance. The authors suggested as a possible explanation that the observed decrease in cell potential resulted from an acceleration of bubble detachment and a change in bubble growth behavior, reducing both cell resistance and membrane dehydration.

Finally, a recent and interesting study - [188] - greatly differs from previous papers because it considers the effect of current pulses in an AWE stack instead of a single cell. Industrial conditions were applied, namely 30 wt% KOH and temperatures between 40-80°C. The authors observe that during DC electrolysis at low loads, bubble evolution occurs only at the first and last bipolar plates but not in the middle ones. As the load increases, the upper part of the middle plates starts to have bubble evolution, but not the lower parts. Finally, at high-loads, all the plates present bubble evolution. It is argued that the electrolyte channel, shared by all the bipolar plates, is the main source of this inconsistency,

as it connects any two bipolar plates. Consequently, the efficiency at low loads is lower than at high loads and, counterintuitively, increases with voltage. More details about this current by-pass can be found in Ch. 3, in refs. [189,190] and in Fig. 24 (bottom left). To counter the inefficiency, the authors propose using current pulses to ensure high-load conditions even at low-loads. They show that using 10 Hz pulses with an optimal on-current value can increase the efficiency by a factor of 2 (Fig. 24). Setting the minimum value for the HHV efficiency at 60%, the operating range can go from 40-100% load at DC to 22-100% load for pulsed operation, increasing electrolyzer flexibility. Nevertheless, since the paper reasons in terms of power, it is unclear if, at a fixed production rate, the efficiency of pulsed operation is higher than that of DC, but it is possible to get some insights on this matter.

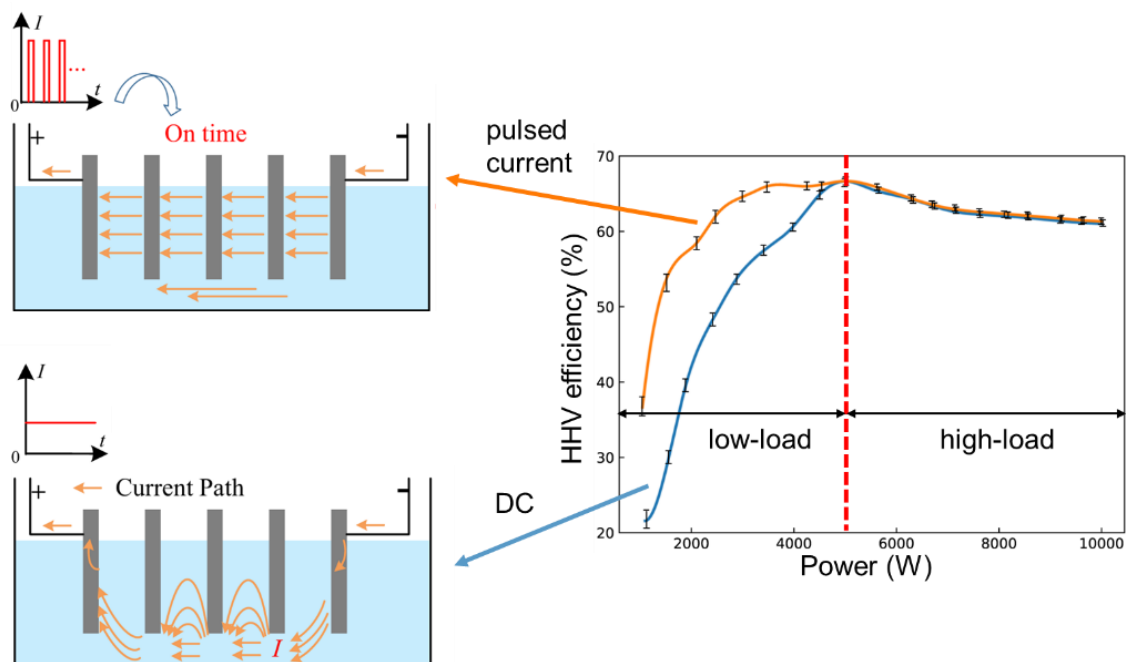


Fig. 24. HHV efficiency as a function of electric power input (right) and schematics of the proposed mechanism at low-loads (left). For pulsed current, current flows in all the electrodes. Current by-pass the middle electrodes for DC, and only the first and last electrodes are active. Adapted from ref. [188]

Fig. 24 shows the results for an on-current of 40 A. Assuming that the voltage at on-period was constant for all duty cycles and equal to the voltage for the DC case (i.e., 92.7 V at 40 A), one has a higher efficiency for pulsed current, which is logical as the current is divided by a larger number of production sites and active electrodes. For example, at a mean current of 20 A, DC efficiency was 34%, while pulsed current efficiency was 56%. Unfortunately, no information about electrode area was given, making it difficult to compare with other systems.

Table 2 provides a critical summary of the works presented above about current pulses

.

Table 2: Summary of current pulse methods

Group	Set-up	Contributions	Water electrolysis efficiency	Limitations	Ref
Mazloomi <i>et al.</i> (2012)	Aluminum plates as electrodes (surface areas between 1.5-10 cm ²) in 0.1-1 M KOH solutions at 25 °C. Frequencies between 10 Hz and 10 MHz. On-currents between 0.05-1.1 A. 50% dutv cvcle.	Showed that there was a resonant frequency that could decrease the cell voltage up to 15%, when the current PWM technique was applied.	3.95-11.07 V at 50 mA/cm ² (against 3.98-11.56 V at DC)	Did not consider oxidation in alkaline solution. Did not collect hydrogen.	Al [168]
Tzvetkoff <i>et al.</i> (2013)	Stainless steel electrodes on 6 M KOH solution. Current amplitudes between 12-250 mA, pulse frequencies of 0.5-10 kHz, and duty cycles between 1 and 99%.	Observed profound modifications in the electrodes surface upon the application of current pulses	Not available	No analysis about the pulsed operation itself e.g. efficiency or cell voltage.	[182]
Yang <i>et al.</i> (2020)	Ni electrodes (0.16 cm ²) in 1 M KOH. Current pulses with a peak current density of 25 A/cm ² , pulse period of 600 s and 50% duty cycle.	Showed that the interruption of current was beneficial for the bubble removal and electrolysis performance.	25 A·cm ² at 3.6 V	Studied only pulses with long periods.	[127]
Xia <i>et al.</i> (2023)	Commercial AWE stack. 30 wt% KOH at 40-80°C.	Showed that current pulses in an electrolyzer stack can improve performance at low power by reducing the current by-pass.	62% HHV efficiency at 2420 W (against 48% for DC).	The efficiency dependence with production rate was not studied.	[188]

3.2.3 Pulses with a redox mediator

Given better management of unstable power inputs coming from renewable sources, which may result in hydrogen and oxygen gas mixing, there is an increasing interest in decoupling the HER from the OER so that they can occur at different times. In this respect, ref. [191] introduced the concept of electron-coupled-proton buffers (ECPB) to separate the two water electrolysis half-reactions. In the first step, electricity was used to oxidize water, while protons and electrons were stored in a solution containing the ECPB (phosphomolybdic acid in their case). Then, the reduced ECPB was re-oxidized, and protons were reduced, producing hydrogen. This method prevented gas mixing and increased the equipment's flexibility with respect to the choice of the membranes and electrode materials. An interesting application of such ECPBs is that solar energy could then be used to produce hydrogen during the day, while during the night, windmills would produce oxygen [192].

Still to facilitate gas separation and to deal with variable energy inputs, Rausch *et al.* [193] developed an electrolysis system with a redox mediator to decouple the two water electrolysis half-reactions. In their case, water was oxidized at the same time that a redox mediator (silicotungstic acid) was reduced. Then, the solution containing the reduced redox-mediator was transferred to a chamber containing catalysts for spontaneous hydrogen evolution. With this method, the HER was no longer coupled to the OER, increasing the rate of H₂ evolution by a factor of 30 compared with state-of-the-art PEM electrolyzers. Chen *et al.* [194] used nickel hydroxide

(Ni(OH)₂/NiOOH) as a redox mediator in a membraneless setup. During the hydrogen production step, electricity was used to reduce water and oxidize Ni(OH)₂. After that, comes the oxygen production step, at which electricity was used to reduce NiOOH and to oxidize hydroxyl ions. This system could also be coupled with a zinc anode to form a NiOOH/Zn battery to produce H₂ during electrolysis and to provide electricity during battery discharge. Coupling this system with solar panels, one could imagine hydrogen production at noon (higher power input) and oxygen production at dusk.

Alternatively, during the day, hydrogen could be produced, and the discharge of the NiOOH/Zn battery could provide electricity during the night. The same solid-state nickel (oxy)hydroxide redox mediator was used by Dotan *et al.* [89]. They created a membraneless two electrodes electrolyzer setup. The authors claimed to have improved the energy efficiency of the decoupled process using cobalt additives to catalyze the Ni(OH)₂/NiOOH reaction and inhibit oxygen evolution during HER. In their setup, hydrogen was produced at a platinized nickel-coated stainless-steel cathode at the same time that a Ni_{0.9}Co_{0.1}(OH)₂ anode was oxidized to Ni_{0.9}Co_{0.1}OOH. Then, a solution of hot electrolyte (95°C) was circulated in the cell, causing the reduction of Ni_{0.9}Co_{0.1}OOH and oxygen production. An issue with this configuration is that the operation has to be periodically stopped, as after hydrogen production the system needs to be flushed with an intermediate electrolyte and then filled with hot (95°C) electrolyte. Furthermore, even though the gases are produced at different times, there is an inevitable liquid mixing and as the electrolytes are saturated with hydrogen or oxygen, the system has an intrinsic gas mixing.

Photoelectrochemical cells were also tested in an ECPB decoupled system [195]. Moreover, redox mediators can also be used to drive chemical reactions other than HER/OER in the other half-cell. For instance, Xiao *et al.* [196] created a battery that produced oxygen during charging and hydrogen at the discharge in a dual-electrolyte set-up with FeO_x as a redox mediator.

Chen *et al.* [194] proposed the use of nickel hydroxide as a redox mediator to decouple hydrogen and oxygen production in water electrolysis. During hydrogen production, a potential difference was imposed between a commercial Pt-coated Ti-mesh (working as a cathode for the HER) and a nickel hydroxide electrode. Hydrogen evolution occurred at the cathode, and Ni(OH)_2 oxidation occurred at the redox mediator, producing NiOOH . Then, an electrical switch connected the redox mediator with an electrode made of commercial RuO_2 / IrO_2 -coated Ti-mesh for the OER. There, NiOOH was reduced to Ni(OH)_2 and at the anode, OH^- was oxidized to O_2 . Each cycle of hydrogen and oxygen production lasted for 10 min.

The authors suggested that this two-step water splitting could be operated in different compartments, the nickel hydroxide electrode being moved from one for H_2 production to another for O_2 production, allowing the production of highly pure gases without using a membrane. Nevertheless, this process does not seem efficient as the operation needs to be periodically stopped to change the position of the redox mediator from one compartment to the other. Moreover, since the power inputs from HER and OER are different, this method allows adapting the power input according to the output from unstable power sources such as wind and solar power.

Using this idea of decoupling the HER and the OER, Vincent *et al.* [197] carried out an experiment with pulsed alkaline water electrolysis. This time, instead of cycles of 10 min, cycles lasted for less than 10 s. An electrical switch alternated the circuit between HER and OER periodically, imposing always the same current each time between 0.1–

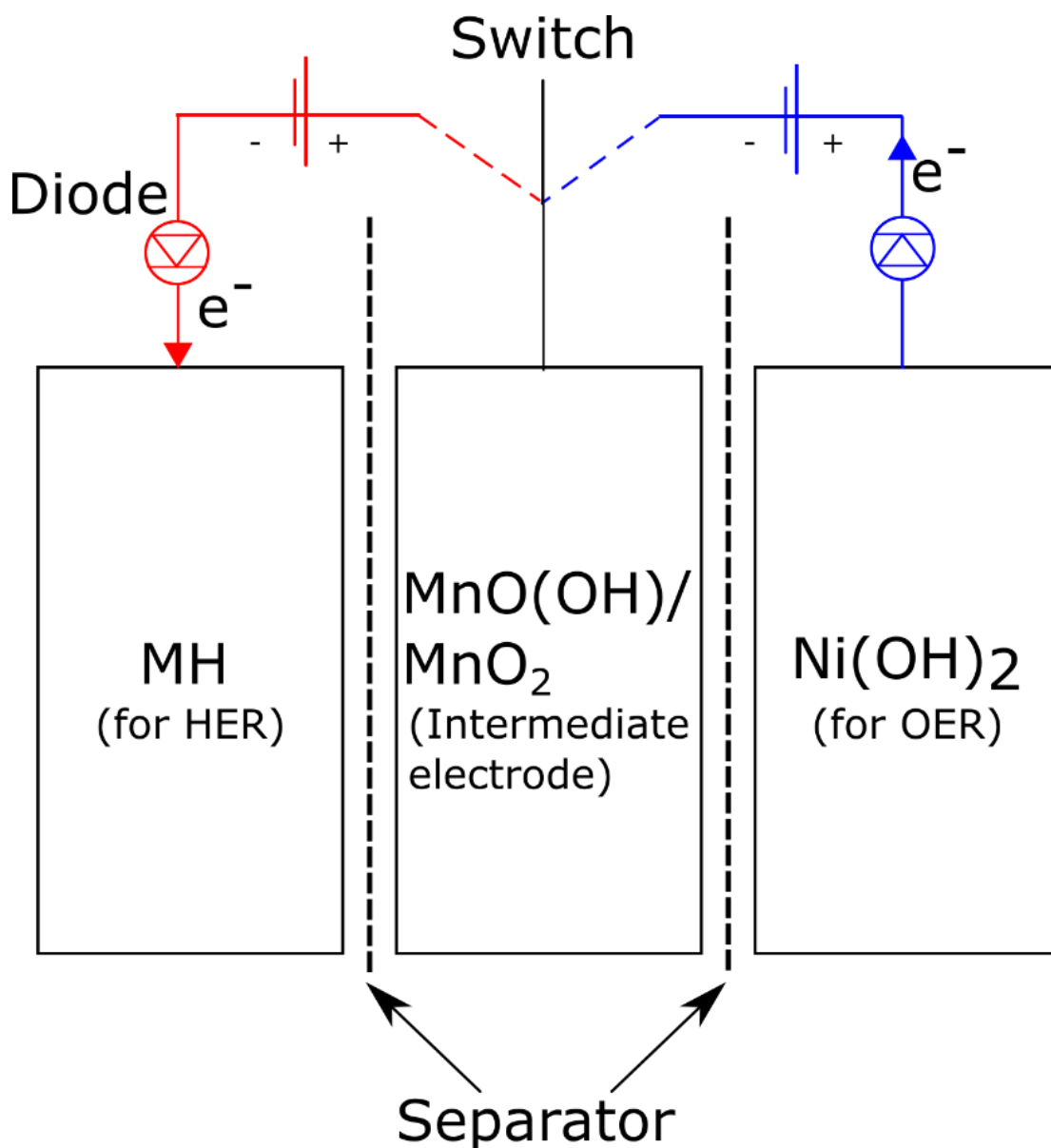
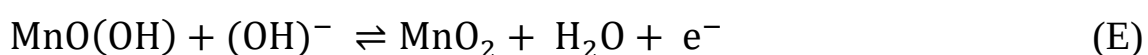


Fig. 25. Schematic view of the pulsed current supply used in [197] for two-step water electrolysis with a MnO(OH)/MnO₂ intermediate electrode, a metal hydride (lanthanum) for hydrogen evolution reaction, and a Ni(OH)₂ electrode for the oxygen evolution reaction. If the switch is connected to the metal hydride electrode, HER occurs; if it is connected to the nickel electrode, OER occurs.

$0.6 \text{ A}\cdot\text{cm}^{-2}$. This process is equivalent to producing square current pulses. The resulting voltage was in the range of 1.4–3.2 V. Diodes controlled the direction of the current. The authors stated that the frequency varied from 0.05–500 Hz. Nevertheless, they affirmed that for a pulse period of 200 ms, the corresponding frequency was 0.5 Hz when the real value would be 5 Hz. The same happened for 2 ms when they said the corresponding frequency was 50 Hz. When analyzing the provided voltage evolution plot, it can be seen that the pulse period values are consistent and the error was in the frequency values. This analysis leads to a frequency between 0.5–5,000 Hz. The electrode used for OER was made mainly of $\text{Ni}(\text{OH})_2$, while the electrode used for HER was made of a metal hydride (mainly lanthanum). The authors also used a 3-D MnO_2 electrode as an intermediate electrode, which was oxidized during HER and reduced during OER. The setup can be seen in Fig. 25. The idea was that during hydrogen on-time, hydrogen would be produced at the metal hydride electrode, and the intermediate electrode would work as an anode where the following reaction occurs:



Then, the hydrogen production would be interrupted, and the oxygen production would start, with the intermediate electrode being reduced ($\text{MnO}_2 \rightarrow \text{MnO}(\text{OH})$) and oxygen being produced at the nickel electrode. This configuration was possible due to the electrical switch from the metal hydride electrode to the nickel electrodes. The results showed that the increase in the alternation frequency could lower the cell voltage for a fixed current density. This result was explained by the model of the pulsating diffusion layer from Ibl [198]. It was argued that in pulsed electrolysis, the thickness of the diffusion layer is reduced

since it has not enough time to be completely formed, and the reactants have time to diffuse back to the electrode surface, enhancing the efficiency of the process by a decrease in ohmic losses caused by mass transport. The higher the pulse frequency, the lower the thickness of the diffusion layer, explaining the observed increase in efficiency with frequency. The results can be seen in Fig. 26, which shows that the voltage was reduced for fixed currents when on-time was lower than 2

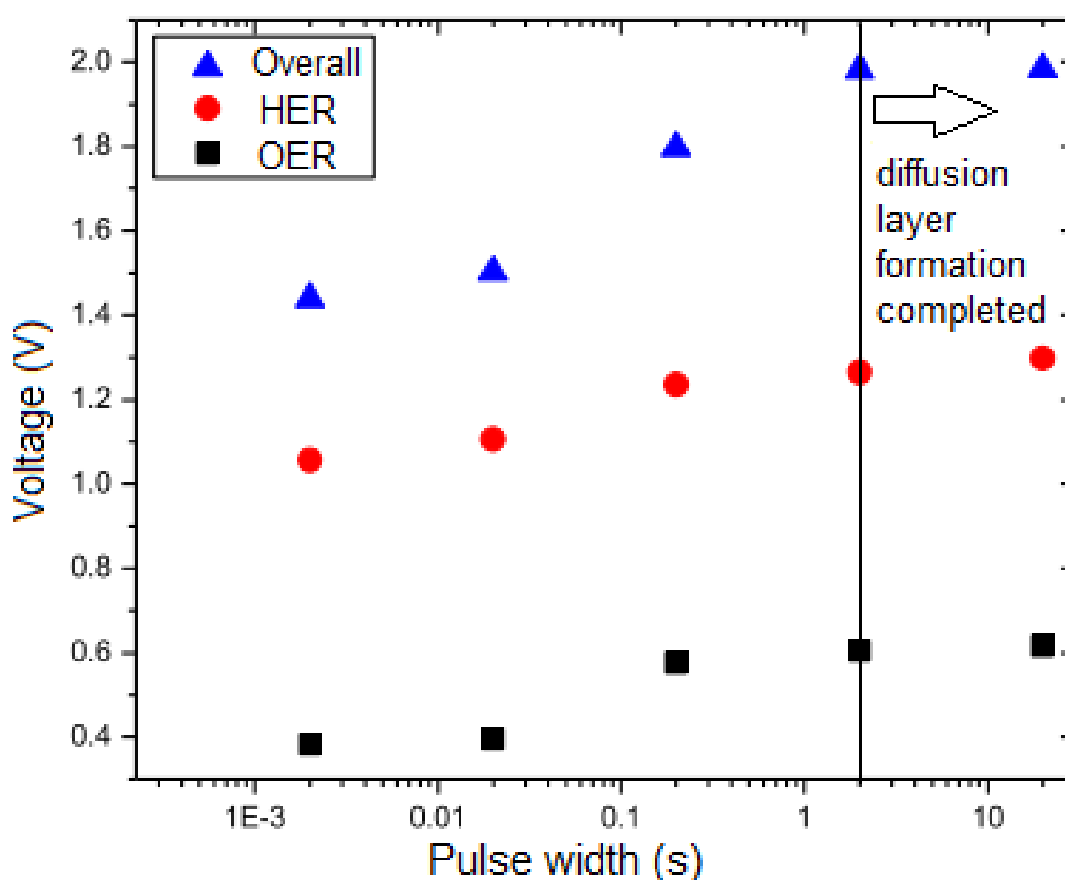


Fig. 26. Pulse width-cell voltage profile at a current density of 0.1 A.cm^{-2} for (black) oxygen evolution reaction at a nickel electrode and the reduction of the intermediate MnO_2 electrode, thermodynamic cell voltage = 0.828 V ; (red) hydrogen evolution reaction in metal hydride electrode and the oxidation of the MnO(OH) electrode, thermodynamic cell voltage = 0.402 V ; (blue) and overall reaction i.g. sum of the two previous cell voltages, thermodynamic cell voltage = 1.229 V (blue). Adapted from [197].

s. The authors explained that the diffusion layer was completely formed after this time of 2 s. Finally, the Faraday efficiency was estimated to be $\sim 100\%$.

Although this pulsed operation could improve the performance of the system, there are some concerns related to it. The first one is related to gas production at the redox mediator, which should be avoided. If the charge and discharge of the redox mediator is not complete, gases will be produced. To illustrate, one could imagine that during the hydrogen production step, the redox mediator is oxidized but an oxidized layer delaminates and leaves the electrode surface. Then, during the oxygen production step, the redox mediator will be reduced, but since it has less oxidized species than what it should have, after the reduction of the remaining oxidized species, hydrogen will be produced. Furthermore, this process suffers with a limited current density, as for high current densities the redox mediator is fully reduced/oxidized quickly and then gases are produced from it. Moreover, the switching between hydrogen and oxygen production takes some time, and increasing the frequency also increases the switching time, thus lowering the production rate. Besides, the switch presents intrinsic ohmic losses, as already seen on Fig. 21. Finally, high-frequency pulsed operation can enhance electrode degradation.

3.2.4 Pulses for other electrochemical applications

In addition to its application in water electrolysis, electric pulses are also studied for the anodic oxidation of organic compounds for wastewater treatment. For instance, a reduction in energy consumption (per mass of impurity) upon the replacement of a constant power by a

pulsed or alternated one was reported by different authors [199–202]. This observation is explained by the rise in the impurities concentration near the electrode surface caused by pulsed power [201]. Othmani *et al.* [200] also observed an electrode lifespan prolongation when using alternated current.

Electric pulses can also be used for the electrodeposition of calcium carbonate present in industrial cooling waters. This approach offers the potential to enhance the compactness of the electrodeposited layer [203].

Chapter 4: Objectives

The primary focus of this Ph.D. thesis is to achieve process intensification of alkaline water electrolysis with the goal of facilitating the energy transition and reducing the capital expenditure (capex) associated with green hydrogen production. The main objective is to investigate several strategies, including:

- 1) **Utilization of three-dimensional (3-D) foam electrodes with forced flow-by electrolyte flow:** this approach aims to maximize the electrode surface area and the removal of gas bubbles from within the intricate and stochastic electrode structure. The forced electrolyte flow will be strategically employed to facilitate efficient gas evacuation, leading to the liberation of electrode surfaces from gas entrapment. This will result in the expansion of the effective active surface area, thereby intensifying hydrogen production. The investigation will include different pore sizes, resulting in the proposal of an innovative laterally-graded bi-layer cell configuration.
- 2) **Integration of pulsed power with 3-D electrode foams:** both current and voltage pulses will be explored as potential strategies to optimize the electrolysis process. By strategically implementing pulsed power, the aim is to investigate the potential synergistic effect of applying pulses in combination of 3-D foams, in view of a further enhancement on the removal of gas bubbles within the electrode structure. During pulse off-times, the electrode surface is replenished with reactants, and gas bubbles have time to leave the 3-D electrode structure, particularly when

influenced by forced electrolyte flow. This would contribute to increased electrode surface availability for hydrogen and oxygen production and elevate the electrolyte conductivity.

- 3) **Development of flow-designed 3-D printed electrode:** focus will be on the development and implementation of flow-designed 3-D printed electrodes in conjunction with a forced flow-by electrolyte system. The objective is to leverage advanced 3-D printing techniques to engineer electrode geometries that maximize gas evacuation. The forced flow of electrolyte will complement these designs, ensuring effective gas removal and electrolyte circulation. This innovative approach aims to optimize both gas bubble liberation and electrolyte conductivity. In contrast to the stochastic structure of foams, the 3-D printed electrodes studied here present a periodic structure, guiding electrolyte flow and exhibiting a high flow sensitivity.

For next-generation high-rate water electrolyzers ($> 1 \text{ A} \cdot \text{cm}^{-2}$), the gas bubble removal efficiency is expected to play a major role in the efficiency. Collectively, these strategies are centered around enhancing bubble evacuation within the 3-D electrode structures. This pivotal objective ultimately translates into two key outcomes: the liberation of electrode surfaces from gases and the enhancement of electrolyte conductivity. By achieving these objectives, this research aims to intensify the alkaline water electrolysis process, contributing to the broader goal of sustainable and efficient green hydrogen production.

Chapter 5: Materials and methods

5.1 Electrochemical measurements

The experimental setup is illustrated in Fig. 27. It comprises an anolyte and a catholyte reservoir, both made of 316 l stainless steel, each one connected to a pump (GJ-N25. FF3S.A gear pumps with polytetrafluoroethylene -PTFE - as gear material, from Micropump, with an ID300/302 pump commander from Nidec) which creates an upward flow of electrolyte inside the cell. This flow is measured by flow transmitters (Honsberg, model LABO-MID1-I/U/F/C). The electrolytic solution was potassium hydroxide (KOH), prepared by dissolving KOH pellets (KOH > 85%, VWR chemicals) in deionized water (18.2 M Ω .cm, Sartorius Arium 611) at room temperature and atmospheric pressure. Stirrer hotplates from IKA are placed below the reservoirs. During an experiment, the temperature of the reservoir is continuously controlled. However, since there is cooling on the way from the reservoir to the cell, there is a temperature gradient. To account for this cooling, the gradient was estimated in a way that the temperature inside the cell could be fixed. For this measurement, a hole of 3 mm in diameter was drilled into the electrode housing to insert a thermocouple. In a configuration without electrodes, the temperature at the catholyte reservoir and at the cell interior (cathodic side) was measured, and the gradient was estimated as a function of the electrolyte flow rate, as shown in Fig. 28. A minimum level of forced flow is needed to maintain the temperature inside the cell higher than the room temperature. The produced hydrogen and oxygen gases can

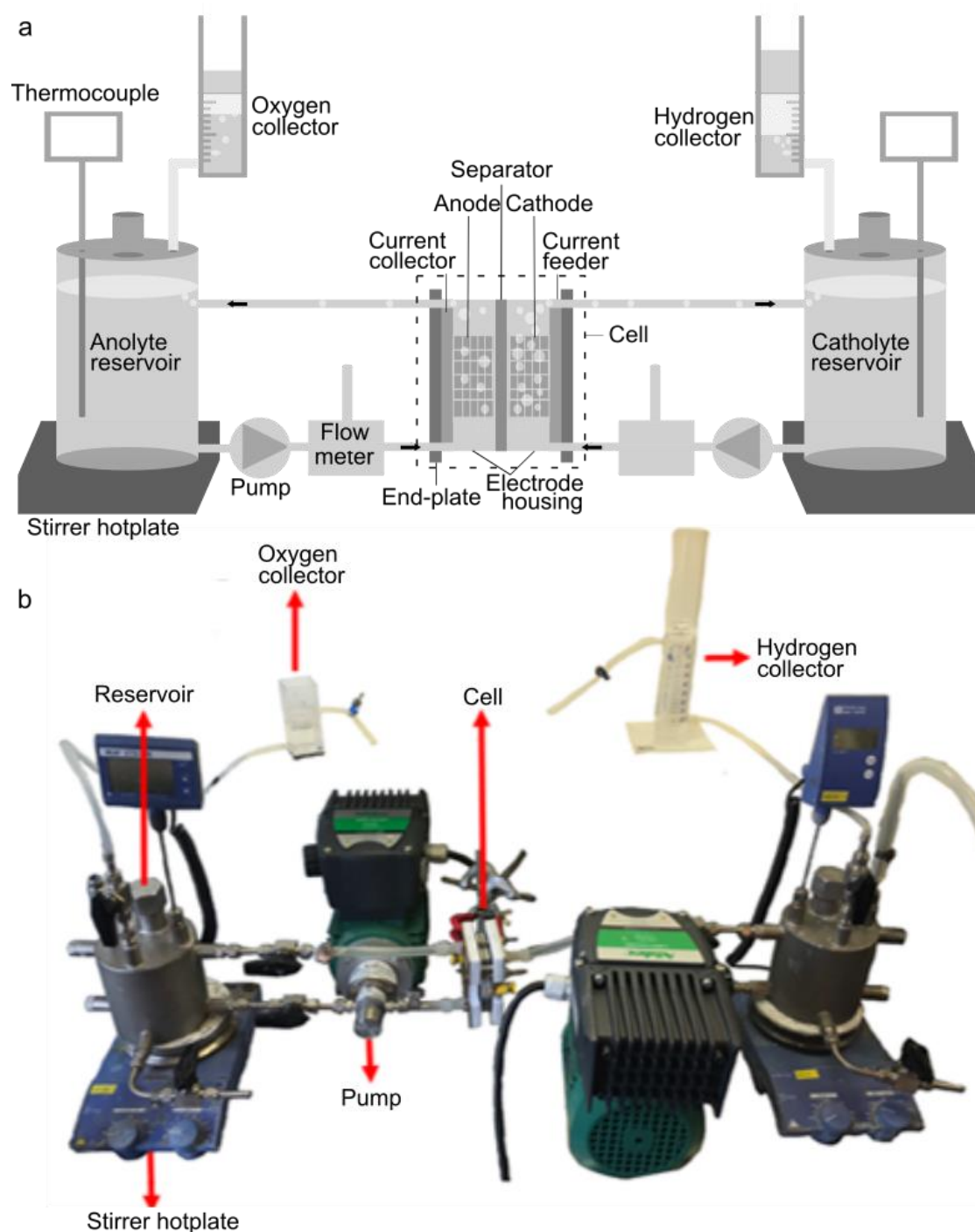


Fig. 27. Experimental setup in: a) Schematic b) Photo documentation. c) Photo documentation of a demounted cell.

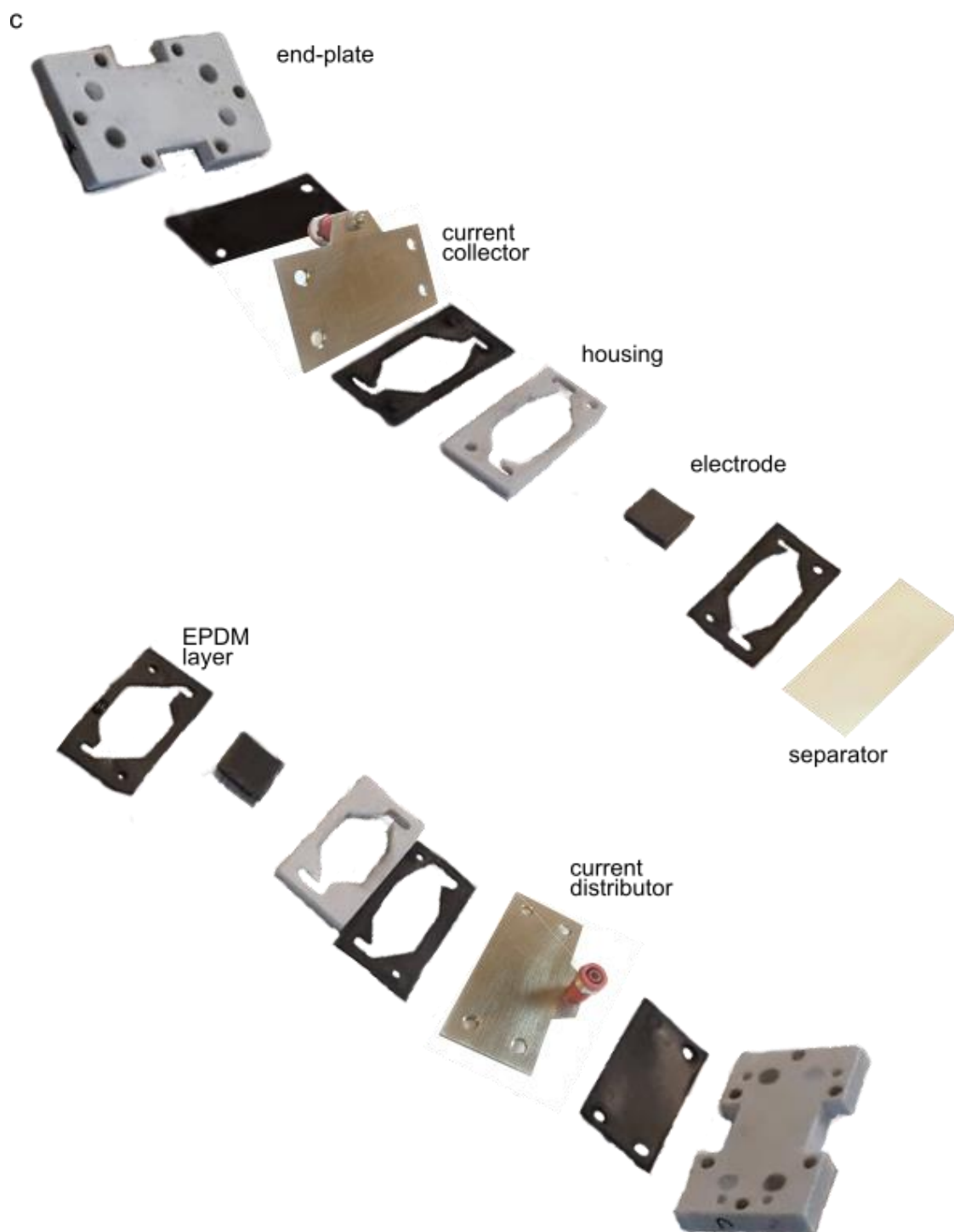


Fig. 27.(continued)

be collected in separated graduated cylinders in a manner that the volumetric production rate can be measured. The electrolytic cell is prepared by sandwiching the following parts, shown in Fig. 27.c: two PTFE end-plates with fittings for electrolyte inlet and outlet; two nickel plate ($> 99.5\%$, Alfa Aesar) current distributors to ensure removal/supply of electrical charge; two PTFE electrode housings to accommodate the electrodes and promote sealing; and a separator (e.g. diaphragm or membrane). Between each one of these parts, there is a 1 mm ethylene propylene diene monomer (EPDM) layer to ensure sealing and prevent mechanical wear. The electrodes had a geometric area of 4 cm^2 ($2 \times 2 \text{ cm}$), and the thickness depended on the specificities of the experiments. To ensure sealing, the cell was pressed using 6 screws with a torque of 3 Nm each.

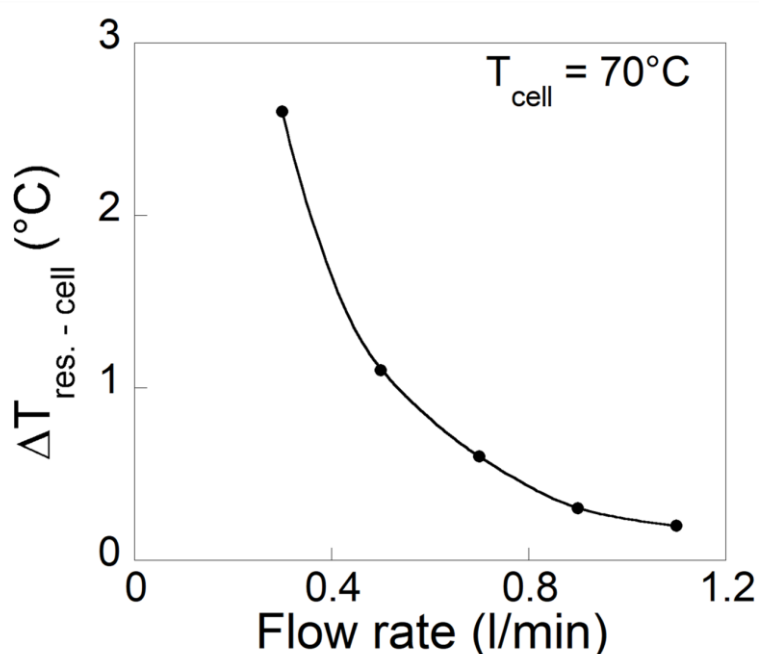


Fig. 28. Temperature difference between the reservoir and the cell as a function of electrolyte flow rate. At natural convection (zero forced flow), the temperature at the cell is close to room temperature.

The separator used for the experiments shown in Chs. 6 and 7 was the state-of-the-art Zirfon Perl UTP 500 from AGFA. It has a thickness of $500 \pm 50 \mu\text{m}$ and can operate at a maximum temperature of 110°C . The ionic resistance is dependent on the one of the electrolyte. At 30 wt% KOH and 90°C , the specified ionic resistance is $0.1 \Omega \cdot \text{cm}^2$ [204]. A Fumasep FAA-3-PK-130 from FumaTech, was employed as an anion-exchange membrane for the experiments shown in Chs. 8 and 9. This membrane is composed of a polyaromatic structure reinforced with polyketone. It contains fixed quaternary ammonium groups and bromide as a counter-ion [205]. The former is a polymeric backbone, important for mechanical and thermal stability, while the latter is an ion exchange group, essential for the ionic conductivity of OH^- [94]. It operates at a maximum temperature of 40°C and a maximum pH of 14. It has a thickness of $130 \pm 20 \mu\text{m}$ and a specified resistance of around $2 - 4 \Omega \cdot \text{cm}^2$ at 25°C [206]. Finally, a commercial PBI-based membrane from Danish power systems (M40 Dapozol PBI membrane) was used as an ion-solvating membrane for one of the tests shown in Ch. 7. Its thickness was $40 \mu\text{m}$, and the reported resistance is in the same order of magnitude as the one of Zirfon [207]. Before each experiment, nitrogen (Alphagaz 1 Azote, $\text{N}_2 > 99.999\%$, from AirLiquide) was circulated in the catholyte to remove residual oxygen from the solution. Electrochemical experiments were performed using a Solartron Modulab XM potentiostat equipped with a 20 A booster.

The experiments present in Chs. 6 and 7 were performed at 30% KOH and 70°C , while the experiments in Chs. 8 and 9 used 1 M KOH at room temperature. The experiments in Ch. 9 were done at a flow rate of $1.9 \text{ l} \cdot \text{min}^{-1}$ (vertical velocity of $0.25 \text{ m} \cdot \text{s}^{-1}$) or natural convection. The

voltage pulses had a base and peak voltage of 1.2 V and 2.0 V, respectively, while the current pulses varied from 0 to 0.3 A. Furthermore, hydrogen gas was collected in a transparent graduated cylinder, and its production volume was recorded with a video-camera. A linear regression of the volumetric hydrogen production versus time gave the hydrogen production rate (in $\text{ml}\cdot\text{s}^{-1}$) and allowed us to calculate the Faraday efficiency.

For the experiment in Ch. 8, room temperature was chosen because the idea was to use natural convection (no forced flow) as a baseline. Current scans from 0 - $0.5 \text{ A}\cdot\text{cm}^{-2}$ were performed with a scan rate of $0.1 \text{ A}\cdot\text{s}^{-1}$ and complemented with 5 minutes of galvanostatic experiments at geometrical current densities of 0.20, 0.25, 0.30, 0.35, and $0.40 \text{ A}\cdot\text{cm}^{-2}$.

The results are often shown in the form of cumulative normal probability plots. This graphical representation sorts the data from the smallest to the largest and plots it against the quantiles of a normal distribution. Consequently, if the data follows a normal distribution (Fig. 29.a), the curve in the probability plot will present a linear behavior with the mean at 50% probability (sometimes also represented as 0 standard normal quantile), as shown in Fig. 29.b. For each variation in the standard deviation, there is 1 standard normal quantile of difference. For instance, there is a probability of 15.9% (-1 standard quantile) to find a value lower than the mean minus the standard deviation and 2.3% of probability (-2 standard quantile) to find values lower than the mean minus two times the standard deviation. A more detailed explanation can be found in ref. [208].

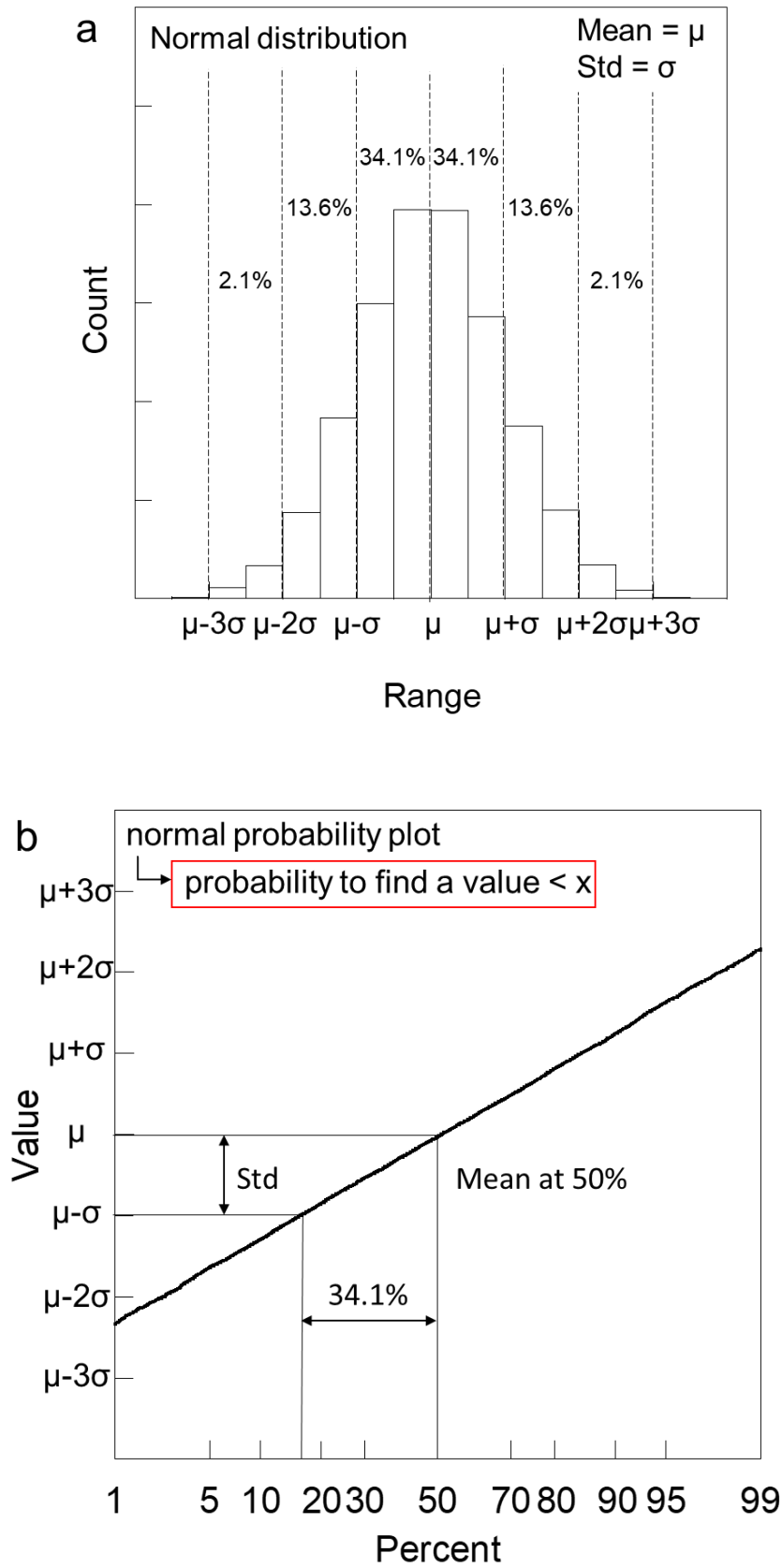


Fig. 29. Schematic illustration of the representation of an experimental data set as a) a normal distribution and b) a cumulative normal distribution.

5.2 Three-dimensional foams

These electrodes were made by cutting commercial sheets of porous foams into pieces of 2·2 cm. The experiments in Chs. 6 and 7 used pure Ni foams (>99%, Alantum) and the experiment in Ch. 9 used Ni-based Inconel 625 alloy (Ni~60%, Cr~22%, Mo~9%, Fe~4%, Nb~3%, Alantum) [209] foams. These 2·2 cm pieces were stacked to fill the gap provided by the electrode housing and the EPDM layers. Different characteristic pore sizes were studied, ranging from 450 to 3000 μm . They were manufactured using an open cell polyurethane (PU) foam as a substrate for nickel sputtering. Then, a 560°C pyrolysis removed the PU, and subsequently, the material was annealed at 950°C, as specified in ref. [210]. For the sputtering to work properly, the layer thickness should also be reduced as the characteristic pore size is reduced. Therefore, in order to accommodate the differently sized foams into our cell, a different number of layers needs to be used. In the case of a pore size of 1200 μm , one of the three layers was sandpapered until its thickness reached 0.2 cm. This way, the total electrode thickness was equal to the housing's gap of 0.8 cm.

Representative micrographs of the foam electrodes, shown in Fig. 30, were used to estimate the average pore size of each foam and its standard deviation. Outliers were removed in order to estimate the pore size better. Even though there is an overlap between the different foams, z-tests were performed, and with an alpha of 0.05, the distributions were proven to be statistically different. The foam thickness was verified using a digital caliper, and the porosity was verified by measuring the dislocated volume of water [$P = (1 - \text{volume dislocated}) / (\text{total volume})$] [211]. The result for the total porous transport layer thickness, later

shown in Table 4, is an average for the cathode and the anode. Four measurements were done in different locations for each electrode. For the porosity measurement, a geometric surface area of 22 cm² of nickel foam was immersed in a graduated cylinder with a precision of ± 0.25 ml.

To reduce the experimental error on the electrode capacitance, the experiment was repeated for each electrode by increasing the number of layers from 1 to 5.

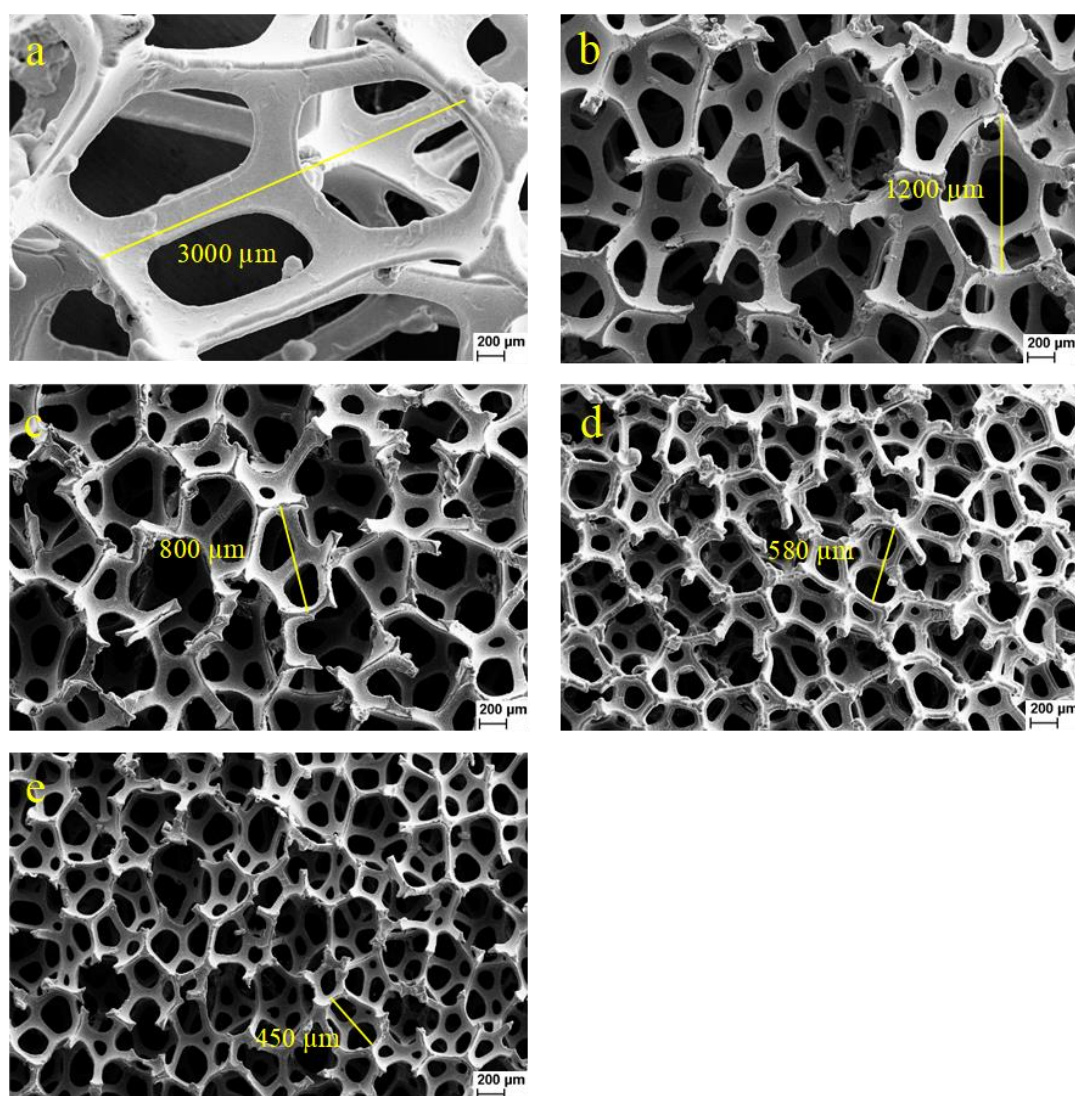


Fig. 30. Scanning electron micrographs taken at the same magnification for porous nickel foams with specified pore sizes of a) 3000 μm , b) 1200 μm , c) 800 μm , d) 580 μm , and e) 450 μm .

5.3 Raney Ni coating and activation

The 450 μm foam was coated by our partner, the German Aerospace Center (DLR), under the context of a Horizon 2020 European project named materials for next generation alkaline electrolyzer (NextAEC). The thermal process used for the plasma spray is reported elsewhere [212], and the aluminum was leached out by immersing the electrode into a solution of 30 wt% KOH (> 85%, VWR chemicals) and 10 wt% potassium-sodium-tartrate-tetrahydrate (>99%, Carl Roth GmbH) at 80°C during 24 h. The composition of the electrode before and after activation is shown in Table 3. Scanning Electron Micrographs (SEM) of both cathode and anode foams before and after coating are shown in Fig. 31. The coated side was put against the separator.

The results from the ex-situ activation (Fig. 32) show that even after 24h, the activation continues. Taking the concentrations obtained after 48h as a base, about half of the total aluminum was leached during the first 15 minutes. Almost all the Mo was leached during this first

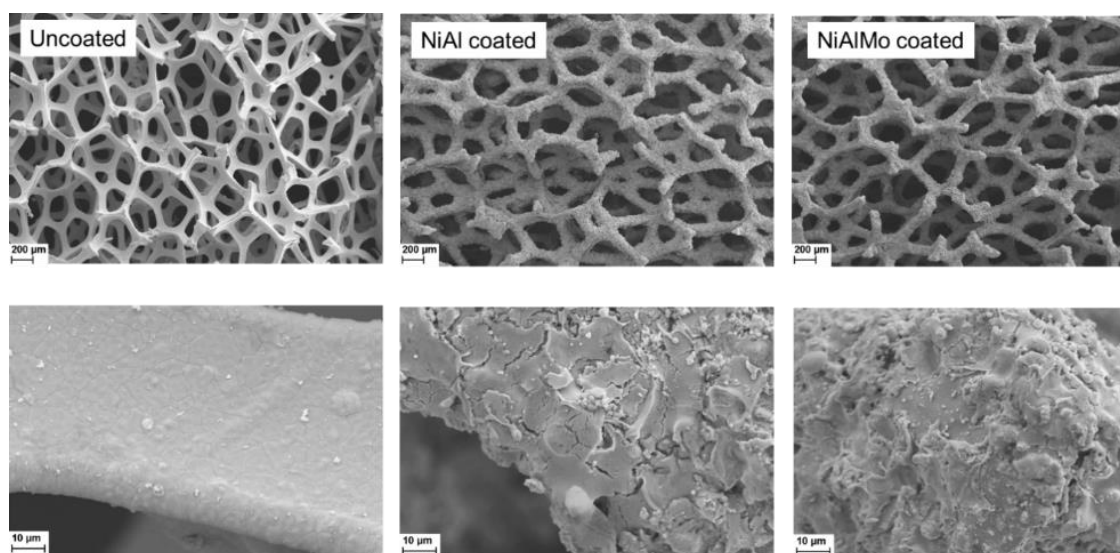


Fig. 31. Scanning electron micrographs of Ni foams before and after coating taken with a field emission gun scanning electron microscope (Zeiss Ultra 55). Electron high tension of 15 kV, working distance of 10 mm, type II secondary electrons.

Table 3. Inductively coupled plasma (ICP) analysis of Raney nickel electrodes

Electrode	Composition before activation (%)	Composition after activation (%)	Ni leached (%)	Al leached (%)	Mo leached (%)
Anode	Ni-57, Al-43	Ni-86, Al-14	17	82	/
Cathode	Ni-41, Al-41, Mo-18	Ni-88, Al-6, Mo-6	22	95	88

activation period. After 24h, about 80-85% of the aluminum was leached. Results from continued in-situ electrochemical activation show that ions crossed the diaphragm, as molybdenum was found at the side of the NiAl-coated foam. As for the ex-situ, the leaching rate is very high during the first minutes. After 24h of in-situ activation, an electrochemical test was carried out (as in Fig. 33). At the side of the NiAl-coated anode foam, there was an important increase in the aluminum ion concentration, evidencing the electrochemical activation step. The quantity of Ni leached was very small.

For the first current scan shown in Fig. 33, there is current even for voltages lower than the reversible cell voltage for water electrolysis of 1.23 V, showing that another electrochemical reaction occurred. This is probably the leaching of aluminum still present at the anode even after 24h of chemical activation. These results indicate that there is also an electrochemical activation of the electrodes. After reaching a current density of about $1.1 \text{ A}\cdot\text{cm}^{-2}$, the polarization curve stabilizes and the curve onset for all subsequent curves becomes 1.4 V. A slight cell voltage decrease is observed over time, but the 3 last polarization curves fully superposed. The total charge consumed during this

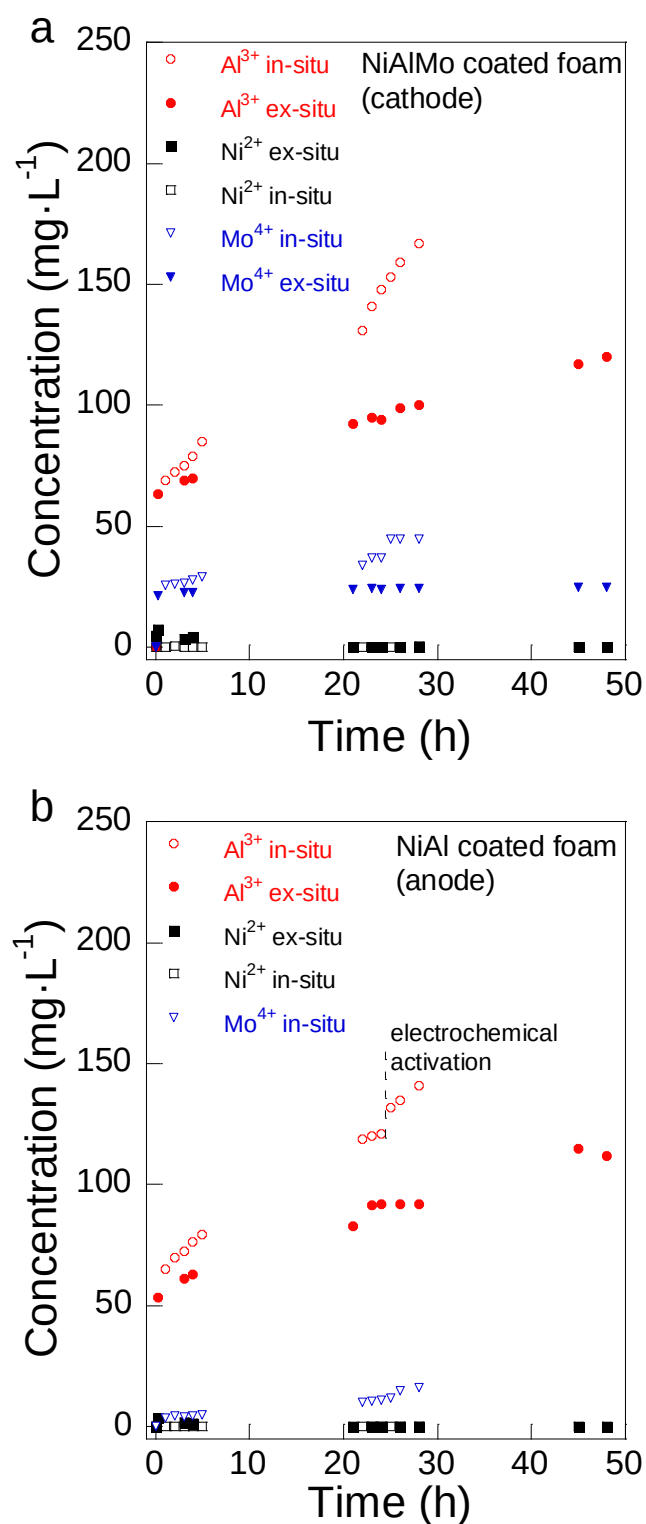


Fig. 32. Ionic concentrations in solution as analyzed by Inductively Coupled Plasma analysis for activation of a) NiAlMo coated foam (cathode) and b) NiAl coated foam (anode). For the in-situ electrochemical activation, the same electrolysis cell presented in the Materials section was used and samples were collected at the reservoir level.

electrochemical activation (from 0 to $1.1 \text{ A}\cdot\text{cm}^{-2}$) was about 100 C, enough to leach out an additional 9 mg of $\text{Al}_{(\text{s})}$. From the ICP analysis shown in Fig. 32, the value obtained for the Al leached at the anolyte during the electrochemical activation is 11 mg. These values are very

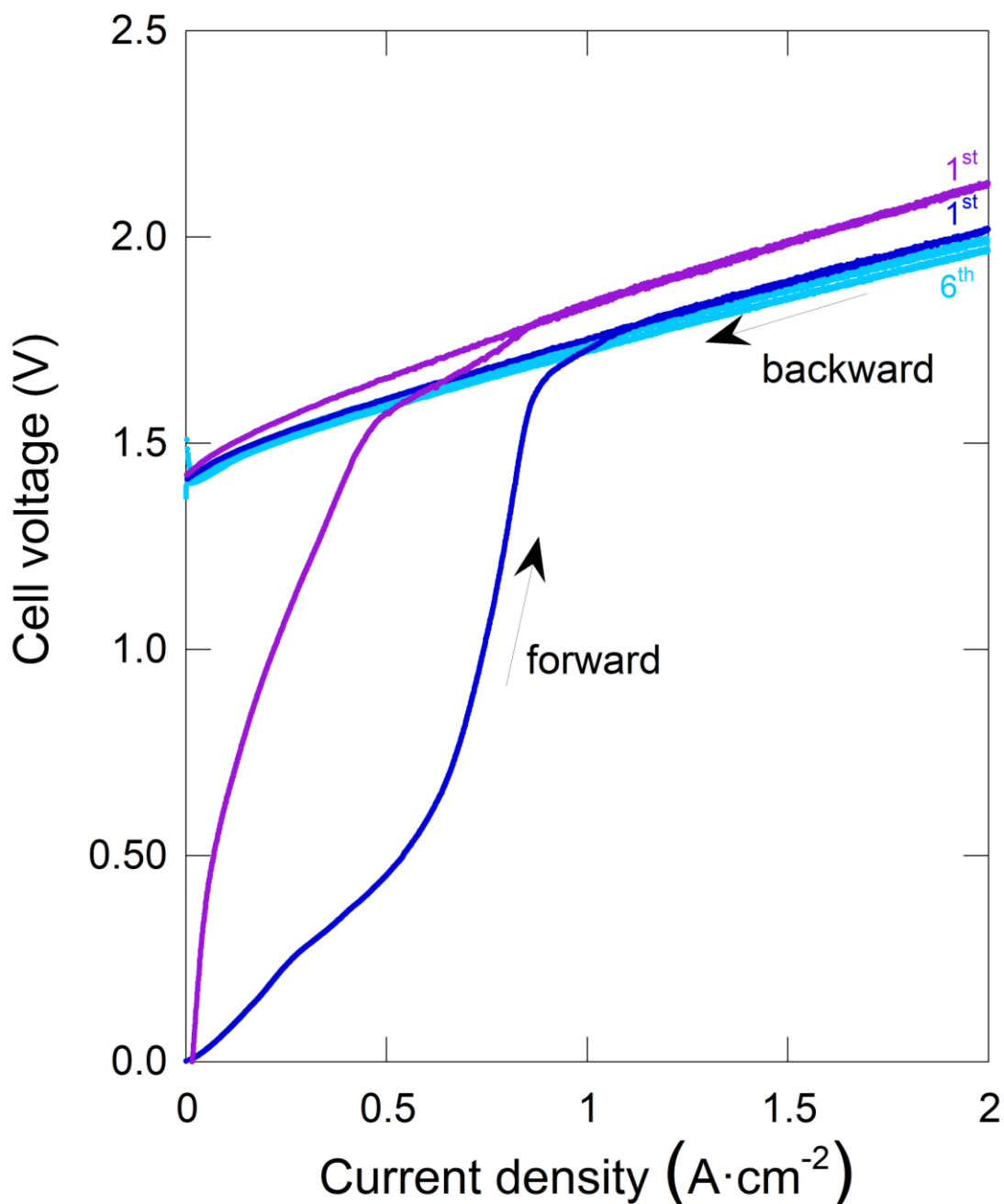


Fig. 33. Polarization curve at 70°C and 30wt% KOH from the first current scan performed on spray-coated and chemically activated Raney nickel foams in dark blue, and subsequent ones in light blue. In purple, the first current scan of another spray-coated and chemically activated Raney Ni foam. The scan rate was $0.025 \text{ A}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$

close, which confirms the theory of Al leaching during the first scan. The curve in purple shows that the electrochemical activation is not very reproducible, but unique to each electrode and its chemical activation pre-history.

5.4 Three-dimensional printed electrodes

Tailored electrodes were made by laser beam melting of a Ni-based Inconel 625 alloy. Inconel was chosen for ease of fabrication, allowing to use an already existing LBM protocol. We realize that this composition might not be the ideal electrocatalyst composition for alkaline water electrolysis. However, since this work was intended to concentrate on the structural aspects of the electrode's geometrical design, our results can still be expected to be highly relevant for other electrode compositions as well. The printing was done by our industrial partner, Sirris, using the LBM process as already described in the Ch. 3. The Inconel 625 electrodes had dimensions of 2·2·0.8 cm (length, width, thickness).

Three triply periodic minimal surfaces (TPMS) geometries were studied: Gyroid, Fischer-Koch, and Schwarz. The following structural equations describe them:

Gyroid

$$\begin{aligned} t = & \cos(g \cdot x) \cdot \sin(g \cdot y) \\ & + \cos(g \cdot y) \cdot \sin(g \cdot z) \\ & + \cos(g \cdot z) \cdot \sin(g \cdot x) \end{aligned} \tag{67}$$

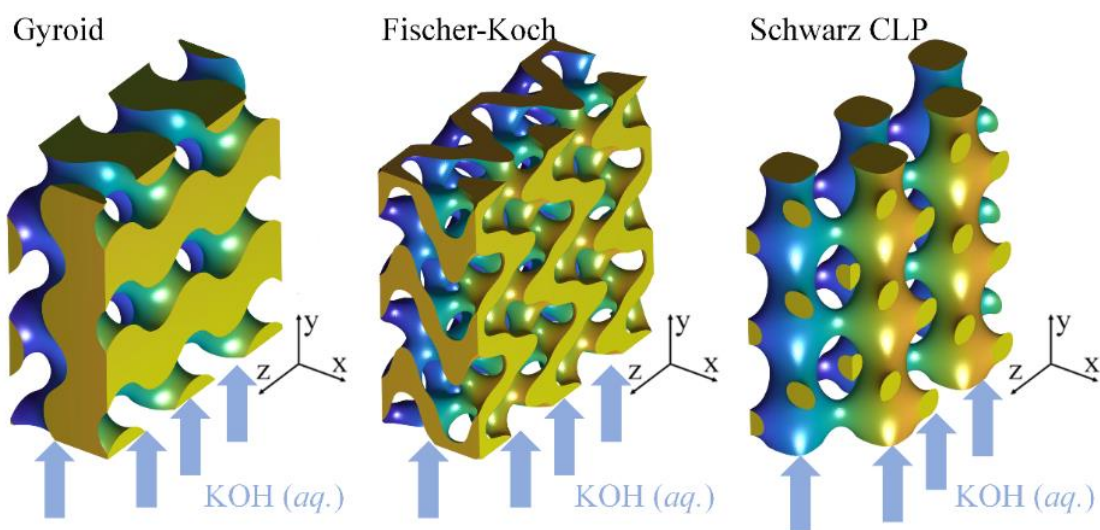


Fig. 34. Examples of TPMS geometries. They all contain a lattice size L of 8 mm and a t parameter of 0.26. Arrows indicate the direction of forced electrolyte flow.

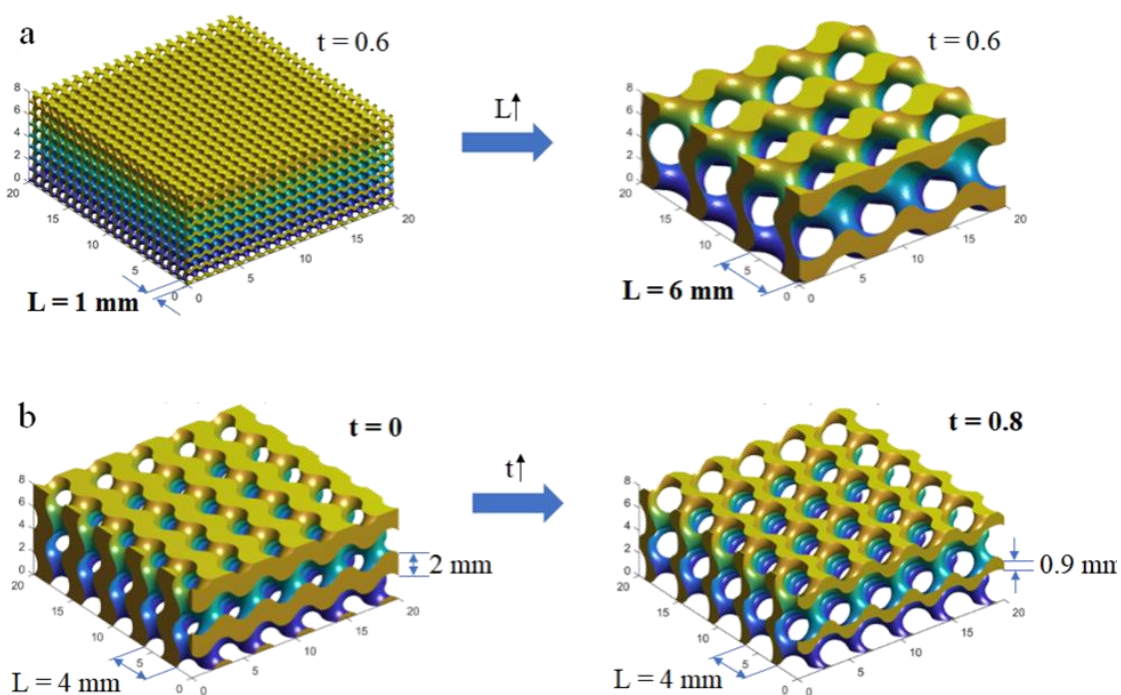


Fig. 35. Gyroidal electrode geometries with different structural parameters: a) L = 1 and 6 mm at t = 0.6; b) t = 0 and 0.8 at L = 4 mm.

Fischer-Koch

$$\begin{aligned}
t = & \cos(2 \cdot g \cdot x) \cdot \cos(g \cdot z) \cdot \sin(g \cdot y) \\
& + \cos(g \cdot x) \cdot \cos(2 \cdot g \cdot y) \cdot \sin(g \cdot z) \\
& + \cos(g \cdot y) \cdot \cos(2 \cdot g \cdot z) \cdot \sin(g \cdot x)
\end{aligned} \tag{68}$$

Schwarz

$$\begin{aligned}
t = & \sin(g \cdot z) \cdot \sin(g \cdot x) - 0.4 \cdot \sin(1.2 \cdot g \cdot y) \cdot \\
& \cdot \cos(g \cdot x)
\end{aligned} \tag{69}$$

with:

$$g = \frac{2 \cdot \pi}{L} \tag{70}$$

In these equations, the lattice size, L , determines the periodicity, and the parameter t is directly related to the porosity, as shown in Fig. 36. It is already worth noticing that while Gyroid and Fischer-Koch-shaped electrodes have the same symmetry in all directions, Schwarz-shaped electrodes have a different symmetry for the vertical (z) direction. An example of each of these three geometries is shown in Fig. 34. For the experiments, the electrolyte will be forced to flow vertically, parallel to the channels inside the Schwarz structure. Fig. 35 illustrates the effect of the parameters L and t on the final electrode geometry for a Gyroidal structure. A lattice size (L) of 4 mm means that the structure repeats itself every 4 mm in all directions. Hence, the lower the L , the higher the surface area. When increasing t , the strut size is reduced and consequently, the void fraction or porosity is raised. The structures shown in Fig. 35.a have the same t parameter, corresponding to the same porosity of 70%. However, since they have different periodicities

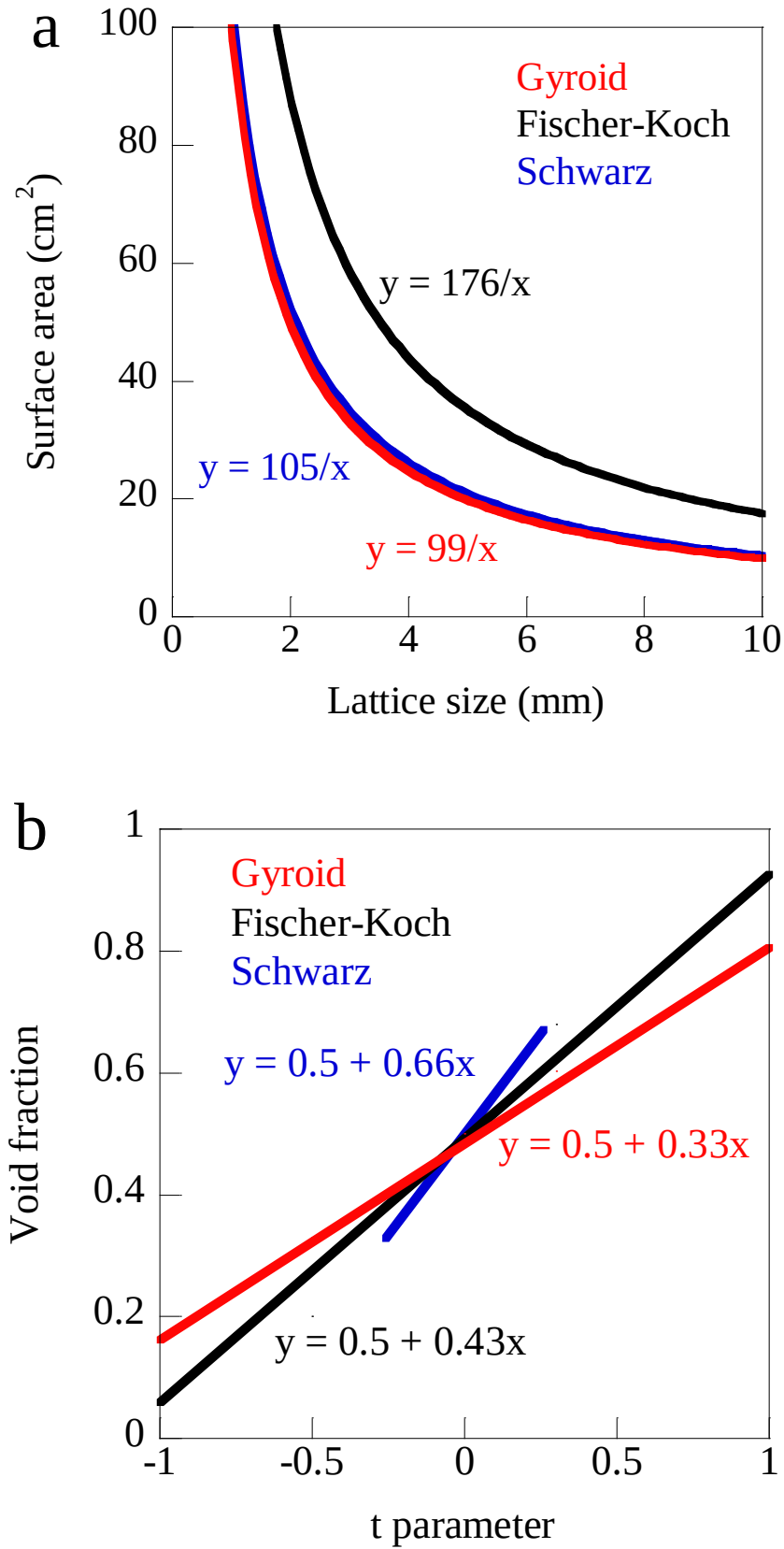


Fig. 36. a) Surface area as a function of lattice size L for $t = 0$; b) porosity as a function of t , the latter relation being independent of L .

($L = 1$ and 6 mm, respectively), they also have different strut sizes (0.3 and 1.8 mm, respectively) and different specific surface areas (29.8 and $6.1 \text{ cm}^2/\text{cm}^3$, respectively). The structures shown in Fig. 35.b have the same periodicity of 4 mm but a different t parameter (0 and 0.8 , respectively). As a consequence, not only the strut sizes are different (2 and 0.9 mm, respectively), but also the porosities (50 to 77% , respectively) and the specific surface area (10.0 and $7.9 \text{ cm}^2 \cdot \text{cm}^{-3}$, respectively). The exact mathematical relations between surface area and periodicity and between porosity and t are shown in Fig. 36.a and b, respectively. Since bubble entrapment and gas evacuation can be expected to vary according to both parameters, we have chosen a systematic set of TPMS structures and parameters for our experimental campaign.

Photographs of some of the 3-D printed electrodes are shown in Fig. 37.

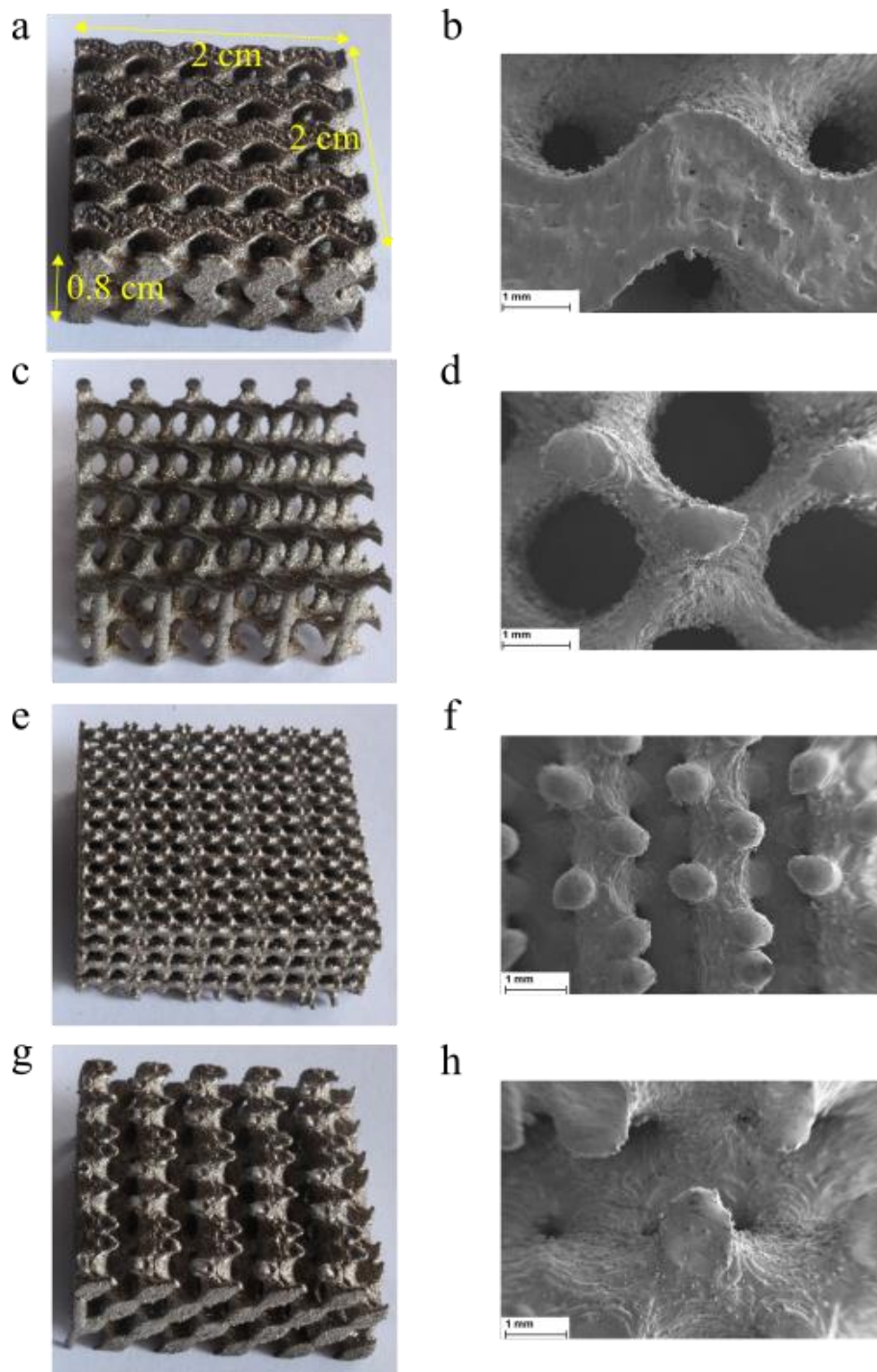


Fig. 37. Photo documentation of SLM 3-D printed electrodes a) Gyroid with an $L = 4$ mm and a $t = 0$ c) Gyroid with an $L = 4$ mm and a $t = 1.2$ e) Schwarz with an $L = 2$ mm and a $t = 0.18$ g) Schwarz with an $L = 4$ mm and a $t = 0.18$. FEGSEM micrographs of 3-D printed electrodes b) Gyroid with an $L = 4$ mm and a $t = 0$ d) Gyroid with an $L = 4$ mm and a $t = 1.2$ f) Schwarz with an $L = 2$ mm and a $t = 0.18$ h) Schwarz with an $L = 4$ mm and a $t = 0.18$. The dimension of the electrodes is $2 \cdot 2 \cdot 0.8$ cm.

5.5 X-ray micro-computed tomography

Samples were imaged using a Phoenix Nanotom M (GE Measurement and Control Solutions, Germany) equipped with a 180kV/15W energy nanofocus X-ray tube and a diamond-coated tungsten target. All μ CT datasets were reconstructed with the Datos|x software (GE Measurement and Control Solutions, Germany) and exported as XY slices (.tiff). The scan resolution was 0.65 and 12 μm for the foams with a characteristic pore size of 450 μm and 3000 μm , respectively.

The specific surface area was estimated by taking the electrode perimeter per μ CT slice and normalizing by the total area of the slice. The coating volume was estimated by taking its area per slice and multiplying by the voxel size.

5.6 Computational fluid dynamics simulations

For single-phase flows, the incompressible Navier-Stokes equations were solved on the domain fusing the Finite Element Method implemented in the open-source MigFlow software [213]. Kinematic viscosity was assumed constant, and values were extracted from ref. [214], according to specific electrolyte conditions. During the post-processing step, the Paraview software (version 5.9.0) was used to visualize streamlines and velocity or vorticity contours.

In order to simulate 2-phase flow, a mixture model formulation was used and implemented on the driftFluxFoam solver available in OpenFOAM. This solver solves the continuity and momentum equations for the gas-liquid mixture by weight-averaging velocity, density and viscosity as a function of gas fraction α and the properties

of both phases. In the simulations, a stagnant gas mixture inlet (considering different values of α) was imposed at the interface of the catalytic foam and the diaphragm, with zero drift velocity. For the 2-phase simulations, the density of hydrogen was set to 0.08 kg/m^3 and the dynamic viscosity to $0.88 \cdot 10^{-5} \text{ Pa.s}$.

In order to validate the simulation, we compare our results with experimental results for the pressure drop that can be found in the relevant literature. Here, two foam samples ($450 \text{ }\mu\text{m}$ and $3000 \text{ }\mu\text{m}$) were scanned by X-ray micro-computed tomography and the scan was processed with Avizo software (version 2019.1), from ThermoFischer scientific. Simulations for both foams were performed for a range of inlet velocities. In Fig. 38, we compare the pressure drop with similar foams from the literature, where we have the expected value range and quadratic profile, meaning that the geometric representation and the simulation are close to reality. The differences are due to small differences in foam characteristics such as porosity and pore sizes.

Reynolds number was estimated using Eq. (31) with a characteristic length defined as:

$$L = \frac{4 \cdot V}{A} \quad (71)$$

with V the volume of the fluid domain inside the electrode region (m^3) and A the electrode surface area (m^2) [215]. For the permeability estimation, a fit using Eq. (29) was done in the pressure drop vs. vertical velocity plot.

For the flow simulation inside 3-D printed structures, a half-cell was modeled using a marching cubes method for the meshing of the TPMS

geometries in the context of Gmsh meshing software. The TPMS geometries were generated on MATLAB and converted to .stl. The physical dimensions of the cell were: circular fluid inlet/outlet with a 3 mm radius and 2.2×0.8 cm electrode. The tetrahedral mesh had an element size in the order of 0.25 mm outside the electrode region and 0.1 mm inside it. These values were determined after a mesh sensitivity analysis. For the simulations, an average fluid velocity was imposed at the half-cell inlet, and the pressure was set at 1 atm at the outlet. We estimate the pressure drop inside the cell as a function of velocity. For simplicity, the separator was approximated by a wall with no fluid crossing.

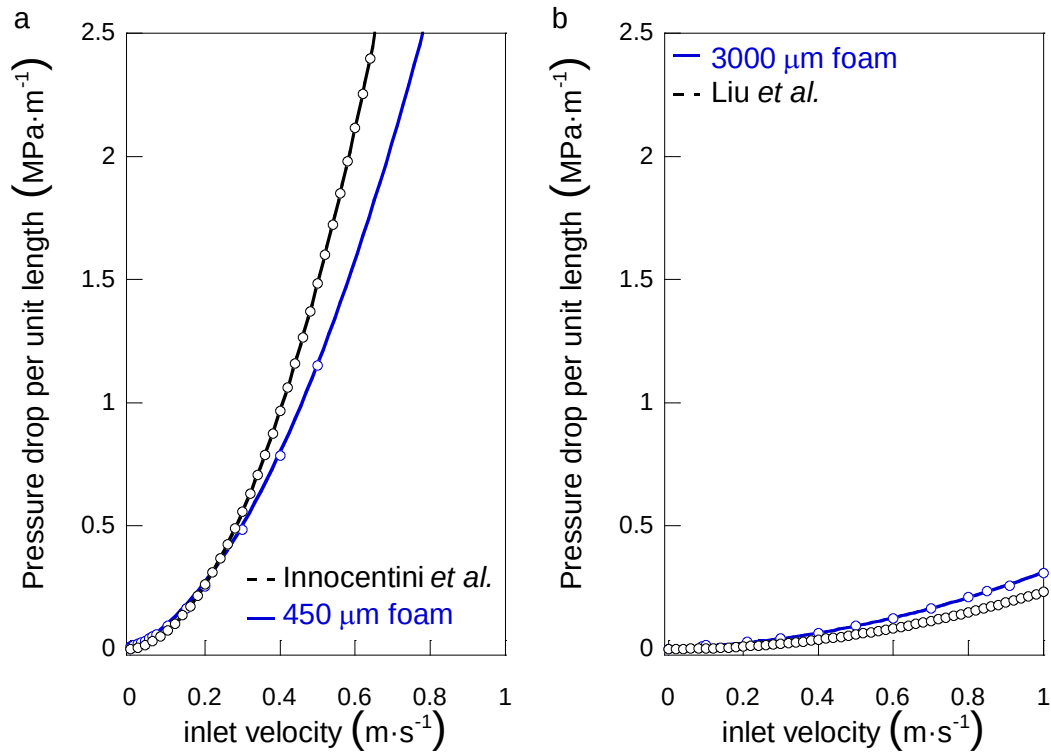


Fig. 38. Evolution of pressure drop versus velocity a) 450 μm foam compared to experimental data from ref. [216] for a 423 μm foam (60 pores per inch) with a porosity of 0.918; b) 3000 μm foam compared to experimental data from ref. [217] for a 2540 μm foam (10 pores per inch) with a porosity of 0.85.

5.7 Characterization techniques

5.7.1 ECSA measurement

The determination of the ECSA was done by measuring the capacitance of the electrode/solution interface. It was calculated by scanning the potential from -0.4 to -0.2 V vs. SHE (-0.6 to -0.4 V vs. Ag|AgCl sat.) at different scanning rates. The rates went from 50 mV s^{-1} to 400 mV s^{-1} in steps of 50 mV s^{-1} . Three cycles were performed for each scan rate. At this potential range, no reaction occurs (the open circuit potential - OCP - is around -0.3 V vs. SHE), but there was the charge and discharge of the electric double layer. This is illustrated in Fig. 39. The current resulting from the scan from -0.4 to -0.2 V vs. SHE is known as anodic

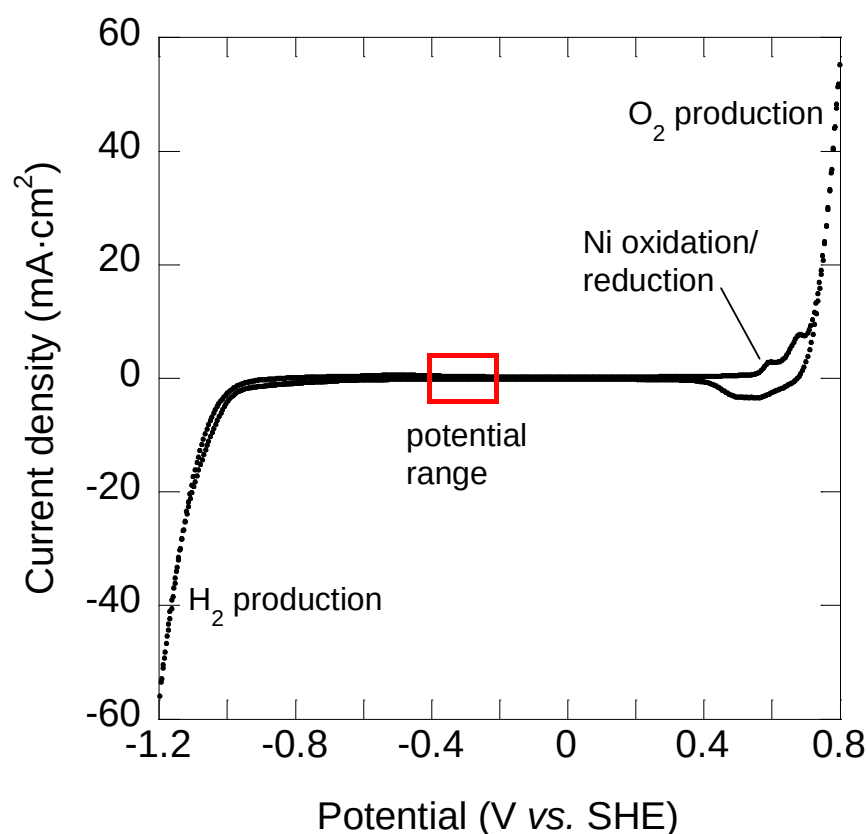


Fig. 39. Cyclic voltammetry for a $2 \cdot 2 \text{ cm}^2$ Ni foam with characteristic pore size of $450 \text{ }\mu\text{m}$. Experimental conditions of 1 M KOH, room temperature. The red rectangle indicates the potential range used for capacitance measurements.

current. When the potential goes from -0.2 to -0.4 V vs. SHE, the current is labeled as cathodic. Half of the difference between these currents at -0.3 V vs. SHE gives the capacitive current at a certain scan rate. A typical plot for the 2 extreme scan rates is shown in Fig. 40.a. The faster the scan rate, the higher this current will be. The slope of the capacitive current (μA) vs. scan rate ($\text{V}\cdot\text{s}^{-1}$) gives the capacitance of the electrode (μF), according to the following equation:

$$\text{Slope} = C_D [\mu\text{F}] = \frac{\Delta i_c [\mu\text{A}]}{\Delta v [\text{V/s}]} \quad (72)$$

with C_{dl} the double layer capacitance, i_c the capacitive current, and v the scan rate. Fig. 40.b shows that there was a linear relation between the capacitive current and the scan rate, which allow us to use the Eq. (72). The capacitance method was chosen following the conclusion of ref. [218] that this method presents a good correlation with the real surface value even in the presence of nickel oxides. Once the capacitance is estimated, the following correlation holds between the electrode capacitance and its total surface area:

$$A_{\text{ECSA}} = \frac{C_D}{c} \quad (73)$$

where c is the specific capacitance ($\mu\text{F}\cdot\text{cm}^{-2}$). A specific capacitance value of $20 \mu\text{F}\cdot\text{cm}^{-2}$ was used as it is commonly employed for Ni electrodes in alkaline solutions [219,220] and it is an approximation of values independently measured by refs. [221,222]. Later on, in Ch. 7, we will also have our own estimation of the specific capacitance comparing our measured capacitance with X-ray tomographic data. Our setup for this test consists of a three-electrode cell with Pt 110 as the

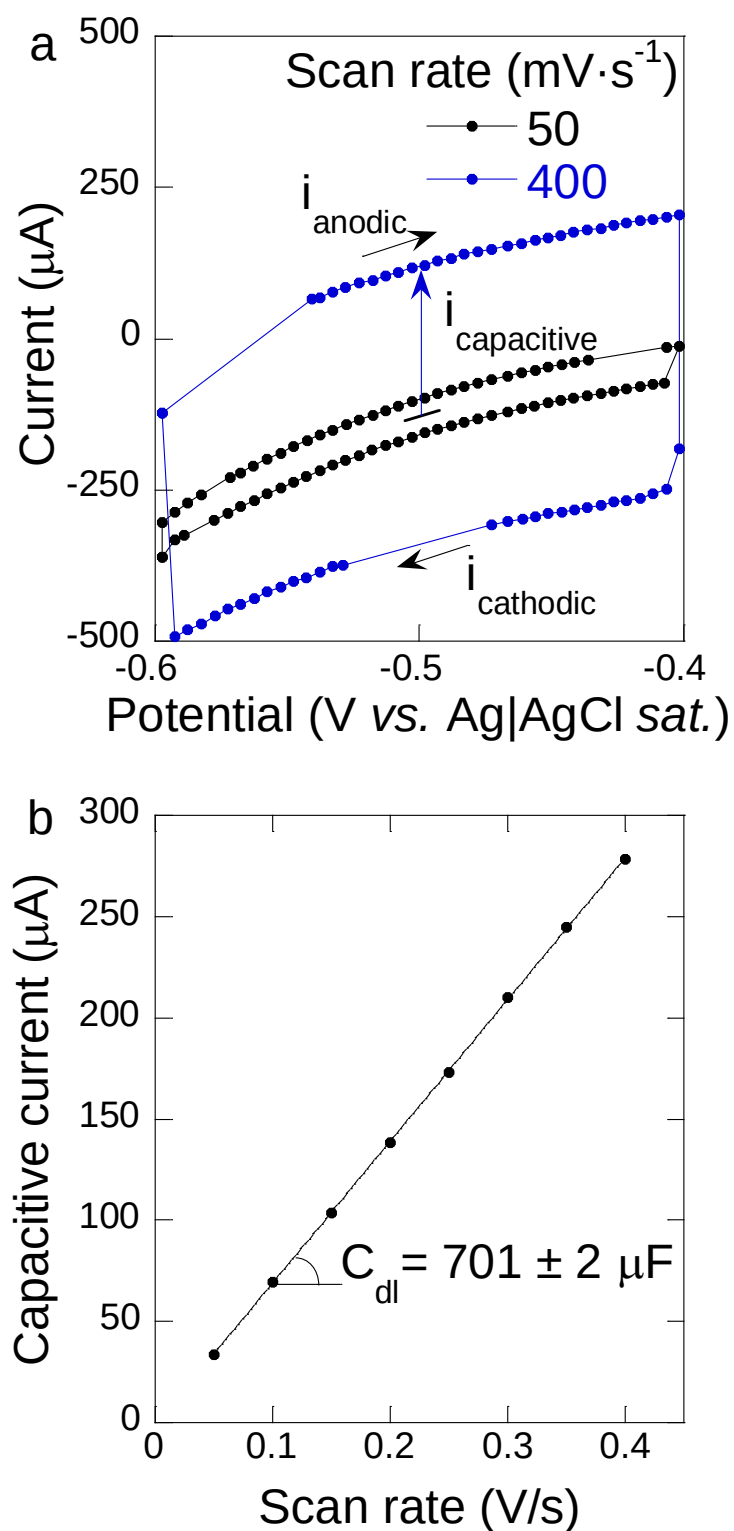


Fig. 40. a) Cyclic voltammetry from -0.6 V vs Ag|AgCl sat. to -0.4 V vs Ag|AgCl sat. at scan rates between 50 mV/s and 400 mV/s for one 2x2 cm² layer of nickel foam with a pore size of 450 μm ; b) Resulting capacitive current as a function of scan rate. Experiments were performed at 1 M KOH, room temperature.

counter- electrode, a saturated Ag|AgCl reference electrode (XR300 from Radiometer Analytical). The solution is 1 M of KOH at room temperature, with the same specifications as before.

5.7.2 Electrochemical impedance spectroscopy

Galvanostatic electrochemical impedance spectroscopy (EIS) measurements were performed as well to have an independent determination of the high frequency Ohmic resistance. The frequency range was set between 10,000 and 0.1 Hz with 3 points per decade for current densities up to 500 mA·cm⁻², and between 2,500 and 0.1 Hz with 3 points per decade for current densities above 500 mA·cm⁻². The AC amplitude was 10% of the DC.

5.7.3 Porosity measurement

The porosity of 3-D printed electrodes was measured by hydrostatic weighting (ISO 18754: 2020). For that, dried electrode samples were weighted (m_d , in grams). Then, the samples were completely submerged in a solution of 70% ethanol and 30% water and weighed again (m_w , in grams). The density of this solution (ρ_{sol} , in g·cm⁻³) was estimated with the help of a pycnometer. Using Archimedes' principle, the volume (cm³) could then be estimated:

$$V = \frac{m_d - m_w}{\rho_{sol}} \quad (74)$$

Knowing the total dimensions of the electrode and the metallic volume, porosity could be estimated, and it was averaged between the two pairs of electrodes (cathode and anode).

This method allows us to estimate the strut porosity as well. For that, the strut density is compared with the massive metallic density (ρ_m):

$$\rho_{strut} = \frac{m_d}{V} = \rho_m \cdot (1 - x) + \rho_{air} \cdot x \quad (75)$$

with ρ_{air} the air density ($0.001225 \text{ g}\cdot\text{cm}^{-3}$ [223]) and x the porosity. The density for Inconel 625 was considered to be $8.44 \text{ g}\cdot\text{cm}^{-3}$ (value from the manufacturer). Note that for massive 3-D printed electrodes, the density equals the density of the metal. In reality, there is some gas entrapped inside the metallic structure, lowering the density of the strut.

5.7.4 Polarization curve fitting

The fit was done based on the work of the ref. [70] using Eq. (23). The reversible cell voltage was estimated using an expression derived from Eq. (9) which considers wet hydrogen and wet oxygen as products and take into account the partial pressure of KOH solutions [224]:

$$\Delta E_{eq} = \Delta E_{eq}^{\circ} + \frac{R \cdot T}{z \cdot F} \cdot \ln \left[\frac{(P - P_e)^{1.5}}{P_{H_2}^{\circ} \cdot (P_{O_2}^{\circ})^{0.5}} \right] + \frac{R \cdot T}{z \cdot F} \cdot \ln \left[\frac{P_w}{P_w^{\circ}} \cdot \frac{P_e^{\circ}}{P_e} \right] \quad (76)$$

with P the total pressure in bar, P_e the vapor pressure of the electrolyte in bar, and P_w the vapor pressure of pure water in bar. The partial and vapor pressures under standard conditions $P_{H_2}^{\circ}$, $P_{O_2}^{\circ}$, P_w° and P_s° are equal to 1 bar. The standard equilibrium cell voltage was estimated as a function of temperature by the following expression [224]:

$$\Delta E_{eq}^{\circ} = 1.5184 - 1.54121 \cdot 10^{-3} \cdot T + 9.523 \cdot 10^{-5} \cdot T \cdot \ln(T) + 9.84 \cdot 10^{-8} \cdot T^2 \quad (77)$$

The vapor pressures of water were estimated using the following expression [224]:

$$\ln P_w = 37.04 - 6276 \cdot T^{-1} - 3.416 \cdot \ln(T) \quad (78)$$

and the one of the electrolyte was estimated by:

$$\ln P_e = 0.01621 - 0.1380 \cdot m + 0.1933 \cdot m^{0.5} + 1.024 \cdot \ln P_w \quad (79)$$

with m the molality in $\text{mol} \cdot \text{kg}^{-1}$.

The Zirfon ohmic resistance was estimated as [70]:

$$R_{zirfon} = R_e \cdot N_m \quad (80)$$

where R_e is the electrolyte resistance in Ω and N_m the dimensionless MacMullin number. The electrolyte resistance was estimated as [91]:

$$\begin{aligned} R_e^{-1} = & -2.041 \cdot M - 0.0028 \cdot M^2 + 5.332 \cdot 10^{-3} \cdot M \cdot T \\ & + 207.2 \cdot M \cdot T^{-1} + 0.001043 \cdot M^3 - 3 \cdot 10^{-7} \\ & \cdot M^2 \cdot T^2 \end{aligned} \quad (81)$$

with M the molarity in $\text{mol} \cdot \text{l}^{-1}$. The MacMullin number was considered to be 2.82, as proposed by ref. [70].

5.7.5 Other techniques

Micrographs of electrode samples were taken with a Zeiss Ultra-55 Field Emission Gun Scanning Electron Microscope (FEGSEM) using an electron high tension of 15 kV and type II secondary electrons.

Analysis of electrolyte composition was done by an Agilent 5100 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Samples of 1 M KOH were analyzed as-is, while samples at 30 wt% KOH were diluted 10 times. A background correction of the emission intensity was performed, and the instrument was calibrated for the KOH solution.

Chapter 6: Electrochemical characterization of 3-D foam-shaped electrodes

In this chapter, the use of macro-porous 3-D pure nickel foams with different pore sizes in the range of 450 – 3000 μm will be studied under well-controlled electrolyte flow conditions. To this end, a dedicated flow-by cell has first been constructed that allows for imposing the same relatively high flow rates on the order of $1 \text{ l}\cdot\text{min}^{-1}$. We then demonstrate that the effect of pore size and the electrochemical performance can be rationalized by considering the cell voltage as a

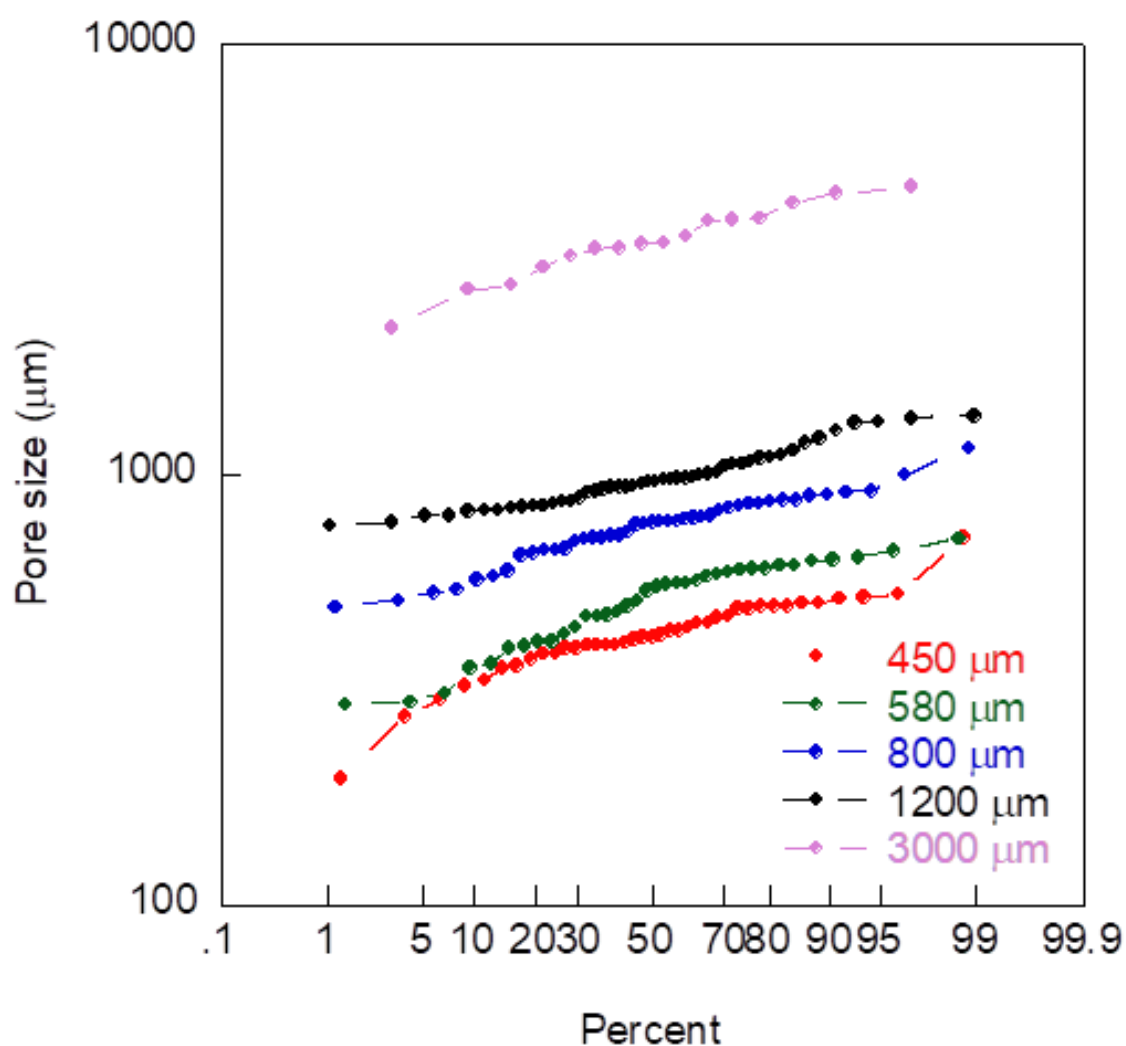


Fig. 41. Probability plot for pore size distribution of foam electrodes

Table 4. Geometrical electrode characteristics

Measured (Specified) pore size (μm)	Measured (Specified) porosity (%)	Measured (Specified) surface area (cm^2/cm^3)	Number of layers	Measured (Specified) total thickness (cm)	Measured foam surface area per cell (cm^2)
430 $\pm$ 60 (450)	87 $\pm$ 8 (85)	42.4 (78)	5	0.81 $\pm$ 0.02 (0.80)	137.4
500 $\pm$ 100 (580)	89 $\pm$ 7 (90)	42.8 (69)	4	0.77 $\pm$ 0.01 (0.76)	131.8
800 $\pm$ 100 (800)	91 $\pm$ 5 (90)	34.7 (60)	3	0.75 $\pm$ 0.01 (0.75)	104.1
1000 $\pm$ 200 (1200)	93 $\pm$ 4 (90)	23.2 (43)	2+2/3	0.78 $\pm$ 0.01 (0.8)	72.4
3500 $\pm$ 700 (3000)	95 $\pm$ 3 (94)	9.9 (11)	2	0.77 $\pm$ 0.03 (0.8)	30.5

function of electrochemical current density, i.e., the current divided by the theoretically available ECSA rather than by the projected electrode area. Based on this analysis, we were also able to quantify the bubble removal efficiency by estimating the effective fraction of the ECSA that is not impeded by bubble coverage.

Specifications of the foams under investigation are shown in Table 4, and the full pore size distributions are shown in Fig. 41.

What is current lacking in the literature is a systematic study on the combining effect of pore size and electrolyte flow rate, in particular under the relatively high flow rates encountered under industrial

conditions. As a consequence, the main objective of the current chapter is to study the electrochemical performance of differently sized pure nickel foams in a zero-gap cell configuration under well-controlled hydrodynamic conditions in a dedicated flow cell. This has allowed for the first time to advance the understanding and interpretation of the influence of their pore size independently from their surface area.

6.1 Effect of pore size on electrochemically active surface area

In what follows, current densities will be presented either as geometric or electrochemical ones. Geometric current density (j_{GEO}) is the total current divided by the projected area of the electrode (4 cm² in this work), while electrochemical current density (j_{ECSA}) is the total current divided by the actual electrochemically active surface area (ECSA). Although values for the electrode specific surface area (in cm²·cm⁻³) as a function of pore size have been specified by the manufacturer (as shown in Table 4), a capacitance test was performed to independently measure the electrochemically active surface area. As shown in Fig. 42, the surface area decreases with pore size in a power law fashion. Furthermore, the measured specific ECSA is systematically lower than the specified value. This result can be due to inhomogeneities in the electrode inherent to the fabrication method, which deviates the value from the specified one. The estimated value of ECSA for the current distributor plate is 19 cm². When estimating the ECSA current density, shown in Fig. 43, the total active surface area was considered including the one from the current distributor.

The capacitance method is a good way to compare electrochemical active surface areas, but the estimation of the exact value is difficult as

it depends on the value chosen for the specific capacitance (here, $20 \mu\text{F}\cdot\text{cm}^{-2}$). Taking as an example the slope of the curve capacitance vs. specified surface area, one has a specific of $9 \pm 1 \mu\text{F}\cdot\text{cm}^{-2}$. There is no consensus in the literature about this value, as experiments are conducted in different conditions and setups. Not all Ni electrodes in the literature are the same: they have different purities and different oxides content. Furthermore, the surface area is often estimated

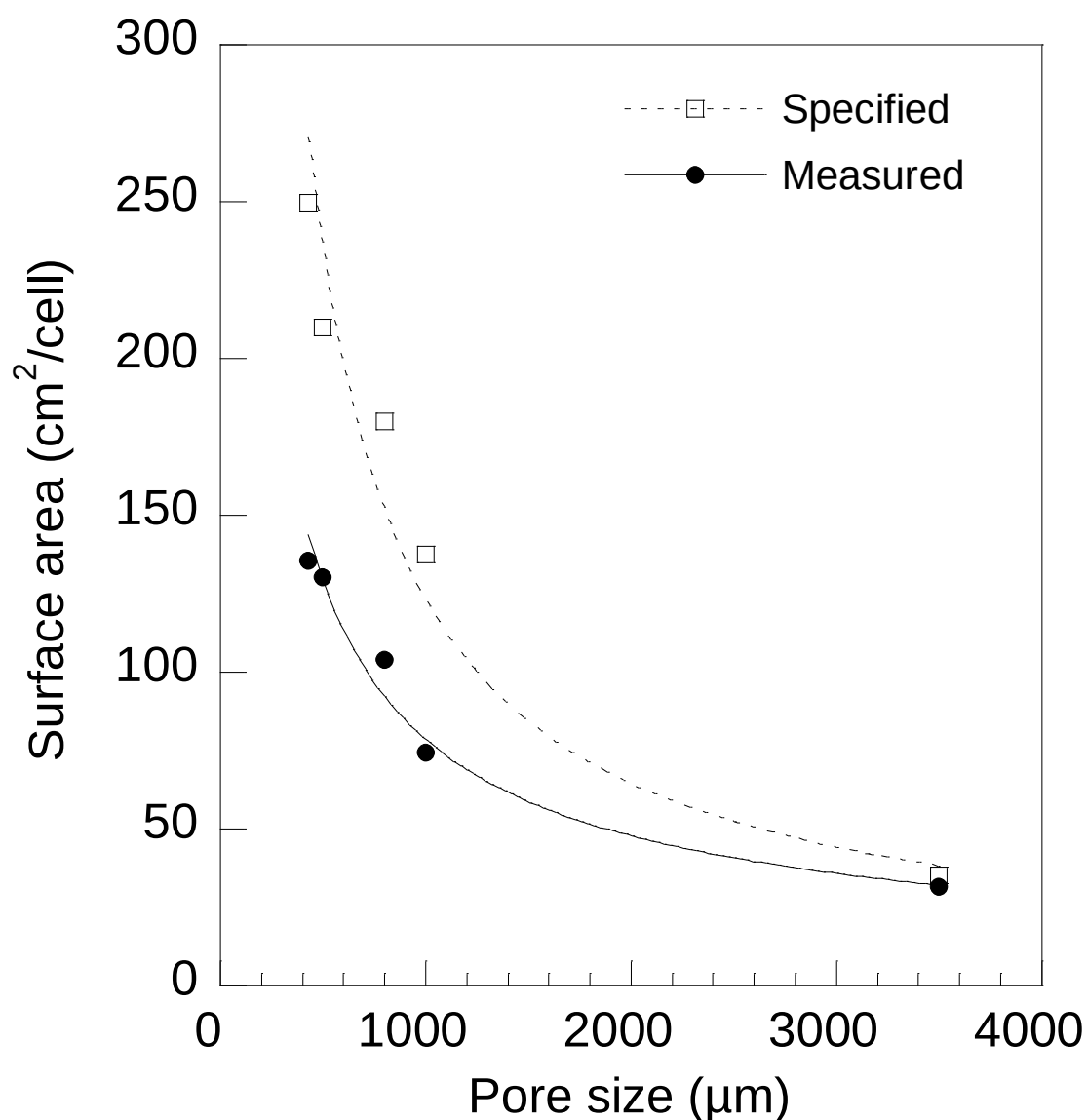


Fig. 42. Specified and measured foam surface area per cell as a function of measured average pore size.

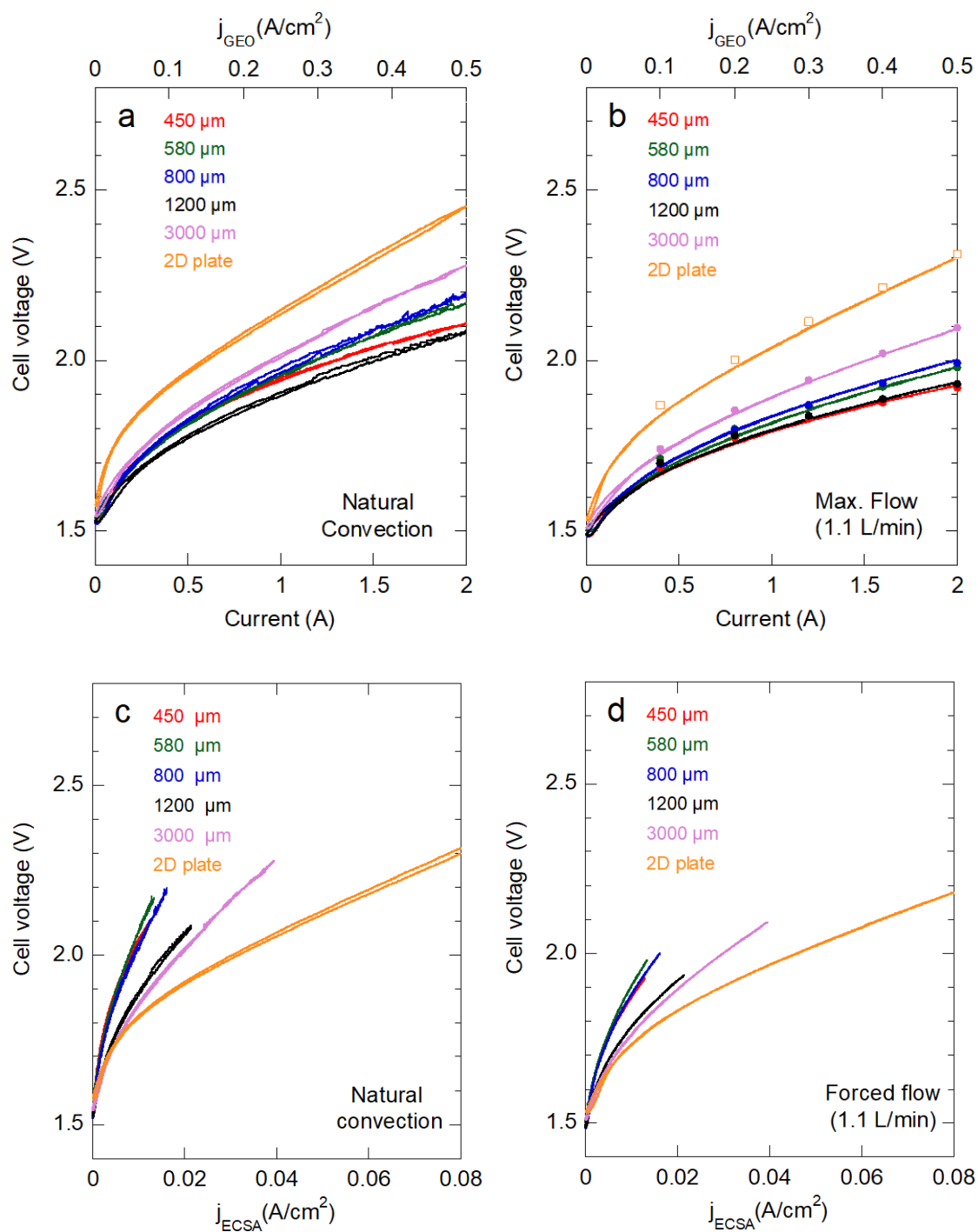


Fig. 43. Cell voltage as a function of a) geometrical current density during natural convection; b) geometric current density for a flow rate of 1.1 L/min; c) electrochemical current density at natural convection; d) electrochemical current density at a flow rate of 1.1 l·min⁻¹. Lines represent the results of CV scans at 100 mA/s, while the additional symbols in b) represent the mean cell voltage during a 5 minutes galvanostatic stay.

differently. While some articles consider the geometrical surface area, others use the BET (Brunauer, Emmett and Teller) surface area. Even for polished Ni electrodes, as in ref. [225], a difference in specific capacitance was observed when considering the geometric surface area of a polished and an etched electrode. Moreover, the electrode holder used to make the electric contact of the nickel electrode, if immersed, will also present a capacitance and will alter the result. If the electrode holder is not immersed it means that the foam will be partially immersed. In this case, the capillary effect in foams will increase the area in contact with the solution and alter the results. Differences in thickness, porosity, and density will change the wicking height and, in turn, the apparent ECSA, making it harder to compare between different studies [226]. This is why it was strictly important here to follow the same protocol to have a good ECSA comparison, with electrodes fully immersed. The effect of the electrode holder was greatly reduced here as the one-foam ECSA value was estimated from the slope of the curve capacitance vs number of layers, with the intercept representing the capacitance of the holder.

6.2 Effect of pore size on the electrochemical performance

When looking at the cell voltage values obtained at a fixed geometric current density (Fig. 44), it can be seen that the use of nickel foams enhances hydrogen production compared to the case where only a 2-D current distributor plate was used. At $0.5 \text{ A}\cdot\text{cm}^{-2}$ one has a decrease between 174 - 389 mV in cell voltage, representing a 14-36% decrease in overvoltage (i.e., the difference between the cell voltage and the sum of the equilibrium cell voltage – 1.195 V - and the ohmic contribution

of the separator), for both natural convection and forced electrolytic flow. This means that even if bubbles get trapped inside the foam's internal structure, hydrogen production can still benefit from the higher surface area of foams and the lower interelectrode gap given by the zero-gap configuration. This result shows the advantage of the zero-gap design over the traditional design, as previously demonstrated by ref. [122].

As illustrated in Fig. 44, the presence of a forced flow promotes a further decrease in cell voltage, between 40-99 mV at $0.1 \text{ A}\cdot\text{cm}^{-2}$ and between 109-189 mV at $0.5 \text{ A}\cdot\text{cm}^{-2}$, dependent on the pore size. This represents a significant decrease of up to 20% in overvoltage. Furthermore, foams are more sensitive to the flow than the 2-D plate.

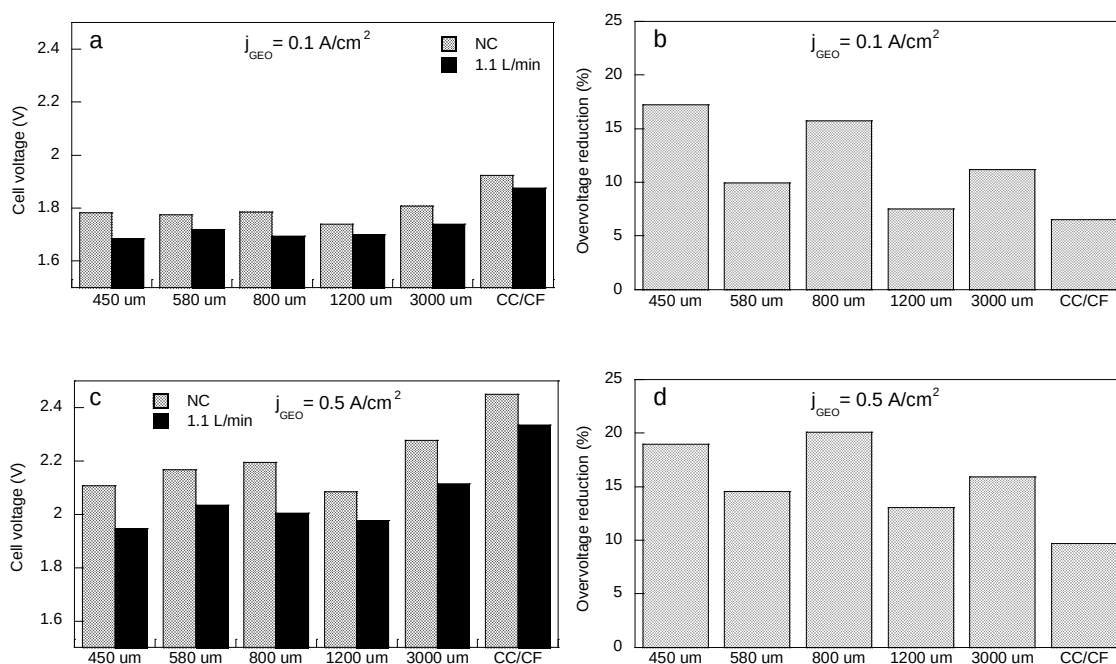


Fig. 44. Cell voltage for the different foams and flow regimes at a) $0.1 \text{ A}\cdot\text{cm}^{-2}$ and c) $0.5 \text{ A}\cdot\text{cm}^{-2}$. Overvoltage reduction caused by a forced electrolytic flow ($1.1 \text{ L}\cdot\text{min}^{-1}$) at b) $0.1 \text{ A}\cdot\text{cm}^{-2}$ and d) $0.5 \text{ A}\cdot\text{cm}^{-2}$.

No clear trend can be observed in Fig. 43.a and Fig. 43.b as to the effect of pore size on the flow-induced performance improvement. The best pore sizes are 450 μm and 1200 μm , as they promote the highest geometric current densities at a fixed cell voltage. At this stage, we might speculate already that the 450 μm foam presents a good performance due to its high surface area of 135.7 cm^2 , while the 1200 μm foam benefits from a better bubble removal efficiency, even if its surface area is lower (74.2 cm^2). The average cell voltage for the 5 minutes galvanostatic experiment - represented by the additional symbols in Fig. 43.b - shows a good agreement with the results from the cyclic voltammetry. The voltage is slightly higher at a fixed current for the galvanostatic one due to the higher time of the experiment, which allows the full development of the diffusion layer and enhances bubble entrapment.

Interestingly, the effect of pore size becomes much more systematic when expressing the cell voltage vs. electrochemical current density, j_{ECSA} (Fig. 43.d). It can be seen that the highest current densities were achieved when no foam was used. Then, as pore size decreases, j_{ECSA} values systematically decrease as well. Since all the electrodes were made of pure nickel, the electrochemical performance normalized by the ECSA should be the same, i.e., all curves in Fig. 43.c and Fig. 43.d should, in principle, be superposed. The observed decrease in j_{ECSA} with smaller pore size can therefore be attributed to bubble entrapment. This decreases the fraction of effectively active surface area, giving the impression of a worse electrochemical activity. It is logical then that the smaller the pore size, the higher the risk of bubble entrapment. To estimate the fraction of effectively available surface area relative to the

theoretically available ECSA values shown in Fig. 42, we propose a new procedure, illustrated in Fig. 45.a. It is based on comparing the 3-D foam's electrochemical current density at a fixed cell voltage to the j_{ECSA} value of the 2-D nickel plate. The fraction of available surface area can then be calculated as the ratio between the current density for each foam divided by the current density without foam, following Eq. (16). Indeed, the position of the foam's polarization curve to the left of the one for a 2-D plate when normalizing by the theoretical ECSA value implies that we have divided the total current by a too high value for the effectively available surface area. The latter fraction can thus be calculated by the correction factor needed to make both curves superpose. The results are shown in Fig. 45.b for the case of natural convection and maximum flow, i.e., $1.1 \text{ l} \cdot \text{min}^{-1}$. It clearly confirms that the lower the pore size, the lower the percentage of available surface. At 1.0 A and natural convection, one has 52% of available surface for $3000 \text{ }\mu\text{m}$ and only 22% for $450 \text{ }\mu\text{m}$. A qualitatively similar effect was observed at the maximum flow rate, going from 60% for $3000 \text{ }\mu\text{m}$ to 34% for $450 \text{ }\mu\text{m}$. This result also demonstrates that a forced electrolytic flow increases surface availability, especially for the lowest pore size. For the latter, an increase in surface availability in the order of 53% was observed, while the others presented an increase between 15-26%.

What can be concluded from all the above is that, when selecting the most appropriate pore size, there is a compromise between surface area and bubble removal efficiency. Since in the case of foams a larger surface area intrinsically implies a smaller pore size and a higher bubble entrapment, there should indeed be an optimum. Here, it was observed

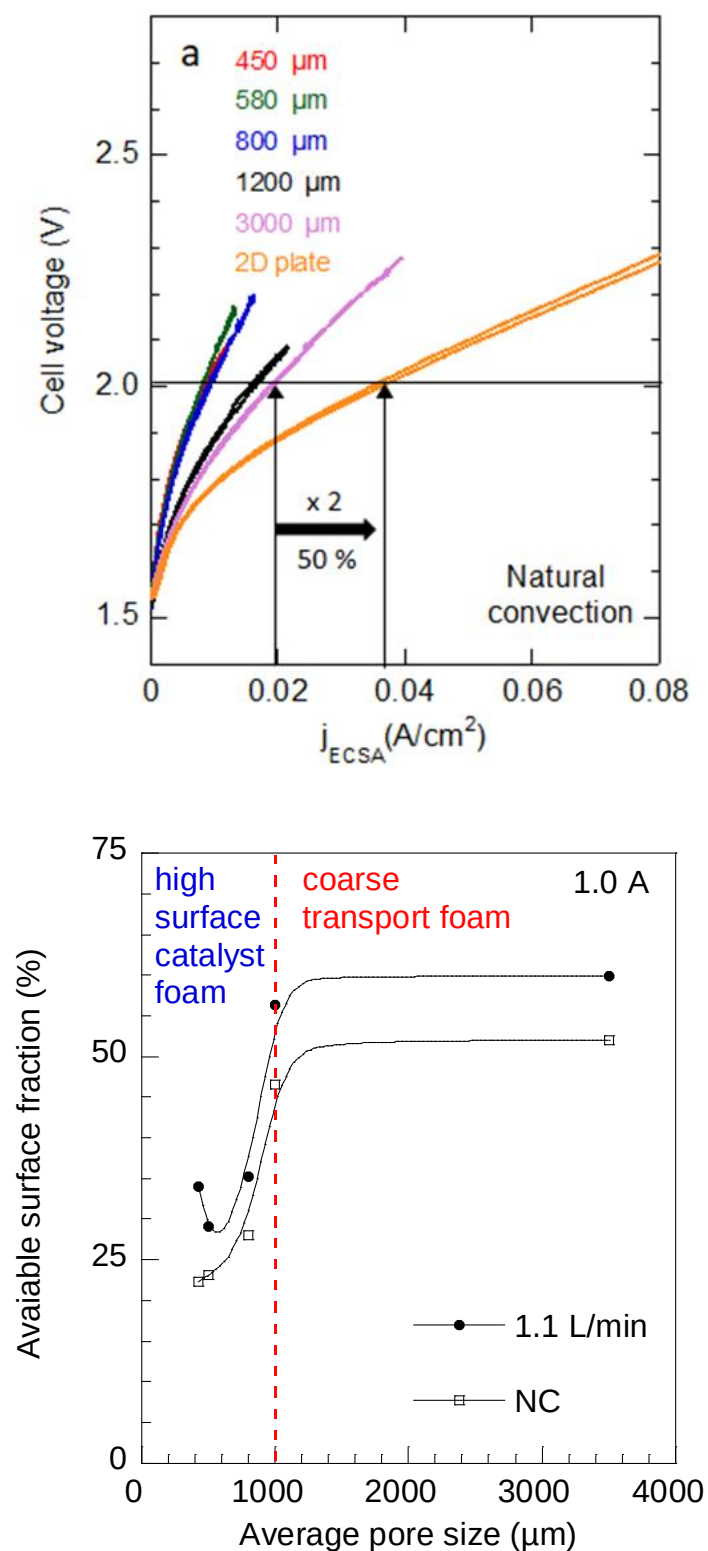


Fig. 45. a) Illustration of the method for calculating the available surface fraction for a foam electrode; b) Fraction of available surface area as a function of measured average pore size at 1 A under natural convection and $1.1 \text{ l} \cdot \text{min}^{-1}$. Solid red lines are merely a guide to the eye.

that for all the pore sizes studied, it could be interesting to maximize the surface area using a relatively small pore size of 450 μm , but it could also be interesting to enhance the bubble removal efficiency by the use of a more open structure, such as a 1200 μm sized foam, compensating for its lesser surface area. This idea will be further explored in the following chapter.

6.3 Effect of pore size on bubble entrapment

In an effort to confirm the hypothesis of bubble entrapment, we compared the foam with the best performance (450 μm) to the one with the worst performance (3000 μm) during three galvanostatic series of 5 minutes at $0.5 \text{ A}\cdot\text{cm}^{-2}$ (geometric current density) followed by a current off period of 5 minutes, both at natural convection and forced flow. In order to ensure the same temperature inside the cell and knowing the existence of a temperature decay at natural convection, this experiment was done at room temperature (21°C). The result is shown in Fig. 46.

At natural convection, the cell voltage increases with time as a consequence of an increase in bubble entrapment, which gradually reduces the active surface area. As expected, this increase is higher for the lowest pore size, as more bubbles are getting trapped within the 3-D structure. At a flow rate of $1.1 \text{ l}\cdot\text{min}^{-1}$, no significant increase in cell voltage was observed, demonstrating that bubble removal was effective at this flow rate. In this case, after a short period of cell voltage increase, there was even a decay in cell voltage, especially for the 450 μm foam.

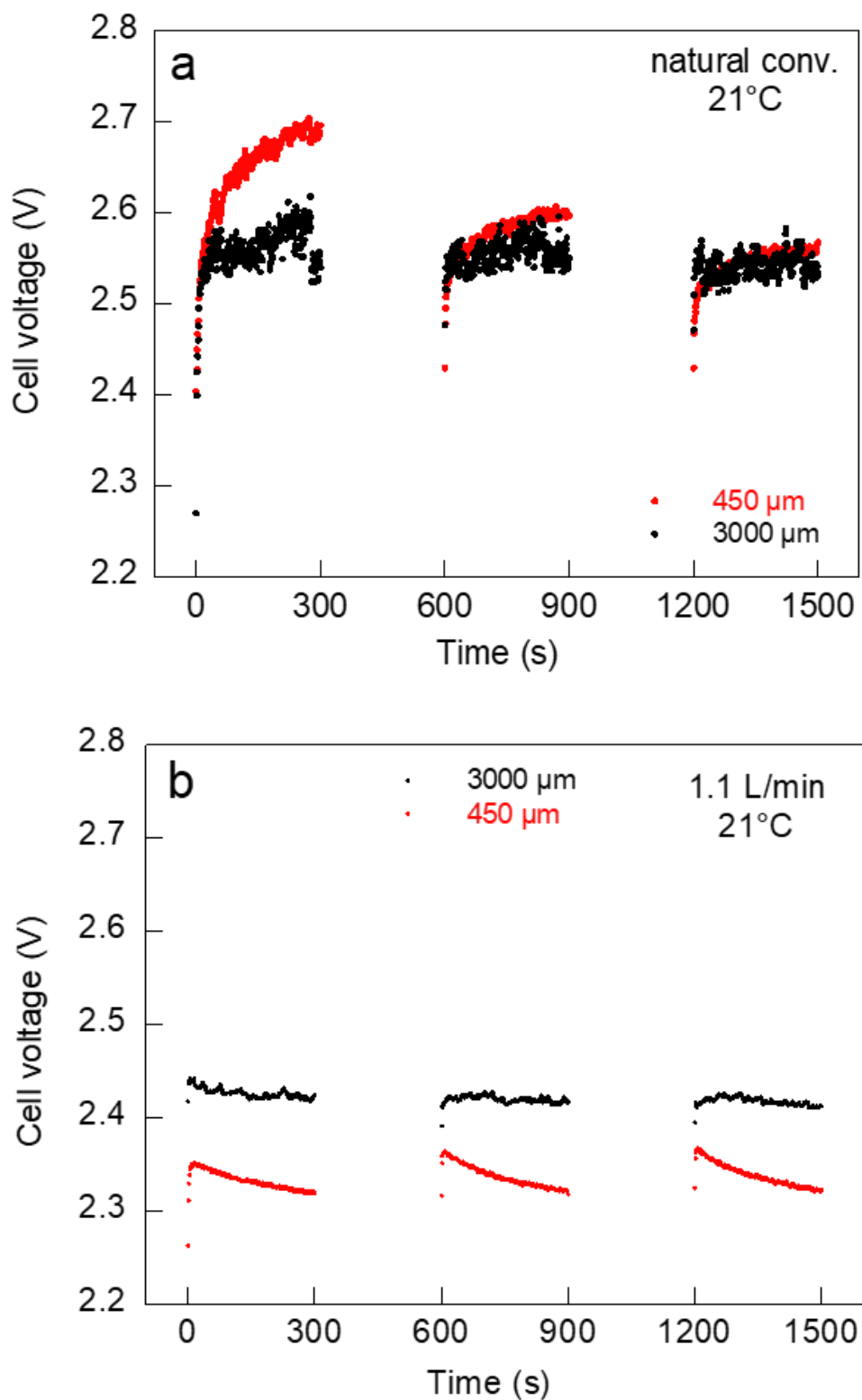


Fig. 46. Evolution of cell voltage for three series of galvanostatic pulses of 5 minutes at a geometric current density of $0.5 \text{ A}\cdot\text{cm}^{-2}$ followed by 5 minutes at zero current; a) natural convection b) $1.1 \text{ l}\cdot\text{min}^{-1}$. Experiments were performed at 30 wt% KOH and room temperature.

This result confirms the importance of a forced electrolytic flow in removing bubbles and avoiding cell voltage build-up. Finally, at natural convection, the foam with a pore size of 450 μm even presented a slightly worse performance than the foam with a pore size of 3000 μm . In other words, using small-sized foams only makes sense if a forced electrolyte flow is imposed; otherwise, bubbles cannot leave the electrode surface.

6.4 Conclusion

In this chapter, it was shown that the choice of a porous foam electrode depends mainly on two opposing factors: surface area and bubble entrapment. To increase surface area, the pore size should be reduced. On the other hand, this will increase bubble entrapment and hinder hydrogen production. When looking at the ECSA current density, it was clear that more closed structures with lower pore sizes caused a decrease in the observed current density. This was mainly a consequence of a higher bubble entrapment. From all the foams studied, the best compromise between surface area and bubble entrapment was found for 450 μm and 1200 μm . For the first one, it makes sense to choose this pore size only when a forced electrolyte flow is imposed. Otherwise, bubble entrapment is too significant and the performance decreases. The electrolytic flow has proven to be promising, promoting a decrease in overvoltage of up to 20%. Furthermore, while pores of 450 μm benefit from the highest surface area, pores of 1200 μm benefit from a more open structure responsible for better bubble removal.

Following the results obtained in this section, we propose a bi-layer cell configuration, combining the best of two foams: a foam with a high

surface area - 450 μm – as production foam; combined with a foam with a low bubble entrapment – 3,000 μm – as a bubble evacuation foam, or porous transport layer, as schematized in Fig. 45.b. The results are discussed in the following chapter.

Chapter 7: PEM-like alkaline water electrolysis using flow-engineered 3-D electrodes

Based on the findings of the previous chapter, we propose a flow-engineered 3-D laterally-graded bi-layer cell configuration allowing for alkaline water electrolysis to become PEM-like ($2 \text{ A} \cdot \text{cm}^{-2}$ at $< 2 \text{ V}$ cell voltage). Detailed CFD simulations, explicitly considering the entire 3-D electrode and cell topology, have shown that under a forced upstream electrolyte flow, such a graded structure induces a high lateral electrolyte velocity at the bi-layer interface. As a result, gas bubbles are

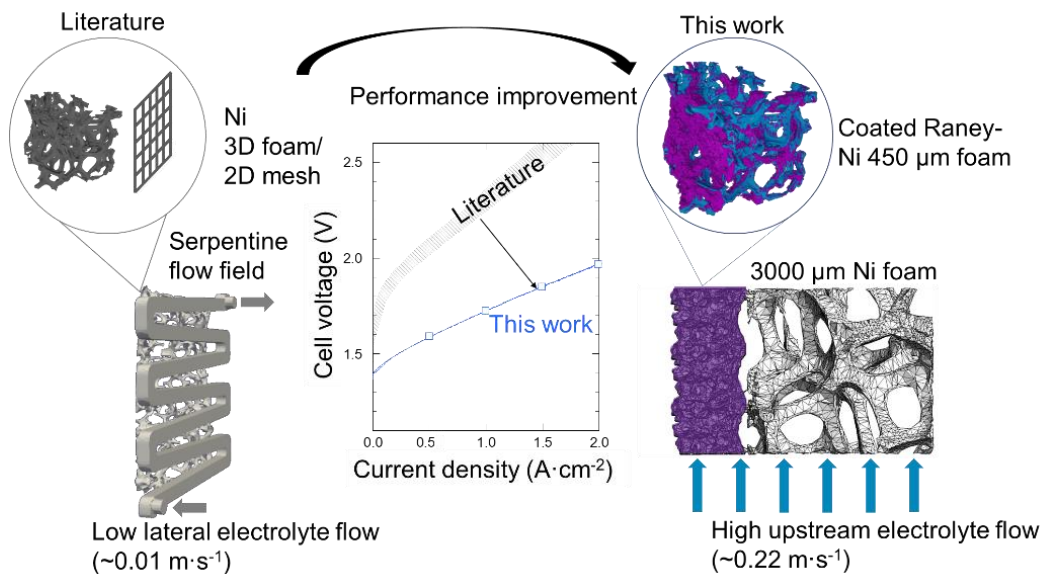


Fig. 47. Graphical abstract of chapter 5 showing the main improvements demonstrated in this work : (1) the use of a high forced upstream electrolyte flow, as opposed to the use of serpentine flow fields in most of the literature reports; (2) the integration of 3-D electrodes in a zero-gap cell using a laterally graded bi-layer configuration consisting of a fine 450 μm foam in contact with a coarse 3000 μm foam, the combination being flow-engineered to enhance gas removal; (3) the application of a Raney Ni coating on the fine foam, resulting in catalytically highly active electrodes free of Pt group metals.

directly evacuated, so that the electrode surface can maintain its high electrochemical activity even at high current densities.

The improved performance was shown to be the synergistic effect of 3 factors, as illustrated in Fig. 47: (1) the use of a high forced upstream electrolyte flow, as opposed to the serpentine flow fields often used in most of the literature so far; (2) the integration of the 3-D electrodes in a zero-gap cell using a bi-layer configuration consisting of a fine thin foam in contact with a thick coarse foam, the combination being flow-engineered to enhance gas removal; (3) the application of a Raney Ni coating on the fine foam in both the anodic and cathodic parts, resulting in highly active electrodes free of PGMs that are able to maintain their activity at high current densities thanks to the improved bubble evacuation.

After analyzing the Ni foams, we propose a new cell configuration based on the previous discussion. The powerful synergy demonstrated in this work between a tailored flow-engineered 3-D electrode and cell geometry using Ni-based electrodes can be best understood and appreciated when compared with available literature data. Several recent papers on alkaline water electrolysis under similar conditions (temperature 70-80°C, KOH concentration 24-30 wt%) and using a Zirfon separator and Ni-based electrode materials are summarized in Table 5. Note that a state-of-the-art Zirfon diaphragm was chosen in this work in order to have the largest possible comparative data set from the literature. A further performance improvement can be expected using our same electrode and cell configuration but replacing the Zirfon diaphragm with more conductive alkaline based membranes [88,227].

Table 5. Details of cell setups for alkaline water electrolysis with Zirfon separator and PGM free electrodes.

Ref.	KOH concn.	Temp. Cathode (°C)	Anode	Flow (ml·min ⁻¹ ·layer)	Transport/contact layer
This work	30%	70	Ni 450 µm foam	350-1600	3000 µm Ni foam
This work	30%	70	Raney-Ni 450 µm foam	350-1600	3000 µm Ni foam
[228]	30%	80	Raney Ni perforated	50	Flow field (shape)
[229]	5% ^a	80	Stainless steel expanded mesh	80	Serpentine flow field
[230]	30%	80 ^b	Ni plate with channels	0.048–28	Flow field (shape)
[88]	24%	80	Ni foam	50	Flow field (shape)
[88]	24%	80	Ni perforated sheet	50	Flow field (shape)
[102,231]	30%	80	Ni foam	450	Serpentine flow
[102,231]	30%	80	Raney Ni foam	450	Serpentine flow
[212]	26% (6	70	Raney Ni multimesh	N/S	Knitted Ni wire
[232]	N/S	80	Ni foam	20	Serpentine flow
[233]	30%	80	Raney Ni foam	400	Ni foam
[234]	30%	80	Porous Raney Ni	400	Serpentine flow
[227]	26% (6	80	Ni foam	50	Serpentine flow
[235]	30%	80	Raney nickel foam	1000	Porous transport

^aNaOH as electrolyte ; b30 bar of pressure ; N/S = not specified

Representative polarization curves are shown in Fig. 48 for two upstream flow velocities for pure Ni bi-layers (a) and bi-layers with a catalytic Raney Ni coating (b). The available literature range is indicated as well. In order to gain a more fundamental insight into the significant performance enhancement obtained in both cases, all polarization curves within the literature range, shown in full detail in Fig. 49, have then been fit using the following Eq. (23).

The total Ohmic resistance, R_{total} , consists of the electrolyte resistance, including any remaining attached or dissolved gas bubbles, and the resistance of the Zirfon diaphragm. As illustrated in Fig. 49, R_{Zirfon} can be subtracted based on known data from the literature, thereby revealing the specific contribution of non-evacuated bubbles as $R_{\text{total}} - R_{\text{Zirfon}}$. All fitting results, including standard deviations, have been summarized in Table 6 and are shown as normal cumulative distributions in Fig. 50 for the Tafel slope b (top) and $R_{\text{total}} - R_{\text{Zirfon}}$ (bottom), respectively.

Two important observations can be made from these graphs. First of all, the use of a catalytic Raney Ni coating results in a significant decrease in Tafel slope and, hence, an improved electrochemical performance, as is already well-documented in the literature. However, fitting results for our own polarization curves do not differ markedly from literature data: the b -values for both our pure Ni and Raney Ni bi-layers fall on the same statistical normal distribution as the respective literature data. Therefore, our observed performance enhancement cannot be ascribed to the use of Raney Ni alone. Secondly, the electrolyte part of the Ohmic resistance ($R_{\text{total}} - R_{\text{Zirfon}}$) for the polarization curves obtained in this

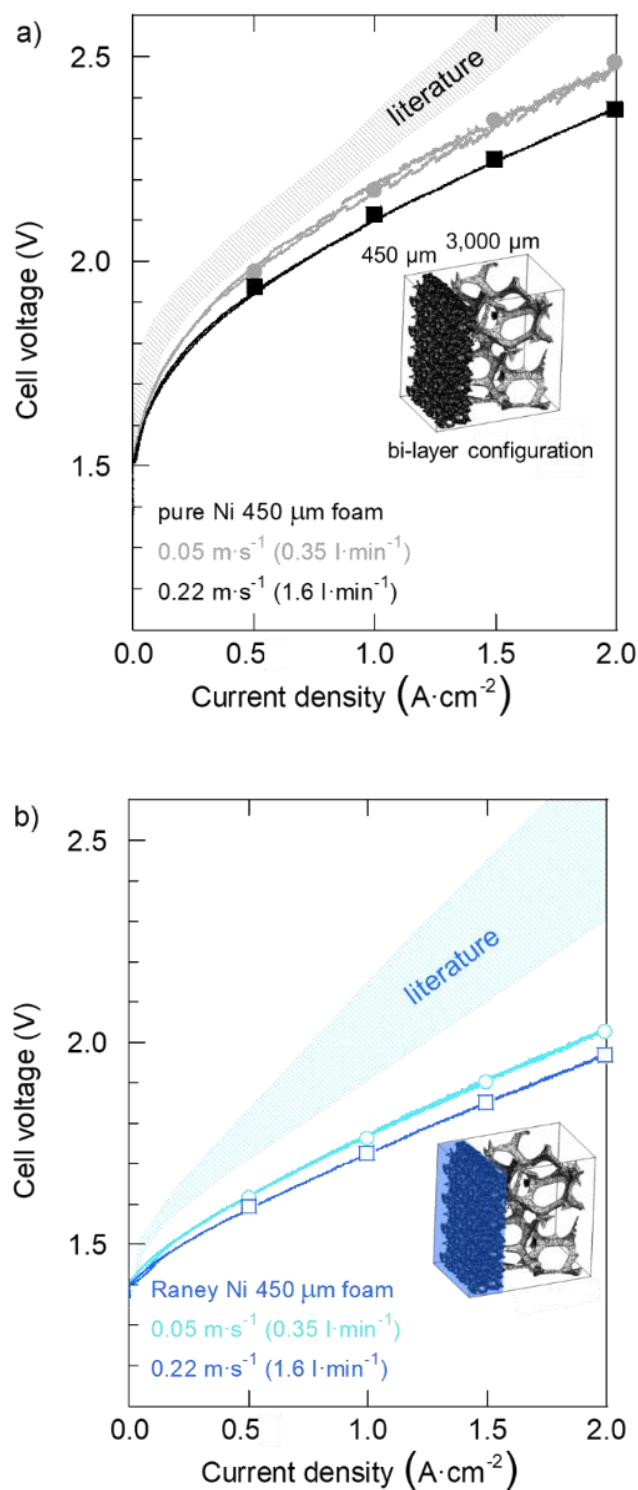


Fig. 48. Representative polarization curves at 70°C and 30wt% KOH for 2 electrolyte upstream flow velocities for pure Ni bi-layers (a) and bi-layers with a catalytic Raney Ni coating (b). Lines are measured from cyclic voltammetry, while bullet points from selected galvanostatic experiments have been superimposed. Hatched zones represent the range of literature data, for which all polarization curves are shown in Fig. 49.

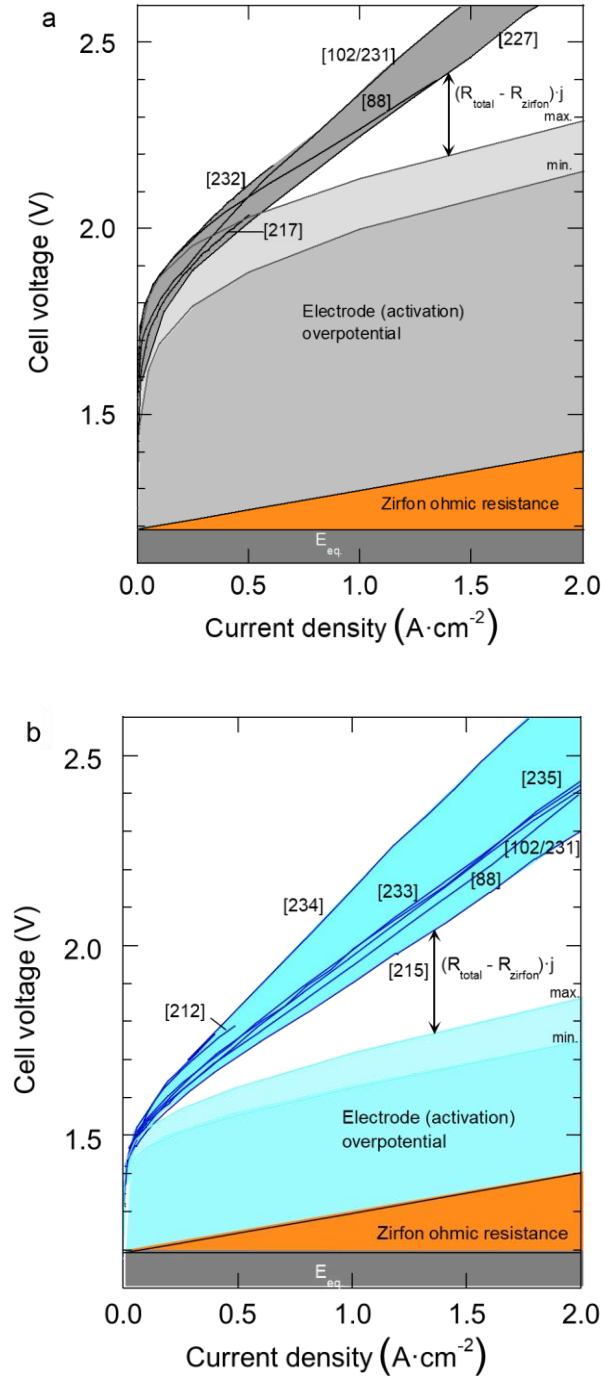


Fig. 49. Polarization curves from literature for Pt group metals (PGM)-free electrodes in alkaline medium using a Zirfon gas separator for a) pure Ni and b) Raney Ni electrodes. Zirfon resistance was estimated individually for each reference in Table 6 considering a MacMullin number of 2.82 (as in ref. [48]), and represented above with an average value of $R_{\text{Zirfon}} = 105 \pm 5 \text{ m}\Omega/\text{cm}^2$. Similarly, values the equilibrium cell voltage were calculated for each reference according to Eq.(76), resulting in the average value for $E_{\text{eq}} = 1.19 \pm 0.02 \text{ V}$ represented above.

Table 6. Electro-kinetic parameters and Ohmic resistance obtained from curve fitting all polarization curves by Eq. (23).

Ref.	Electrode composition	E_{eq} (V)	b (mV·dec ⁻¹)	$j_0 \cdot 10^{-5}$ (A·cm ⁻²)	$R_{\Omega, total}$ (mΩ·cm ²)	R_{Zirfon} (mΩ·cm ²)	$R_{\Omega, total} - R_{Zirfon}$ (mΩ·cm ²)
This work	Pure Ni (0.35 l·min ⁻¹)	1.195	189.8 ± 0.9	19.3 ± 0.6	266.3 ± 0.7	114	152.3 ± 0.7
This work	Pure Ni (1.6 l·min ⁻¹)	1.195	168.0 ± 0.6	13.1 ± 0.4	244.4 ± 0.5	114	130.4 ± 0.5
This work	Raney Ni (0.35 l·min ⁻¹)	1.195	54.6 ± 0.3	0.20 ± 0.01	259.9 ± 0.3	114	145.9 ± 0.3
This work	Raney Ni (1.6 l·min ⁻¹)	1.195	43.8 ± 0.3	0.033 ± 0.002	242.4 ± 0.2	114	128.4 ± 0.2
[228]	Raney Ni	1.184	60 ± 4	0.2 ± 0.1	372 ± 4	102	270 ± 4
[230]	Pure Ni	1.269	215 ± 3	54 ± 3	246 ± 8	103	143 ± 8
[88]	Pure Ni	1.179	169 ± 11	1.1 ± 0.6	260 ± 20	110	150 ± 20
[88]	Raney Ni	1.179	70 ± 4	0.6 ± 0.3	407 ± 5	110	297 ± 5
[102,231]	Pure Ni	1.184	138 ± 7	0.7 ± 0.3	472 ± 9	102	369 ± 9
[102,231]	Raney Ni/NiFe-LDH	1.184	95 ± 9	7 ± 4	400 ± 10	102	300 ± 10
[212]	Raney Ni	1.192	90 ± 5	2.1 ± 0.8	430 ± 20	119	310 ± 20
[232]	Pure Ni	1.184	153 ± 3	0.49 ± 0.08	330 ± 20	102	230 ± 20
[233]	Raney Ni/NiFe-LDH	1.184	65 ± 4	0.12 ± 0.08	420 ± 30	102	320 ± 30
[234]	Raney Ni/NiFe-LDH	1.184	123 ± 8	29 ± 10	530 ± 10	102	430 ± 10
[227]	Pure Ni	1.18	200 ± 14	20 ± 9	340 ± 10	106	230 ± 10
[235]	Raney Ni/NiFe-LDH	1.184	61 ± 5	0.08 ± 0.08	427 ± 5	102	325 ± 5

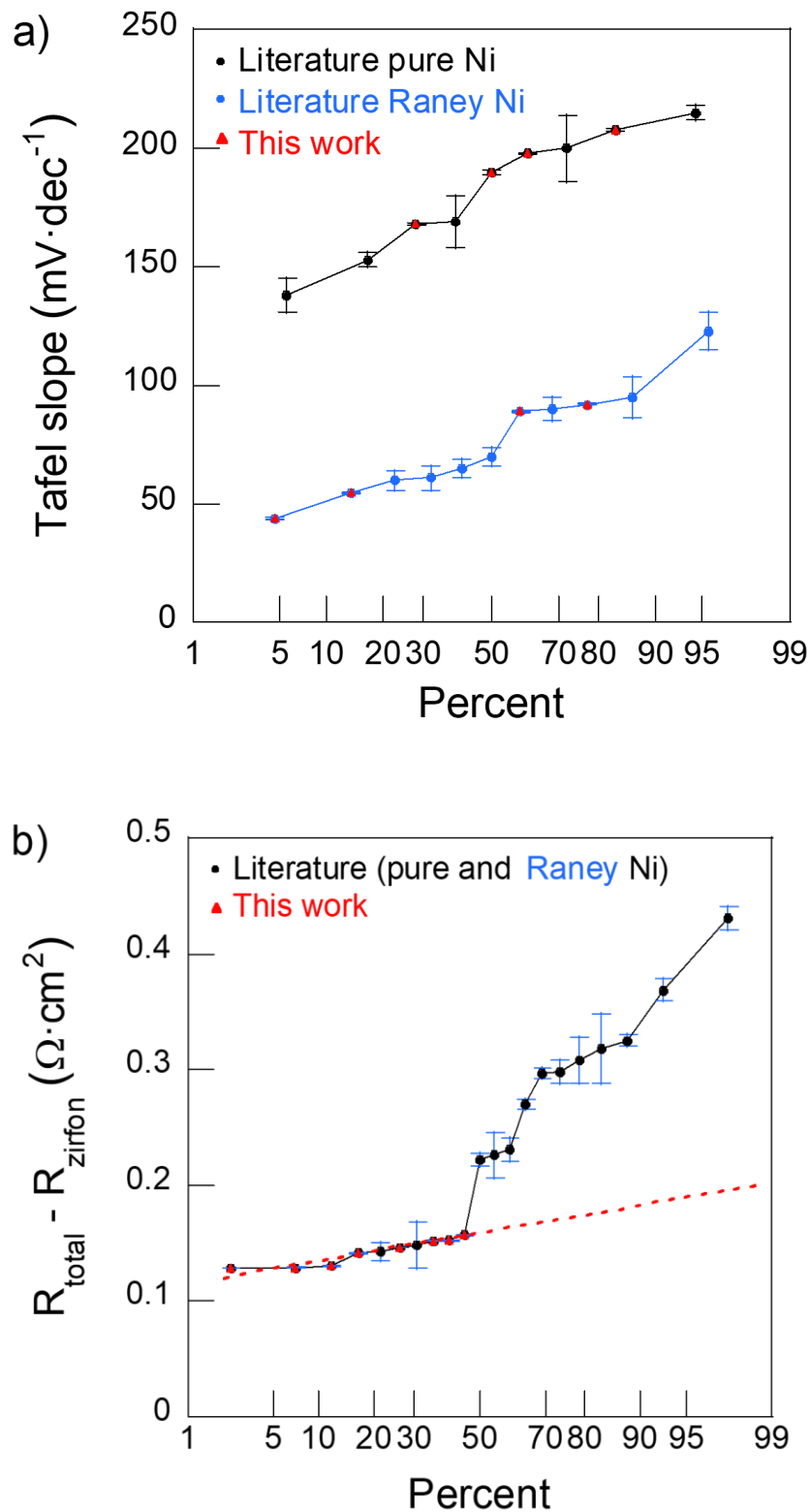


Fig. 50. Cumulative normal probability plots comparing our own data to relevant data from the literature using Ni-based electrodes and a Zirfon diaphragm for a) Tafel slopes and b) Ohmic resistance minus Zirfon resistance. Raw data are compiled in Table 6 and obtained by fitting all polarization curves by Eq. (23).

work clearly does fall on a different normal distribution, and the obtained values are also significantly lower than most of previously reported literature values. This indicates that, although applying a Raney Ni coating is a necessary contribution to the here reported PEM-like performance enhancement, it is the lowering of the electrolyte contribution to the Ohmic resistance that allows to make the difference. Since the latter mainly comes from any attached or remaining gas bubbles, we will show below through detailed CFD simulations that it is the use of a flow-engineered bi-layer configuration, combined with applying a forced upstream electrolyte flow that allows for the PEM-like performance enhancement.

7.1 Forced upstream electrolyte flow

From Fig. 48 and Table 6, it can be seen that an increase in the electrolyte flow from the minimum to the maximum value caused a decrease of $12.0 \pm 0.2 \%$ and $14.4 \pm 0.5 \%$ in Ohmic resistance for the coated and the non-coated foam, respectively. The observed effect can be attributed to enhanced bubble removal caused by the forced upstream electrolyte flow. Before the start of hydrogen and oxygen production, both the electrode surface and the electrolyte are free of bubbles. As soon as gas evolution starts, bubbles start to nucleate and grow on the electrode surface and pass into the electrolyte once a critical size is achieved. Such adhering insulating bubbles decrease the electrochemically active electrode surface (screening effect), while detached bubbles tend to lower the electrolyte conductivity (voidage effect) [21]. An increase in upstream flow rate (i.e., in the direction of gas evacuation) is capable of shortening the bubble growth time and

decrease its maximum size, thereby lowering the bubble-induced overpotential [237]. Also note in Fig. 48 how the polarization curves at minimum flow show many irregularities, indicative of poor bubble evacuation, while it becomes fully stabilized when increasing the flow.

Looking first at the data for our pure Ni electrodes, their performance clearly outperforms the ones previously reported in the literature. At a constant current density of $1.8 \text{ A}\cdot\text{cm}^{-2}$, the best result from the literature was a cell voltage of 2.6 V [227], whereas our own study achieved a significantly lower voltage of only 2.3 V. Both studies utilized $2 \times 2 \text{ cm}^2$ Ni foam electrodes, but instead of using a coarse porous transport foam as we did, ref. [227] used a serpentine-like flow plate at a flow rate of only $0.05 \text{ ml}\cdot\text{min}^{-1}$, 7 times lower than the minimum flow used in our work. In terms of Zirfon corrected Ohmic resistance ($R_{\text{total}} - R_{\text{Zirfon}}$), our work achieved a minimum value of $130 \pm 1 \text{ m}\Omega\cdot\text{cm}^2$ for pure Ni electrodes, which is still lower than the lowest literature value of $143 \pm 8 \text{ m}\Omega\cdot\text{cm}^2$, reported in ref. [230] at a pressure of 30 bar. While it is known that at higher pressures, the bubble size decreases, thereby reducing their contribution to the overall cell voltage, our flow-engineered 3-D electrodes proved to be superior even under atmospheric conditions.

Secondly, as to the coating effect, in ref. [88] the Ohmic resistance doubled when going from pure Ni to Raney Ni, reaching $297 \pm 5 \text{ m}\Omega\cdot\text{cm}^2$. This indicates that in that work, the use of serpentine-like flow plates was unable to efficiently remove the higher amount of gas bubbles produced at the Raney Ni electrodes. In ref. [228], 2-D perforated coated Raney Ni plates were used as electrodes, but again in

the presence of non-optimized flow fields and a low flow rate of $0.05 \text{ l}\cdot\text{min}^{-1}$. As a result, their Ohmic resistance was $270 \pm 4 \text{ m}\Omega\cdot\text{cm}^2$, twice as high as in our work. Refs. [102] and [231] compared different Raney Ni-based foams as electrodes. The electrolyte flow rate was set at $0.45 \text{ l}\cdot\text{min}^{-1}$, similar as in our work. In ref. [231], the nature of the porous transport layer was not specified, but in ref. [102] a single serpentine flow field was used. The result was an Ohmic resistance of $297 \pm 5 \text{ m}\Omega\cdot\text{cm}^2$, more than double the value we obtained by our flow-engineered bi-layer configuration.

Based on the above comparisons with literature data, we can conclude that the serpentine flow fields often used in the literature so far are not the best way to enhance bubble removal. It appears that they have been simply adopted without further question from transport studies related to fuel cells [28,30]. However, mass transport in fuel cells relates to the transport of gases as reactants away from the flow field into the catalyst layer and to the transport of liquid water as a product from the electrode into the flow field. This is fundamentally different from the basic functioning of a water electrolyzer, where the main transport issue is the extraction of gas bubbles as the reaction product away from the electrode. Our own novel cell design and electrode configuration mitigate the negative effects of high electrolyte flows, most notably the occurrence of jet-like, unstable flows due to small inlet diameters [239]. Instead, in our cell, the flow is uniformly distributed at the entrance of the bi-layer electrode, as illustrated by the CFD simulations shown in Fig. 51. This results in an enhanced transport of bubbles away from the catalytic foam, either directly to the outlet or laterally towards the

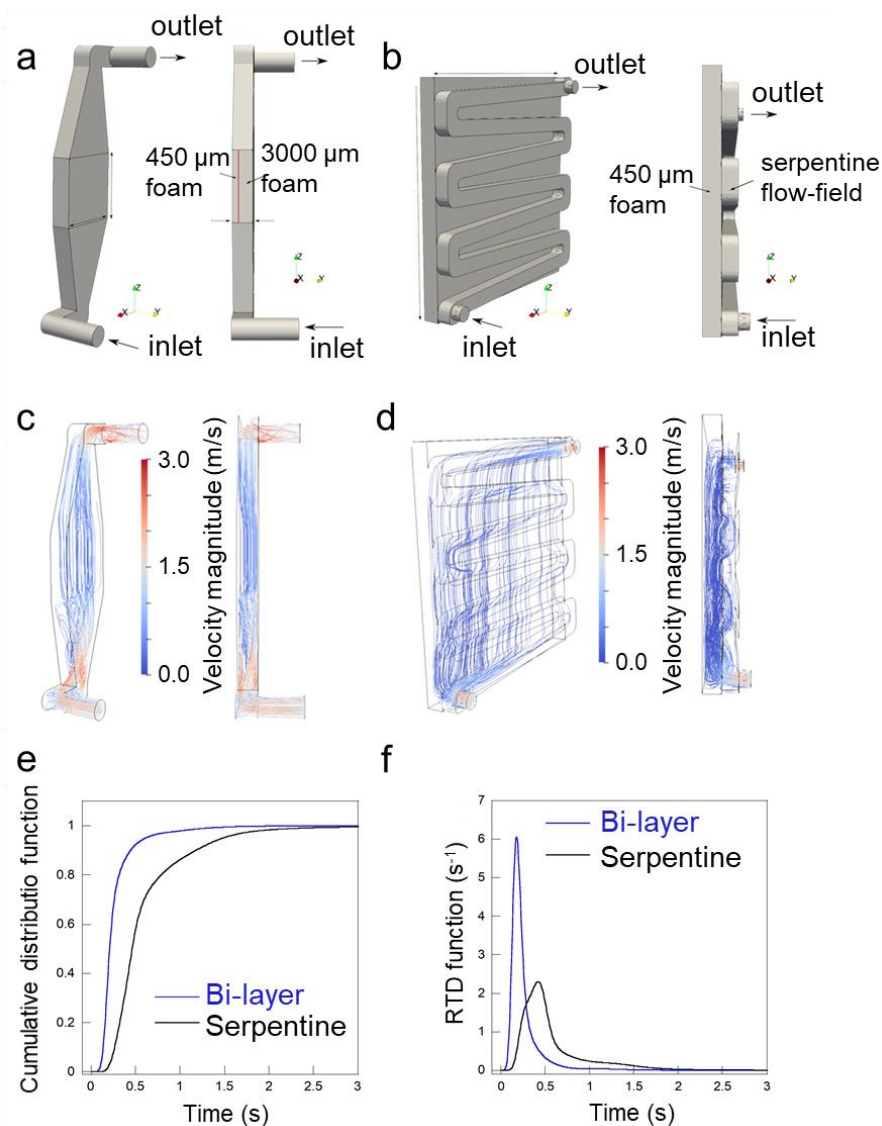


Fig. 51. Graphical representation of a) our own flow-engineered cell with the bi-layer configuration consisting of a catalytic 450 μm foam and a porous transport foam of 3000 μm ; b) serpentine flow field along with a 450 μm foam. Flow streamlines for an inlet velocity of 1.5 $\text{m}\cdot\text{s}^{-1}$ for c) our own cell and d) serpentine flow field; e) cumulative distribution function at the outlet, representing the fraction of tracers exiting the electrolyzer that have spent a time t or less in the electrolyzer; f) residence time distribution function $E(t)$. The product $E(t)\cdot dt$ represents the fraction of tracers exiting the electrolyzer that have spent a time between (t) and $(t + dt)$ in the electrolyzer. The mean residence time was 0.26 s and 0.60 s for the bi-layer configuration and for the serpentine, respectively.

coarse porous transport foam, as will be demonstrated in the next section by single and 2-phase simulations that explicitly take into account the 3-D bi-layer electrode topology. Also shown in Fig. 51 is that serpentine flow fields rather impede such a bubble extraction,

due to a back-and-forth flow circulation in the interface between the catalytic region and the flow channels, as visualized by the streamlines on Fig. 51.d. This becomes even more obvious by comparing the Residence Time Distribution (RTD) for both cases in Fig. 51.f: a passive scalar convected by the electrolyte flow has a much lower RTD in our flow-engineered cell, meaning that hydrogen bubbles are extracted much more efficiently.

By using Eq. (23), an important assumption was made, namely that the value of the Ohmic resistance R_{tot} obtained from fitting can be considered independent of current density. If we associate this value (and therefore also the value of $R_{\text{tot}} - R_{\text{Zirfon}}$) with any remaining attached or dissolved gas bubbles, then it is not unlikely that it might change (increase) upon increasing current density, as a result of an increased gas production rate. Therefore, we also performed additional Electrochemical Impedance Spectroscopy (EIS) measurements at 2 different flow rates on our pure Ni bi-layers, and compared the obtained results for the high frequency resistance at different current densities in the range $0.01 - 2 \text{ A}\cdot\text{cm}^{-2}$ to the (single) value of R_{tot} obtained from fitting the entire polarization curve to Eq. (23). Results are shown in Fig. 52. A first important observation is that for both flow rates, the EIS-derived ohmic resistance shows very little variation with imposed current density: for an electrolyte flow rate of $0.35 \text{ l}\cdot\text{min}^{-1}$ and $1.2 \text{ l}\cdot\text{min}^{-1}$, it ranges between 0.24 to $0.30 \text{ }\Omega\cdot\text{cm}^2$ and 0.23 and $0.27 \text{ m}\Omega\cdot\text{cm}^2$,

respectively, leading to an average value of $0.26 \pm 0.02 \Omega \cdot \text{cm}^2$ and $0.24 \pm 0.02 \Omega \cdot \text{cm}^2$, respectively. Moreover, these average values (with a relative error in both cases of less than 10%) are also statistically equal to the polarization curve-fitted values for R_{tot} of $0.27 \Omega \cdot \text{cm}^2$ and $0.24 \Omega \cdot \text{cm}^2$, already reported in Table 6. Both of these findings give further confidence to the $R_{\text{tot}} - R_{\text{Zirfon}}$ data from our own polarization curves as

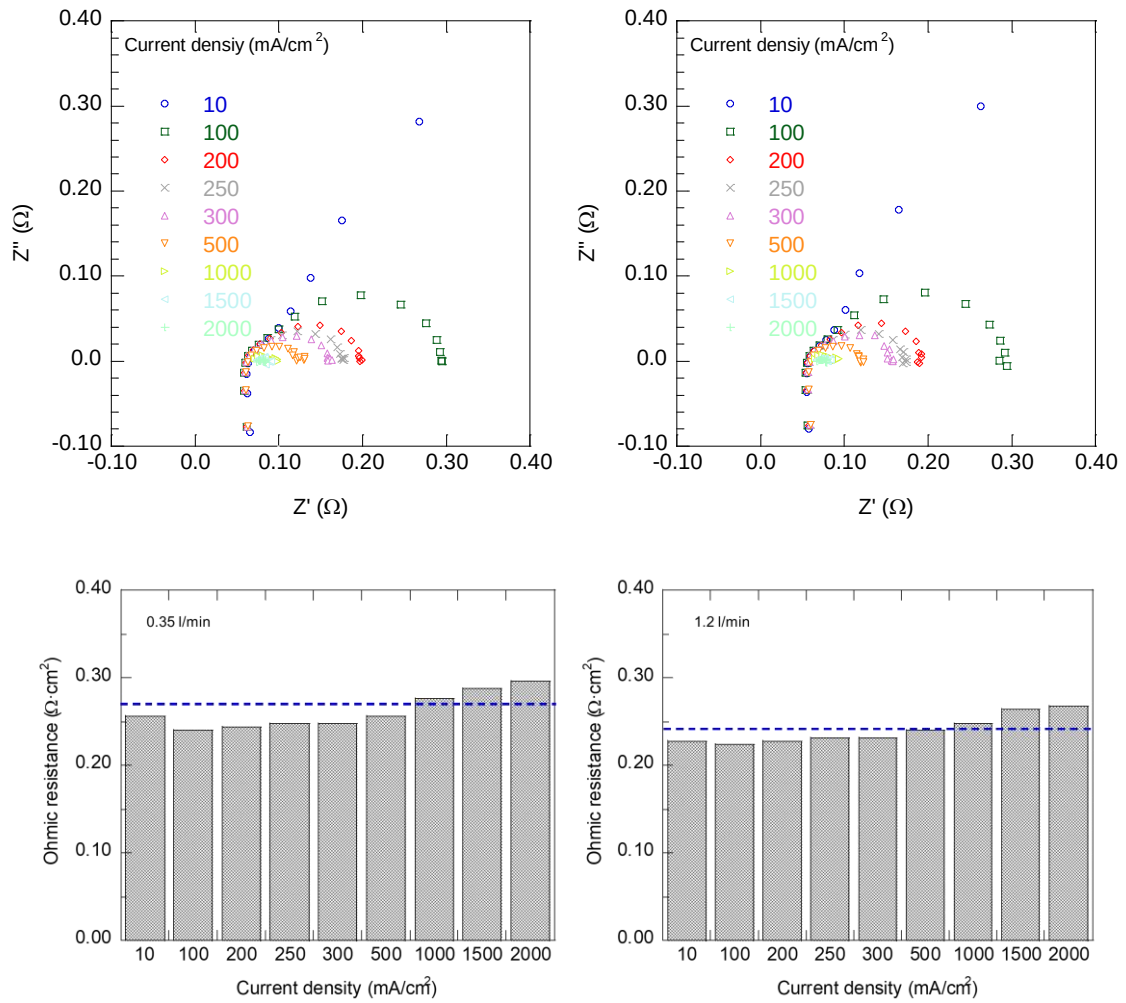


Fig. 52. TOP: Cole-Cole plot for an electrochemical cell containing pure Ni bi-layer electrodes at 70°C, 30 wt% KOH, and an electrolyte flow rate of 0.35 L·min⁻¹ (left) and b) 1.2 L·min⁻¹ (right); BOTTOM: EIS-measured Ohmic resistance derived from the high frequency region of the Cole-Cole plot; the dashed horizontal lines represent the value obtained from curve fitting of the polarization curves using Eq. (23).

presented in Fig. 50.b, and in the validity of the associated conclusions related to enhanced bubble removal. They also allow to exclude any significant contribution of current inhomogeneities, which was estimated in ref. [70] as $0.02 \Omega \cdot \text{cm}^2$ in the case of a perforated 2-D plate electrode, much smaller than our reported $R_{\text{tot}} - R_{\text{Zirfon}}$ values. Moreover, in the case of 3-D electrodes, ref. [240] convincingly showed that the frontal area of mesh electrodes, i.e. the area facing the diaphragm, was not electrically active in a standard zero-gap cell using a Zirfon separator. This was attributed to the fact that gas bubbles may enter the separator and block the electrode surface in the region between the electrode and the separator, hence creating a screening effect which increases the ohmic resistance. The fact that our $R_{\text{tot}} - R_{\text{Zirfon}}$ values are significantly lower than the literature is therefore indeed an indication of a much better bubble removal efficiency in our flow-engineered bilayer zero-gap cell, not only in the interior of the 3-D electrode itself but also in the region between the 3-D electrode and the separator. This enhanced removal of bubbles will in turn also lead to a more homogeneous current distribution and a decrease in the effective tortuosity.

7.2 Laterally-graded bi-layer cell configuration

Secondly, the integration of our 3-D electrodes into a zero-gap cell configuration was then optimized for enhanced bubble evacuation with the help of both single-phase and 2-phase CFD simulations. Particular attention was given to the understanding of the dynamics of electrolyte flow through macro-porous 3-D electrodes. Traditionally, flow in such porous media has been simulated by averaged equations based on the Representative Elementary Volume theory [241]. Progress in

computational power has now made it possible to tackle the problem by explicitly describing the full topology of the porous electrode. The latter involves the use of X-ray micro-computed tomography to obtain high-resolution scanning data of the foam topology [242–244]. Based on these scanned data, a meshing workflow was then applied to obtain computationally ready meshes for our electrode foams, similarly as in refs. [245] and [246]. The detailed flow characteristics are then investigated, with a particular focus on the interface dynamics between a fine catalytic foam acting as a gas production layer and a coarse porous transport foam (PTF) acting as a bubble extraction layer.

In a first step, we have based our initial bi-layer configuration on the experimental results of bubble evacuation efficiency as a function of pore size already discussed in the previous chapter. As seen in Fig. 45.b, a drastic increase in available surface fraction, indicative of enhanced bubble removal, was observed from 1000 μm pore sizes onwards. Therefore, our initial bi-layer configuration consisted of a fine, high surface 450 μm foam as a gas production layer, combined with a coarse 3000 μm porous transport foam used as a bubble extraction layer. Fig. 53.a then shows for this initial configuration the resulting velocity streamlines at the maximum upstream electrolyte inlet velocity. Two different sets of streamlines are visualized: one starting from an x-y seed plane on the catalyst layer and one from an x-y seed plane on the PTF, with both seed planes situated at a height $z = 1\text{ mm}$ in order to be well within the porous flow region. A clear tendency is observed for the flow to pass through the interface from the catalyst layer to the PTF, while the flow starting within the PTF remains confined to it. In order to further quantify this phenomenon, we also calculated the average y-

velocity component through x-z planes, i.e. parallel to the diaphragm. This scalar quantity can be taken as indicative of mass transfer in the lateral y-direction, i.e. in the direction normal to the diaphragm. Fig. 53.b shows a clear velocity increase as we move towards the coarse

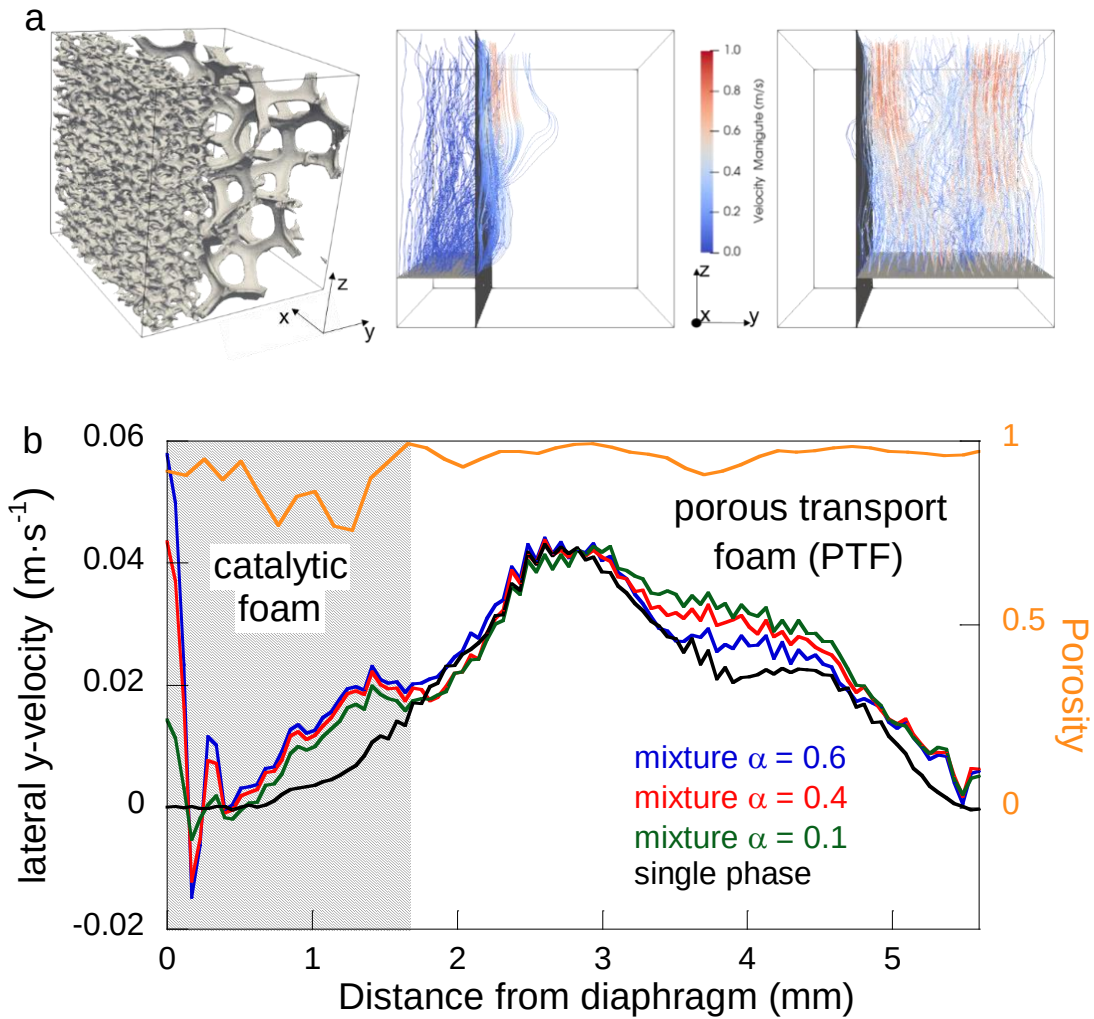


Fig. 53. a) Pore-resolved bi-layer geometry and simulation domain (left), velocity streamlines emanating from the catalyst (middle), and from the porous transport foam (right); b) Averaged lateral (in the direction normal to the diaphragm) velocity of x-z plans as a function of distance for single-phase and 2-phase simulations, the latter with different gas fractions α . The upstream electrolyte inlet velocity was set at 0.22 m/s. The fine 450 μm pore size catalytic foam is indicated by the dashed region.

bubble evacuation layer, with peaks that depend on the local foam morphology.

The driving mechanism behind this is the pressure discontinuity on the interface. Indeed, the finer foam acting as the gas production layer exhibits a much higher flow resistance as compared to the PTF because of its much higher form coefficient (3305 m^{-1} vs. 260 m^{-1} for the PTF, see Fig. 38). As a result, for the maximum inlet velocity of $0.22 \text{ m}\cdot\text{s}^{-1}$, the upstream z-velocity through the coarse PTF is $0.30 \text{ m}\cdot\text{s}^{-1}$ while for the fine gas production layer it is only $0.06 \text{ m}\cdot\text{s}^{-1}$. As a consequence, bubbles that are produced at the fine catalytic foam will be evacuated laterally into the porous transport foam, so that the high catalytically active surface area of the former is no longer hindered by bubble entrapment.

The above conclusions derived from single phase simulations are further confirmed (and even enhanced) when considering 2-phase flow, as shown in Fig. 53 as well. Our 2-phase modeling approach, which was based on simple mixture model with hydrodynamic dispersion, was to start with a stagnant gas mixture inlet with different gas fractions α at the interface of the catalytic foam and the diaphragm (i.e. distance 0 in Fig. 53) and then see the variations as a function of gas fraction in the lateral velocity profiles as a function of distance in the direction normal to the diaphragm. As shown in Fig. 53, the lateral velocity obtained from our simulations for the 2-phase mixtures is now significantly higher over the entire thickness of the fine catalytic foam (where bubble generation is mainly located) as compared to the single phase case. In other words, bubble evacuation from the catalytic foam into the coarse

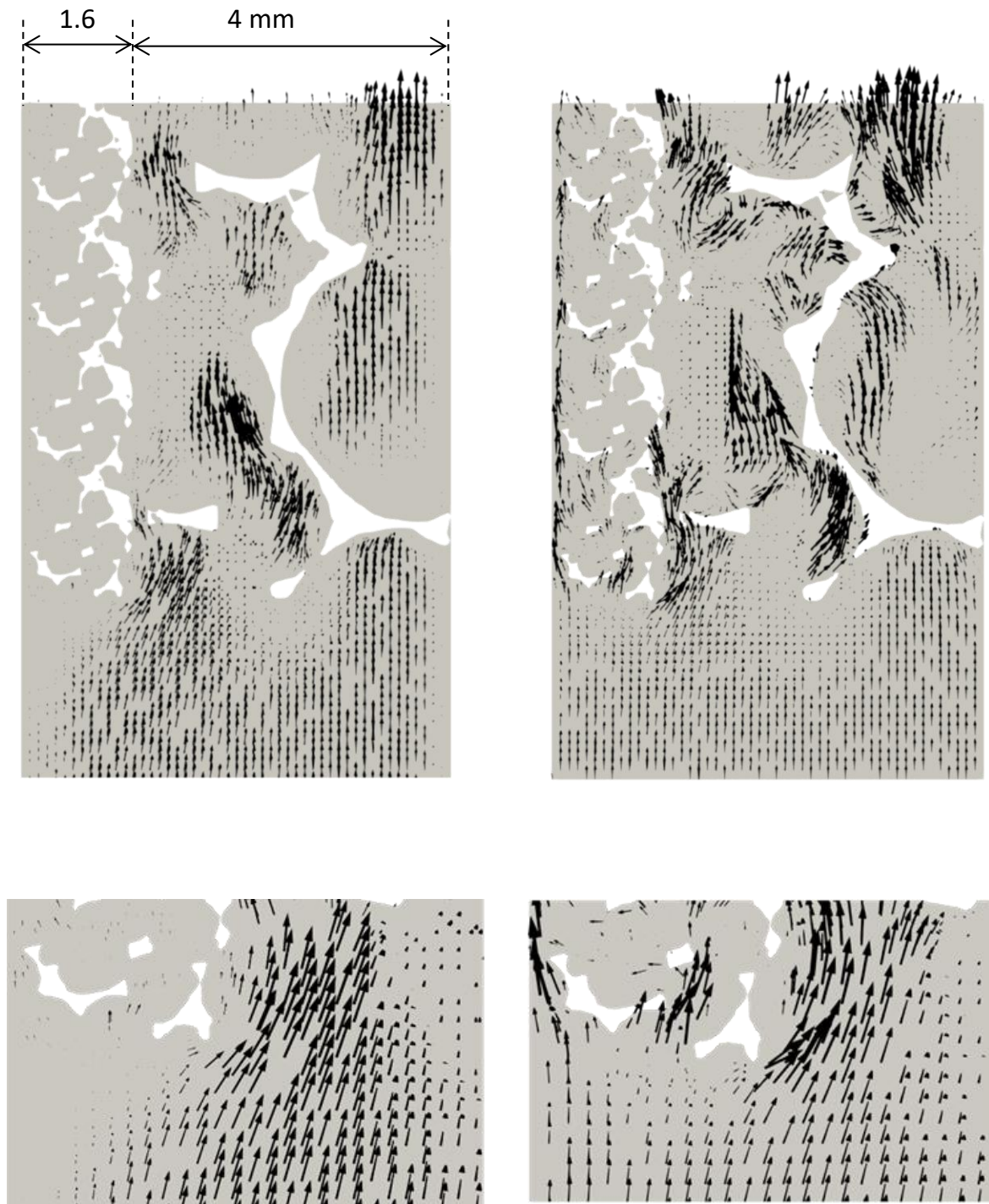


Fig. 54. Velocity vectors scaled by magnitude for the single-phase (left) and 2-phase (right) simulations, the latter with a gas fraction of 40%. The electrolyte upstream inlet velocity was set at 0.22 m/s, as in Fig. 53. The bottom figures are details at the entrance section of the bi-layer region. The fine catalytic foam is on the left, with a thickness of 1.6 mm. The top figures cover the entire cell width of 5.6 mm.

PTL foam can be expected to be even more enhanced as compared to the single phase simulations. We associate this enhanced lateral velocity of the 2-phase mixture with an increased fraction of upstreaming electrolyte being sucked into the catalytic foam, as a result of a less dense mixture situated near the diaphragm (i.e. at $x = 0$ in our simulations). The latter is shown more clearly in Fig. 54, which compares the velocity vectors for the single-phase and 2-phase simulations (the latter for $\alpha = 0.4$). By looking in detail at the entrance section of the bi-layer region (bottom figures), we can see that for the single phase the largest fraction of upstream electrolyte flow deviates into the coarse 3000 μm foam, while for the 2-phase simulations a significant fraction of electrolyte also enters the fine 450 μm catalytic foam. These figures also demonstrate the importance of performing 2-phase simulations using the explicit topological description of the 3-D foam bilayer configuration. Indeed, the negative velocities observed in Fig. 53 are directly associated with the local morphological details of the catalyst foam at the entrance section of the bi-layer region.

In a second step, our simulations then revealed that a coarser foam, such as the 3000 μm one, is a more suitable choice compared to finer available foams (see Fig. 55). It indeed exhibits a lower resistance to the upstream flow, thus creating a higher pressure difference between the catalytic and the porous transport foam. At the same time, it offers a rigid structure to electrically connect the electrode to the bipolar plate and to press the catalytic foam against the separator, maintaining the structural stability of our zero-gap configuration. In a final step, we then fixed the catalytic foam thickness at 1.6 mm and simulated the flow with different PTF thicknesses. Since a 3000 μm sized foam was

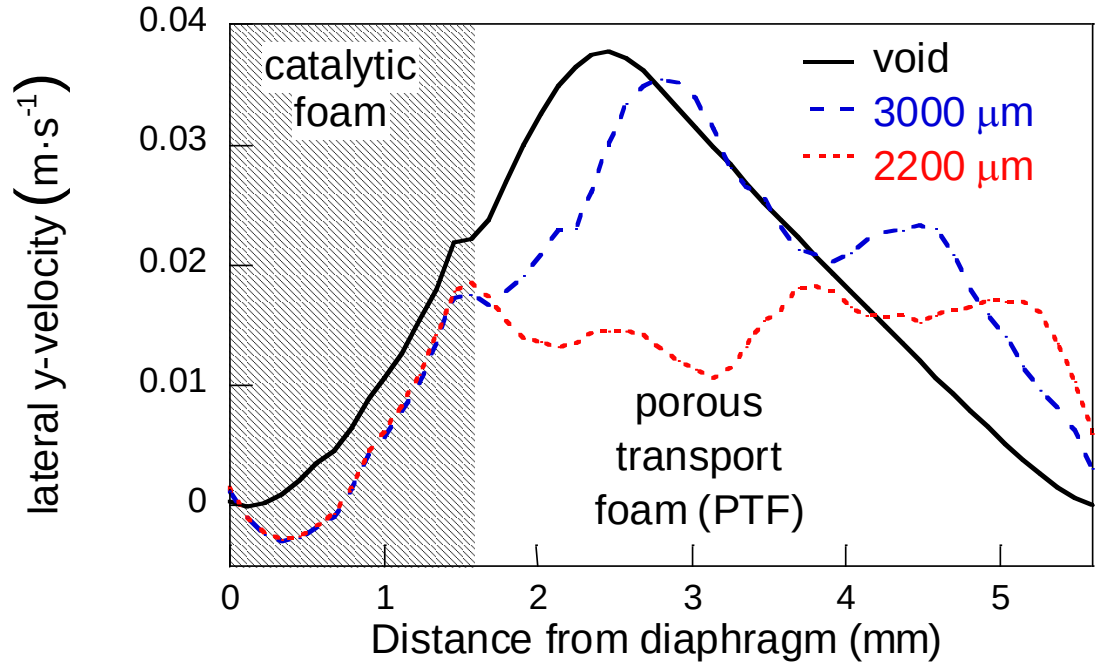


Fig. 55. Comparison of mass transfer in the lateral (y-) direction for different porous transport foam porosities.

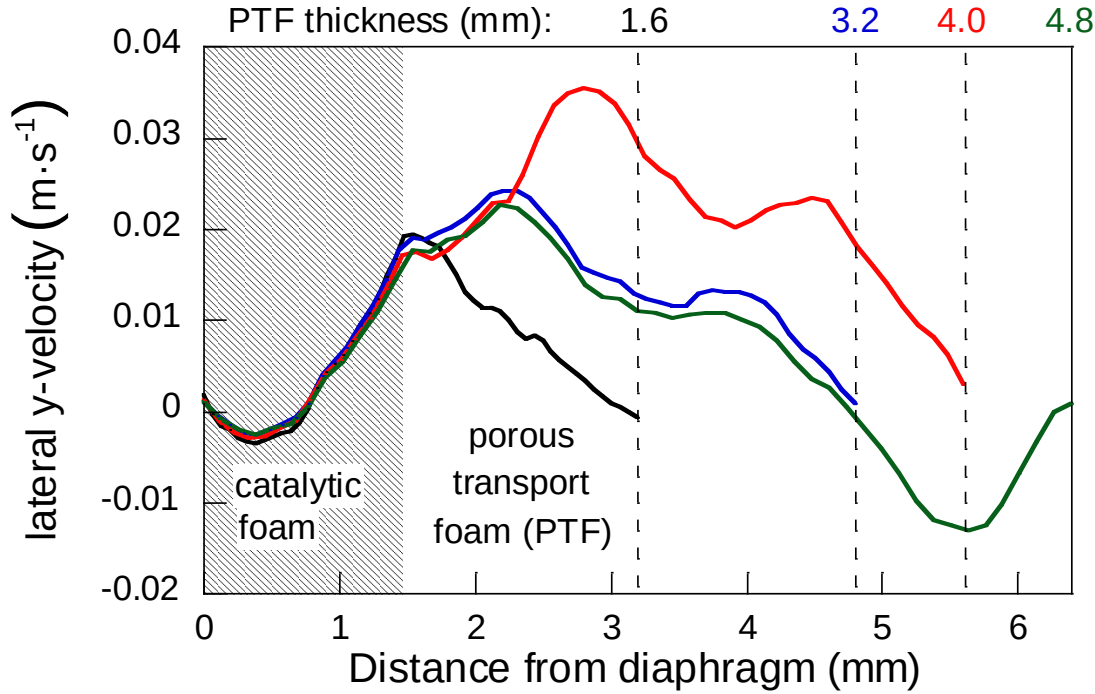


Fig. 56. Comparison of mass transfer in the lateral (y-) direction for different porous transport foam (PTF) thicknesses. The catalytic foam thickness was set at 1.6 mm and the PTF thickness was varied between 1.6 and 4.8 mm.

selected as the optimal PTF, a width of at least 4 mm is needed in order to ensure homogeneity and structural stability along the lateral y-direction with at least one pore per width. For thicknesses larger than 4 mm, the high upstream electrolyte flow may generate vortical flow instabilities and recirculation zones in the PTF, as revealed in Fig. 56 by the negative lateral velocity values in the PTF. As a result, the PTF thickness was kept at 4 mm.

7.3 Ni-Al-(Mo) coating and activation

A final performance enhancement was realized by applying a thermal spray coating of Ni-Al and Ni-Al-Mo to the fine foams in the bi-layer configuration, followed by alkaline activation to form Raney Ni. As was already shown in Fig. 50.a, the expected improvement was fully in line with existing literature data, and therefore does not represent any real novelty as such. Nonetheless, to the best of our knowledge, this is the first time that the application of such a spray coating and its subsequent activation has been successfully demonstrated on small pore sized foams [247]. More quantitative surface area data have been extracted as well from high-resolution X-ray tomography analysis and presented in Fig. 57.

Comparing the surface area estimated here from X-ray tomography data ($80 \pm 20 \text{ cm}^2 \cdot \text{cm}^{-3}$) with the capacitance estimated in Ch. 6 ($848 \text{ } \mu\text{F} \cdot \text{cm}^{-3}$), one has a specific capacitance for the $450 \text{ } \mu\text{m}$ foam of $11 \pm 3 \text{ } \mu\text{F} \cdot \text{cm}^{-2}$, statistically equal to the $9 \pm 1 \text{ } \mu\text{F} \cdot \text{cm}^{-2}$ obtained in Ch. 6 when doing a linear regression of the curve capacitance vs. specified surface area.

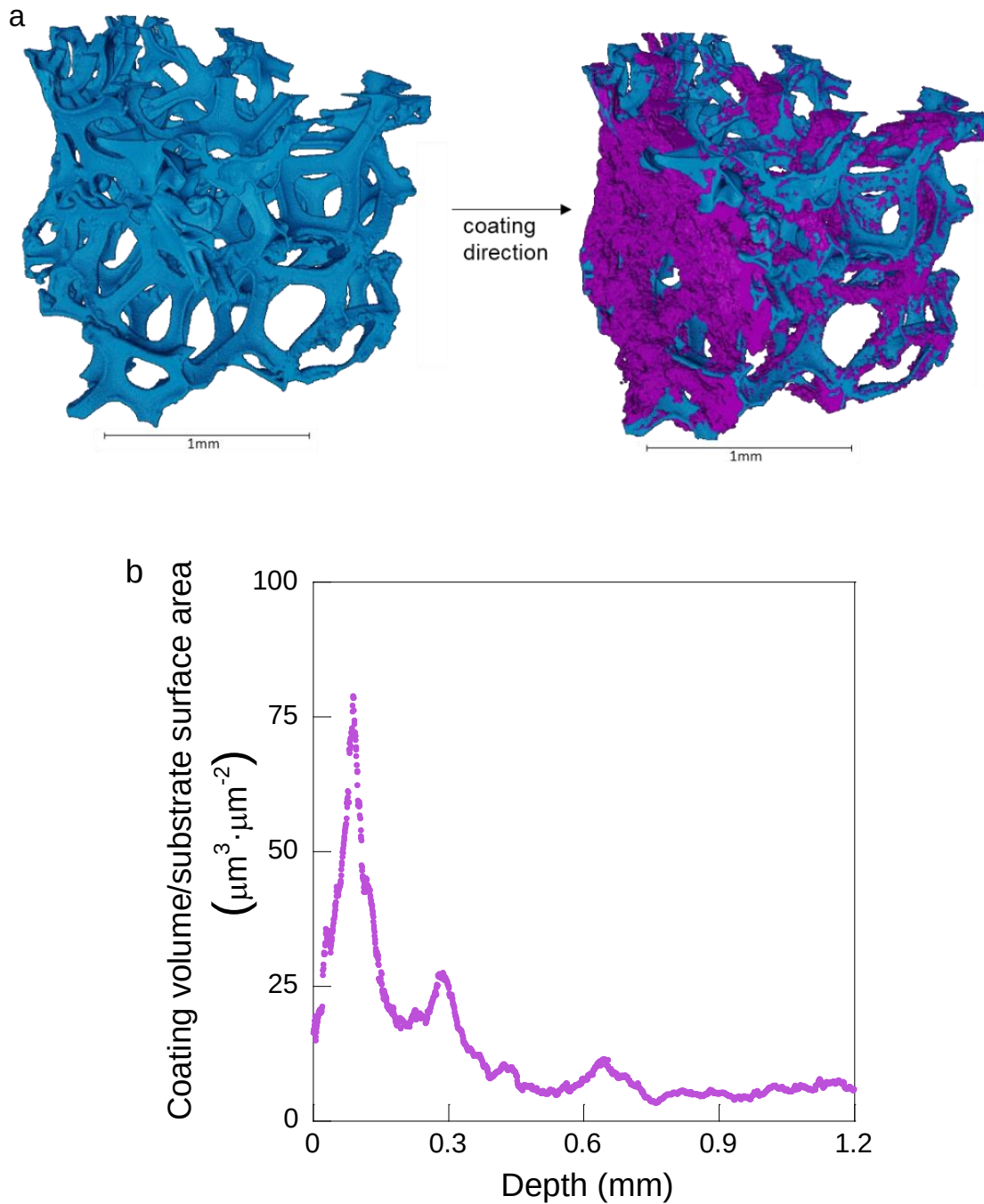


Fig. 57. a) X-ray micro-computed tomography of a coated and activated 450 μm foam showing pure Ni in blue and coating in purple; b) Coating volume per substrate surface area as a function of thickness for the coated 450 μm Ni foam, c) Specific surface area per slice of 0.65 μm thickness for the 450 μm pure Ni foam as a function of scanning depth.

The higher electrochemical activity of our Raney Ni bi-layer electrodes as compared to pure Ni translated into a significantly lower Tafel slope: $49 \pm 7 \text{ mV} \cdot \text{dec}^{-1}$ vs. $180 \pm 15 \text{ mV} \cdot \text{dec}^{-1}$ for Raney Ni and pure Ni, respectively. Interestingly, from Table 6, no significant difference in ohmic resistance was observed after coating: the value of $R_{\text{tot}} - R_{\text{Zirfon}}$, which can be taken as indicative of bubbles remaining inside the porous foam, was $152.3 \pm 0.7 \text{ m}\Omega \cdot \text{cm}^2$ and $130.4 \pm 0.5 \text{ m}\Omega \cdot \text{cm}^2$ for pure Ni foams and $145.9 \pm 0.3 \text{ m}\Omega \cdot \text{cm}^2$ and $128.4 \pm 0.2 \text{ m}\Omega \cdot \text{cm}^2$ for Raney Ni foams at $0.35 \text{ l} \cdot \text{min}^{-1}$ and $1.60 \text{ l} \cdot \text{min}^{-1}$, respectively. This indicates that the Raney Ni coating does not improve nor hinder the bubble evacuation capacity of our flow-engineered bi-layer configuration.

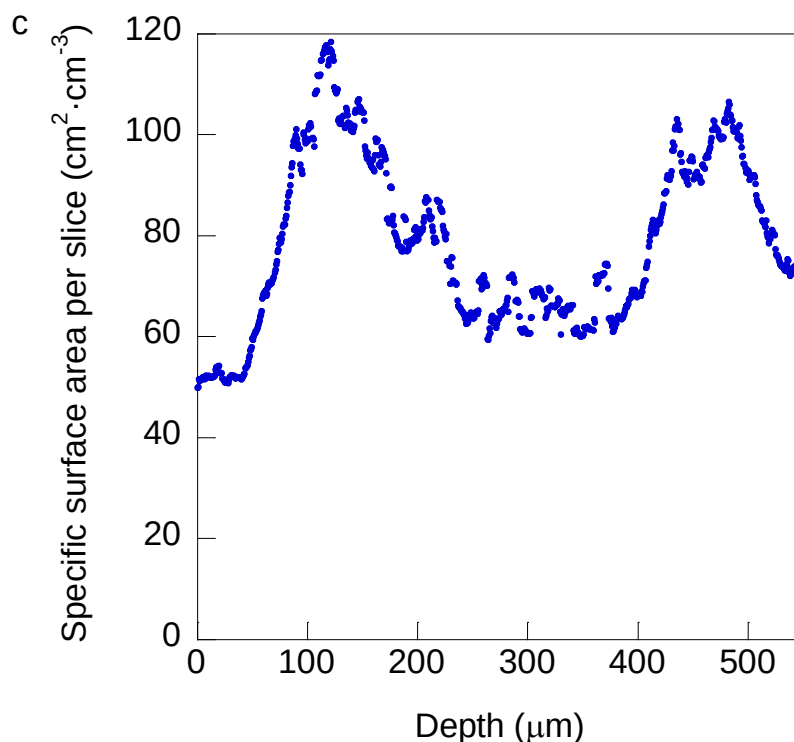


Fig. 57 (continued)

7.4 Perspectives and strategies for future electrolyzer developments

The performance improvement for alkaline water electrolysis demonstrated in this work, with cell voltages less than 2 V at $2 \text{ A}\cdot\text{cm}^{-2}$, has a number of important positive consequences for future electrolyzer developments. First of all, it allows for a significant process intensification, meaning less alkaline cell stacks are needed for a given hydrogen output. With a significantly increased power density of $2 \text{ V}\cdot 2 \text{ A}\cdot\text{cm}^{-2} = 4 \text{ W}\cdot\text{cm}^{-2}$, a 1 MW electrolyzer would only require 25 m^2 of electrode surface, which is 5 to 10 times less than current alkaline water electrolyzers producing only $0.2\text{-}0.4 \text{ A}\cdot\text{cm}^{-2}$ at 2 V. With today's alkaline electrodes being circular with a diameter on the order of 1 m, they typically require 160 to 320 cells for a 1 MW stack. Given that the significant electrode's surface area reduction allowed by our flow-engineered 3-D electrodes also allows for an easier pressurization and sealing, and hence the use of square electrodes (as is the case for PEM), a 1 MW alkaline stack would now only require 25 cells consisting of $1\cdot 1 \text{ cm}^2$ squared electrodes.

From an economical point of view, the contribution of our Ni-based flow-engineered electrodes to the estimated cost per kW of hydrogen produced using our Ni-based electrodes is the lowest among any other electrolyzer technology. This is demonstrated in Fig. 58, where polarization curves for different water electrolysis technologies expressing cell voltage as a function of current density (in $\text{A}\cdot\text{m}^{-2}$) have been re-considered by dividing the latter by the electrode cost (in $\text{€}\cdot\text{m}^{-2}$). This then allows to express the cell voltage as a function of current per € invested. On such plots, PEM electrolyzers clearly come out to be

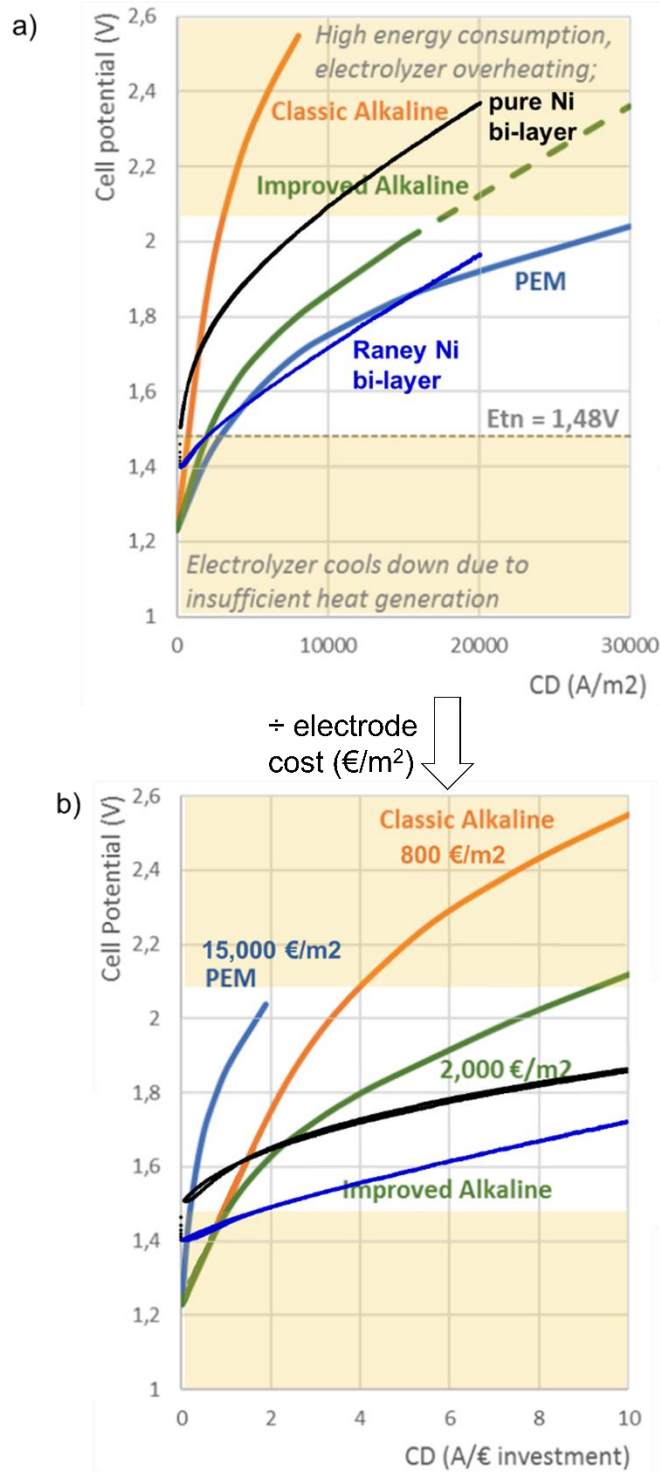


Fig. 58. a) Polarization curves for different water electrolysis technologies including the ones reported in this work; b) Cell-voltage as a function of current density in amperes per euro. Data for PEM, classic and improved alkaline have been reproduced from DeNora [248]. The cost of our own bi-layer foams was estimated based on Alantum projections ($90 \text{ €} \cdot \text{m}^{-2}$ for each layer) and the cost of plasma spray coating was set at $314 \text{ €} \cdot \text{m}^{-2}$ as specified in ref. [249].

the worst as a result of the use of expensive and scarce catalyst like Pt and Ir, resulting in an electrode cost up to $15,000 \text{ €}\cdot\text{m}^{-2}$. Interestingly, both our pure Ni and Raney Ni 3-D bi-layers, with electrode costs estimated at about 400 and $1000 \text{ €}\cdot\text{m}^{-2}$, respectively, economically outperform any other electrolyzer technology. Their low electrode cost is not only related to the use of Ni as electrode material, but also to the high porosity ($>90\%$) and associated decreased materials needs when implemented as macro-porous 3-D foams.

Furthermore, the substitution of the Zirfon diaphragm by recently developed alkaline-based membranes could improve even more the electrochemical performance, as shown in Fig. 59. The resulting total ohmic resistance was reduced by 40% going from $259.9 \pm 0.3 \text{ m}\Omega\cdot\text{cm}^2$ to $153.2 \pm 0.4 \text{ m}\Omega\cdot\text{cm}^2$. This can be explained by the reduction in the separator thickness – from $500 \text{ }\mu\text{m}$ to $40 \text{ }\mu\text{m}$ – and by the fact that the membrane used is an ion-solvating one, more performing than the anion-exchange types.

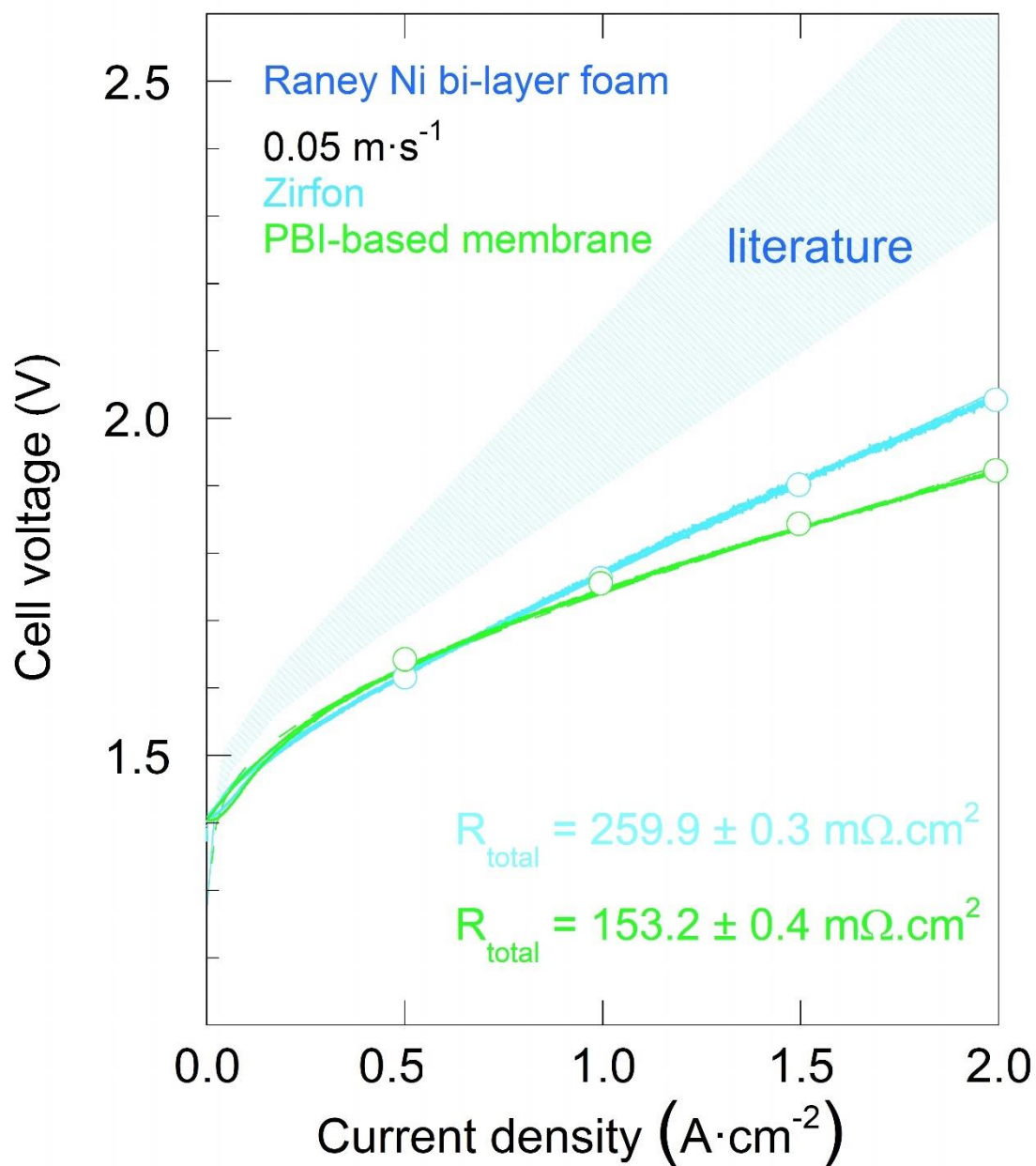


Fig. 59. Polarization curves for Raney-Ni bi-layer foams with different separators. Tafel slopes are within the range for Raney-Ni: $54.5 \pm 0.3 \text{ mV}\cdot\text{dec}^{-1}$ and $119.1 \pm 0.5 \text{ mV}\cdot\text{dec}^{-1}$ for the experiment using Zirfon and Dapozol, respectively.

7.5 Conclusion

In this chapter, it was shown that efforts in optimizing the electrode's geometrical structure in all of its 3 dimensions towards enhanced gas evacuation has the potential of a much more pronounced performance improvement than when merely optimizing the electrode's electrocatalytic composition. In particular, by a combined experimental and CFD modeling approach, we demonstrated that integrating flow-engineered 3-D Ni-based electrodes into a laterally-graded bi-layer cell configuration allows to significantly boost the electrochemical performance of alkaline water electrolysis ($2 \text{ A}\cdot\text{cm}^{-2}$ at $< 2 \text{ V}$ cell

voltage). Under high upstream electrolyte flow conditions, such a graded structure induces a high lateral velocity component in the direction normal to the diaphragm. As a result, gas bubbles, once formed on the electrode's surface, are evacuated much more efficiently, so that the electrode surface can maintain its high electrochemical activity even at high current densities. Such a PEM-like performance improvement allows for a significant process intensification: a 1 MW stack would now only require 25 m^2 of electrode surface, which is 5 to 10 times less than current alkaline water electrolyzers. Moreover, the contribution of our Ni-based flow-engineered electrodes to the estimated cost per kW of hydrogen produced using our flow-engineered Ni-based electrodes is the lowest among any other electrolyser technology.

Chapter 8: Performance of 3-D printed electrodes

As demonstrated in the previous chapter, a zero-gap cell with porous electrodes is a promising configuration for alkaline water electrolysis. However, gas evacuation becomes a challenge in that case, as bubbles can get trapped within the electrode's 3-D structure. The previously studied electrode geometry, foam, has a stochastic form. Consequently, gas removal may not be optimal as bubbles follow a large path until they get out of the electrode. While the fastest path would be to travel upwards, the path of bubbles inside nickel foams will be deviated by the collision with the metallic electrode, presenting a higher residence time. Trying to achieve a better bubble evacuation, tailored 3-D electrodes were printed and tested and the results are discussed in the present chapter.

This work considers several 3-D printed electrode geometries with so-called triply periodic minimal surfaces (TPMS). The latter is a mathematically defined structure that repeats itself in three dimensions with zero mean curvature [250] and can therefore be expected to be particularly well-suited to enhance gas evacuation. The use of TPMS geometries was inspired by a study of membrane distillation for desalination, which has successfully shown that TPMS 3-D printed spacers can enhance heat and mass transfer and reduce the formation of dead zones [251]. Later, these spacers were tested for reverse osmosis and ultrafiltration, showing not only an enhancement in the mass transfer but also a reduction in fouling when compared with commercial stochastically-structured spacers [252]. Following these observations, the present chapter aims at the analysis of different TPMS electrode

geometries for alkaline water electrolysis in view of enhanced gas evacuation.

Another advantage of TPMS 3-D printed geometries as compared to other state-of-the-art 3-D electrodes like foams or felts lies in the fact that their porosity, which determines the available surface area, and their pore size or flow channel dimensions, which determines the degree of bubble entrapment, can be varied independently. By a combined experimental and modelling approach, this chapter then identifies the structural parameters that direct the performance of such 3-D printed TPMS geometries towards enhanced gas evacuation. It is demonstrated that an optimal combination of these parameters allows under a forced electrolyte flow for a reduction in cell overvoltage of more than 40%. This indicates that efforts in optimizing the electrode's geometry can give a similar electrochemical performance enhancement as optimizing its electro-catalytic composition.

The main objective of this chapter is, first of all, to demonstrate the performance enhancement of using such 3-D printed electrodes during alkaline water electrolysis and, secondly, to link this enhancement to the underlying variations in structural geometry by assessing gas evacuation under forced electrolyte flow conditions.

8.1 Geometrical and Structural Characterization of 3-D printed TPMS electrodes

Results for the geometrical (ECSA) and structural (porosity) measurements have been included in Table 7 and are summarized in Fig. 60 as well. Porosity was lower than expected for all the cases, mainly due to the thickening of the strut, inherent from the laser beam

Table 7. Structural and geometrical characteristics of selected 3-D printed triply periodic minimal surface (TPMS) electrodes

TPMS type	L (mm)	t	Theoretical (measured) porosity (%)	Theoretical (measured) surface area (cm ²)	Measured strut porosity (%)
Gyroid	2	0.80	77 (67±1)	46.9 (173.5)	6 ± 2
	2	0	50 (43±1)	56.9 (225.4)	1.2 ± 0.2
	4	0	50 (46±1)	32.0 (160.6)	1.6 ± 0.1
	4	1.20	90 (86±1)	16.6 (95.9)	0.92 ± 0.01
Schwarz	2	0.18	61 (51±1)	55.8 (169.1)	0.90 ± 0.06
	4	0.18	61 (57±1)	29.5 (115.2)	0.8 ± 0.2
	4	0.26	66 (62±1)	27.6 (98.7)	0.73 ± 0.03
Fischer-Koch	2	0	50 (35±1)	95.4 (288.5)	1.4 ± 0.4
	4	0	50 (44±1)	50.8 (191.8)	0.74 ± 0.02
	8	0.70	86 (84±1)	18.1(85.9)	0.5 ± 0.5

melting process. Briefly, when the laser beam is scanning a strut, the surrounding powder heats up due to thermal diffusion, enlarging the melting pool and thickening the strut [253]. It is shown that, generally, the deviation from the expected value is higher for lower expected porosities. Concerning the surface area, the measured value is always higher than the theoretical one. This is an expected result since the theoretical value considers a perfectly flat surface, not accounting for the roughness. It is intrinsic to SLM that unmelted particles coming from the initial metallic powder adhere to the surface, increasing surface area (Fig. 37). This happens because there is partial melting of

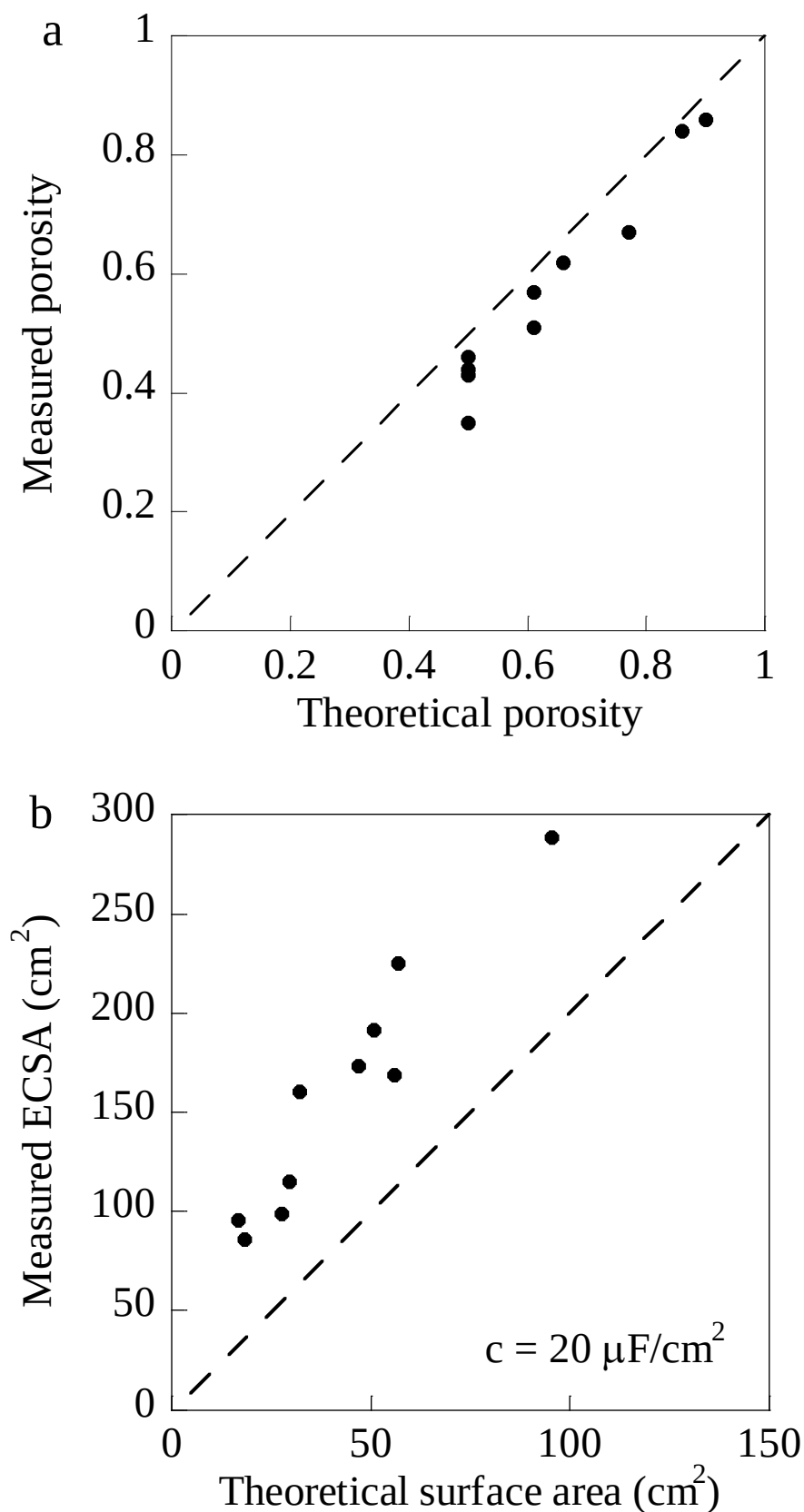


Fig. 60. a) Measured porosity as a function of expected porosity b) Electrochemical active surface area as a function of theoretical surface area.

boundary particles and also an important thermal diffusion between solidified metal underneath and the loose particles due to the big temperature difference [254]. Strategies to remove powder particles attached to the surface include mechanical milling, polishing [255], electrochemical polishing [256], and a combination of abrasion and electrochemical polishing [257]. The roughness factor (ratio between real surface and completely flat one) decreases with surface area, starting at 6 and going to 3, with 4 being the average value for our 3-D printed structures. Regarding strut porosity, i.e., the porosity inside the strut, values were in the range of 0.5-1.6%, which agrees with the literature. To illustrate, another study found porosities between 0.01-1.73% for SLM-printed Inconel 625 structures, depending on strut diameter (200-1000 μm) and angle (20-90°) [258]. The exception is the gyroid-shaped electrode with $L = 2\text{ mm}$ and $t = 0.8$, with a strut porosity of 6%. This difference may be related to printing parameters such as laser power (P), beam diameter (S), and scanning speed (V). A study shows that low volume energy density [$P \cdot S^{-1} \cdot V^{-1}$] is related to high porosities of up to 7% [259].

8.2 Electrochemical performance of 3-D printed TPMS electrodes

Polarization curves have been summarised in Fig. 61 for two series of structures with similar measured ECSA values, both at natural convection (left) and forced electrolytic flow (right). It is shown that for all electrodes, the presence of a forced flow caused an increase in electrochemical performance. This is mainly due to bubble removal and confirms previous results on foam-shaped electrodes. Furthermore, at natural convection, an increase in ECSA from around 100 cm^2 (Fig.

61.a) to around 175 cm² (Fig. 61.c) caused a significant increase in performance only for the gyroid-shaped electrode. For Schwarz and Fischer-Koch, the increase in surface area came along with an equal increase in bubble entrapment. In other words, there was no benefit in increasing the surface area because the excess surface was covered by gas bubbles. It is interesting to observe for these two electrodes at

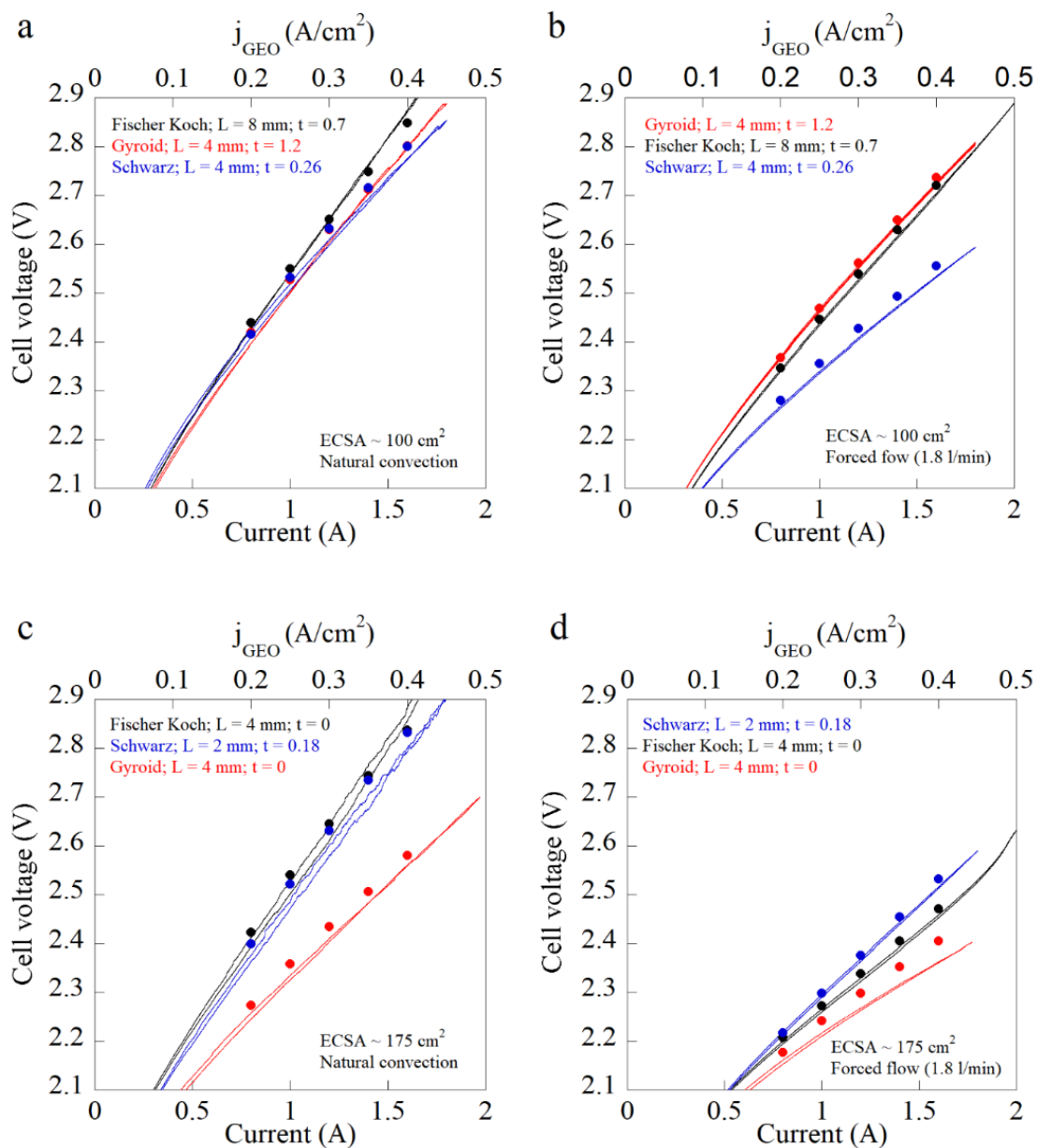


Fig. 61. Evolution of cell voltage vs. current for structures with an ECSA of 100 cm² at natural convection (a) and forced flow (b), and for structures with an ECSA of 175 cm² at natural convection (c) and at forced flow (d).

natural convection and ECSA near 175 cm^2 that the upward and downward current scans differ from one another, and both present instabilities/variations. This is a result of bubbles being created and leaving the surface, altering the active surface area by its removal. The fact that this was observed for the same electrodes that did not present a performance enhancement when increasing the surface area confirms

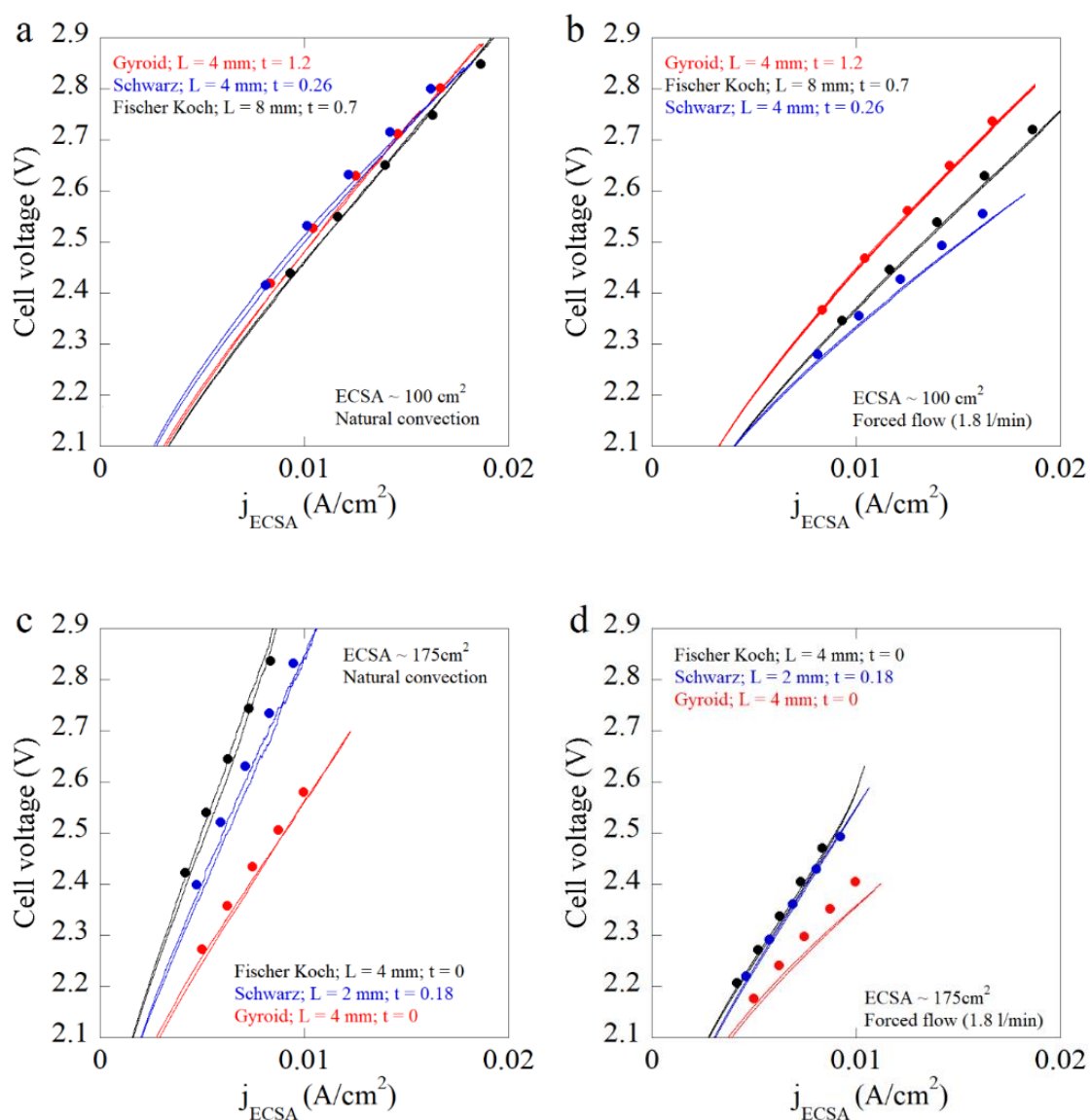


Fig. 62. Evolution of the cell voltage vs. electrochemical current density for structures with an ECSA of 100 cm^2 at natural convection (a) and forced flow (b), and for structures with an ECSA of 175 cm^2 at natural convection (c) and at forced flow (d).

that bubble entrapment is a dominant factor in this case. The situation is different, however, at forced flow. At this condition, an increase in ECSA caused an increase in performance for all the structures. This result shows the relevance of forcing the electrolyte to circulate and remove gas from inside 3-D electrodes, allowing the use of a higher percentage of the metallic surface.

Besides the global electrochemical behavior (cell voltage vs. total current), it is important to have a closer look at the effect of bubble entrapment. Since water electrolysis is a heterogeneous reaction and surface matters, the polarization curves were therefore normalized by the surface area, as shown in Fig. 62. As discussed in Ch. 6, without the presence of bubbles, all the curves should superpose, as the electrode material is the same. The onset of all polarization curves is indeed the same (near 1.7 V), showing that the 3-D printed electrodes have the same intrinsic electrocatalytic activity.

However, the normalized polarization curves do not superpose, as shown in Fig. 62, showing that there is a difference in bubble evacuation for these structures. A forced flow helps to get rid of bubbles, decreasing the bubble coverage and therefore increasing the available surface area. Nevertheless, this effect is not always the same for all structures. For the series at 100 cm², they have a similar starting point at natural convection and different curves when a flow is imposed, showing different flow sensitivities. When analyzing structures with a surface area of 175 cm², a lower current density is observed when compared to the ones obtained for structures with a surface area of 100 cm² as a consequence of a higher bubble entrapment. In summary, an increase in the surface area comes along with an increase in bubble

coverage. What allows to benefit from the higher surface area is the forced electrolyte flow, increasing the overall performance and making electrodes with higher surface areas better than the others.

In this respect, some general trends are shown in Fig. 63. At a constant cell voltage of 2.6 V, it is shown that the current density increases with the flow as a consequence of gas removal. An alternative way of seeing this effect is to look at the ohmic resistance ($\partial V/\partial A$). The advantage of this method is that it does not depend on the cell voltage or current

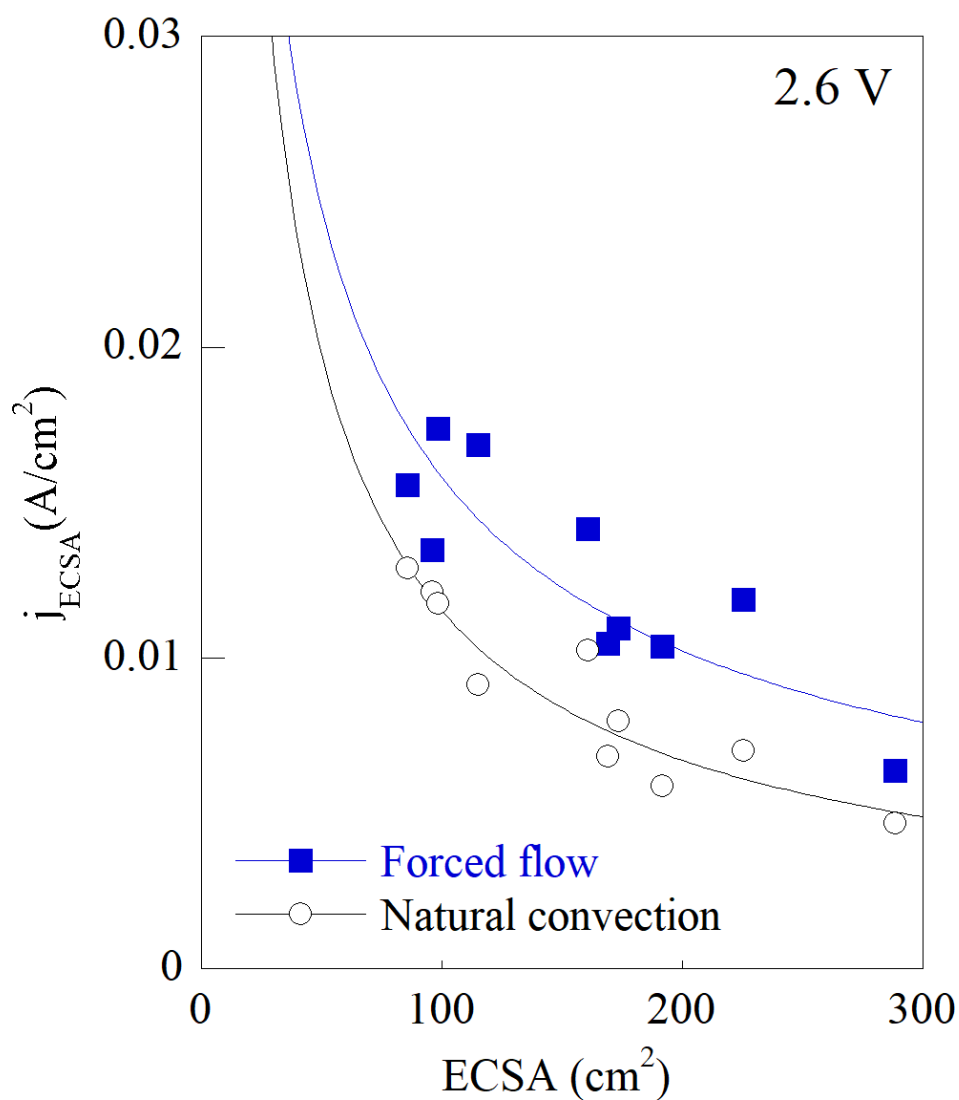


Fig. 63. Electrochemical current density as a function of surface area at a constant voltage of 2.6 V

chosen. Flow caused a reduction of at least 30% in ohmic resistance when going from natural convection to a vertical velocity of $0.36 \text{ m}\cdot\text{s}^{-1}$ for most of the electrode geometries. Furthermore, as the ECSA increases, there is a decrease in current density as a consequence of a higher bubble coverage. Finally, the curves for natural convection and forced flow seem to be diverging with ECSA, meaning that flow sensitivity is higher at higher surface areas.

8.3 Simulation of electrolyte flow inside 3-D printed TPMS electrodes

Looking at the results from the CFD simulations (Fig. 64), it is shown that the different electrode geometries create different flow patterns, and that these patterns can be related to the pressure drop along the flow direction (Fig. 65). Structures such as Gyroids and Fischer-Koch, with

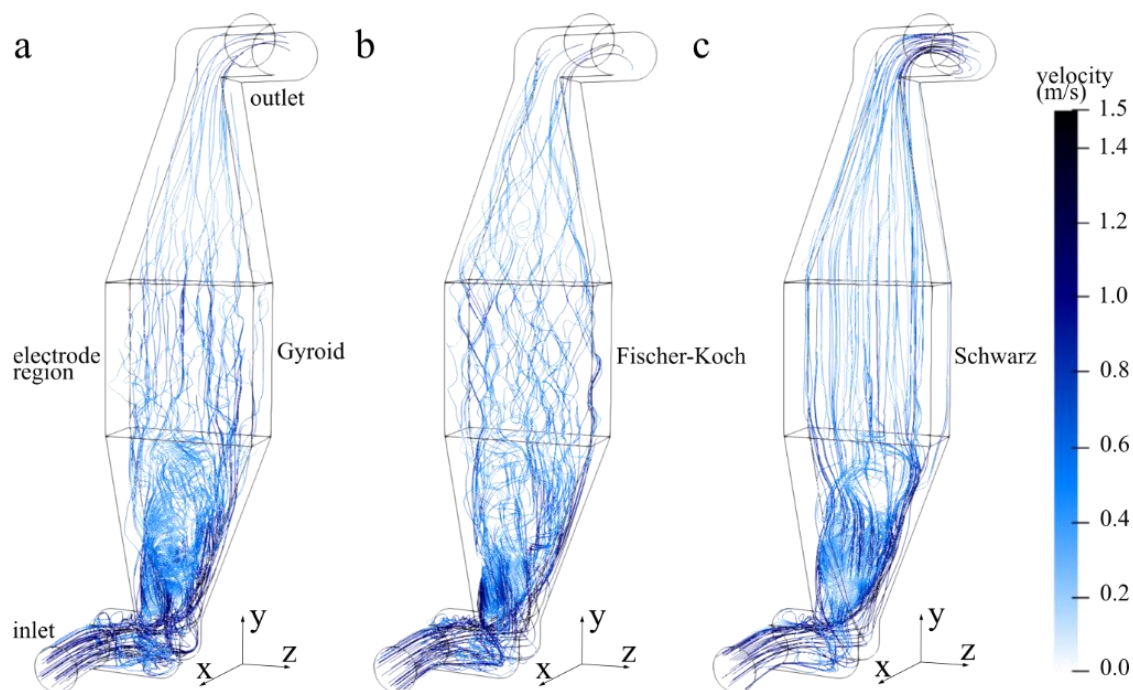


Fig. 64. Velocity streamlines for structures with the same theoretical surface area (32 cm^2) and porosity (61%): a) Schwarz $L = 4$ and $t = 0.18$; b) Gyroid $L = 3.94$ and $t = 0.34$; c) Fischer-Koch $L = 6.5$ and $t = 0.25$.

the same symmetry in all directions, cause flow mixing in the lateral direction and therefore an increase in pressure drop at constant vertical velocity. This mixing can be beneficial for processes such as desalination, where water needs to cross a separator and mixing in a flow-by cell can deviate the flow and force it against the separator, improving the mass transport. However, in the case of water electrolysis, the main objective is to get rid of bubbles as fast and as effectively as possible. As a consequence, lateral mixing may promote the coalescence of bubbles. For this case, structures able to channel the flow and reduce pressure drop will be privileged. Since the Schwarz

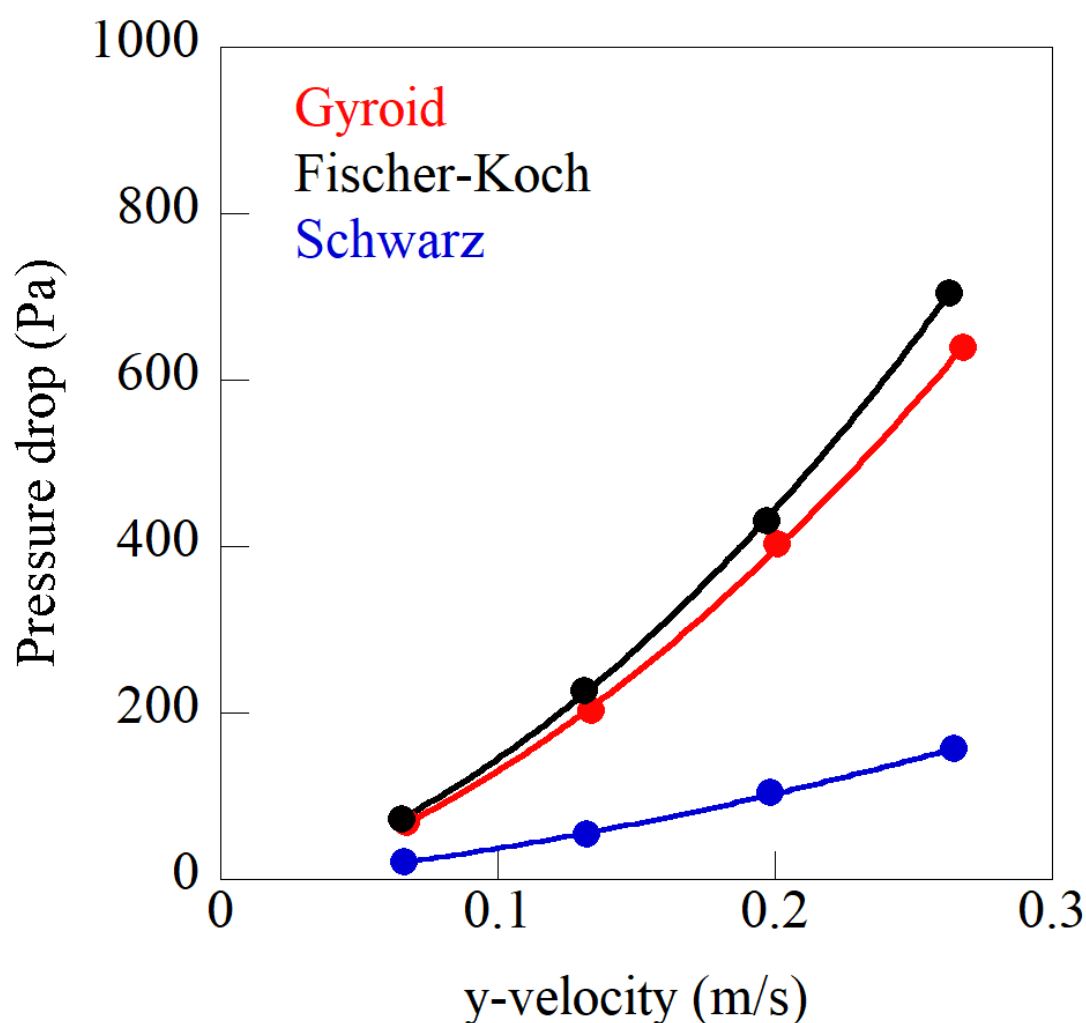


Fig. 65. Resulting pressure drop as a function of vertical velocity.

geometry presents a different symmetry for one axis, it can guide the flow in the vertical direction, reducing pressure drop. The flow rate imposed during the experiments was in the range of $0.4\text{-}1.8\text{ l}\cdot\text{min}^{-1}$, representing a Reynolds number between 50 and 1600, depending on the structure. For a flow inside a pipe, a Reynolds number close to 2,000 is normally considered the transition value between laminar and turbulent regimes [260]. Even though the transition Reynolds value is unknown for TPMS geometries, it is reasonable to estimate that at a Reynolds number below 1,600, the flow is at a laminar regime. At laminar flow, different regimes are defined by their governing equations: Darcy, weak inertia, and Forchheimer (strong inertia). The latter is used for $Re \gg 1$, which happens to be the case for the flow inside the analyzed structures [261]. Applying the Forchheimer equation (Eq.(29)) to the plot shown in Fig. 65, the obtained Darcian permeability values for Schwarz, Gyroid, and Fischer-Koch are $(8 \pm 1) \cdot 10^{-8}$, $(3 \pm 0.4) \cdot 10^{-8}$, and $(2.9 \pm 0.3) \cdot 10^{-8}\text{ m}^2$. For the form coefficient, the estimated values are 68 ± 6 , 320 ± 20 , and $380 \pm 10\text{ m}^{-1}$, respectively. In other words, for structures with the same surface area (32 cm^2) and porosity (61%), there are intrinsic differences due to the differences in geometries. Schwarz intrinsically has a Darcian permeability that is about 3 times higher than the two others and a form coefficient about 5 times lower. This is a consequence of the flow channeling. Between Gyroids and Fischer-Koch, they both cause flow mixing in the x-z plane, but even if permeabilities values are close, the form coefficient is about 20% higher for Fischer-Koch. This analysis covers intrinsic properties when comparing structures with same surface and porosity, but different geometries. Nevertheless, these

properties depend on the chosen periodicity (L) and t factor, consequently, they should be analysed carefully case by case.

8.4 Electrochemical performance of 3-D printed TPMS electrodes as a function of electrolyte flow

Flow sensitivity at the highest production rate studied here ($0.4 \text{ A}\cdot\text{cm}^{-2}$) is shown in Fig. 66 for the two electrode series with similar ECSA. For this comparison, natural convection is used as a baseline. In other words, the cell overvoltage at $0.4 \text{ A}\cdot\text{cm}^{-2}$ is normalized by the value found at natural convection. This gives 100% at natural convection and as the flow increases, there is a decrease in the relative overvoltage. The first important observation is that all the electrodes are flow sensitive and flow alone can cause a reduction of more than 40% in cell overvoltage. Furthermore, the sensitivity becomes more important as the ECSA increases, confirming the observation made previously when analyzing Fig. 63. At 100 cm^2 of surface, the relative overvoltage reduction ranges from 8-32%, while for 175 cm^2 , it is between 32-45%. Having a closer look at Fig. 66.a, it is shown that there is a difference in sensitivity for the different structures, with Schwarz being the most sensitive. It could be argued, however, that the observed difference does not arise from differences in geometry but differences in porosity. In this series, the higher the porosity, the less flow-sensitive the electrode was. Porosity can indeed play a role in flow sensitivity. It could be supposed that at a constant ECSA, structures with higher porosities have less bubble entrapment and, consequently, are less sensitive to flow. To deepen the understanding of the phenomena and confirm that there are intrinsic differences in flow sensitivity caused by the electrode

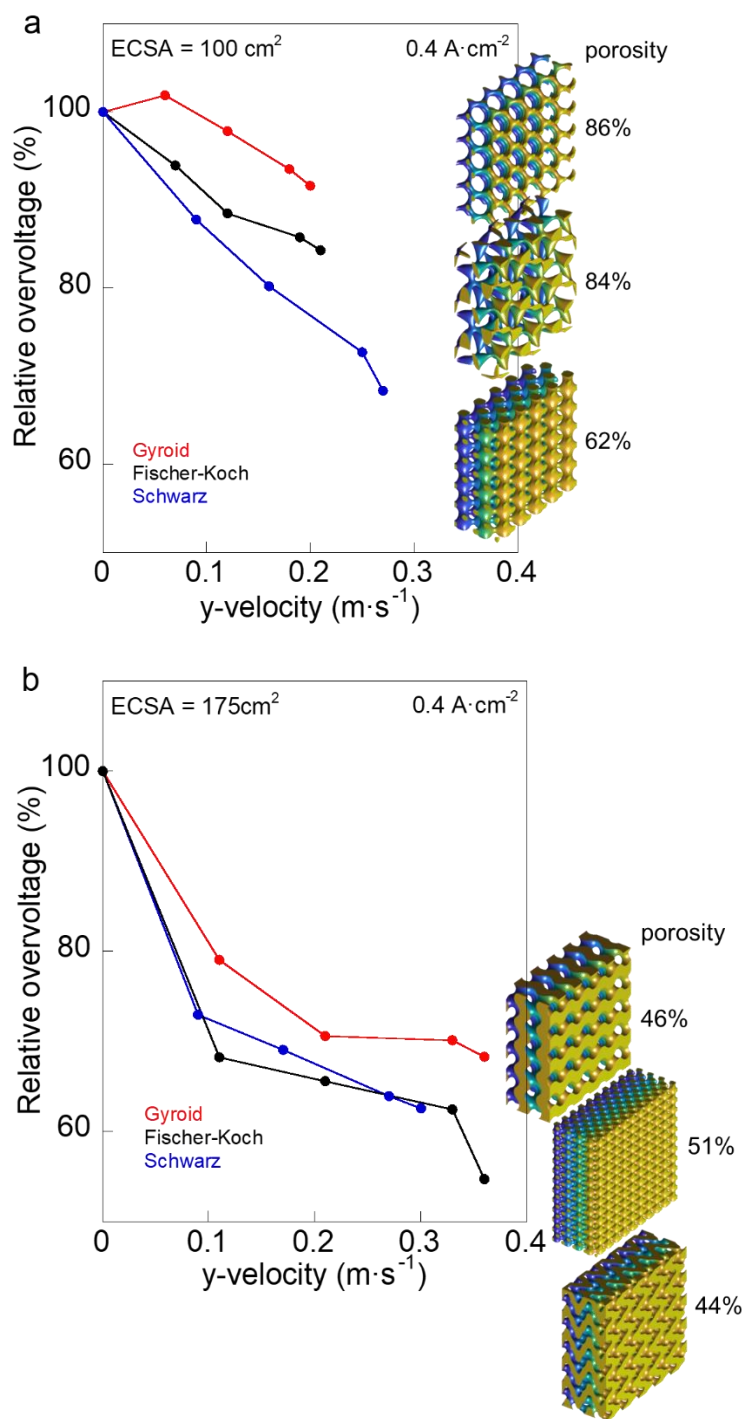


Fig. 66. Flow sensitivity at projected current density of 0.4 A·cm⁻² for: a) Structures with a measured ECSA around 100 cm² (Gyroid L = 4 mm, t = 1.2; Fischer-Koch L = 8 mm, t = 0.7; Schwarz L = 4 mm, t = 0.26); b) Structures with a measured ECSA around 175 cm² (Gyroid L = 4 mm, t = 0; Fischer-Koch L = 4 mm, t = 0; Schwarz L = 2 mm, t = 0.18). Overvoltage is the difference between the cell voltage and the sum of the equilibrium cell voltage – 1.23 V - and the ohmic contribution of the separator – 0.8 V.

geometry, structures with similar ECSA (160.6-191.8 cm²) and porosities (44-51%) should be compared. This comparison is shown in Fig. 66.b. For the Gyroid and Fischer-Koch, they have the same properties, yet, the flow sensitivity is higher for Fischer-Koch. The Schwarz-shaped electrode has a sensitivity that is comparable to the one for Fischer-Koch, even though its porosity is higher. Consequently, Schwarz can potentially be the most flow-sensitive if structures with the same porosity and ECSA are compared.

The 3-D printed electrodes present here have also the potential to be used as substrates for catalysts. As demonstrated in the previous chapter, plasma spray Raney Ni coating results in a significant performance improvement. Here we could image plasma-spraying 3-D printed electrodes or printing directly in Raney Ni (Ni/Al). Unlike metal foams, 3-D printed electrodes are rigid, which prevents damage during cell/stack assemblage [262]. Furthermore, by enhancing bubble removal, these electrodes can increase the use of catalytic sites and the stability of the electrodes [262].

8.5 Conclusion

In this chapter, 3-D printed Inconel electrodes were tested and simulated. It was first shown that it is feasible to print electrodes and use them in an alkaline electrolyser. This proof of concept opens new possibilities for electrode geometries, combining high surface area with effective gas removal. Furthermore, it was confirmed that forced electrolyte flow is an important tool to get rid of bubbles and liberate the electrode surface, increasing process performance by reducing the overvoltage by up to 45%. Moreover, it was shown that at the length

scale used here, there was a compromise between surface area and bubble coverage. It was also shown that intrinsically, for structures with the same surface area and porosity, geometries that channel the flow and avoid mixing in the transversal plane present lower pressure drop, higher permeabilities, and lower form coefficient. Finally, when looking at flow sensitivity, it was shown that structures present different sensitivities depending on the surface area, porosity, and geometry. The sensitivity was higher for electrodes with higher surface areas. Schwarz-shaped electrodes are potentially the best of the analyzed structures, as they have intrinsically high Darcian permeability and important flow sensitivity.

Chapter 9: Experimental validation of pulsed water electrolysis

The present chapter presents an investigation of the effect of applying voltage and current pulses during alkaline water electrolysis using 3-D Ni foam electrodes. It was already shown the process intensification that 3-D Ni electrodes can offer. This chapter aims to verify whether pulses offer a further process intensification.

The motivation for this work is a previous study conducted in our laboratory - [176] - which investigated the application of pulsed voltage in AWE using 3-D electrodes, specifically Ni foams. The primary aim of introducing pulses in the electrolysis process with 3-D electrodes is to enhance the removal of gas bubbles that would otherwise accumulate and become trapped within the porous structure of the electrodes. As previously shown, the accumulation of bubbles negatively impacts the electrode's active surface area and increases the electrolytic cell's overall resistance. In this previous investigation, a synergistic effect was observed, where the combination of 3-D electrodes, forced electrolyte flow, and pulsed voltage resulted in a twofold increase in current when on-times were on the order of a few milliseconds and optimal parameters were applied [176].

Building upon these previous findings, this chapter aims to delve deeper into the underlying mechanism of pulsed water electrolysis and to discriminate between the distinct impacts of pulse width and duty cycle when employing both voltage and current pulses in alkaline water electrolysis. Furthermore, this investigation expands upon our previous study by prolonging the experimental duration and collecting produced

gases to verify the effectiveness of the reported improvements. Additionally, the analysis includes the examination of current pulses with varying periods, ranging from 10 seconds down to 1 millisecond, highlighting their advantages over voltage pulses in the context of alkaline water electrolysis.

9.1 Voltage pulses with a duty cycle of 50%

At first, pulses were applied with a duty cycle of 50% and pulse widths (on-times) between 1 ms and 100 s. Fig. 67.a compares the current evolution during on-time for the first applied pulse. It can be seen that the highest current was obtained during the first milliseconds of the pulse application, after which it gradually decreased with time. Consequently, the sooner the pulse was stopped, i.e., the shorter the pulse width, the higher the average on-current. Pulses with higher widths were also a continuation of pulses with lower widths, confirming the experiment's reproducibility. Looking at the time evolution of the off-current in Fig. 67.b, a change in polarization was observed. This change indicates either a discharge of the electrical double layer or the reversal of the redox reaction. Contrary to the on-current, the temporal evolution of the off-current was not the same for the different pulse widths. It reached lower initial values for higher pulse widths and stabilized for pulse widths equal to or higher than 100 ms. Fig. 68 shows the resulting average current for these first pulses. It was calculated by integrating both the on- and off-currents over time and normalizing by the pulse period. It can be seen that the combination of a higher on-current with a higher off-current still resulted in an apparent better performance for the shortest pulses: for the first pulse, a pulse width of

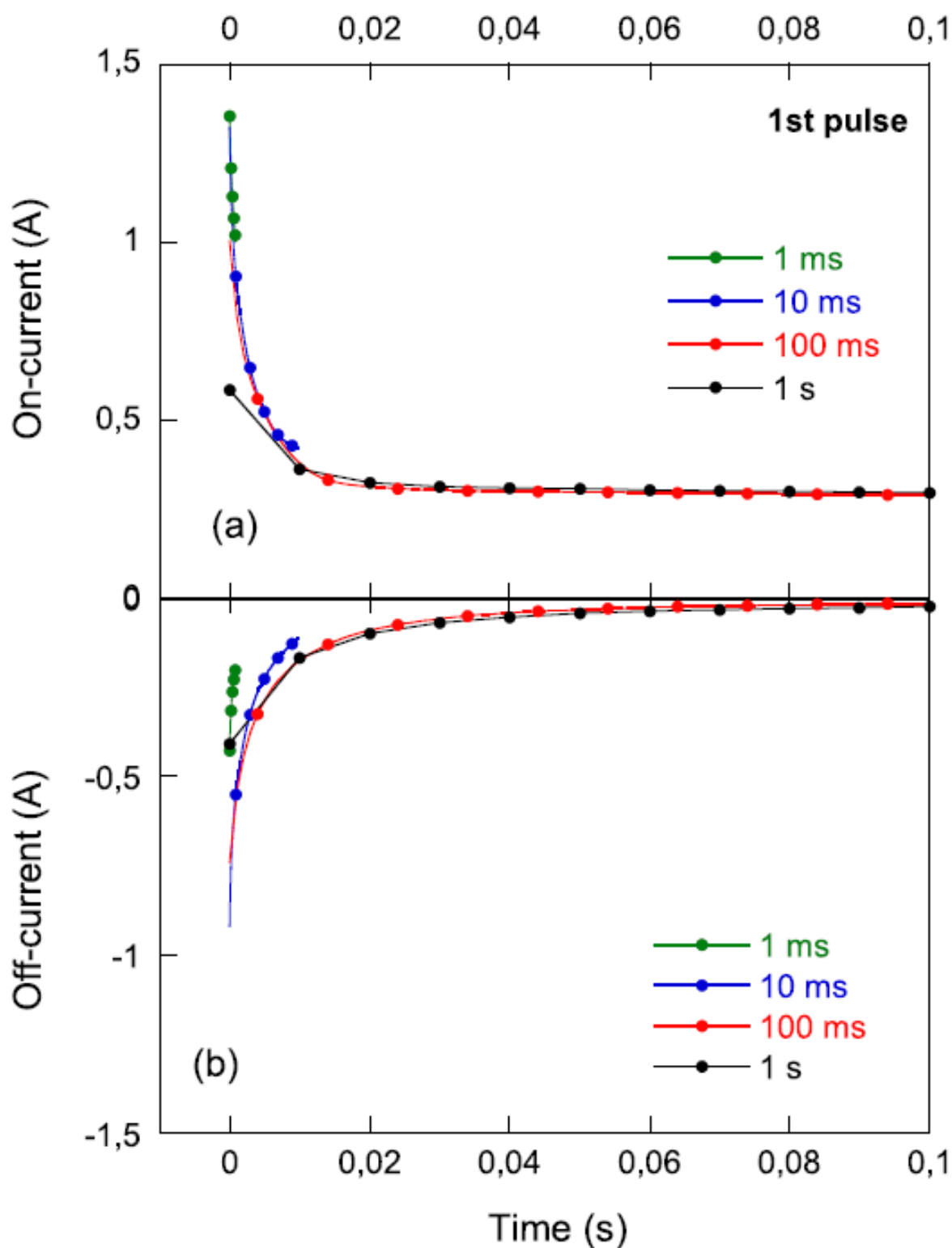


Fig. 67. Time evolution of the on-current at 2.0 V (a) and off-current at 1.2 V (b) during the first voltage pulse for different pulse widths. Duty cycle of 50%, natural convection. The time resolution was 1% of the pulse period, except for the pulse with a period of 1 ms, where the resolution was 10% of pulse period.

1 ms resulted in a more than 2-fold increase in average current as compared to a 100 s pulse, in agreement with our previous findings (ref. [176]).

However, this apparent better performance was not observed over the long term, as the shortest pulses showed a rapid decrease in current, as shown in Fig. 69, for a series of both 1 ms and 10 ms pulses. Both the on- and off-currents decreased over time, their difference remaining constant at about 1.4 A. This decrease continued until a stabilization occurred after about 10 s of the experiment. As a result, if the average current of a pulse was measured after 10 s, a decrease in pulse width caused a decrease in average current. This effect is illustrated in Fig. 70.a and suggests that capacitive processes become important for pulse widths lower than 1 s. In this respect, the ratio between the charge

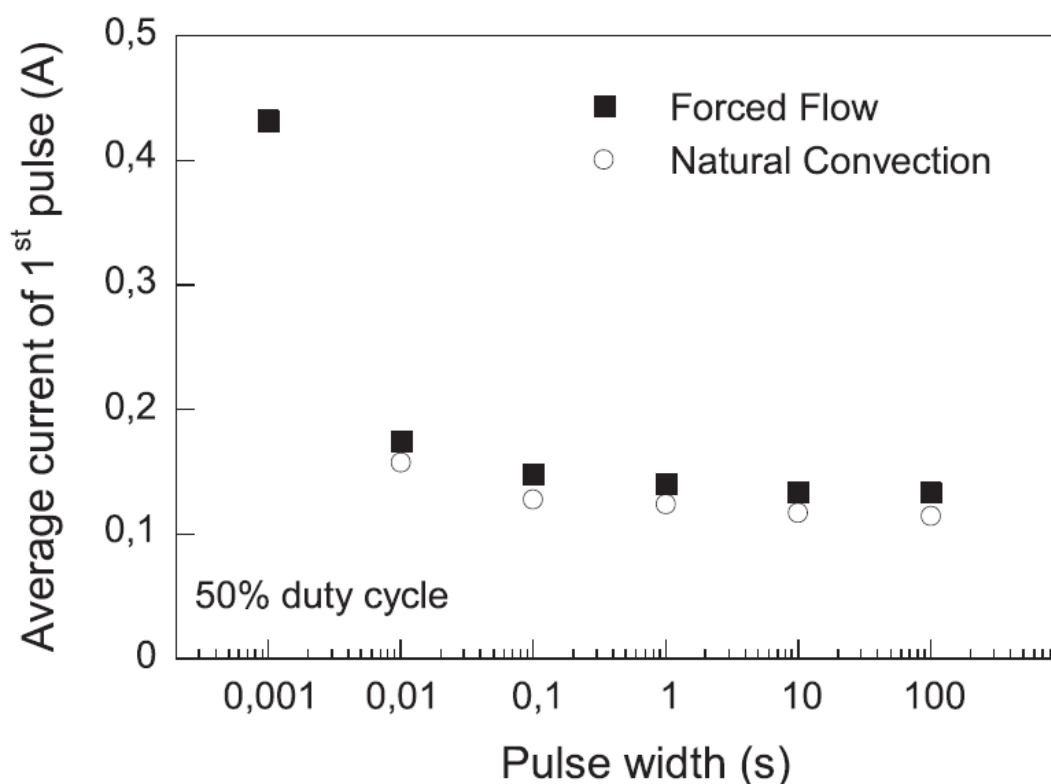


Fig. 68. Average current of the first voltage pulse as a function of pulse width. Duty cycle of 50%, both natural convection and forced flow.

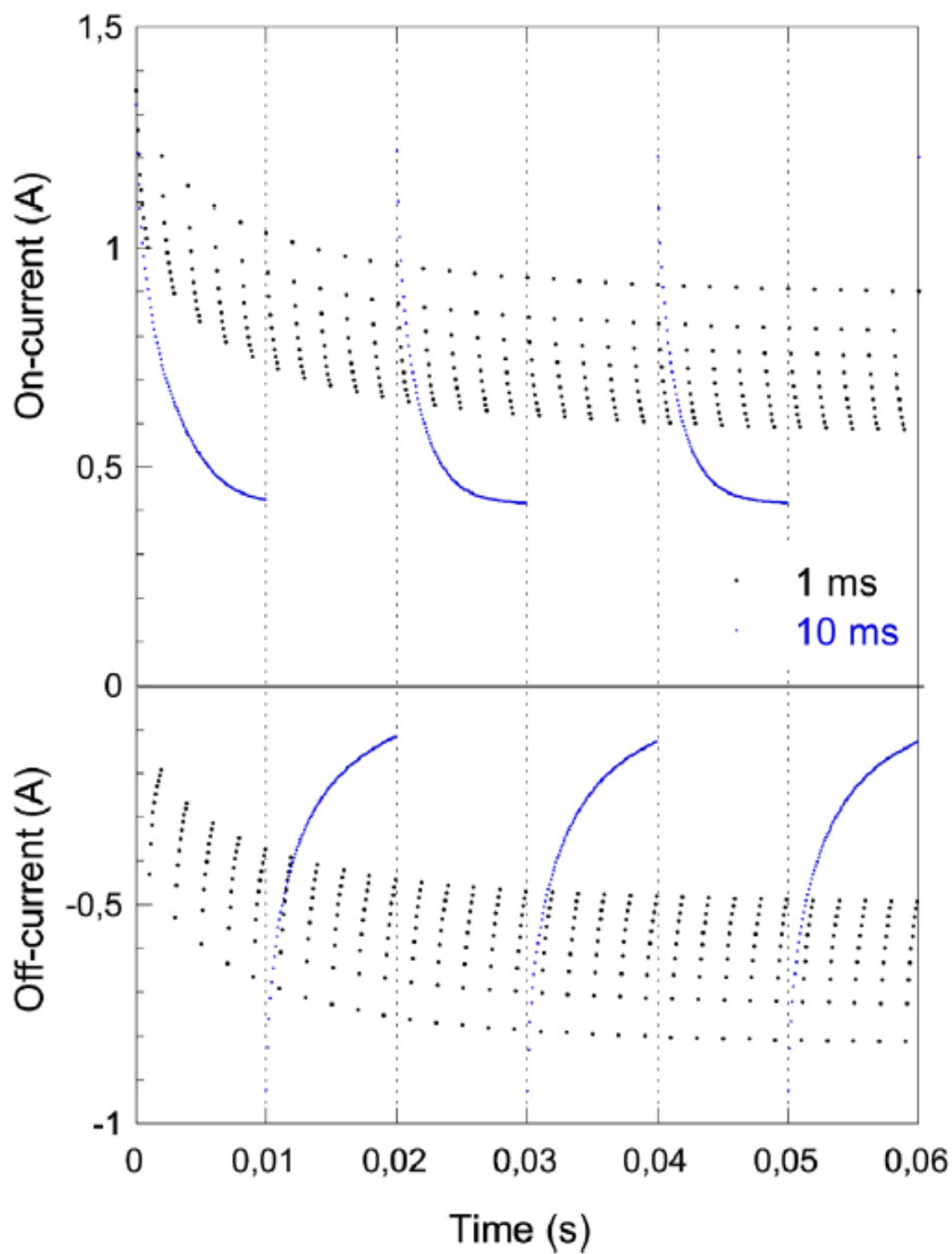


Fig. 69. Time evolution of the on- and off-current during the first 60 ms for a pulse width of 1 and 10 ms. Duty cycle of 50%, natural convection.

gained by the system during the pulse on-time and the total charge during an entire period gives an idea of the contribution of faradaic processes. From the results shown in Fig. 70.b, it can be seen that for pulses with a width of 1 ms, only 3% of the on-current was used to conduct faradaic processes. This ratio steeply increased with pulse width until 1 s, where the current was predominantly (> 90%) faradaic.

Moreover, no change was observed when comparing the average current in Fig. 70.a at forced flow and natural convection for a pulse width of 1 ms, while at 10 ms, we measured an inversion of the flow effect. This result confirms that diffusion and bubble evacuation were not dominant and that almost all the current was capacitive. In other words, the electrical double layer was continuously being charged and discharged, and almost no hydrogen generation occurred. Additionally, the application of Eq. (48) to the current decay curves shown in Fig. 69 allows to provide an estimate of the time constant ($R_s \cdot C_{dl}$) for EDL charging. An average value of 3.2 ms was calculated, confirming the predominance of capacitive processes for pulse widths from 1 to 10 ms.

As to the effect of forced electrolyte flow, it can be seen in Fig. 70.a that forced flow increases the average current by 12-14% in case faradaic processes are dominant. This improvement can be attributed to an increase in the bubble removal rate and a decrease in the thickness of the diffusion layer, as previously demonstrated. It also reinforces the idea of a predominance of capacitive processes for the shortest pulses, as there is neither diffusion layer nor bubble formation in pure capacitive processes.

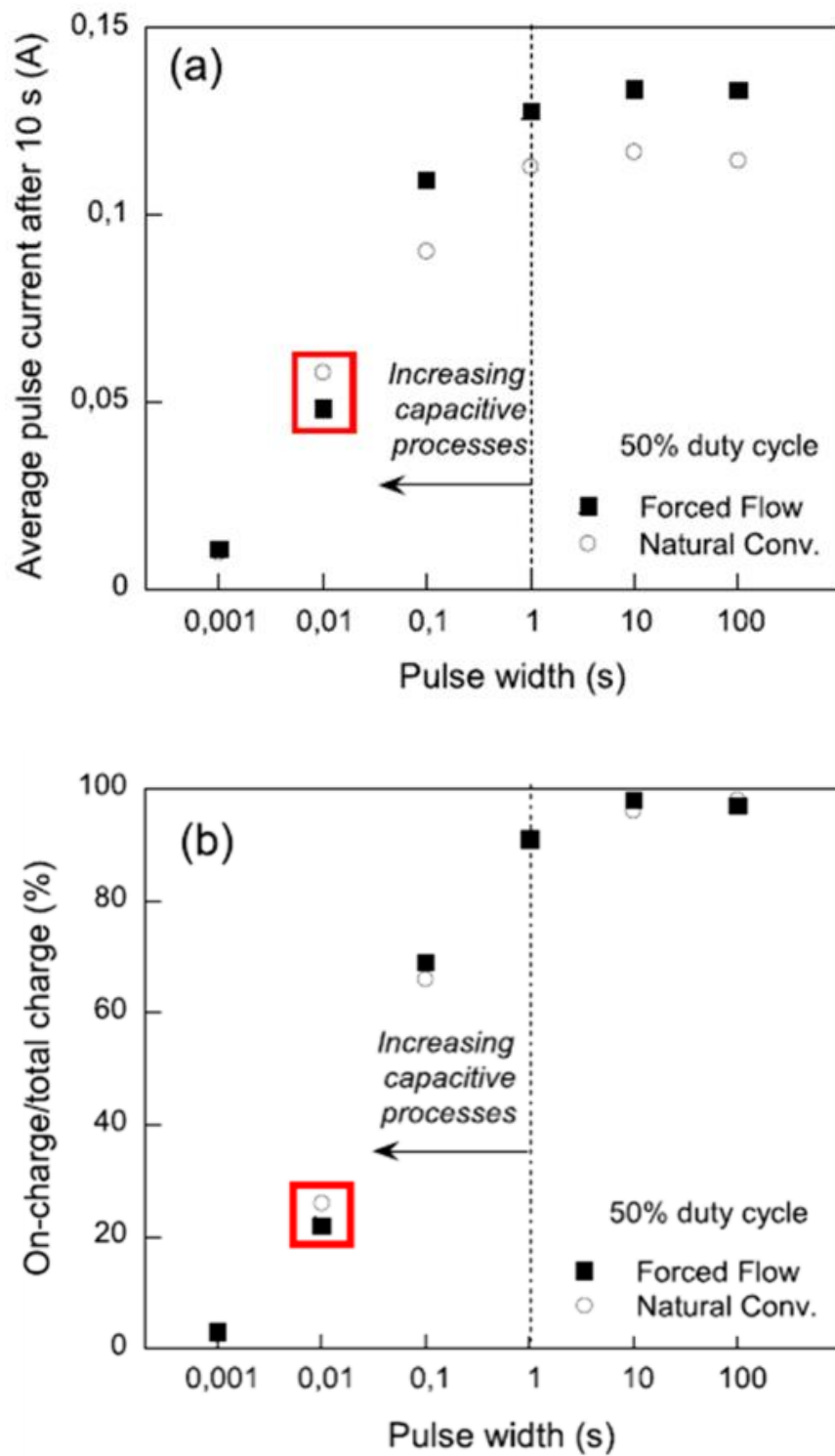


Fig. 70. (a) Average current after 10 s of experiment as a function of voltage pulse width. For a pulse width of 10 s and 100 s, the second applied pulse was used to calculate the average; (b) Pulse width dependence of the ratio between on-charge and total charge during one voltage pulse period. Duty cycle of 50%, both natural convection and forced flow.

Finally, our result confirms what was demonstrated previously in the literature by refs. [174,263] (shown in Ch. 3), notably an on-current enhancement and a decrease in average current upon the application of voltage pulses. The present analysis went further on the investigation by explicitly including off-current in the analysis and clearly demonstrating the need to do so since the apparently higher current at on-times can be due to capacitive effects. By doing so, it was possible to demonstrate that the result obtained by ref. [176] was wrongly attributed to a better hydrogen performance when in reality, it was mainly due to the EDL charging current.

9.2 Voltage pulses with a higher duty cycle

In a second stage, the effect of the duty cycle was studied. This investigation was done by applying pulses with a short off-time (1 and 10 ms, respectively) and a long total pulse period (from 1 ms to 100 s), resulting in a duty cycle between 50 and 99.9%. One of the purposes was to verify the observation made in ref. [183] that it is beneficial to interrupt the power supply occasionally. The experiment was run for 1000 s to allow for a simultaneous in-situ hydrogen collection as well. The results are shown in Fig. 71 for a fixed pulse off-time of (a) 1 ms and (b) 10 ms, respectively. Comparing both figures indicates that from a duty cycle of 99% onwards, i.e., an on-time which is at least 100 times higher than the off-time, the pulsed voltage signal approaches the DC production rate, but never overcomes it.

When looking at the effect of forced flow, the hydrogen production rate was improved by 4-7% for voltage pulses with a 10 ms off-time,

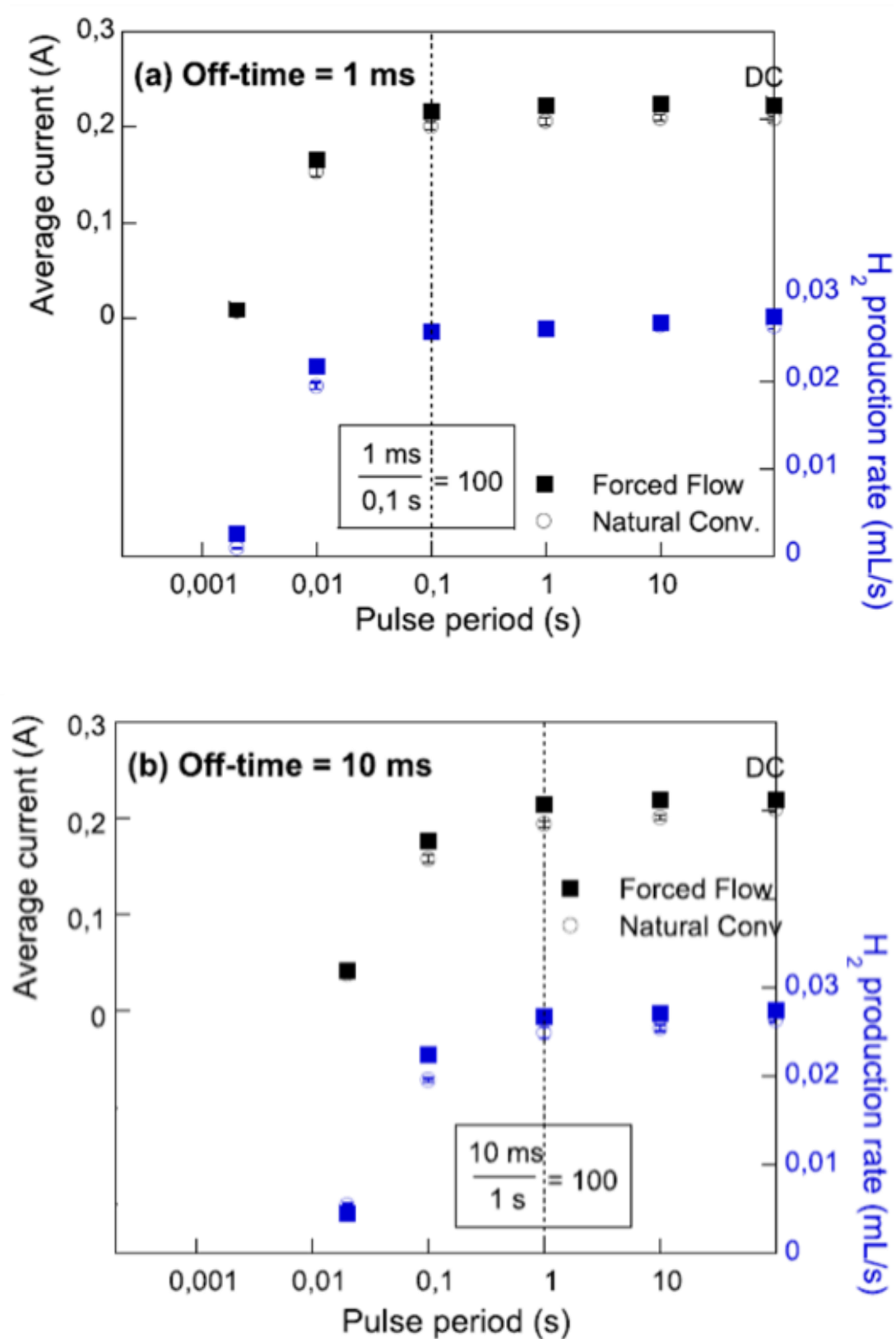


Fig. 71. Average current (left ordinate) and hydrogen production rate (right ordinate) as a function of voltage pulse period for an off-time of (a) 1 ms and (b) 10 ms. Both natural convection and forced flow.

compared to only 0.2 and 4% for a 1 ms off-time. In other words, lower duty cycles (i.e., longer off- times) reinforce the effect of forced flow. As for voltage pulses with a 50% duty cycle, the performance of pulsed operation was worse than at DC.

Moreover, comparing the measured H₂ production rates (shown on the right-side ordinate in Fig. 71) to the total current response during pulsation, the Faraday efficiency was found under these conditions to be around 100% for most of the cases, as shown in Fig. 72. In other words, almost all the charge was used to produce hydrogen and no significative parasitic reaction occurred. For pulse periods of 2 ms, the hydrogen production rate was one order of magnitude lower than the values obtained for all the other periods. Since the measurement of the gas volume was done with a graduated cylinder with 0.5 ml of uncertainty, the reduced hydrogen production greatly reduced the precision of the estimation. As a consequence, the values for this pulse period deviates from 100%. For instance, the value for forced flow and off time of 1 ms at a pulse period of 2 ms was 2 ± 1 and is not shown in the graph. For an off-time of 1 ms and forced flow, efficiency is a bit lower than the expected, with a minimum value of 93 ± 3 %. Nonetheless, in order to estimate the Faraday efficiency, pressure is assumed to be 1 bar and the temperature is considered to be constant along the duration of the experiment. It is worth noticing that 5% of change in pressure or temperature causes 5% of change in the Faraday efficiency. To increase the precision of the Faraday efficiency estimation, one solution is the use of a mass spectrometer with inline measurement of the produced gases [264].

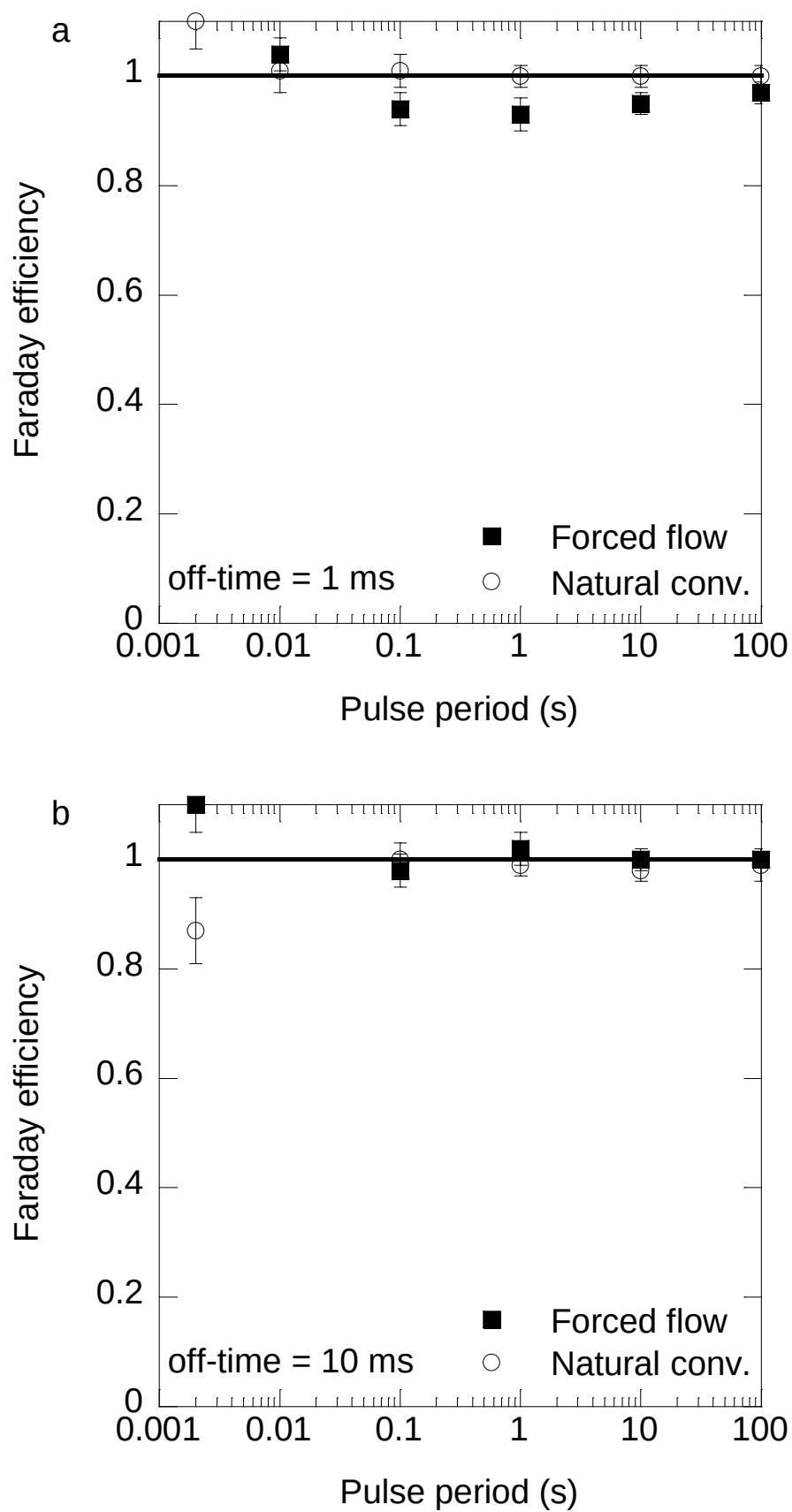


Fig. 72. Faraday efficiency for voltage pulses with an off-time of a) 1 ms and b) 10 ms.

9.3 Current pulses with a duty cycle of 50%

As opposed to the application of voltage pulses, there can be no polarity reversal in the case of current pulses as the current during off time is set at 0 A. The electrical double layer is then charged at the beginning, and it is never discharged in the course of the experiment. This then allows for net hydrogen production even at low pulse widths on the order of a few milliseconds. As shown in Fig. 73, after the first pulse, we observed a significant reduction in the cell voltage needed to reach 0.3 A (corresponding to a geometric current density of $0.075 \text{ A}\cdot\text{cm}^{-2}$). This is especially the case at high pulse frequencies, although the time evolution of the cell voltage at the beginning of all pulses was similar to DC. Since the duty cycle was the same in all cases (i.e., 50%), the best pulse configuration was the one with the smallest pulse width (10 ms). In this case, as shown in Fig. 74.a, a reduction in cell potential (averaged over 10 min) on the order of 30 mV was observed compared to DC for both natural convection and forced flow. This represents a reduction of 5% in cell overvoltage. It is important to notice that DC water electrolysis at 0.3 A was performed before and after the pulse experiment, as illustrated in Fig. 74.b. This was to ensure that no modification in the electrode behavior had occurred. In all cases, the DC behavior was the same at the beginning and the end of each experiment.

When comparing the above results to available literature data, they are in qualitative agreement with the ones obtained by Vincent *et al.* [197] for water electrolysis with a redox mediator. The authors reported a 23% reduction in cell voltage when applying 20 ms current pulses and

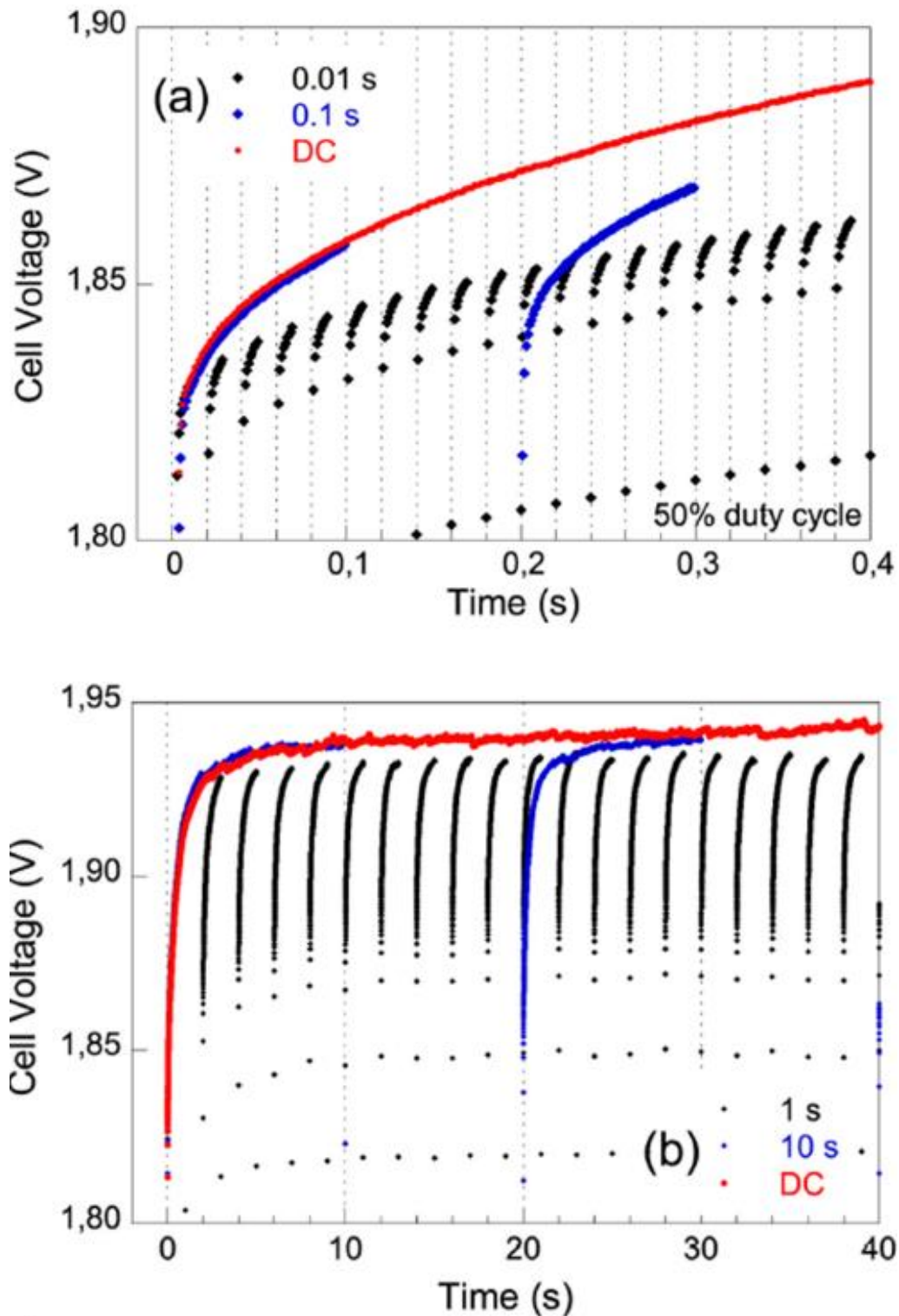


Fig. 73. Time evolution of the cell voltage for current pulses between 0 and $0.075 \text{ A} \cdot \text{cm}^{-2}$ for pulse widths of a) 0.01 and 0.1 s, and b) 1 and 10 s. The DC behavior at $0.075 \text{ A} \cdot \text{cm}^{-2}$ is shown for comparison. Duty cycle of 50%, natural convection.

27% reduction for pulse periods of 2 ms. The current went from 0 to $0.1 \text{ A}\cdot\text{cm}^{-2}$ with a 50% duty cycle. As in our case, they also observed a better performance for pulses with higher frequencies. However, as

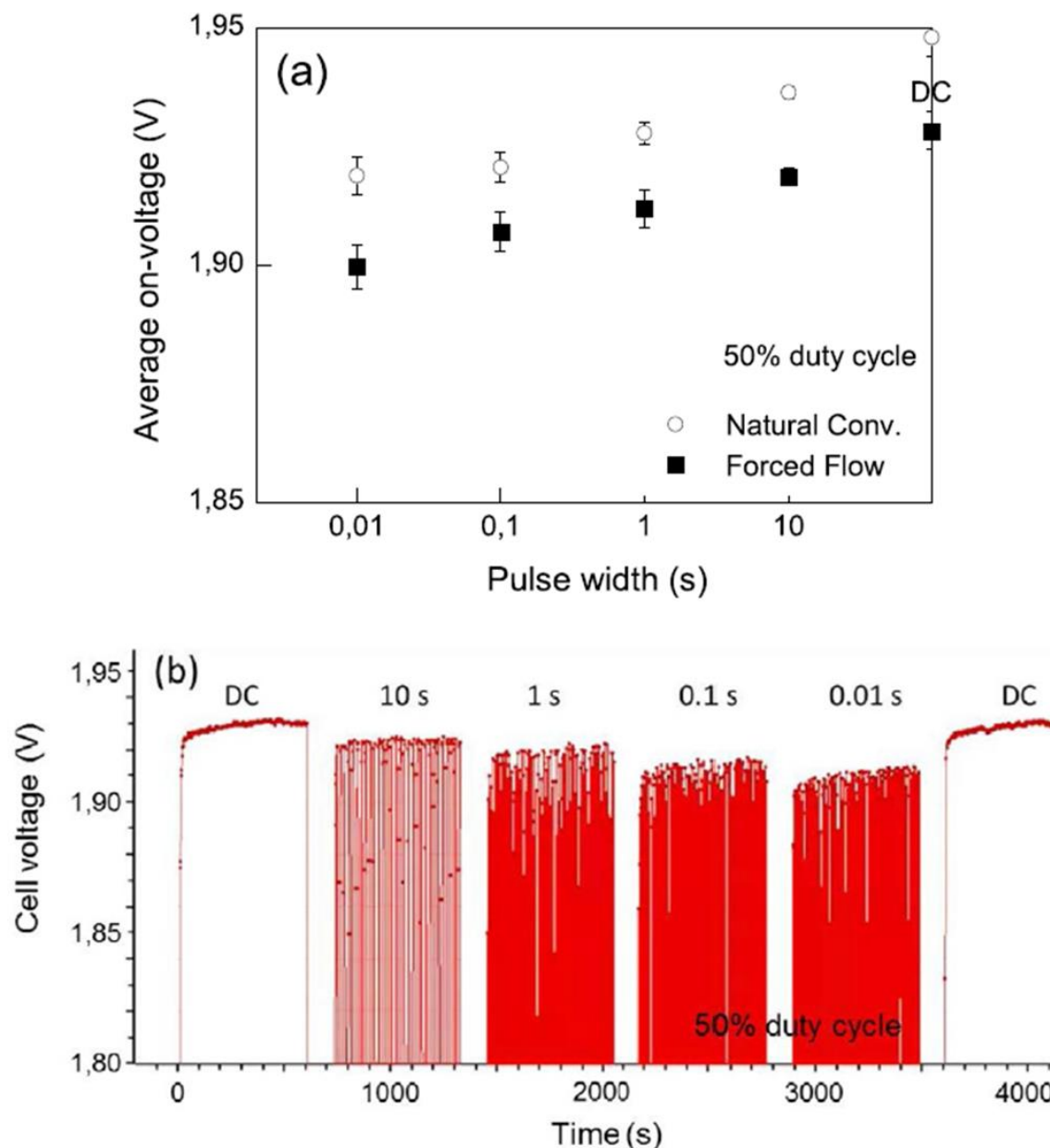


Fig. 74. (a) Average cell voltage during 10 min of experiment as a function of the current pulse width. Duty cycle of 50%, both natural convection and forced flow; (b) Time evolution profile of the cell voltage during a typical pulsed current experiment, showing that the DC behavior measured at the end of each experiment was the same as the one at the beginning.

opposed to the results obtained in ref. [197], we did not observe any plateau at high pulse periods when plotting the average cell voltage vs. pulse period in Fig. 74.a. Since this plateau can be attributed to the complete establishment of the diffusional boundary layer, it also implies that this layer was still not fully established after 10 s in our experimental setup.

9.4 Current pulses with duty cycles other than 50%

The effect of applying current pulses with duty cycles higher than 50% is shown in Fig. 75. No statistically significant decrease in cell voltage relative to DC could be observed. With the introduction of a forced flow, an overvoltage reduction of about 11-12% and 6% was obtained for current pulses with off-times of 10 and 100 ms, respectively, confirming once more the flow effect.

The fact that current pulses only have a statistically significant effect for duty cycles equal to or lower than 50% is confirmed in Fig. 76. In this case, the combined effect of low pulse periods with low duty cycles gave the lowest on-voltage: for a 20% duty cycle and a 2 ms pulse period, we observed a 260 mV (i.e., 25%) reduction in cell overvoltage, as opposed to only 11% for a 50% duty cycle. Such an increase in performance when decreasing the duty cycle is in line with the observations from Lin *et al.* [174] in the case of voltage pulses. The effect of lower duty cycles is also beneficial for all pulse periods but most pronounced for the lower ones (i.e., the highest frequencies). Therefore, our results indicate that the application of current pulses with short pulse periods (ms-range) and low duty cycles (10-20%) can be a

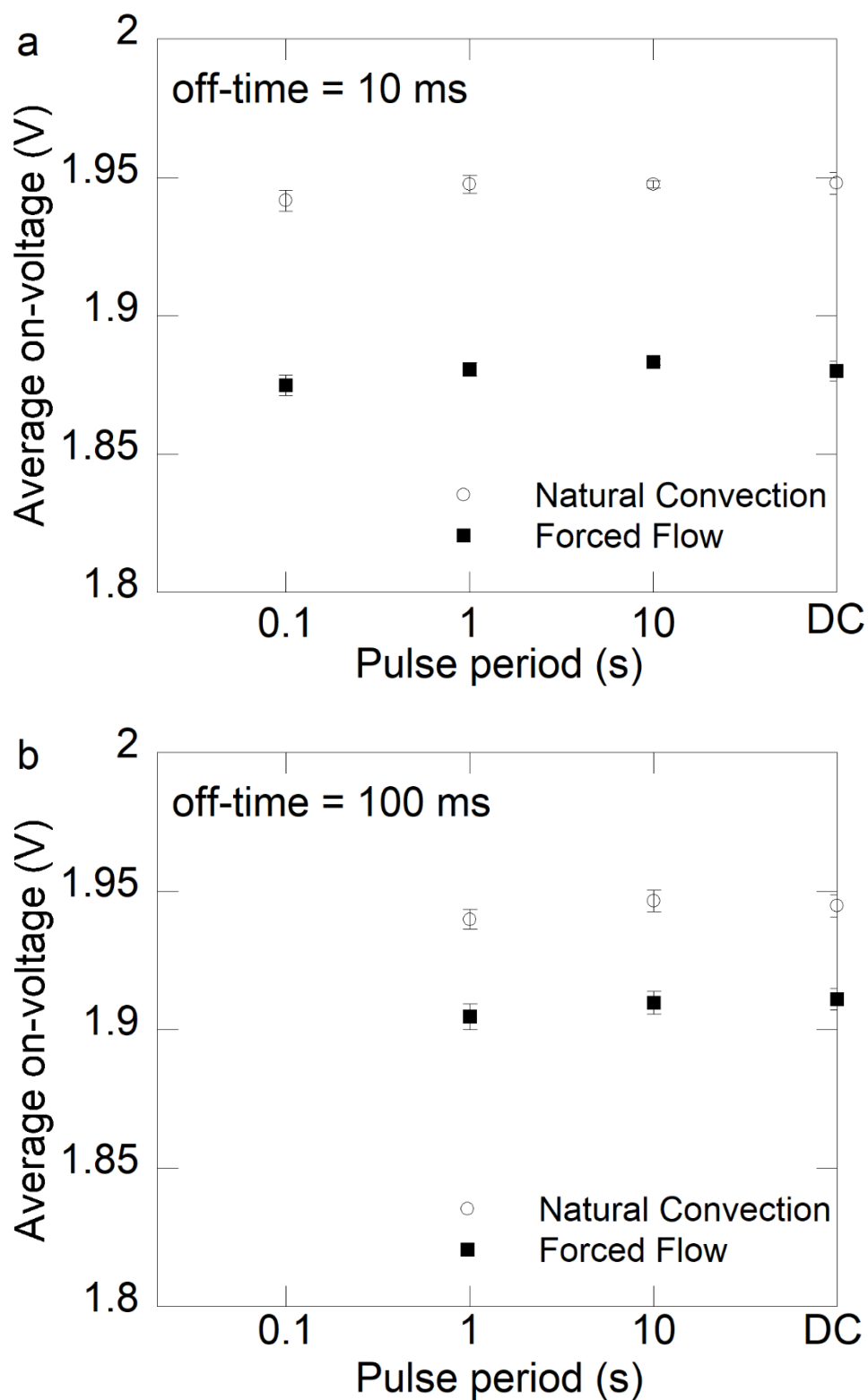


Fig. 75. Average cell voltage as a function of current pulse period for an off-time of (a) 10 ms and (b) 100 ms. Both natural convection and forced flow.

promising method for improving cell performance during alkaline water electrolysis. Nevertheless, lowering the duty cycle also lowers the production rate; thus, the reduction in cell voltage may not compensate for the reduction in hydrogen production rate.

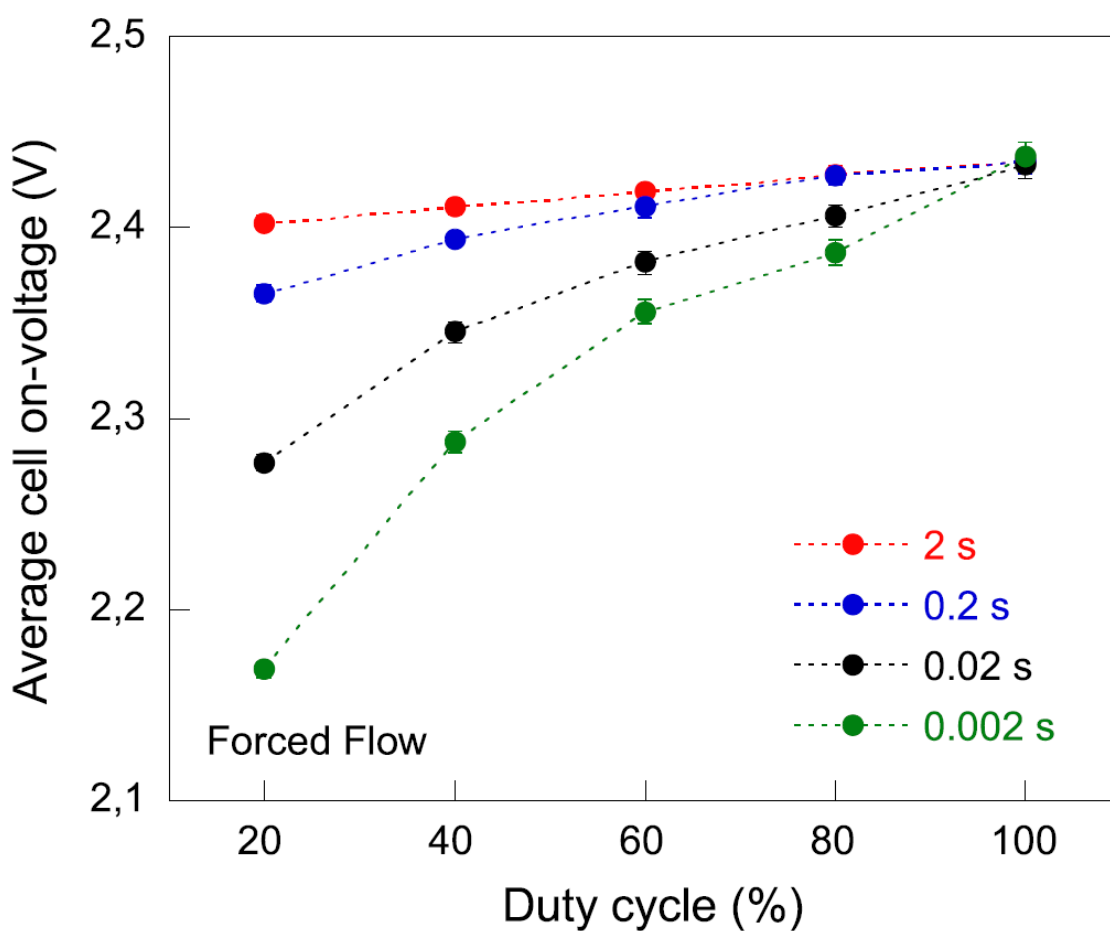


Fig. 76. Duty cycle dependence of the average cell on-voltage for current pulses with different pulse periods. Peak current of $0.075 \text{ A} \cdot \text{cm}^{-2}$, forced flow.

9.5 Literature overview

The results present here confirm the general trend observed in the literature, namely an increase in the on-current upon the application of voltage pulses and a reduction in the on-voltage upon the application of current pulses. Some authors explained this as a consequence of better bubble removal, as during the off-time, bubbles had time to leave the electrode surface [172]. Others attributed this result to a higher concentration of reactants at the electrode surface as the surface is replenished of reactants during the off-time [169,197]. Vanags *et al.* [265] proposed that during pulsed operation, the diffusion layer is characterized by pulsating concentrations of active ions. Another given reason is related to the relaxation time of the ionic atmosphere around reactant ions [170]. However, even though pulsed electrolysis enhanced performance during on-time, this improvement was not high enough to compensate for the pulse behavior during off-time. For instance, for voltage pulses with a 50% duty cycle, the increase in current was generally lower than two times the direct current. In other words, to maintain the same production rate, the pulsed voltage needs to be higher than the DC voltage, which reduces the overall efficiency. Furthermore, we demonstrated with our experiments that voltage pulses can be significantly influenced by the charge and discharge of the EDL, not being ideal for process intensification.

Despite the fact that experimental evidences point out to the failure of pulsed power as a way to improve electrolyzer performance, there is a noteworthy exception. For stacks working at low load conditions, current pulses may enhance the performance due to the reduction in current by-pass [188]. This is particular important when considering

that green hydrogen needs to deal with varying renewable power inputs, which can sometimes be low.

Nevertheless, the application of pulsed power in commercial stacks has yet many challenges. Notably, more research is needed on gas crossover and electrode degradation during pulsed operation [183].

Additionally, a process that is intrinsically pulsed/alternated is the decoupled process of production of hydrogen and oxygen using a redox mediator, as studied by Vincent *et al.* [197]. In this process, an increase in the alternation frequency seems promising in improving the performance, but the process is limited to a certain current density, not being able to achieve the high current densities needed for modern alkaline electrolyzers. Furthermore, the increase in alternation frequency can enhance degradation, total switching time, and possibly anticipate the generation of gas bubbles at the redox mediator.

Finally, pulsed water electrolysis could be useful in processes in which there is a reaction controlled by mass transfer. This includes the work of ref. [173], at which hydrogen was produced at the cathode, and at the anode, there was the mass transfer controlled oxidation of sulfite ions. It could also be helpful to control the quality of electrodeposition and to improve the performance of wastewater oxidation, as discussed in Ch. 3.

9.6 Conclusion

In this chapter, our focus centered on the application of square-shaped pulses to advance the process of hydrogen production using 3-D electrodes and forced electrolyte flow. The pulses promoted gas

production during the on-time and resting during the off-time. Through our experiments, a series of noteworthy insights emerged.

When voltage pulses were applied, it was observed that the current at on-time was systematically higher than the current during DC electrolysis. However, during off-time, a change in polarization was observed, demonstrating that a considerable part of this on-current was capacitive. Notably, focusing only at the first pulse, the on-current of the pulsed operation was significantly higher than DC operation, confirming the results obtained previously by our research group. Yet, we demonstrated that this apparent better performance was in reality the result of the EDL charging, not representing any improvement in production rate, on the contrary. As an example, almost no hydrogen production occurred when applying pulses with a 50% duty cycle and an on-time of 1 ms, but its first pulse presented a more than 2-fold increase in current when compared to DC. Once the charge/discharge cycle of the electrical double layer achieves a steady state, such short pulses could no longer provide significant average currents. This observation underlines the necessity for comprehensive investigation of voltage pulses over extended experiment duration. Furthermore, the voltage pulses studied here presented no advantage compared to conventional DC electrolysis.

Current pulses, on the other hand, were proven to be more promising in intensifying the process. These pulses were able to block double layer discharge during off-time, as well as the possible reduction of nickel hydroxides at the anode and the oxidation at the cathode. As a result, all the current could be used for hydrogen and oxygen production. For example, when the pulse period was 2 ms, and the duty cycle was 50%,

there was a 11% reduction in overvoltage. When the duty cycle went to 20%, there was a 25% overvoltage reduction. This is a consequence of a reduction in the thickness of the diffusion layer and the facilitation of bubble removal, as previously proposed in the literature. Furthermore, applying a forced electrolyte flow was beneficial in all cases where faradaic processes were dominant, as already demonstrated in previous chapters.

Additionally, literature review shows that pulsed power could potentially be used at low-load conditions, as it can limit gas cross-over and improve efficiency by reducing current by-pass. Moreover, the inherent alternated decoupled process can benefit from the higher on-current/lower on-voltage promoted by pulsed power, without the drawback presented by the resting (off)-time. Therefore, it is a potential field for future studies.

Finally, pulses can be used for other applications than water electrolysis. They appear to be a manner to better control the quality of electrodeposition and to reduce the energy consumption during anodic oxidation of organic compounds. Moreover, the conclusions obtained in terms of enhanced mass transport during pulsed water electrolysis could also be applied to refine several electroanalytical techniques, e.g., enhancing the current density in voltammetry to detect low-concentration species or to determine the electrode capacitance.

Chapter 10: Conclusions and perspectives

In this work, we explored different process intensification strategies for alkaline water electrolysis aiming at the increase in scalability and the capex reduction of green hydrogen production. At first, 3-D foam electrodes were investigated and several conclusions can be outlined including:

- Forced electrolyte flow showed promising results in decreasing cell voltage and liberating electrode surfaces for better performance when using 3-D electrodes.
- The performance of 3-D foams could be better understood when normalizing the polarization curves by the ECSA.
- Using the normalized curves, a method to estimate available electrode surface was proposed and a compromise was found between surface area and bubble entrapment for foam-shaped electrodes. It was demonstrated that foams with pore sizes higher than 1000 μm are better to evacuate bubbles, while foams with lower pore sizes are fit for hydrogen/oxygen production due to their high surface area.
- Following the previous observation, a lateral-graded bi-layer electrode configuration was proposed, combining a high-surface area foam (450 μm) for hydrogen/oxygen production with an open structure for gas removal (3,000 μm), boosting the forced electrolyte flow effect.
- It was shown that in this bi-layer configuration, the mean residence time was lower than the one obtained with flow fields,

and there was mass transfer from the production layer to the porous transport foam.

- Thermal-sprayed NiAl and NiAlMo coating has shown to be a very effective way to improve electrolysis performance due to the substantial increase in surface area and to catalytic effects provided by the Mo.
- The use of Raney Ni bi-layer foam electrodes showed remarkable performance improvements, making alkaline water electrolysis more akin to PEM-like systems.

Then, SLM 3-D printed electrodes were fabricated and tested and it was concluded that:

- It was feasible to combine SLM technology with alkaline water electrolysis, which opens new possibilities for electrode geometries that can combine high surface area with effective gas removal.
- Flow sensitivity analysis revealed varying sensitivities depending on surface area, porosity, and geometry, with Schwarz-shaped electrodes showing great potential as they channel the flow in the upward direction, avoiding flow lateral mixing and the consequent bubble collision and coalescence.

Finally, the effectiveness of pulsed water electrolysis was investigated, and it was concluded that:

- Even if some improvements in performance were observed during on-time, the performance gains were not sufficient to compensate for the non-production during off-time. This

statement is valid for our experiments and for most of the existing literature.

- When applying pulsed-voltage, a change in current polarization was observed during off-time, representing the discharge of the EDL. At high pulse frequencies, the current was controlled by the charge and discharge of the EDL and almost no faradaic current was observed. In other words, no hydrogen could be produced.
- Current pulses, on the other hand, were more promising, as the EDL was charged during the application of the first pulses and it was not discharged. Consequently, the electrolysis was not controlled by capacitive processes.
- Pulsed power appears to be worth using in situations with low power inputs, as it may enhance efficiency of stacks. Since the energy sources for green hydrogen are often intermittent, it is reasonable to expect changes in power input and the ability to adapt to those changes is an asset.

In conclusion, this research has shed light on various aspects of alkaline water electrolysis, offering valuable insights into intensifying the process and enhancing its performance. The findings provide important considerations not only for industrial electrolyzer manufacturers but also to other gas-evolving processes and contribute to the development of sustainable hydrogen production technologies.

Furthermore, some perspectives can be outlined:

- To better understand bubble behavior inside porous electrodes, it is recommended to be able to dissociate the HER from the OER, as hydrogen and oxygen bubbles have different sizes and are

produced at different rates. It is much easier to use reference electrodes in a Becker, but the situation is more complex when using a zero-gap cells, especially because the reference electrode should be placed between the cathode and the anode. An alternative would be to use a reference electrode at the electrolyte inlet and another in a Becker ionically connected to the separator, as suggested by ref. [220].

- High speed photography could be used to estimate bubble size and residence time inside porous electrodes. To be able to visualize inside cells, the PTFE electrode housing should be replaced by a transparent or translucent material resistant to corrosion in alkaline media. One alternative is acrylic.
- The laterally graded bi-layer electrode configuration caused a remarkable intensification of the electrolysis process at a lab-scale. Further research is needed in terms of the scalability and long-term stability of this configuration; especially at high current densities.
- It was shown that increasing the electrolyte flow rate improves the electrochemical performance. It is recommended for future works to study the mechanical damage, corrosion, and shunt current that can be caused by this increased flow rate.
- Here, the Raney Ni coating was obtained by means of the thermal spraying technique, but other techniques could be studied as well. One possibility would be to first coat the foam with a binder solution using a spraying technique and then with a high alloyed powder, as done by ref. [266]. Another possibility is to co-deposit Ni with Zn or Sn.

- To show the feasibility of using a pulsed power supply at low-load conditions, more research is needed on the gas crossover and electrode degradation phenomena during pulsed operation.
- After demonstrating the significant performance increase caused by thermal spraying NiAl and NiAlMo on foams, it would be interesting to study 3-D printed electrodes printed using NiAl/NiAlMo powder.
- As a consequence of the benefits observed when using a graduated electrode structure on bubble removal, it is recommended to study graded 3-D printed structures.
- The development of flow-engineered 3-D electrodes could be combined with other bubble removal strategies, including superaerophobic surfaces, superaerophilic sacrificial sites, the use of ultrasound or an external field (magnetic fields, photothermal, supergravity), or pressure modulation.
- For future developments, it is recommended to design electrodes with geometrical variations not only in the direction perpendicular to the separator, but also along the flow direction, considering the differences in the gas fraction. Furthermore, different designs should be tested for the anode and the cathode. Heat management could also be taken into account for future designs.

References

- [1] Cook J, Nuccitelli D, Green SA, et al. Quantifying the consensus on anthropogenic global warming in the scientific literature. *Environ Res Lett* 2013;8:24024.
- [2] IPCC. Synthesis report of the IPCC sixth assesement report. 2023.
- [3] Rennert K, Errickson F, Prest BC, et al. Comprehensive evidence implies a higher social cost of CO₂. *Nature* 2022;610:687–92.
- [4] Urban MC. Accelerating extinction risk from climate change. *Science* (80-) 2015;348:571–3.
- [5] O'Neill BC, Oppenheimer M, Warren R, et al. IPCC reasons for concern regarding climate change risks. *Nat Clim Chang* 2017;7:28–37.
- [6] United Nations Framework Convention on Climate Change, May 9, 1992, S. Treaty Doc. No. 102-38.
- [7] Kyoto Protocol to the United Nations Framework Convention on Climate Change, Dec. 10, 1997, 2303 U.N.T.S. 162.
- [8] Paris Agreement to the United Nations Framework Convention on Climate Change, Dec. 12, 2015, T.I.A.S. No. 16-1104.
- [9] Brecha RJ, Ganti G, Lamboll RD, et al. Institutional decarbonization scenarios evaluated against the Paris Agreement 1.5 °C goal. *Nat Commun* 2022;13:4304.
- [10] IEA. Energy Technology Perspectives 2023. Paris: 2023.
- [11] IEA. Net Zero by 2050. Paris: 2021.
- [12] Dawood F, Anda M, Shafiullah GM. Hydrogen production for energy: An overview. *Int J Hydrog Energy* 2020;45:3847–69.
- [13] Öberg S, Odenberger M, Johnsson F. The value of flexible fuel mixing in hydrogen-fueled gas turbines – A techno-economic study. *Int J Hydrogen Energy* 2022;47:31684–702.
- [14] Steilen M, Jörisen L. Chapter 10 - Hydrogen Conversion into Electricity and Thermal Energy by Fuel Cells: Use of H₂-Systems and Batteries. In: Moseley PT, Garche JBT-EES for RS and GB, editors., Amsterdam: Elsevier; 2015, p. 143–58.

- [15] Öberg S, Odenberger M, Johnsson F. Exploring the competitiveness of hydrogen-fueled gas turbines in future energy systems. *Int J Hydrogen Energy* 2022;47:624–44.
- [16] Marocco P, Gandiglio M, Audisio D, et al. Assessment of the role of hydrogen to produce high-temperature heat in the steel industry. *J Clean Prod* 2023;388:135969.
- [17] Nemmour A, Inayat A, Janajreh I, et al. Green hydrogen-based E-fuels (E-methane, E-methanol, E-ammonia) to support clean energy transition: A literature review. *Int J Hydrogen Energy* 2023.
- [18] Colelli L, Segneri V, Bassano C, et al. E-fuels, technical and economic analysis of the production of synthetic kerosene precursor as sustainable aviation fuel. *Energy Convers Manag* 2023;288:117165.
- [19] Inal OB, Zincir B, Deniz C. Investigation on the decarbonization of shipping: An approach to hydrogen and ammonia. *Int J Hydrogen Energy* 2022;47:19888–900.
- [20] Capurso T, Stefanizzi M, Torresi M, et al. Perspective of the role of hydrogen in the 21st century energy transition. *Energy Convers Manag* 2022;251:114898.
- [21] Becken S, Mackey B, Lee DS. Implications of preferential access to land and clean energy for Sustainable Aviation Fuels. *Sci Total Environ* 2023;886:163883.
- [22] Nurdiawati A, Zaini IN, Wei W, et al. Towards fossil-free steel: Life cycle assessment of biosyngas-based direct reduced iron (DRI) production process. *J Clean Prod* 2023;393:136262.
- [23] IEA. The future of Hydrogen. 2019.
- [24] Joseph A, Oghenegare E. Recent Advances in White Hydrogen Exploration and Production: A Mini Review. *J Energy Res Rev* 2023;13:64–79.
- [25] Wang L, Jin Z, Chen X, et al. The Origin and Occurrence of Natural Hydrogen. *Energies* 2023;16.
- [26] Zgonnik V. The occurrence and geoscience of natural hydrogen: A comprehensive review. *Earth-Science Rev* 2020;203:103140.
- [27] Taylor SR, McLennan S. Planetary crusts: their composition,

- origin and evolution. vol. 10. Cambridge University Press; 2009.
- [28] Ajanovic A, Sayer M, Haas R. The economics and the environmental benignity of different colors of hydrogen. *Int J Hydrogen Energy* 2022;47:24136–54.
 - [29] IEA. Global Hydrogen Review 2022. Paris: 2022.
 - [30] Howarth RW, Jacobson MZ. How green is blue hydrogen? *Energy Sci Eng* 2021;9:1676–87.
 - [31] Ursua A, Gandia LM, Sanchis P. Hydrogen Production From Water Electrolysis: Current Status and Future Trends. *Proc IEEE* 2012;100:410–26.
 - [32] Mohammadpour H, Cord-Ruwisch R, Pivrikas A, et al. Utilisation of oxygen from water electrolysis – Assessment for wastewater treatment and aquaculture. *Chem Eng Sci* 2021;246:117008.
 - [33] Tonelli D, Rosa L, Gabrielli P, et al. Global land and water limits to electrolytic hydrogen production using wind and solar resources. *Nat Commun* 2023;14:5532.
 - [34] IRENA. Green Hydrogen Cost Reduction: Scaling up Electrolysers to Meet the 1.5°C Climate Goal. Abu Dhabi: 2020.
 - [35] Proost J. State-of-the art CAPEX data for water electrolysers, and their impact on renewable hydrogen price settings. *Int J Hydrogen Energy* 2019;44:4406–13.
 - [36] Guillet N, Millet P. Alkaline Water Electrolysis, 2015, p. 117–66.
 - [37] IEA. The Role of Critical Minerals in Clean Energy Transitions. Paris: 2021.
 - [38] Minke C, Suermann M, Bensmann B, et al. Is iridium demand a potential bottleneck in the realization of large-scale PEM water electrolysis? *Int J Hydrogen Energy* 2021;46:23581–90.
 - [39] C. Reichl MS. World Mining Data 2023. Vienna: 2023.
 - [40] Commission E, Directorate-General for Internal Market Entrepreneurship and SMEs I, Blengini G, et al. Study on the EU's list of critical raw materials (2020) – Final report. Publications Office of the European Union; 2020.
 - [41] Sen D, Hamurcuoglu KI, Ersoy MZ, et al. Forecasting long-term world annual natural gas production by machine learning. *Resour*

Policy 2023;80:103224.

- [42] Sens L, Neuling U, Kaltschmitt M. Capital expenditure and levelized cost of electricity of photovoltaic plants and wind turbines – Development by 2050. *Renew Energy* 2022;185:525–37.
- [43] Proost J. Critical assessment of the production scale required for fossil parity of green electrolytic hydrogen. *Proc. 23rd World Hydrog. Energy Conf.*, 2022.
- [44] George JF, Müller VP, Winkler J, et al. Is blue hydrogen a bridging technology? - The limits of a CO₂ price and the role of state-induced price components for green hydrogen production in Germany. *Energy Policy* 2022;167:113072.
- [45] Swiegers GF, Terrett RNL, Tsekouras G, et al. The prospects of developing a highly energy-efficient water electrolyser by eliminating or mitigating bubble effects. *Sustain Energy Fuels* 2021;5:1280–310.
- [46] Smolinka T, Bergmann H, Garche J, et al. Chapter 4 - The history of water electrolysis from its beginnings to the present. In: Smolinka T, Garche Systems, and Applications JBT-EPSF, editors., Elsevier; 2022, p. 83–164.
- [47] Feiner A-S, McEvoy AJ. The nernst equation. *J Chem Educ* 1994;71:493.
- [48] Lubert K-H, Kalcher K. History of Electroanalytical Methods. *Electroanalysis* 2010;22:1937–46.
- [49] Pourbaix M. Lectures on electrochemical corrosion. Springer Science & Business Media; 2012.
- [50] Atkins P, Atkins PW, de Paula J. Atkins' physical chemistry. Oxford university press; 2014.
- [51] Millet P. Chapter 2 - Fundamentals of water electrolysis. In: Smolinka T, Garche Systems, and Applications JBT-EPSF, editors., Elsevier; 2022, p. 37–62.
- [52] Hammoudi M, Henao C, Agbossou K, et al. New multi-physics approach for modelling and design of alkaline electrolyzers. *Int J Hydrogen Energy* 2012;37:13895–913.
- [53] Adibi T, Sojoudi A, Saha SC. Modeling of thermal performance

of a commercial alkaline electrolyzer supplied with various electrical currents. *Int J Thermofluids* 2022;13:100126.

- [54] Dickinson EJJ, Wain AJ. The Butler-Volmer equation in electrochemical theory: Origins, value, and practical application. *J Electroanal Chem* 2020;872:114145.
- [55] Newman J, Balsara NP. *Electrochemical systems*. John Wiley & Sons; 2021.
- [56] Bard AJ, Faulkner LR, Allen JB, et al. *Electrochemical methods fundamentals and applications*. 2nd ed. New York: Wiley; 2001.
- [57] Compton RG, Banks CE. *Understanding voltammetry*. 2nd ed. London: Imperial College Press; 2011.
- [58] Wang M, Wang Z, Gong X, et al. The intensification technologies to water electrolysis for hydrogen production – A review. *Renew Sustain Energy Rev* 2014;29:573–88.
- [59] Quaino P, Juarez F, Santos E, et al. Volcano plots in hydrogen electrocatalysis – uses and abuses. *Beilstein J Nanotechnol* 2014;5:846–54.
- [60] Zaman N, Noor T, Iqbal N. Recent advances in the metal–organic framework-based electrocatalysts for the hydrogen evolution reaction in water splitting: a review. *RSC Adv* 2021;11:21904–25.
- [61] Bao F, Kemppainen E, Dorbandt I, et al. Understanding the Hydrogen Evolution Reaction Kinetics of Electrodeposited Nickel-Molybdenum in Acidic, Near-Neutral, and Alkaline Conditions. *ChemElectroChem* 2021;8:195–208.
- [62] Ooka H, Huang J, Exner KS. The Sabatier Principle in Electrocatalysis: Basics, Limitations, and Extensions . *Front Energy Res* 2021;9.
- [63] Liang Q, Brocks G, Bieberle-Hütter A. Oxygen evolution reaction (OER) mechanism under alkaline and acidic conditions. *J Phys Energy* 2021;3:26001.
- [64] Seh ZW, Kibsgaard J, Dickens CF, et al. Combining theory and experiment in electrocatalysis: Insights into materials design. *Science* (80-) 2017;355:eaad4998.
- [65] Fabbri E, Haberer A, Walzer K, et al. Developments and perspectives of oxide-based catalysts for the oxygen evolution

reaction. *Catal Sci Technol* 2014;4:3800–21.

- [66] Plevová M, Hnát J, Bouzek K. Electrocatalysts for the oxygen evolution reaction in alkaline and neutral media. A comparative review. *J Power Sources* 2021;507:230072.
- [67] Santos DMF, Sequeira CAC, Figueiredo JL. Hydrogen production by alkaline water electrolysis. *Quim Nova* 2013;36.
- [68] Selamet OF, Ergoktas MS. Effects of bolt torque and contact resistance on the performance of the polymer electrolyte membrane electrolyzers. *J Power Sources* 2015;281:103–13.
- [69] Wosiak G, Silva J da, Sena SS, et al. Investigation of the influence of the void fraction on the energy consumption of a vertical electrolyser under natural convection. *J Environ Chem Eng* 2022;10:107577.
- [70] de Groot MT, Vreman AW. Ohmic resistance in zero gap alkaline electrolysis with a Zirfon diaphragm. *Electrochim Acta* 2021;369:137684.
- [71] Vogt H. The Quantities Affecting the Bubble Coverage of Gas-Evolving Electrodes. *Electrochim Acta* 2017;235:495–9.
- [72] Janssen LJJ, van Stralen SJD. Bubble behaviour on and mass transfer to an oxygen-evolving transparent nickel electrode in alkaline solution. *Electrochim Acta* 1981;26:1011–22.
- [73] de Jonge RM, Barendrecht E, Janssen LJJ, et al. Gas bubble behaviour and electrolyte resistance during water electrolysis. *Int J Hydrogen Energy* 1982;7:883–94.
- [74] Khalighi F, Deen NG, Tang Y, et al. Hydrogen bubble growth in alkaline water electrolysis: An immersed boundary simulation study. *Chem Eng Sci* 2023;267:118280.
- [75] Eigeldinger J, Vogt H. The bubble coverage of gas-evolving electrodes in a flowing electrolyte. *Electrochim Acta* 2000;45:4449–56.
- [76] Zeng K, Zhang D. Recent progress in alkaline water electrolysis for hydrogen production and applications. *Prog Energy Combust Sci* 2010;36:307–26.
- [77] Buttler A, Spliethoff H. Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-

- gas and power-to-liquids: A review. *Renew Sustain Energy Rev* 2018;82:2440–54.
- [78] Council NR. The hydrogen economy: opportunities, costs, barriers, and R&D needs. National Academies Press; 2004.
- [79] Smolinka T, Günther M, Garche J. Stand und Entwicklungspotenzial der Wasserelektrolyse zur Herstellung von Wasserstoff aus regenerativen Energien. Kurzfassung Des Abschlussberichtes NOW-Studie, Freibg Im Breisgau 2011.
- [80] Pletcher D, Walsh F. Three-Dimensional Electrodes. In: GENDERS JD, WEINBERG NL, editors. *Electrochem. Technol. a Clean. Environ.*, New York: 1992.
- [81] Goodall R, Mortensen A. 24 - Porous Metals. In: Laughlin DE, Hono KBT-PM (Fifth E, editors., Oxford: Elsevier; 2014, p. 2399–595.
- [82] Haverkort JW. A theoretical analysis of the optimal electrode thickness and porosity. *Electrochim Acta* 2019;295:846–60.
- [83] Chen Z, Danilov DL, Eichel R-A, et al. On the reaction rate distribution in porous electrodes. *Electrochem Commun* 2020;121:106865.
- [84] Olmstead ML, Nicholson RS. Influence of double-layer charging in chronopotentiometry. *J Phys Chem* 1968;72:1650–6.
- [85] Puippe JC, Ibl N. Influence of charge and discharge of electric double layer in pulse plating. *J Appl Electrochem* 1980;10:775–84.
- [86] Li Y, Zhang T, Ma J, et al. Study the effect of lye flow rate, temperature, system pressure and different current density on energy consumption in catalyst test and 500W commercial alkaline water electrolysis. *Mater Today Phys* 2022;22:100606.
- [87] Schmidt O, Gambhir A, Staffell I, et al. Future cost and performance of water electrolysis: An expert elicitation study. *Int J Hydrogen Energy* 2017;42:30470–92.
- [88] Kraglund MR, Carmo M, Schiller G, et al. Ion-solvating membranes as a new approach towards high rate alkaline electrolyzers. *Energy Environ Sci* 2019;12:3313–8.
- [89] Dotan H, Landman A, Sheehan SW, et al. Decoupled hydrogen

and oxygen evolution by a two-step electrochemical–chemical cycle for efficient overall water splitting. *Nat Energy* 2019;4:786–95.

- [90] Gambou F, Guilbert D, Zasadzinski M, et al. A Comprehensive Survey of Alkaline Electrolyzer Modeling: Electrical Domain and Specific Electrolyte Conductivity. *Energies* 2022;15.
- [91] Gilliam RJ, Graydon JW, Kirk DW, et al. A review of specific conductivities of potassium hydroxide solutions for various concentrations and temperatures. *Int J Hydrogen Energy* 2007;32:359–64.
- [92] Cekic-Laskovic I, Wölke C, Xu K, et al. Electrolytes: From a Thorn Comes a Rose, and from a Rose, a Thorn. *Isr J Chem* 2021;61:85–93.
- [93] Brauns J, Turek T. Alkaline Water Electrolysis Powered by Renewable Energy: A Review. *Processes* 2020;8.
- [94] Vincent I, Bessarabov D. Low cost hydrogen production by anion exchange membrane electrolysis: A review. *Renew Sust Energ Rev* 2018;81:1690–704.
- [95] Brauns J, Schönebeck J, Kraglund MR, et al. Evaluation of Diaphragms and Membranes as Separators for Alkaline Water Electrolysis. *J Electrochem Soc* 2021;168:14510.
- [96] de Groot MT, Kraakman J, Garcia Barros RL. Optimal operating parameters for advanced alkaline water electrolysis. *Int J Hydrogen Energy* 2022;47:34773–83.
- [97] Trinke P, Haug P, Brauns J, et al. Hydrogen Crossover in PEM and Alkaline Water Electrolysis: Mechanisms, Direct Comparison and Mitigation Strategies. *J Electrochem Soc* 2018;165:F502.
- [98] Aili D, Kraglund MR, Rajappan SC, et al. Electrode Separators for the Next-Generation Alkaline Water Electrolyzers. *ACS Energy Lett* 2023;8:1900–10.
- [99] Frank AL, Joshi TK. The Global Spread of Asbestos. *Ann Glob Heal* 2014;80:257–62.
- [100] Rodríguez J, Palmas S, Sánchez-Molina M, et al. Simple and Precise Approach for Determination of Ohmic Contribution of Diaphragms in Alkaline Water Electrolysis. *Membranes (Basel)*

2019;9.

- [101] Ito H, Maeda T, Nakano A, et al. Properties of Nafion membranes under PEM water electrolysis conditions. *Int J Hydrogen Energy* 2011;36:10527–40.
- [102] Lee HI, Mehdi M, Kim SK, et al. Advanced Zirfon-type porous separator for a high-rate alkaline electrolyser operating in a dynamic mode. *J Memb Sci* 2020;616:118541.
- [103] Hagesteijn KFL, Jiang S, Ladewig BP. A review of the synthesis and characterization of anion exchange membranes. *J Mater Sci* 2018;53:11131–50.
- [104] Manzotti A, Robson MJ, Ciucci F. Recent developments in membraneless electrolysis. *Curr Opin Green Sustain Chem* 2023;40:100765.
- [105] Safizadeh F, Ghali E, Houlachi G. Electrocatalysis developments for hydrogen evolution reaction in alkaline solutions – A Review. *Int J Hydrogen Energy* 2015;40:256–74.
- [106] Ďurovič M, Hnát J, Bouzek K. Electrocatalysts for the hydrogen evolution reaction in alkaline and neutral media. A comparative review. *J Power Sources* 2021;493:229708.
- [107] Zhang J, Wang T, Liu P, et al. Efficient hydrogen production on MoNi₄ electrocatalysts with fast water dissociation kinetics. *Nat Commun* 2017;8:15437.
- [108] Park SH, To DT, Myung N V. A review of nickel-molybdenum based hydrogen evolution electrocatalysts from theory to experiment. *Appl Catal A Gen* 2023;651:119013.
- [109] Huang L-F, Hutchison MJ, Santucci RJJ, et al. Improved Electrochemical Phase Diagrams from Theory and Experiment: The Ni–Water System and Its Complex Compounds. *J Phys Chem C* 2017;121:9782–9.
- [110] Smith AJ, Wainwright MS. Skeletal Metal Catalysts. *Handb. Heterog. Catal.*, 2008, p. 92–100.
- [111] Razmjooei F, Liu T, Azevedo DA, et al. Improving plasma sprayed Raney-type nickel–molybdenum electrodes towards high-performance hydrogen evolution in alkaline medium. *Sci Rep* 2020;10:10948.

- [112] Gannon WJF, Dunnill CW. Raney Nickel 2.0: Development of a high-performance bifunctional electrocatalyst. *Electrochim Acta* 2019;322:134687.
- [113] Zhu Y, Zhang X, Song J, et al. Microstructure and hydrogen evolution catalytic properties of Ni-Sn alloys prepared by electrodeposition method. *Appl Catal A Gen* 2015;500:51–7.
- [114] Maniam KK, Paul S. A Review on the Electrodeposition of Aluminum and Aluminum Alloys in Ionic Liquids. *Coatings* 2021;11.
- [115] Fow KL, Ganapathi M, Stassen I, et al. Catalytically active gauze-supported skeletal nickel prepared from Ni-Zn alloys electrodeposited from an acetamide–dimethyl sulfone eutectic mixture. *Catal Today* 2015;246:191–7.
- [116] Schalenbach M, Kasian O, Mayrhofer KJJ. An alkaline water electrolyzer with nickel electrodes enables efficient high current density operation. *Int J Hydrogen Energy* 2018;43:11932–8.
- [117] Kim J-H, Lee J-N, Yoo C-Y, et al. Low-cost and energy-efficient asymmetric nickel electrode for alkaline water electrolysis. *Int J Hydrogen Energy* 2015;40:10720–5.
- [118] Han W-B, Kim I-S, Kim M, et al. Directly sputtered nickel electrodes for alkaline water electrolysis. *Electrochim Acta* 2021;386:138458.
- [119] Kou T, Wang S, Li Y. Perspective on High-Rate Alkaline Water Splitting. *ACS Mater Lett* 2021;3:224–34.
- [120] Heath MM, Poureshghi F, Seland F, et al. The Enhancing Effect of α -FeOOH on Ni Surfaces Toward Electrolytic Water Splitting. *Energy Technol* 2023;11:2300313.
- [121] Voitic G, Pichler B, Basile A, et al. Chapter 10 - Hydrogen Production. In: Hacker V, Mitsushima SBT-FC and H, editors., Elsevier; 2018, p. 215–41.
- [122] Phillips R, Dunnill CW. Zero gap alkaline electrolysis cell design for renewable energy storage as hydrogen gas. *RSC Adv* 2016;6:100643–51.
- [123] Grigoriev SA, Fateev VN, Bessarabov DG, et al. Current status, research trends, and challenges in water electrolysis science and

- technology. *Int J Hydrogen Energy* 2020;45:26036–58.
- [124] Wendt H, Hofmann H. Cermet diaphragms and integrated electrode-diaphragm units for advanced alkaline water electrolysis. *Int J Hydrogen Energy* 1985;10:375–81.
- [125] Fischer J, Hofmann H, Luft G, et al. Fundamental investigations and electrochemical engineering aspects concerning an advanced concept for alkaline water electrolysis. *AIChE J* 1980;26:794–802.
- [126] Záchenská J, Ábel M, Mičušík M, et al. Nickel-based nanocoatings on 3D Ni foam for zero-gap alkaline water electrolysis. *J Appl Electrochem* 2020;50:959–71.
- [127] Yang F, Kim MJ, Brown M, et al. Alkaline Water Electrolysis at 25 A cm^{-2} with a Microfibrous Flow-through Electrode. *Adv Energy Mater* 2020:2001174.
- [128] Liu PS, Chen GF. Chapter Three - Application of Porous Metals. In: Liu PS, Chen GF BT-PM, editors., Boston: Butterworth-Heinemann; 2014, p. 113–88.
- [129] Duan DL, Zhang RL, Ding XJ, et al. Calculation of specific surface area of foam metals using dodecahedron model. *Mater Sci Technol* 2006;22:1364–7.
- [130] Kou T, Wang S, Shi R, et al. Periodic Porous 3D Electrodes Mitigate Gas Bubble Traffic during Alkaline Water Electrolysis at High Current Densities. *Adv Energy Mater* 2020;10:2002955.
- [131] Huang B, Lei C, Sun X, et al. Improving mass transfer in anion exchange membrane water electrolysis by ordered gas diffusion layer. *Int J Hydrogen Energy* 2023.
- [132] Lyu Z, Lim GJH, Koh JJ, et al. Design and Manufacture of 3D-Printed Batteries. *Joule* 2021;5:89–114.
- [133] Saadi MASR, Maguire A, Pottackal NT, et al. Direct Ink Writing: A 3D Printing Technology for Diverse Materials. *Adv Mater* 2022;34:2108855.
- [134] Xu X, Fu G, Wang Y, et al. Highly Efficient All-3D-Printed Electrolyzer toward Ultrastable Water Electrolysis. *Nano Lett* 2023;23:629–36.
- [135] Izdebska-Podsiadły J. Polymers for 3D Printing: Methods,

Properties, and Characteristics. William Andrew; 2022.

- [136] Mertens A, Dedry O, Reuter D, et al. Thermal treatments of AlSi₁₀Mg processed by laser beam melting, Proceedings - 26th Annual International Solid Freeform Fabrication Symposium - An Additive Manufacturing Conference; 2020, p. 1007–16.
- [137] Gokuldoss PK, Kolla S, Eckert J. Additive Manufacturing Processes: Selective Laser Melting, Electron Beam Melting and Binder Jetting—Selection Guidelines. Mater 2017;10.
- [138] Abdelghani-Idrissi S, Dubouis N, Grimaud A, et al. Effect of electrolyte flow on a gas evolution electrode. Sci Rep 2021;11:4677.
- [139] Phillips R, Dunnill C. Zero Gap Cell Design for Alkaline Electrolysis. 2019.
- [140] Đukić A, Firak M. Hydrogen production using alkaline electrolyzer and photovoltaic (PV) module. Int J Hydrogen Energy 2011;36:7799–806.
- [141] Kovač A, Marciuš D, Budin L. Solar hydrogen production via alkaline water electrolysis. Int J Hydrogen Energy 2019;44:9841–8.
- [142] Amores E, Rodríguez J, Oviedo J, et al. Development of an operation strategy for hydrogen production using solar PV energy based on fluid dynamic aspects. Open Eng 2017;7:141–52.
- [143] Abdelghani-Idrissi S, Colin A. Numerical computation of electrical potential on a gas evolving electrode. Sci Rep 2023;13:1722.
- [144] Hao J, Yang W, Huang Z, et al. Superhydrophilic and Superaerophobic Copper Phosphide Microsheets for Efficient Electrocatalytic Hydrogen and Oxygen Evolution. Adv Mater Interfaces 2016;3:1600236.
- [145] Tiwari P, Tsekouras G, Wagner K, et al. A new class of bubble-free water electrolyzer that is intrinsically highly efficient. Int J Hydrogen Energy 2019;44:23568–79.
- [146] Brussieux C, Viers P, Roustan H, et al. Controlled electrochemical gas bubble release from electrodes entirely and partially covered with hydrophobic materials. Electrochim Acta

2011;56:7194–201.

- [147] Foroughi F, Immanuel Bernäcker C, Röntzsch L, et al. Understanding the Effects of Ultrasound (408 kHz) on the Hydrogen Evolution Reaction (HER) and the Oxygen Evolution Reaction (OER) on Raney-Ni in Alkaline Media. *Ultrason Sonochem* 2022;84:105979.
- [148] Li Y-H, Chen Y-J. The effect of magnetic field on the dynamics of gas bubbles in water electrolysis. *Sci Rep* 2021;11:9346.
- [149] Zhang X, Pan S, Song H, et al. Photothermal effect enables markedly enhanced oxygen reduction and evolution activities for high-performance Zn–air batteries. *J Mater Chem A* 2021;9:19734–40.
- [150] Yin X, Sun G, Song A, et al. A novel structure of Ni-(MoS₂/GO) composite coatings deposited on Ni foam under supergravity field as efficient hydrogen evolution reaction catalysts in alkaline solution. *Electrochim Acta* 2017;249:52–63.
- [151] Xie Q, Zhou D, Li P, et al. Enhancing oxygen evolution reaction by cationic surfactants. *Nano Res* 2019;12:2302–6.
- [152] Bakker MM, Vermaas DA. Gas bubble removal in alkaline water electrolysis with utilization of pressure swings. *Electrochim Acta* 2019;319:148–57.
- [153] He Y, Cui Y, Zhao Z, et al. Strategies for bubble removal in electrochemical systems. *Energy Rev* 2023;2:100015.
- [154] Yin W, Yuan L, Huang H, et al. Strategies to accelerate bubble detachment for efficient hydrogen evolution. *Chinese Chem Lett* 2023:108351.
- [155] Darband GB, Aliofkhazraei M, Shanmugam S. Recent advances in methods and technologies for enhancing bubble detachment during electrochemical water splitting. *Renew Sustain Energy Rev* 2019;114:109300.
- [156] Hodges A, Hoang AL, Tsekouras G, et al. A high-performance capillary-fed electrolysis cell promises more cost-competitive renewable hydrogen. *Nat Commun* 2022;13:1304.
- [157] Zhang H, Lin G, Chen J. Evaluation and calculation on the efficiency of a water electrolysis system for hydrogen production.

Int J Hydrogen Energy 2010;35:10851–8.

- [158] Grimes PG, Bellows RJ. Shunt Current Control Methods In Electrochemical Systems — Applications BT - Electrochemical Cell Design. In: White RE, editor., Boston, MA: Springer US; 1984, p. 277–92.
- [159] Bennett WR, Hoberecht MA, Lvovich VF. Analysis of shunt currents and associated corrosion of bipolar plates in PEM fuel cells. J Electroanal Chem 2015;737:162–73.
- [160] Monk N, Watson S. Review of pulsed power for efficient hydrogen production. Int J Hydrog Energy 2016;41:7782–91.
- [161] Liu T, Wang J, Yang X, et al. A review of pulse electrolysis for efficient energy conversion and chemical production. J Energy Chem 2021;59:69–82.
- [162] David M, Ocampo-Martínez C, Sánchez-Peña R. Advances in alkaline water electrolyzers: A review. J Energy Storage 2019;23:392–403.
- [163] Mazloomi K, Sulaiman N. Influencing factors of water electrolysis electrical efficiency. Renew Sust Energ Rev 2012;16:4257–63.
- [164] Burton NA, Padilla R V, Rose A, et al. Increasing the efficiency of hydrogen production from solar powered water electrolysis. Renew Sustain Energy Rev 2021;135:110255.
- [165] Rocha F, de Radiguès Q, Thunis G, et al. Pulsed water electrolysis: A review. Electrochim Acta 2021;377:138052.
- [166] Mazloomi K, Sulaiman N. Efficiency Enhancement of PWM Controlled Water Electrolysis Cells. Int J Electron Commun 2011;5:198–202.
- [167] Mazloomi K, Sulaiman N, Moayedi H. Electrical Efficiency of Electrolytic Hydrogen Production. Int J Electrochem Sc 2012;7:3314–26.
- [168] Mazloomi K, Sulaiman N, Moayedi H. An Investigation into the Electrical Impedance of Water Electrolysis Cells – With a View to Saving Energy. Int J Electrochem Sc 2012.
- [169] Mazloomi K, Sulaiman N, Ahmad SA, et al. Analysis of the frequency response of a water electrolysis cell. Int J Electrochem

Sci 2013;8:3731–9.

- [170] Mazloomi K, Sulaiman N. Retarding Forces Cancellation in Electrolyte Solutions - An Electrical Approach. *Int J App Electron Phys Robot* 2013;1.
- [171] Martiningsih W, Alfanz R, Akbar MA, et al. Effect of PWM Signal on Hydrogen Production Using Hoffman Voltameter Methods. *Adv Sci Lett* 2017;23:11897–901.
- [172] Demir N, Kaya MF, Albawabiji MS. Effect of pulse potential on alkaline water electrolysis performance. *Int J Hydrog Energy* 2018;43:17013–20.
- [173] Huang C. Solar hydrogen production via pulse electrolysis of aqueous ammonium sulfite solution. *Sol Energy* 2013;91:394–401.
- [174] Lin M-Y, Hourng L-W. Effects of magnetic field and pulse potential on hydrogen production via water electrolysis. *Int J Energy Res* 2014;38:106–16.
- [175] Al-Hasnawi DMH. Experimental Study of Wave Shape and Frequency of the Power Supply on the Energy Efficiency of Hydrogen Production by Water Electrolysis. *Int J Innov Res Sci Eng Technol* 2015;4:12239–50.
- [176] de Radiguès Q, Thunis G, Proost J. On the use of 3-D electrodes and pulsed voltage for the process intensification of alkaline water electrolysis. *Int J Hydrog Energy* 2019;44:29432–40.
- [177] Singh A, Ahamad I, Quraishi MA. Piper longum extract as green corrosion inhibitor for aluminium in NaOH solution. *Arab J Chem* 2016;9:S1584–9.
- [178] Katsoufis P, Doukas E, Politis C, et al. Enhanced rate of hydrogen production by corrosion of commercial aluminum. *Int J Hydrogen Energy* 2020;45:10729–34.
- [179] Trasatti S. Work function, electronegativity, and electrochemical behaviour of metals: III. Electrolytic hydrogen evolution in acid solutions. *J Electroanal Chem Interfacial Electrochem* 1972;39:163–84.
- [180] Vanags M, Shipkovs P, Kleperis J, et al. Water Electrolyses - Unconventional Aspects. *IHEC 2007 Sel. Artic. Hydrog. Phenom.*

from 2nd Int. Hydrog. Energy Congr. 2007 Jul 13-15; Istanbul, Turkey, Izmit: Umuttepe Yayinlari; 2009, p. 39–45.

- [181] Shimizu N, Hotta S, Sekiya T, et al. A novel method of hydrogen generation by water electrolysis using an ultra-short-pulse power supply. *J Appl Electrochem* 2006;36:419–23.
- [182] Hristova D, Betova I, Tzvetkoff T. An electrochemical and analytical characterization of surface films on AISI 316 as electrode material for pulse electrolysis of water. *Int J Hydrog Energy* 2013;38:8232–43.
- [183] Siracusano S, Trocino S, Briguglio N, et al. Analysis of performance degradation during steady-state and load-thermal cycles of proton exchange membrane water electrolysis cells. *J Power Sources* 2020;468:228390.
- [184] Rakousky C, Reimer U, Wippermann K, et al. An analysis of degradation phenomena in polymer electrolyte membrane water electrolysis. *J Power Sources* 2016;326:120–8.
- [185] Rakousky C, Reimer U, Wippermann K, et al. Polymer electrolyte membrane water electrolysis: Restraining degradation in the presence of fluctuating power. *J Power Sources* 2017;342:38–47.
- [186] Dobó Z, Palotás ÁB. Impact of the current fluctuation on the efficiency of Alkaline Water Electrolysis. *Int J Hydrog Energy* 2016.
- [187] Frensch SH, Fouda-Onana F, Serre G, et al. Influence of the operation mode on PEM water electrolysis degradation. *Int J Hydrogen Energy* 2019;44:29889–98.
- [188] Xia Y, Cheng H, He H, et al. Efficiency and consistency enhancement for alkaline electrolyzers driven by renewable energy sources. *Commun Eng* 2023;2:22.
- [189] Hu S, Guo B, Ding S, et al. A comprehensive review of alkaline water electrolysis mathematical modeling. *Appl Energy* 2022;327:120099.
- [190] Hnát J, Kodým R, Denk K, et al. Design of a Zero-Gap Laboratory-Scale Polymer Electrolyte Membrane Alkaline Water Electrolysis Stack. *Chemie Ing Tech* 2019;91:821–32.

- [191] Symes MD, Cronin L. Decoupling hydrogen and oxygen evolution during electrolytic water splitting using an electron-coupled-proton buffer. *Nat Chem* 2013;5:403–9.
- [192] Mallouk TE. Divide and conquer. *Nat Chem* 2013;5:362–3.
- [193] Rausch B, Symes MD, Chisholm G, et al. Decoupled catalytic hydrogen evolution from a molecular metal oxide redox mediator in water splitting. *Science* (80-) 2014;345:1326 LP – 1330.
- [194] Chen L, Dong X, Wang Y, et al. Separating hydrogen and oxygen evolution in alkaline water electrolysis using nickel hydroxide. *Nat Commun* 2016;7:11741.
- [195] Bloor LG, Solarska R, Bienkowski K, et al. Solar-Driven Water Oxidation and Decoupled Hydrogen Production Mediated by an Electron-Coupled-Proton Buffer. *J Am Chem Soc* 2016;138:6707–10.
- [196] Jin Z, Li P, Xiao D. A Hydrogen-Evolving Hybrid-Electrolyte Battery with Electrochemical/Photoelectrochemical Charging from Water Oxidation. *Chem Sus Chem* 2017;10:483–8.
- [197] Vincent I, Choi B, Nakoji M, et al. Pulsed current water splitting electrochemical cycle for hydrogen production. *Int J Hydrog Energy* 2018;43.
- [198] Ibl N. Some theoretical aspects of pulse electrolysis. *Surf Technol* 1980;10:81–104.
- [199] Chao H-J, Xue D, Jiang W, et al. A low-voltage pulse electrolysis method for the degradation of anthraquinone and azo dyes in chloride medium by anodic oxidation on Ti/IrO₂-RuO₂-SnO₂ electrodes. *Water Environ Res* 2020;92:779–88.
- [200] Othmani A, Kesraoui A, HaneneAkrou, et al. Coupling anodic oxidation, biosorption and alternating current as alternative for wastewater purification. *Chemosphere* 2020;249:126480.
- [201] Pei S, You S, Zhang J. Application of Pulsed Electrochemistry to Enhanced Water Decontamination. *ACS ES&T Eng* 2021;1:1502–8.
- [202] Jiang Z, Cheng Z, Yan C, et al. Simultaneous Removal of Nitrogen and Refractory Organics from a Biologically Treated Leachate by Pulse Electrochemical Oxidation in a Multi-channel

- Flow Reactor. ACS Omega 2021;6:25539–50.
- [203] Wang X, Tang R, Chen Z, et al. Influence of pulse current on the electrodeposition behaviors of CaCO_3 scale in the industrial circulating water system. Desalination 2023;554:116495.
- [204] AGFA. Technical Data Sheet ZIRFON PERL UTP 500 2020:3–5.
- [205] Garcia-Herrero I, Alvarez-Guerra M, Irabien A. Electrosynthesis of dimethyl carbonate from methanol and CO_2 using potassium methoxide and the ionic liquid [bmim][Br] in a filter-press cell: a study of the influence of cell configuration. J Chem Technol Biotechnol 2016;91:507–13.
- [206] Fuel Cell Store. Technical Data Sheet - fumapesp FAA-3-PK-130.
- [207] Herranz D, Escudero-Cid R, Montiel M, et al. Poly (vinyl alcohol) and poly (benzimidazole) blend membranes for high performance alkaline direct ethanol fuel cells. Renew Energy 2018;127:883–95.
- [208] Chambers JM. Graphical methods for data analysis. CRC Press; 2018.
- [209] Ramenatte N, Vernouillet A, Mathieu S, et al. A comparison of the high-temperature oxidation behaviour of conventional wrought and laser beam melted Inconel 625. Corros Sci 2020;164:108347.
- [210] Oh K, Lee E, Bae JS, et al. Large scale production and applications of alloy metal foam. Proc. 7th Int. Conf. Porous Met. Met. Foam. MetFoam, 2011.
- [211] Zankowski SP, Vereecken PM. Electrochemical Determination of Porosity and Surface Area of Thin Films of Interconnected Nickel Nanowires. J Electrochem Soc 2019;166:D227–35.
- [212] Razmjooei F, Farooqui A, Reissner R, et al. Elucidating the Performance Limitations of Alkaline Electrolyte Membrane Electrolysis: Dominance of Anion Concentration in Membrane Electrode Assembly. ChemElectroChem 2020;7:3951–60.
- [213] Constant M, Dubois F, Lambrechts J, et al. Implementation of an unresolved stabilised FEM–DEM model to solve immersed

- granular flows. *Comput Part Mech* 2019;6:213–26.
- [214] Le Bideau D, Mandin P, Benbouzid M, et al. Review of necessary thermophysical properties and their sensitivities with temperature and electrolyte mass fractions for alkaline water electrolysis multiphysics modelling. *Int J Hydrogen Energy* 2019;44:4553–69.
- [215] Ouda M, Al-Ketan O, Sreedhar N, et al. Novel static mixers based on triply periodic minimal surface (TPMS) architectures. *J Environ Chem Eng* 2020;8:104289.
- [216] Innocentini MDM, Salvini VR, Macedo A, et al. Prediction of ceramic foams permeability using Ergun's equation. *Mater Res* 1999;2:283–9.
- [217] Liu JF, Wu WT, Chiu WC, et al. Measurement and correlation of friction characteristic of flow through foam matrixes. *Exp Therm Fluid Sci* 2006;30:329–36.
- [218] Cossar E, Houache MSE, Zhang Z, et al. Comparison of electrochemical active surface area methods for various nickel nanostructures. *J Electroanal Chem* 2020;870:114246.
- [219] van Drunen J, Kinkead B, Wang MCP, et al. Comprehensive Structural, Surface-Chemical and Electrochemical Characterization of Nickel-Based Metallic Foams. *ACS Appl Mater Interfaces* 2013;5:6712–22.
- [220] Chatzichristodoulou C, Leuaa P, Kraglund MR. Integration of Reference Electrodes in Zero-Gap Alkaline Electrolysis Cells for the Deconvolution of Reaction Overpotentials and Ionic Transport Losses Across the Anode, Cathode, and Separator. 4th Int. Conf. Electrolysis, Sun City: 2023.
- [221] Weininger JL, Breiter MW. Hydrogen Evolution and Surface Oxidation of Nickel Electrodes in Alkaline Solution. *J Electrochem Soc* 1964;111:707.
- [222] Lasia A, Rami A. Kinetics of hydrogen evolution on nickel electrodes. *J Electroanal Chem Interfacial Electrochem* 1990;294:123–41.
- [223] Ulazia A, Sáenz J, Ibarra-Berastegi G, et al. Global estimations of wind energy potential considering seasonal air density changes. *Energy* 2019;187:115938.

- [224] LeRoy RL, Bowen CT, LeRoy DJ. The Thermodynamics of Aqueous Water Electrolysis. *J Electrochem Soc* 1980;127:1954.
- [225] Grdeń M, Alsabet M, Jerkiewicz G. Surface Science and Electrochemical Analysis of Nickel Foams. *ACS Appl Mater Interfaces* 2012;4:3012–21.
- [226] Zheng W, Liu M, Lee LYS. Best Practices in Using Foam-Type Electrodes for Electrocatalytic Performance Benchmark. *ACS Energy Lett* 2020;5:3260–4.
- [227] Hu X, Liu M, Huang Y, et al. Sulfonate-functionalized polybenzimidazole as ion-solvating membrane toward high-performance alkaline water electrolysis. *J Memb Sci* 2022;663:121005.
- [228] Schalenbach M, Tjarks G, Carmo M, et al. Acidic or Alkaline? Towards a New Perspective on the Efficiency of Water Electrolysis. *J Electrochem Soc* 2016;163:F3197.
- [229] Phillips R, Edwards A, Rome B, et al. Minimising the ohmic resistance of an alkaline electrolysis cell through effective cell design. *Int J Hydrogen Energy* 2017;42:23986–94.
- [230] Ju W, Heinz MVF, Pusterla L, et al. Lab-Scale Alkaline Water Electrolyzer for Bridging Material Fundamentals with Realistic Operation. *ACS Sustain Chem Eng* 2018;6:4829–37.
- [231] Lee JW, Lee JH, Lee C, et al. Cellulose nanocrystals–blended zirconia/polysulfone composite separator for alkaline electrolyzer at low electrolyte contents. *Chem Eng J* 2022;428:131149.
- [232] Karacan C, Lohmann-Richters FP, Keeley GP, et al. Challenges and important considerations when benchmarking single-cell alkaline electrolyzers. *Int J Hydrogen Energy* 2022;47:4294–303.
- [233] Lopata JS, Kang S-G, Cho H-S, et al. Investigating influence of geometry and operating conditions on local current, concentration, and crossover in alkaline water electrolysis using computational fluid dynamics. *Electrochim Acta* 2021;390:138802.
- [234] Kim S, Han JH, Yuk J, et al. Highly selective porous separator with thin skin layer for alkaline water electrolysis. *J Power Sources* 2022;524:231059.
- [235] Ali MF, Lee HI, Bernäcker CI, et al. Zirconia Toughened

Alumina-Based Separator Membrane for Advanced Alkaline Water Electrolyzer. *Polymers (Basel)* 2022;14.

- [236] Deng X, Yang F, Li Y, et al. Quantitative study on gas evolution effects under large current density in zero-gap alkaline water electrolyzers. *J Power Sources* 2023;555:232378.
- [237] Angulo AE, Frey D, Modestino MA. Understanding Bubble-Induced Overpotential Losses in Multiphase Flow Electrochemical Reactors. *Energy & Fuels* 2022;36:7908–14.
- [238] Wang J. Theory and practice of flow field designs for fuel cell scaling-up: A critical review. *Appl Energy* 2015;157:640–63.
- [239] Rocha F, Delmelle R, Georgiadis C, et al. Effect of pore size and electrolyte flow rate on the bubble removal efficiency of 3D pure Ni foam electrodes during alkaline water electrolysis. *J Environ Chem Eng* 2022;10:107648.
- [240] Haverkort JW, Rajaei H. Voltage losses in zero-gap alkaline water electrolysis. *J Power Sources* 2021;497:229864.
- [241] Bear J, Bachmat Y. Introduction to modeling of transport phenomena in porous media. vol. 4. Springer Science & Business Media; 2012.
- [242] Meinicke S, Möller C-O, Dietrich B, et al. Experimental and numerical investigation of single-phase hydrodynamics in glass sponges by means of combined μ PIV measurements and CFD simulation. *Chem Eng Sci* 2017;160:131–43.
- [243] Zafari M, Panjepour M, Davazdah Emami M, et al. Microtomography-based numerical simulation of fluid flow and heat transfer in open cell metal foams. *Appl Therm Eng* 2015;80:347–54.
- [244] Ranut P, Nobile E, Mancini L. Microtomography-based CFD Analysis of Transport in Open-Cell Aluminum Metal Foams. *J Phys Conf Ser* 2014;501:12021.
- [245] Sadeghi M, Mirdrikvand M, Pesch GR, et al. Full-field analysis of gas flow within open-cell foams: comparison of micro-computed tomography-based CFD simulations with experimental magnetic resonance flow mapping data. *Exp Fluids* 2020;61:124.
- [246] Kuhlmann K, Sinn C, Siebert JMU, et al. From μ CT data to CFD:

- an open-source workflow for engineering applications. *Eng Appl Comput Fluid Mech* 2022;16:1706–23.
- [247] Schiller G, Henne R, Borck V. Vacuum plasma spraying of high-performance electrodes for alkaline water electrolysis. *J Therm Spray Technol* 1995;4:185–94.
- [248] De Nora electrodic package for Alkaline Water Electrolysis 2016.
- [249] Ansar A, Reissner R, Aguiar D, et al. Raney-nickel alloy electrodes for alkaline water electrolysis. *Int. Conf. Electrolysis (ICE)*, Copenhagen, DTU, Copenhagen, 2017.
- [250] Yu S, Sun J, Bai J. Investigation of functionally graded TPMS structures fabricated by additive manufacturing. *Mater Des* 2019;182:108021.
- [251] Thomas N, Sreedhar N, Al-Ketan O, et al. 3D printed triply periodic minimal surfaces as spacers for enhanced heat and mass transfer in membrane distillation. *Desalination* 2018;443:256–71.
- [252] Sreedhar N, Thomas N, Al-Ketan O, et al. 3D printed feed spacers based on triply periodic minimal surfaces for flux enhancement and biofouling mitigation in RO and UF. *Desalination* 2018;425:12–21.
- [253] Van Bael S, Kerckhofs G, Moesen M, et al. Micro-CT-based improvement of geometrical and mechanical controllability of selective laser melted Ti₆Al₄V porous structures. *Mater Sci Eng A* 2011;528:7423–31.
- [254] Fousová M, Vojtěch D, Doubrava K, et al. Influence of Inherent Surface and Internal Defects on Mechanical Properties of Additively Manufactured Ti₆Al₄V Alloy: Comparison between Selective Laser Melting and Electron Beam Melting. *Materials (Basel)* 2018;11.
- [255] Milton S, Morandeau A, Chalon F, et al. Influence of Finish Machining on the Surface Integrity of Ti₆Al₄V Produced by Selective Laser Melting. *Procedia CIRP* 2016;45:127–30.
- [256] Jain S, Corliss M, Tai B, et al. Electrochemical polishing of selective laser melted Inconel 718. *Procedia Manuf* 2019;34:239–46.
- [257] Zhao C, Qu N, Tang X. Electrochemical mechanical polishing of

- internal holes created by selective laser melting. *J Manuf Process* 2021;64:1544–62.
- [258] Leary M, Mazur M, Williams H, et al. Inconel 625 lattice structures manufactured by selective laser melting (SLM): Mechanical properties, deformation and failure modes. *Mater Des* 2018;157:179–99.
- [259] Koutiri I, Pessard E, Peyre P, et al. Influence of SLM process parameters on the surface finish, porosity rate and fatigue behavior of as-built Inconel 625 parts. *J Mater Process Technol* 2018;255:536–46.
- [260] Iyer J, Moore T, Nguyen D, et al. Heat transfer and pressure drop characteristics of heat exchangers based on triply periodic minimal and periodic nodal surfaces. *Appl Therm Eng* 2022;209:118192.
- [261] Santos J, Pires T, Gouveia BP, et al. On the permeability of TPMS scaffolds. *J Mech Behav Biomed Mater* 2020;110:103932.
- [262] Xu HG, Zhang XY, Ding Y, et al. Rational Design of Hydrogen Evolution Reaction Electrocatalysts for Commercial Alkaline Water Electrolysis. *Small Struct* 2023;n/a:2200404.
- [263] Hourng L-W, Wu W-H, Lin M-Y. The improvement of water electrolysis efficiency by using acid-alkaline electrolysis with multi-electrode and pulsed current. *Eng. Innov. Des.*, London: CRC Press; 2019, p. 143–7.
- [264] Dresp S, Ngo Thanh T, Klingenhof M, et al. Efficient direct seawater electrolyzers using selective alkaline NiFe-LDH as OER catalyst in asymmetric electrolyte feeds. *Energy Environ Sci* 2020;13:1725–9.
- [265] Vanags M, Kleperis J, Bajars G. Water electrolysis with inductive voltage pulses. *Electrolysis*, IntechOpen; 2012.
- [266] Kim S, Lee C-W. A Review on Manufacturing and Application of Open-cell Metal Foam. *Procedia Mater Sci* 2014;4:305–9.