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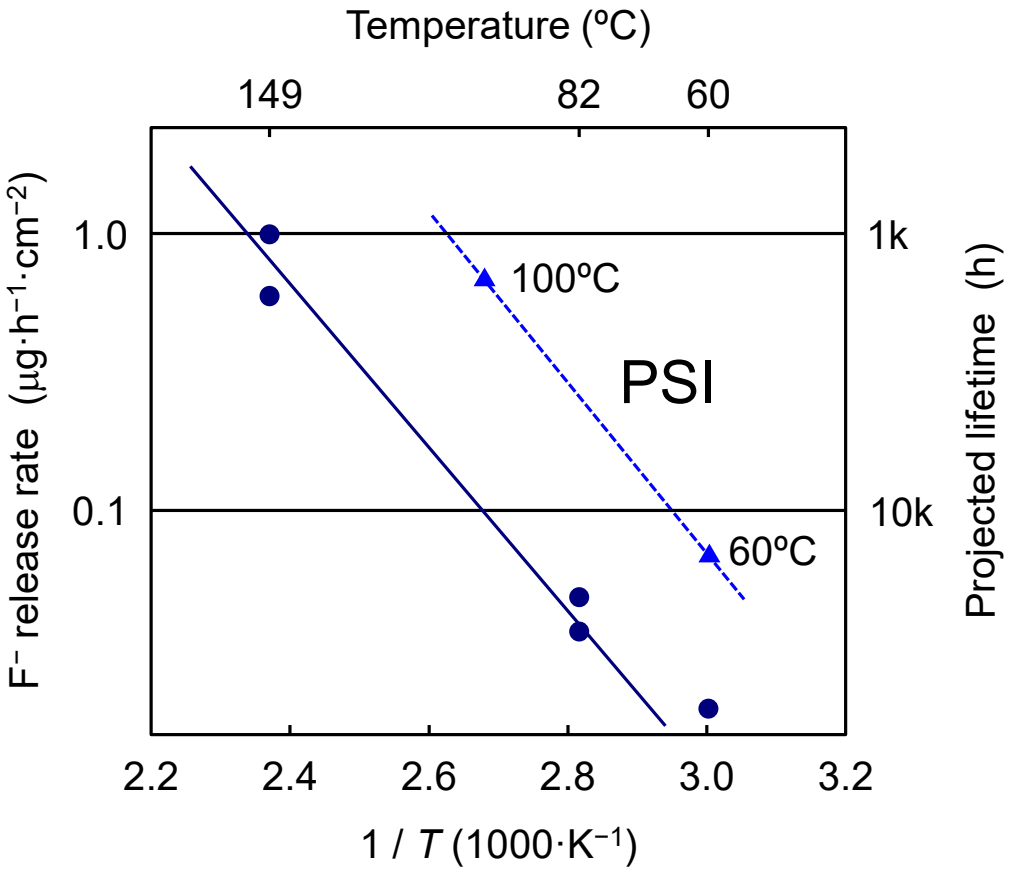
Final report

ELY-TEMP

Polymer electrolyte water electrolysis at elevated temperature for reduced cost of hydrogen for energy applications



Influence of temperature on the rate of membrane degradation in a polymer electrolyte water electrolyzer, represented in an Arrhenius diagram. Here, commercial Nafion™ membranes were used, which release fluoride ions, F−, during chemical degradation. The projected lifetime corresponds to a loss of 10% of the fluoride inventory of the membrane. Data obtained at PSI in this project and data reported in the literature (ECS Trans. 1(8), 2006, 199) show the same activation energy. (Source: ©PSI 2021)

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Summary

Decarbonization of the energy system across different sectors (Power-to-X) relies heavily on the availability of low-cost hydrogen produced from renewable power by water electrolysis. The increase in conversion efficiency of H_2 production in a polymer electrolyte water electrolyte (PEWE) is imperative to lower the cost of green hydrogen to be competitive to blue and grey hydrogen in industrial applications and mobility. In this project, we demonstrated that the efficiency of H_2 production on the cell-level can be increased by 14% at a current density of 3 A/cm^2 using a thin (50 μm) standard membrane material (Nafion™) and an elevated operating temperature of 120°C. The increased gas crossover can be successfully mitigated through the incorporation of a Pt gas recombine catalyst into the membrane at a loading of 0.06 mg(Pt)/cm^2. Elevated temperature operation, however, comes at the cost of an increased rate of membrane degradation, leading to projected cell lifetime that is a tenfold lower at 100°C than at today's standard operating temperature 60°C. This calls for the further development of membrane materials for water electrolysis applications.

Zusammenfassung

Szenarien zur Dekarboniserung des Energiesystems im Rahmen von Power-to-X basieren zu einem wesentlichen Teil auf der Verfügbarkeit von elektrolytisch aus Wasser hergestelltem, kostengünstigem Wasserstoff unter der Verwendung von Strom aus erneuerbaren Quellen. Eine Erhöhung des Umwandlungswirkungsgrades in Polymerelektrolyt-Wasserelektrolyseuren ist unabdingbar, um grünen Wasserstoff zu erzeugen, welcher bezüglich Kosten konkurrenzfähig ist mit blauem und grauem Wasserstoff für Anwendung in Industrie und Mobilität. Im Rahmen dieses Projektes konnte gezeigt werden, dass mit der Verwendung von dünnen Membranen (50 μm) aus kommerziellem Ionomer (Nafion™) und einer erhöhten Betriebstemperatur von 120°C der Wirkungsgrad bei einer Stromdichte von 3 A/cm^2 um 14% erhöht werden kann. Der erhöhte Gasdurchtritt kann durch Einbringen von Pt-Nanopartikeln in die Membran als Rekombinationskatalysator mit einer Beladung von 0.06 mg(Pt)/cm^2 deutlich verringert werden. Erhöhte Temperaturen bringen jedoch eine verringerte Lebensdauer der Membran mit sich. Die erwartete Lebensdauer sinkt bei einer Erhöhung der Temperatur von heute 60°C auf 100°C um einen Faktor 10. Dies verlangt nach weiterer Forschung auf dem Gebiet der Membranmaterialien für die Wasserelektrolyse.

Résumé

Les scénarios de décarbonisation du système énergétique dans le cadre de Power-to-X reposent en grande partie sur la disponibilité d'hydrogène produit par électrolyse de l'eau à un prix avantageux, en utilisant de l'électricité issue de sources renouvelables. Une augmentation de l'efficacité de conversion dans les électrolyseurs d'eau à électrolyte polymère est indispensable pour produire de l'hydrogène vert qui soit compétitif en termes de coûts avec l'hydrogène bleu et gris utilisé dans l'industrie et la mobilité. Dans le cadre de ce projet, il a été démontré que l'utilisation de membranes minces (50 μm) en ionomère commercial (Nafion™) et une température de fonctionnement élevée de 120°C permettent d'augmenter le rendement de 14% pour une densité de courant de 3 A/cm2. L'augmentation du perméabilité des gaz peut être considérablement réduite en introduisant des nanoparticules de Pt dans la membrane comme catalyseur de recombinaison avec une charge de 0,06 mg(Pt)/cm^2. Des températures plus élevées entraînent toutefois une réduction de la durée de vie de la membrane. La durée de vie attendue diminue d'un facteur 10 lorsque la température passe de 60°C aujourd'hui à 100°C. Cela nécessite de poursuivre les recherches dans le domaine des matériaux membranaires pour l'électrolyse de l'eau.

Main findings

- Cell performance and, thus, H_2 production efficiency using state-of-the-art components can be significantly improved by using thinner membranes and higher operating temperatures.
- An increase in the operating temperature from 60 to 100°C leads to a tenfold reduction of the projected membrane and electrolyzer lifetime.
- The incorporation of a recombination catalyst into the membrane leads to a lower gas crossover and therefore allows the dynamic operation of an electrolyzer over a wider load range.
- Next generation membranes for electrolyzers need to contain radical scavengers to increase lifetime.

Contents

Abbreviations

CCM	Catalyst Coated Membrane
PEM	Proton Exchange Membrane
PEWE	Polymer Electrolyte Water Electrolysis / Electrolyzer
PTL	Porous Transport Layer

1 Introduction

1.1 Background information and current situation

Water electrolysis forms a core technology in many Power-to-X scenarios. For applications with variable electricity input and with frequent periods of idling or shutdown, low temperature water electrolysis using membrane technology offers distinct advances over other electrolyzer technologies in terms of responsiveness, attainable current density, and possibility of differential pressure operation. The reduction of the production cost of hydrogen is essential for the technology to be economically viable in providing fuel (hydrogen or, after methanation, synthetic natural gas) for mobility applications or for the chemical or heavy industry.

In Switzerland, electricity generation based on hydroelectric and nuclear power is largely CO_2 free, and the Federal Energy Strategy (Energiestrategie des Bundes) envisions a replacement of the nuclear power plants by power generation from renewables, mainly photovoltaics, wind and biomass, along with energy imports. However, the use of oil and gas for transport, heating and industrial processes accounts for about 70 % of final energy consumption of 230 TWh today. Therefore, since the potential for biomass based energy is limited to around 100 PJ = 28 TWh, Power-to-X is a necessary route to translate low-carbon energy from power generation to the other sectors.

1.2 Purpose of the project

Future economic prospects of Power-to-X and penetration of the energy market by large polymer electrolyte water electrolysis (PEWE) systems will largely be determined by the cost of the hydrogen produced. Hydrogen cost is composed of operating expenditure (opex), which is dominated by the cost of electricity, and investment cost (capital expenditure, capex) comprising stack, power electronics, gas cleaning installation and other up-front costs. Today's cost of electrolytically produced hydrogen of ~7 CHF/kg is in the range required for mobility applications to compete with gasoline fueled cars on a cost per driven kilometer basis. However, the cost of hydrogen produced by steam methane reforming is ~4 CHF/kWh, which is the relevant comparison for the use in industrial processes. Therefore, to widen the applicability of green hydrogen and to render P2X concepts economically viable, the cost of electrolytically produced hydrogen needs to be significantly reduced.

1.3 Objectives

The aim of this project is to study the prospects of increasing the operating temperature of polymer electrolyte water electrolyzers to 90-95°C and introduce relevant modifications of key cell components, in particular the proton exchange membrane, to enable cost reduction of the produced hydrogen by increasing the cell current density and / or improve the efficiency by reducing the cell voltage. The challenges of chemical and mechanical stability of the membrane under the more demanding conditions will be investigated and approaches for mitigating lifetime limitations identified and implemented.

2 Procedures and methodology

A specific aim of this project was to enable operation of a single cell water electrolyzer up to a temperature of 90 to 95°C. This required the modification of the test bench. In particular, it necessitated the introduction of an anode water feed loop with two temperature levels, as the chemical stability of the ion-exchange resin used in the loop to maintain water quality significantly decreases above 60°C. Therefore, an electric heater was implemented, with which the feed water could be heated to 120°C (at elevated pressure) (**Figure 1a**). The product gas on the anode side (oxygen with percent level hydrogen) was separated from the effluent water in a gas-water separator, and the water was subsequently cooled down to 40°C or below in a heat exchanger and fed to the ion-exchange bed.

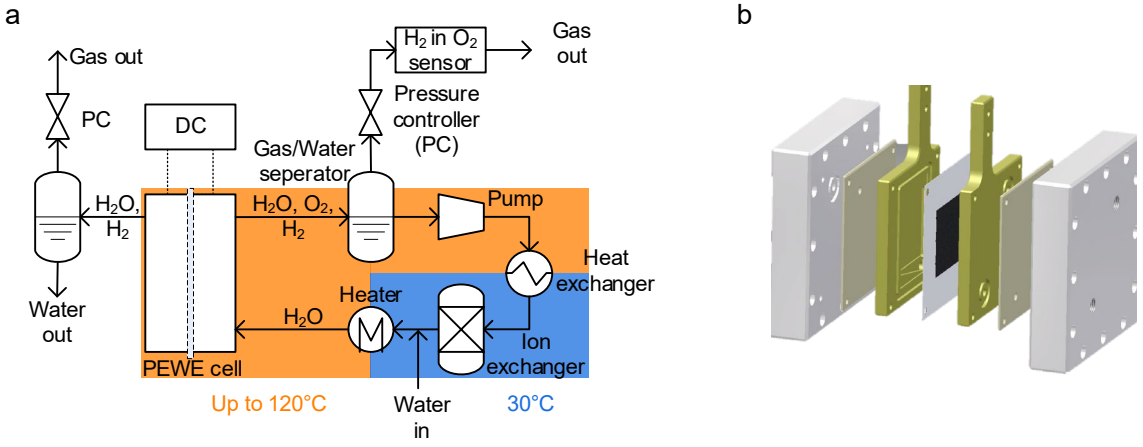

Figure 1. a) Schematic of the electrolyzer testbench with two temperature levels for elevated temperature operation of up to 120 °C. EH = electrical heater, GW = gas-water separator, HE = heat exchanger, IE = ion exchanger, P = pump, PC = pressure controller. b) Sketch of the new 25 cm2 water electrolysis single cell designed in-house, allowing the flexible use of electrochemical components.

Towards the end of the project, a new cell design was devised (**Figure 1b**), based on the experience gained during the project with the cell originally supplied by the Fraunhofer Institut für solare Energiesysteme (ISE) in Freiburg, Germany. Its active area is identical (25 cm^2), but it allows a more flexible use of components for testing and also exerts less mechanical stress on the membrane, which is important in particular in the case of the use of thin membranes.

3 Results and discussion

With the aim of reducing the cost of electrolytically produced hydrogen, the first, seemingly straightforward approach is to lower the operating cell voltage of the water electrolyzer while maintaining a given conversion rate, expressed as current density. The polarization behavior of a water electrolysis cell shows an increase of cell voltage as a function of current density, which indicates increasing deviation from the equilibrium, reversible (=thermodynamically ideal) cell voltage U_{rev}. The voltage increase can be assigned to different loss mechanisms, characterized as overpotentials. In **Figure 2a**, a polarization curve and the respective overpotential breakdown of a state-of-the-art cell is reported at 60°C, a common operating temperature of commercial PEWE stacks. We see that the loss term is dominated at low current densities by the activation / kinetic overpotential η_{kin} of the oxygen evolution reaction (OER). The overpotential of the hydrogen oxidation reaction (HOR) is in fact negligible. At increasing current density, the ohmic losses, which are largely given by the membrane resistance, become appreciable and dominant. Therefore, in the first approach the limitation of existing state-of-the-art cell components was studied by reducing the membrane thickness from 175 µm (Nafion™ 117) to 50 µm (Nafion™ 212), and increasing the operating temperature to 120°C. The resulting polarization curve (**Figure 2b**) is significantly depressed, concomitant with a higher conversion efficiency. In particular, the ohmic losses are considerably lower, but also the OER activaton overpotential due to thermal activation of the reaction. We also note that the reversible voltage decreases with temperature due to the positive reaction entropy.

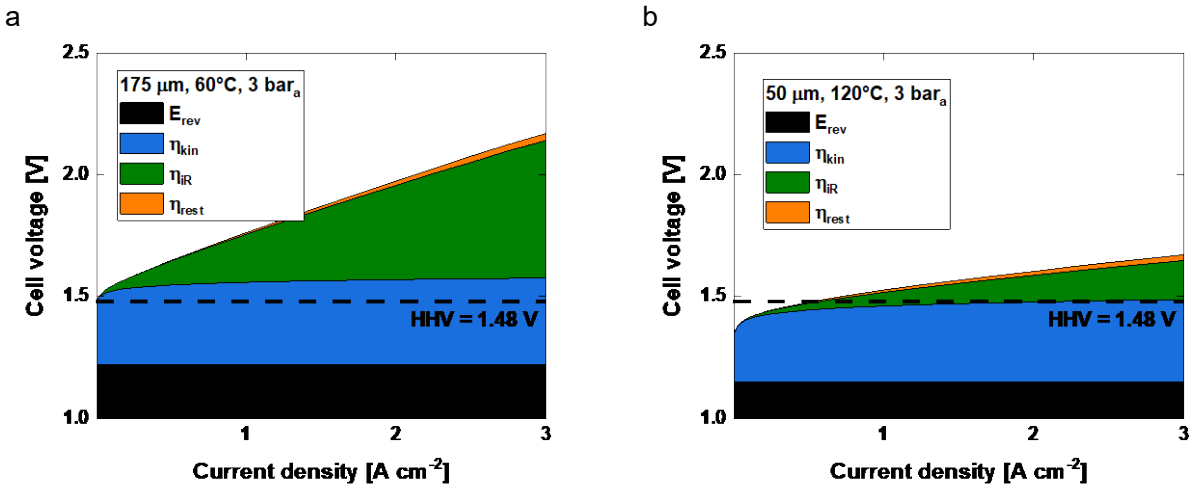

Figure 2. Overpotential breakdown of polarization curves for PEWE single cells, recorded at a balanced pressure of 3 bar$_a$. E_{rev} = reversible cell potential, η_{kin} = kinetic overpotential (dominated by the oxygen evolution reaction, OER), η_{iR} = ohmic overpotential, η_{rest} = residual overpotential. HHV = 1.48 V indicates the thermoneutral voltage given by the higher heating value (HHV) of hydrogen. a) Thick membrane (Nafion™ 117, 175 µm dry thickness), 60°C cell temperature. b) Thin membrane (Nafion™ 212, 50 µm dry thickness), 120°C cell temperature.

The improved cell performance at 120°C using a thin Nafion™ membrane, however, comes at a cost. On the one hand, the degradation rate of the cell components increases with temperature, which leads to a lower expected lifetime of the electrolyzer. On the other hand, gas crossover through the membrane is more pronounced, which can lead to the formation of an explosive gas mixture. The lower explosion limit of H_2 in O_2 is 4 %, hence the safety limit is often defined at 2% H_2 in O_2.

The impact of temperature on the stability of cell components, especially the membrane, was therefore studied in detail. For this, two cells containing a Nafion™ 117 membrane were operated at a constant

current density of 2 A/cm^2 at different cell temperatures: cell 1 was operated at 60°C, cell 2 at 100°C, both at a balanced pressure of 3 bar$_a$. The performance of the two cells was compared at the end of test at a temperature of 60°C. The overpotential breakdown indicates that the ohmic overpotential and the OER activation overpotential show a significant increase of several hundred mV at 2 A/cm^2 for the cell tested at 100°C, whereas the cell operated at 60°C shows negligible change (**Figure 3a**). The increase in OER overpotential can be correlated to the change of the anode catalyst layer thickness. For the sample tested at 100°C, the thickness of the anode catalyst layer decreased on average (**Figure 3b**). This indicates loss or dissolution of active catalyst material.

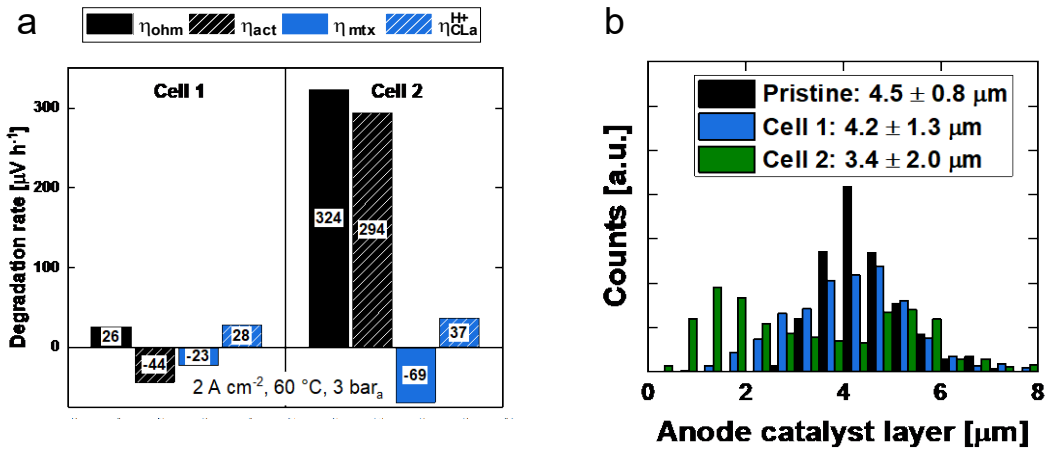

Figure 3. a) Degradation rate assigned to overpotentials for cells operated for 300 h at a temperature of 60°C (Cell 1) and 100°C (Cell 2), respectively. b) Anode catalyst layer thickness distribution obtained from scanning electron microscopy cross-sectional analysis for a pristine sample and the two samples tested for 300 h.

The degradation rate of the membrane was quantified by measuring the fluoride ion concentration in the cathode water loop. The chemical degradation of perfluoroalkylsulfonic acid (PFSA) type membranes, such as Nafion™, is triggered by radical intermediates, which attack the ionomer and lead to the release of fluoride ions into the water. Based on the measured concentration of F− ions in the cathode loop, the fluoride release rate of the membrane in $\mu g \cdot h^{-1} \cdot cm^{-2}$ can be calculated. This is shown on the title page in an Arrhenius-type diagram for the two cells tested at 60 and 100°C. The results are compared with data from the literature [1]. We see that, although the absolute values of the fluoride release rate differ notably, the temperature dependence is almost identical. Membrane degradation increases with temperature with an apparent activation energy of around 60 kJ/mol. This means that the rate of membrane degradation increases by about a tenfold in going from 60 to 100°C operating temperature. Concomitantly, the projected lifetime of an electrolyzer decreases by an order of magnitude if the time to failure is governed by chemical membrane degradation. Therefore, next generation membrane materials must be chemically stabilized to reduce thermal and radical induced aging. Lessons learned from fuell cells can be adopted here, namely the incorporation of radical scavengers in to the membrane [2]. This is the subject of the follow-up project ELY-MAT, which started in 2021 (see below).

The second challenge associated with the use of thin membranes at elevated temperature in PEWE is, as mentioned, the gas crossover. Accumulation of H_2 in the oxygen product stream can be reduced if a recombination catalyst is incorporated into the membrane. The H_2 and O_2 dissolved in the membrane react on the surface of this noble metal catalyst (e.g., Pt) to produce water. Hence the gas escaping to the opposite gas compartment is reduced. It is important to note that recombination catalysts do not improve the faradaic efficiency of the cell, as the gases produced in the electrochemical reaction are

still lost due to recombination. Recombination catalysts are used to reduce the risk of the formation of an explosive gas mixture in the product stream. In the course of this project, we have developed a method of Pt doping of proton exchange membranes, which leads to a uniform distribution of Pt particles in the membrane with a typical particle size of 20-30 nm (**Figure 4**). The method of Pt doping was submitted as a patent application (see below).

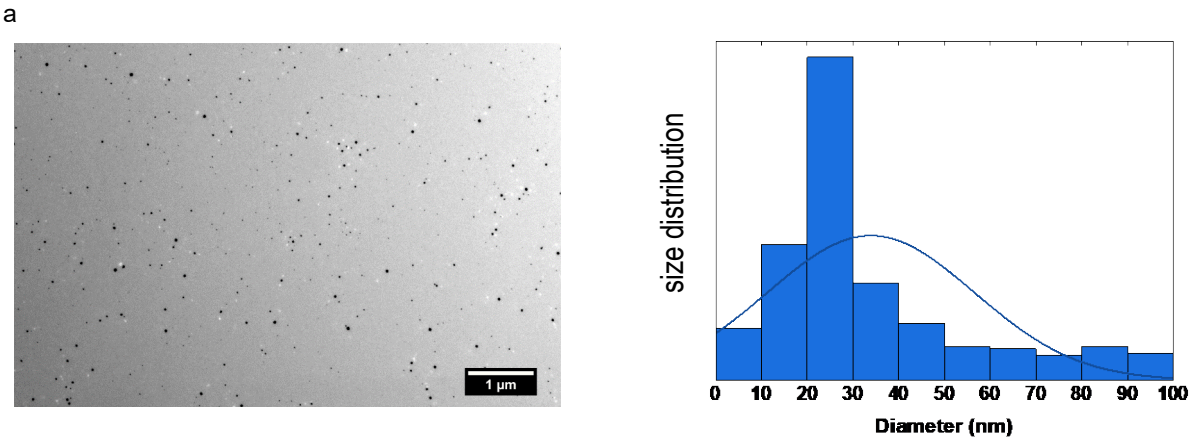

Figure 4. a) Transmission electron microscopy (TEM) image of a Pt doped Nafion™ 212 membrane with a loading of 0.1 mg_{Pt}/cm^2. b) Pt particle size distribution in the membrane obtained from TEM image analysis.

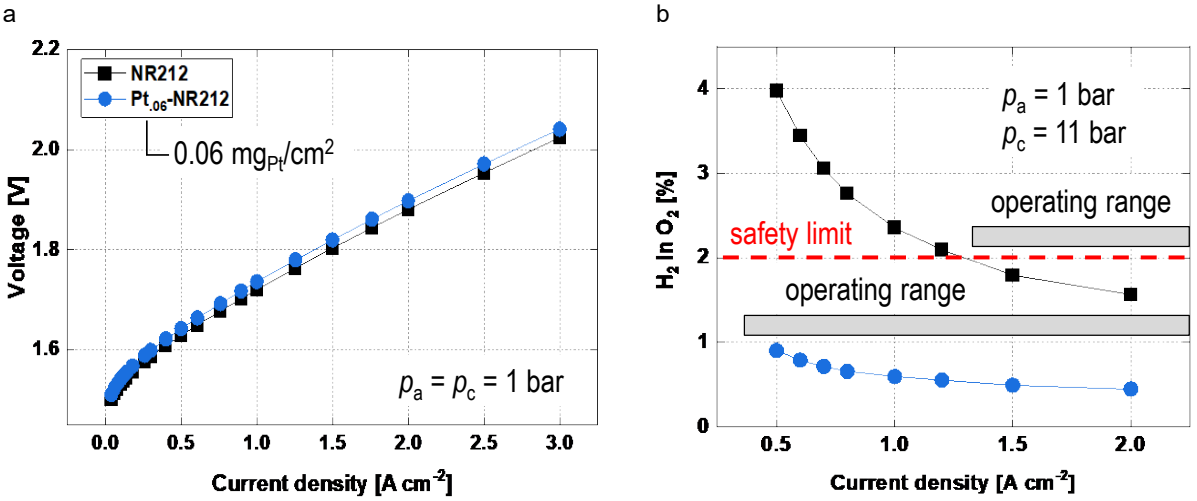

Figure 5. a) Polarization curve recorded at 80°C using a pristine Nafion™ 212 membrane (black symbols) and a Nafion™ 212 membrane doped with Pt recombination catalyst with a loading of 0.06 mg_{Pt}/cm^2. b) Content of H_2 in the O_2 product stream for the same samples. The common technical safety limit of 2% is indicated (the lower explosion limit is at 4%). The grey bars indicate the associated operating range of the cell.

The doping level of Pt as recombination catalyst is below 0.1 mg_{Pt}/cm^2. Therefore, this does not add dramatically to the noble metal use in the electrochemical cell components of a PEWE cell. **Figure 5a** shows the resulting performance of a Pt-doped Nafion™ 212 membrane compared to a pristine membrane. The performance of the two cells is almost identical, the presence of Pt in the membrane does

not lead to a significant change in the ohmic resistance of the membrane. At the same time, the content of H_2 in the O_2 stream is significantly reduced in case of the membrane containing the recombination catalyst (**Figure 5b**). Whereas the safety limit of 2% is exceeded below a current density of 1.3 A/cm^2 in case of the undoped membrane, the operating range of the electrolyzer can be significantly enhanced with the Pt-doped membrane down to below 0.5 A/cm^2. This is important from the point of view of a dynamic operation of a water electrolyzer. If the system is designed to provide grid stabilization services, it needs to be able to operate at different nominal loads. Hence, with a higher turndown ratio, the range of dynamically accessible operating range is enhanced and thus the value of the electrolyzer as a grid stabilizing component increased.

4 Conclusions

The efficiency of hydrogen production in a water electrolyzer can be significantly enhanced using state-of-the-art electrochemical materials by using thinner membranes and increasing the operating temperature from 60 to 100 or 120°C. However, this leads to an increase in the rate of component aging and therefore to a reduction in the projected lifetime of the water electrolyzer by an estimated factor of ten in going from 60 to 100°C. Chemical degradation of the membrane and aging of the anode catalyst layer is a topic of future work required to develop next generation cell components. In addition, gas crossover limits the dynamic operation of an electrolyzer because of the risk of formation of an explosive gas mixture. Therefore, membranes need to be doped with a recombination catalyst. We have developed a method for uniform Pt-doping of membranes, which does not affect cell performance yet significantly reduces H_2 crossover. Therefore, the dynamic operating range of the electrolyzer can be considerably enhanced.

5 Outlook and next steps

The follow-up work to this project is already underway: the project ‘New materials for electrolysis cells and next generation electrochemical water splitting devices (ELY-MAT)’ started in January 2021. The study is focused on next generation membrane materials for electrolyzers. In particular, the objective is to incorporate nano-particles into the membrane to act as recombination catalyst as well as radical scavenger. This is expected to significantly reduce the rate of membrane degradation and push the boundaries of current state-of-the-art materials. In addition to using commonly employed perfluorinated ionomers, such as Nafion™, we also aim to explore hydrocarbon based membranes, as they offer intrinsically improved gas barrier properties and a lower tendency to creep at elevated temperatures.

6 National and international cooperation

The different water electrolysis projects in the Electrochemistry Laboratory at PSI are linked by overarching research questions. Results and key insights are exchanged and discussed formally on a quarterly basis.

We are collaborating with the Max Planck Institute for Solid State Research in Stuttgart on hydrocarbon membranes for water electrolysis. Initial tests using poly(phenylene sulfone) membranes have been performed. The experimental work will be continued in the framework of the follow-up project ELY-MAT, with the aim of a joint publication.

PSI joined a consortium, coordinated by Forschungszentrum Jülich, to prepare a Horizon – European Innovation Council (EIC) proposal for the 'EIC Pathfinder Challenges 2021' call. The proposed study is entitled 'Design of Membrane Electrode Assembly with Hierarchical Structures for H_2 Production (DIMENSION)', the planned duration 48 months.

Furthermore, PSI established a service contract with an industrial partner for the evaluation of membrane-electrode components for water electrolyzers. The scope of the project is around 2 person months.

7 Dissemination

7.1 Peer-reviewed publications

S. Garbe, U. Babic, E. Nilsson, T.J. Schmidt, L. Gubler, "Communication—Pt-Doped Thin Membranes for Gas Crossover Suppression in Polymer Electrolyte Water Electrolysis", Journal of The Electrochemical Society 166 (2019), 13, F873-F875

S. Garbe, J. Futter, T.J. Schmidt, L. Gubler, "Insight into Elevated Temperature and Thin Membrane Application for High Efficiency in Polymer Electrolyte Water Electrolysis", Electrochimica Acta (2021), 138046

S. Garbe, J. Futter, A. Agarwal, M. Tarik, A.A. Mularczyk, T.J. Schmidt, L. Gubler, "Understanding Degradation Effects of Elevated Temperature Operating Conditions in Polymer Electrolyte Water Electrolyzers", Journal of The Electrochemical Society 168 (2021), 044515

S. Garbe, E. Samuelsson, T.J. Schmidt, L. Gubler, "Comparison of Pt-Doped Membranes for Gas Crossover Suppression in Polymer Electrolyte Water Electrolysis", Journal of The Electrochemical Society 168 (2021), 104502

7.2 Conference contributions

(* = presenter)

S. Garbe*, U. Babic, E. Nilsson, T.J. Schmidt, L. Gubler, "Hydrogen Cross-over Suppression in PEWE through Pt-doped Thin Membranes", International Summer School on Power-to-X: Fundamentals and Applications of Modern Electrosynthesis, Villars-sur-Ollon, Switzerland, August 27-31, 2019 (Poster)

S. Garbe*, U. Babic, E. Nilsson, T.J. Schmidt, L. Gubler, "Pt-doped Thin Membranes for Gas Crossover Suppression in Polymer Electrolyte Water Electrolysis", 35th Swiss Electrochemistry Symposium, Aarau, Switzerland, May 22, 2019 (Poster)

S. Garbe*, U. Babic, T.J. Schmidt, L. Gubler, "Pt-doped Thin Membranes for Hydrogen Crossover Suppression in Polymer Electrolyte Water Electrolysis", 2nd International Conference on Electrolysis (ICE), Loen, Norway, June 9-13, 2019 (Poster)

S. Garbe*, T.J. Schmidt, L. Gubler, "Elevated Temperature Proton Exchange Membrane Water Electrolysis for Reduced Cost of Green Hydrogen Production", Pacific Rim Meeting (PRiME), Joint International Meeting of The Electrochemical Society (ECS), The Electrochemical Society of Japan (ECSJ) and The Korean Electrochemical Society (KECS), Symposium I01F - Polymer Electrolyte Fuel Cells & Electrolyzers 20 (PEFC&E 20) - Polymer-Electrolyte Electrolysis, Oct 4 – 9, 2020, Honolulu (HI), USA (held online due to the Covid-19 pandemic), Contribution I01F-2452 (Talk)

S. Garbe, T.J. Schmidt, L. Gubler*, "Towards Thin Membrane Use in Polymer Electrolyte Water Electrolysis Using Pt Recombination Catalyst", 240th Meeting of The Electrochemical Society Meeting, Orlando, Florida (USA) (held online due to the Covid-19 pandemic), October 10-14, 2021 (Talk)

Patent applications

S. Garbe, U. Babic, L. Gubler, T.J. Schmidt, "Method for Preparing a Polymer Membrane for a Polymer Electrolyte Water Electrolyser", Paul Scherrer Institut, European Patent Application No. EP3739678A1 (2019)

8 References

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2. P. Trogadas, J. Parrondo, V. Ramani, "Degradation Mitigation in PEM Fuel Cells Using Metal Nanoparticle and Metal Oxide Additives", in Functional Polymer Nanocomposites for Energy Storage and Conversion, American Chemical Society, 2010, 187-207