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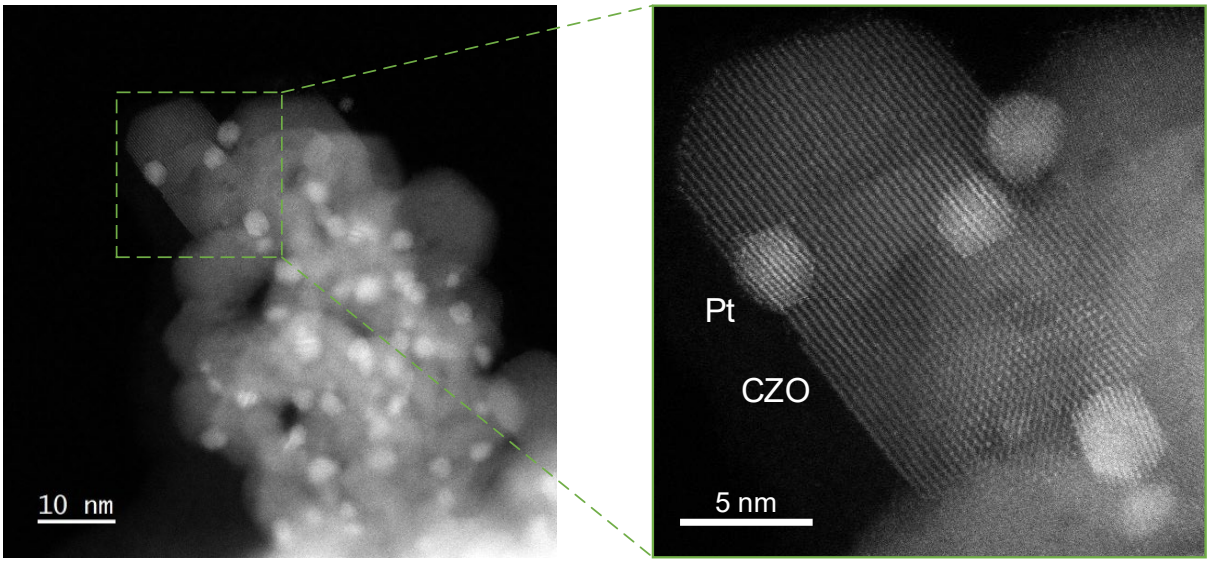
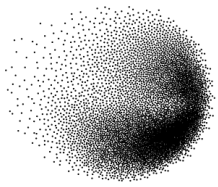
ELY-MAT

New materials for electrolysis cells and next generation electrochemical water splitting devices



High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of bi-functional catalyst $Pt/Ce_{0.25}Zr_{0.75}O_2$ used as additive in the polymer electrolyte membrane of an electrochemical water splitting cell for the reduction of gas crossover and scavenging of radicals: © PSI, 2024



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Summary

Water electrolysis is an anticipated core technology to produce green hydrogen for power-to-X processes. The levelized cost of electrolytically produced hydrogen is determined by the capital expenditure of the electrolyzer and, in particular, electricity cost. Therefore, improvement of the conversion efficiency and durability of cell components is necessary. The aim of the project was to identify and study new electrolyzer components with improved performance and stability, especially at elevated cell temperature, i.e. 90°C. Specifically, strategies for the use of platinum gas recombination and cerium-zirconium oxide (CZO) antioxidant additives in connection with the use of thin perfluorinated membranes (Nafion™ type) with a thickness of ~50 μm were developed. Both additives are essential to ensure safe operation of the cell over a large current density range and obtain membrane lifetimes of several tens of thousands of hours. Since the presence of platinum in the membrane increases the formation of reactive intermediates, which exacerbates membrane degradation, a bifunctional catalyst of Pt supported on CZO was successfully implemented for the first time. Furthermore, we showed that the effectiveness of the recombination catalyst and antioxidant can be maximized when located in defined layers in the membrane close to the cathode and anode, respectively. With the optimized configuration, the projected membrane lifetime is approximately 30’000 h at 90°C, compared to 4’000 h for an undoped membrane. A critical aspect that needs further investigation is the chemical stability of cerium-based oxides, which may be critical for long-term operation of an electrolyzer. In another aspect of the work, the influence of the compositional parameters of the hydrogen electrode was studied, which was shown to be important to minimize hydrogen crossover to the anode side. Overall, this project explores advanced design strategies to mitigate hydrogen crossover and ionomer degradation in catalyst coated proton exchange membranes (PEMs). The findings contribute to the development of next generation PEM water electrolysis cells.

Zusammenfassung

Die Wasserelektrolyse wird als Schlüsseltechnologie zur Erzeugung von grünem Wasserstoff für Power-to-X-Prozesse angesehen. Die Kosten für elektrolytisch erzeugten Wasserstoff werden durch den Investitionsaufwand für den Elektrolyseur und insbesondere durch die Stromkosten bestimmt. Daher ist eine Verbesserung des Umwandlungswirkungsgrads und der Haltbarkeit der Zellkomponenten unumgänglich. Ziel des Projekts war die Erforschung neuer Elektrolyseurkomponenten mit verbesserter Leistung und Stabilität, insbesondere bei erhöhter Zelltemperatur, d.h. 90°C. Konkret wurden Strategien für den Einsatz von Platin Gasrekombinationskatalysatoren und Cer-Zirkonium-Oxid (CZO) als antioxidative Zusätze in Verbindung mit dem Einsatz dünner perfluorierter Membranen (Typ Nafion™) mit einer Dicke von ~50 μm entwickelt. Beide Zusätze sind notwendig, um einen sicheren Betrieb der Zelle über einen großen Stromdichtebereich zu gewährleisten und eine Membranlebensdauer von mehreren zehntausend Stunden zu ermöglichen. Da das Vorhandensein von Platin in der Membran die Bildung reaktiver Zwischenprodukte verstärkt, was die Degradation der Membran beschleunigt, wurde erstmals ein bifunktionaler Katalysator aus CZO-geträgertem Pt erfolgreich eingesetzt. Darüber hinaus wurde gezeigt, dass die Wirksamkeit des Rekombinationskatalysators und des Antioxidations maximiert werden kann, wenn sie in definierten Schichten in der Membran in der Nähe der Kathode bzw. Anode angeordnet sind. Mit einer optimierten Konfiguration beträgt die hochgerechnete Lebensdauer der Membran 30'000 Stunden bei 90°C, im Vergleich zu 4'000 Stunden bei einer undotierten Membran. Ein kritischer Aspekt, der weiter untersucht werden muss, ist die chemische Stabilität von Oxiden auf Cer-Basis, die für den langfristigen Betrieb eines Elektrolyseurs entscheidend sein kann. Ein weiterer Aspekt der Arbeit war die Untersuchung des Einflusses der Zusammensetzung der Wasserstoff-Elektrode, was sich als bedeutend für die Minimierung des Wasserstoffdurchtritts auf die Anodenseite erwiesen hat. Zusammenfassend werden als Ergebnis dieses Projektes Ansätze für die Ausgestaltung von Membrane-Elektrodeneinheiten von Wasserelektrolyseuren vorgeschlagen, um Wasserstoffdurchtritt und Ionomeralterung in katalysatorbeschichteten Protonenaustauschmembranen zu verringern. Die Ergebnisse tragen zur Entwicklung von PEM-Wasserelektrolysezellen der nächsten Generation bei.

Résumé

L'électrolyse de l'eau est une technologie clé attendue pour produire de l'hydrogène vert destiné aux processus « power-to-X ». Le coût actualisé de l'hydrogène produit par électrolyse est déterminé par les dépenses d'investissement de l'électrolyseur et, en particulier, par le coût de l'électricité. Il est donc nécessaire d'améliorer le rendement de conversion et la durabilité des composants des cellules. L'objectif du projet était d'identifier et d'étudier de nouveaux composants d'électrolyseurs offrant des performances et une stabilité améliorées, en particulier à une température élevée de la cellule, c'est-à-dire 90°C. Plus précisément, des stratégies ont été élaborées pour l'utilisation d'additifs antioxydants à base de platine et d'oxyde de cérium-zirconium (CZO) en association avec des membranes perfluorées minces (de type Nafion™) d'une épaisseur d'environ 50 μm. Ces deux additifs sont essentiels pour garantir le fonctionnement sûr de la cellule sur une large plage de densité de courant et obtenir une durée de vie de la membrane de plusieurs dizaines de milliers d'heures. Étant donné que la présence de platine dans la membrane augmente la formation d'intermédiaires réactifs, ce qui aggrave la dégradation de la membrane, un catalyseur bifonctionnel de Pt supporté par du CZO a été mis en œuvre avec succès pour la première fois. De plus, nous avons montré que l'efficacité du catalyseur de recombinaison et de l'antioxydant peut être maximisée lorsqu'ils sont situés dans des couches définies de la membrane, respectivement près de la cathode et de l'anode. Avec cette configuration optimisée, la durée de vie prévue de la membrane est d'environ 30’000 heures à 90°C, contre 4’000 heures pour une membrane non dopée. Un aspect critique qui nécessite des recherches supplémentaires est la stabilité chimique des oxydes à base de cérium, qui peut être déterminante pour le fonctionnement à long terme d'un électrolyseur. Dans un autre aspect du travail, l'influence des paramètres de composition de l'électrode à hydrogène a été étudiée, qui s'est avérée importante pour minimiser le transfert d'hydrogène vers le côté anode. Dans l'ensemble, ce projet explore des stratégies de conception avancées pour atténuer le transfert d'hydrogène et la dégradation des ionomères dans les membranes échangeuses de protons (PEM) recouvertes de catalyseur. Les résultats contribuent au développement de la prochaine génération de cellules d'électrolyse de l'eau PEM.

Main findings («Take-Home Messages»)

- **Next generation electrochemical water splitting devices**: the reduction of the electrolyte membrane thickness for water electrolyzers requires a strategy to manage hydrogen crossover and improve membrane stability.
- **Improved control of hydrogen crossover**: Compositional optimization of the hydrogen electrode and targeted placement of a H_2-O_2 recombination catalyst minimizes hydrogen crossover and ensures safe operation over a wide current density range.
- **Advanced membrane stabilization strategy**: A cerium-zirconium-oxide nanoparticle containing catalyst layer for radical scavenging placed in the thin (~50 µm) Nafion™ membrane near the anode reduced degradation by a factor of 7.5.
- **Contribution to Swiss energy policy**: By enabling more efficient and durable electrolyzers for green hydrogen production, the results support cost reduction of power-to-X technologies and align with Switzerland's energy strategy to expand renewable energy storage and sector coupling.

Contents

List of abbreviations

AEM	Anion Exchange Membrane
AEMWE	Anion Exchange Membrane Water Electrolyzer
CAPEX	Capital Expenditure
CCM	Catalyst Coated Membrane
CL_A	Anode Catalyst Layer
CL_C	Cathode Catalyst Layer
CZO	Cerium-Zirconium Oxide
FRR	Fluoride Release Rate
GDL	Gas Diffusion Layer
HSAC	High Surface Area Carbon
I/C	Ionomer-to-Carbon
OPEX	Operational Expenditure
PEM	Proton Exchange Membrane
PEWE	Polymer Electrolyte Water Electrolysis / Electrolyzer
PFSA	Perfluoroalkylsulfonic Acid
PTL	Porous Transport Layer

1 Introduction

1.1 Context and motivation

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. Reducing the production cost of hydrogen is an essential driver of research & development of cell materials and components.

The membranes and other components used in today's polymer electrolyte water electrolysis (PEWE) technology are largely over-engineered and have not been specifically designed for this application. In particular, the desire to increase operating temperature and reduce the ohmic resistance of the cell by using thin membranes leads to gas crossover issues, which can result in explosive gas mixtures. Furthermore, since the components for water electrolyzers are expected to be durable for several tens of thousands of hours, membranes need a dedicated antioxidant strategy. There is a strong desire by industry for next generation water electrolyzer membranes and membrane electrode assemblies.

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 (green) 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. In order for green hydrogen to be competitive with hydrogen produced by steam methane reforming combined with carbon capture (blue hydrogen), both capex and opex of the electrolyzer have to be improved. This can be achieved by improving the performance and durability of cell components. This project aims to contribute to the development of next generation cell components, in particular composite proton exchange membranes, to tackle this challenge.

1.2 Project objectives

The main objective of this project is to modify existing water electrolyzer components and introduce new material concepts with improved performance and stability, especially at elevated temperature, to improve conversion efficiency. On the one hand, membranes co-doped with recombination catalyst (platinum or palladium) and a radical scavenger based on cerium-zirconium oxide (CZO) is developed and characterized. The positioning of these two dopants is studied based on single cell tests. Furthermore, the structure of the cathode catalyst layer is systematically varied to investigate the effect on the crossover of hydrogen to the oxygen side. A reduction of crossover allows the use of thinner membranes and/or higher operating temperature. Durability studies are performed *ex situ* and *in situ* to determine the projected electrolyzer lifetime.

Specifically, following topics have been tackled with defined measurable output:

- $Ce_xZr_{1-x}O_{2-\delta}$ nanoparticles, optionally decorated with Pt-nanoparticles, are synthesized and incorporated into the proton exchange membrane as catalyst for radical scavenging and, with Pt-decoration, additionally for recombination of H_2 and O_2. The structure and morphology of the particles are characterized by standard laboratory techniques and synchrotron-based methods, with their stability characterized in model acid solutions.
- The particles are incorporated into the membrane in different configurations: i) even distribution throughout the membrane, and ii) deposition as a thin interlayer at specific locations between anode and cathode. The membranes are assembled into a single cell for *in situ* characterization. The improvement of cell performance and component stability will be assessed in comparison with benchmark materials.

- The structure of the cathode catalyst layer is systematically varied to investigate the effect on the crossover of hydrogen to the oxygen side. A reduction of crossover will allow the use of thinner membranes and/or higher operating temperature (up to 120°C).

2 Approach, method, results and discussion

2.1 Procedures and methodology

The synthesis of CZO nanoparticles is carried out in collaboration with Dr. Andrea Testino from the Laboratory for Sustainable Energy Carriers & Processes (LEP) at PSI. In short, the route chosen is a wet chemical process based on co-precipitation of Ce and Zr, followed by drying and calcination to obtain the final oxide. The methods used to characterize the obtained powder, such as XRD and BET, are all available at PSI. Initially, a one-pot polyol method was employed for synthesizing ceria-zirconia and Pt-doped ceria-zirconia nanoparticles. At a later stage, the synthesis process was varied by exploring possible hydrothermal routes to achieve more desirable properties of the nanoparticles, such as reduced particle size and increased specific surface area.

The ionomer used throughout this project is a perfluoroalkylsulfonic acid (PFSA) ionomer, the commercial Nafion™. This is the state-of-the-art electrolyte and ionomer for PEM water electrolysis cells. PFSA ionomers have come under scrutiny recently, owing to their fluorinated nature, in the context of the environmental concerns associated with fluorinated chemicals. Nafion™ is used in this project as it is considered the industry standard, and it is very likely that it will continue to be used in PEM water electrolysis cells in the next couple of years or even decades. In any case, the research topic related to membrane dopants is of generic nature and results could be transferred in straightforward manner to other ionomer types, such as sulfonated aromatic hydrocarbons.

Two different methods are used to prepare the composite membranes containing catalyst nanoparticles. In the first approach, the proton exchange membranes are prepared using a solution casting method from commercial Nafion™ ionomer dispersions. Target thickness is around 50 μm. For doped and co-doped membranes, oxide or Pt-decorated oxide and/or Pt-black nanoparticles are dispersed in the ionomer solution prior to the casting process. After casting, the samples are dried and cured to prevent redissolution of the ionomer when in contact with liquid water. In another approach, a Nafion™ 212 membrane (dry thickness: 50 μm) is used as a substrate and mixtures of Nafion™ ionomer and catalyst nanoparticles are coated on one or both sides of the membrane via ultrasonic spray deposition. The catalyst layers, using carbon-supported Pt and IrO_2-TiO_2 electrocatalyst for cathode and anode, respectively, are subsequently coated onto the (composite) membrane, also by ultrasonic spray-coating, to obtain a catalyst coated membrane (CCM).

Device-level experiments are performed in a single cell with a parallel flow field and an active area of 25 cm^2. The CCM is assembled together with a carbon-fiber based gas diffusion layer (GDL) on the cathode side and a titanium porous transport layer (PTL) on the anode side, using PTFE gaskets and sub-gaskets of appropriate thickness for sealing and edge-protection, respectively. The cell is mounted onto an in-house built testbench, built in the framework of the ELY-DEG project (SI/501198-01), and upgraded later in the ELY-TEMP project (SI/501603-01). The cell operating temperature was generally 80 or 90°C, with hydrogen pressure up to 11 bar and oxygen pressure maintained at ambient conditions. A smaller version of the cell with an active area of 4 cm2 is also available. A modification thereof was used in the beamline campaign at the Synchrotron Light Source (SLS) of PSI at the Materials Science beamline (MS-X04SA) in November 2022.

A schematic of the synthesis of Pt-decorated CZO nanoparticles, their incorporation into the membrane by solution-casting, preparation of the CCM, and assembly into the single cell is given in Figure 1.

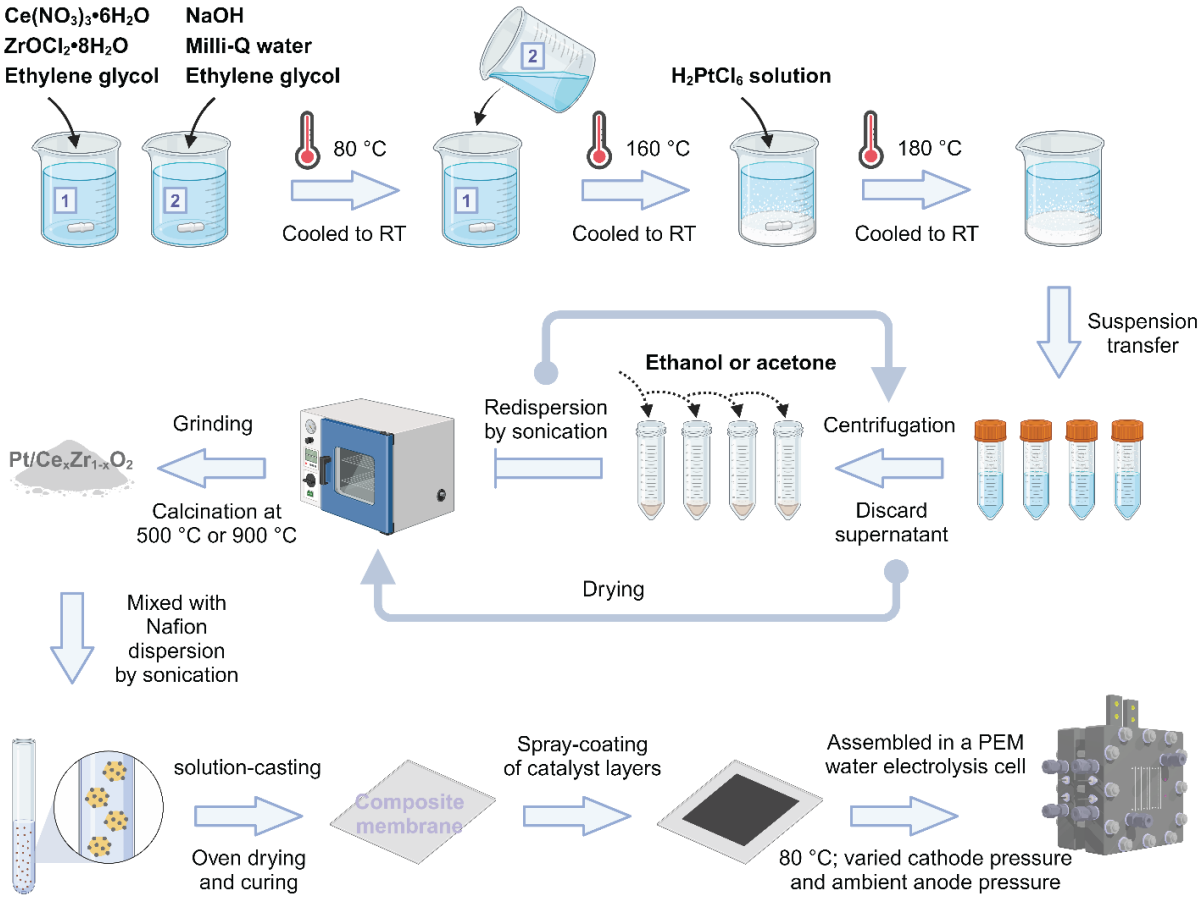

Figure 1: An overview of the particle synthesis process of $Pt/Ce_xZr_{1-x}O_2$ via one-pot polyol method and the incorporation of the catalyst in solution-cast Nafion™ membrane for PEM water electrolysis measurements [1]. (Created with BioRender.com)

2.2 Results and discussion

A total of four peer-reviewed articles will be published as a main outcome of the research work performed, two of which have already been published, and two being under review / in preparation. The doctoral exam of the PhD student financed by the project funds is scheduled on February 12, 2025, and his contract will expire after 4 years on February 28, 2025.

2.2.1. Effect of cathode catalyst layer design on H_2 crossover to anode side

A detailed study was performed of the cathode catalyst layer compositional parameters to concurrently decrease the loading of Pt and minimize the rate of hydrogen crossover. The Pt/C catalyst was chosen from two types of the carbon support: Vulcan carbon (low specific surface area of ~250 m^2/g) and high surface area carbon (HSAC), and from a range of Pt wt.% in Pt/C between nominally 5 and 50 wt.%. Two levels of the ionomer content, represented by an ionomer-to-carbon (I/C) mass ratio of 0.35 and 0.69, were employed. Electrolysis single cell measurements were carried out and the electrochemical performance of the cell containing the various cathode configurations was compared. A decrease of Pt wt.% in Pt/C, I/C ratio or an increase of the Pt loading was proven to be typically beneficial in decreasing the rate of hydrogen permeation. At a Pt loading of 0.025 mg/cm^2, the cathode of 40 wt.% Pt on HSAC support with an I/C ratio of 0.35 shows the highest calculated hydrogen mass transfer coefficient, which is seen as the optimal configuration. These findings help to provide guidance for the design criteria of the next-generation PEM water electrolysis cells. As an example, a comparison of the single cell performance and H_2 crossover using the optimized cathode design is shown in Figure 2 in comparison to the

previously used standard composition at two different Pt loadings. A further four-fold reduction of Pt loading to 0.025 mg/cm^2 could be achieved without loss of performance [2].

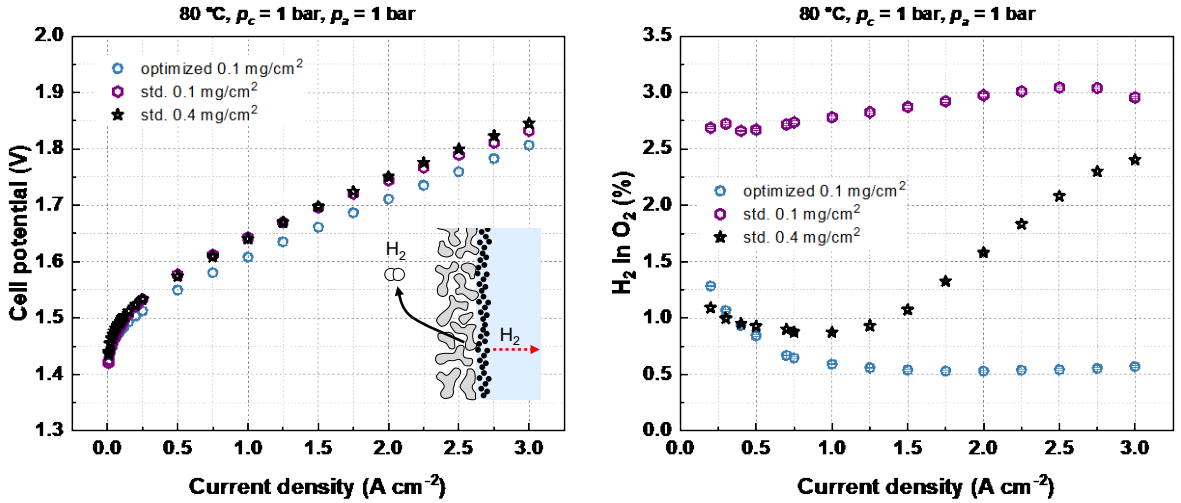

Figure 2: Comparison of cathode catalyst layer designs before and after lowering of the loading and compositional/structural optimization. a, polarization curves. b, H_2 content in O_2 product gas. Membrane: Nafion™ 212, cell temperature: 80°C, anode and cathode pressure: 1 bar.

2.2.2. Nanoparticle Catalysts for Gas Recombination and Radical Scavenging

Incorporating platinum (Pt) as a gas recombination catalyst in the membrane of a polymer electrolyte water electrolyzer (PEWE) effectively addresses the challenge of pronounced hydrogen crossover from the cathode to the anode, particularly when thin membranes with a thickness of 50 μm or below are employed. However, the Pt-catalyzed formation of reactive oxygen species, including hydroxyl radicals (HO•), accelerates membrane degradation, which can be alleviated by additionally incorporating a radical scavenger such as cerium-zirconium oxide (CZO) into the membrane [3]. Figure 3a shows the result of 100 h single cell tests in terms of the release of fluoride into the cathode effluent, which is a measure for the rate of membrane degradation. Incorporation of CZO leads to a decrease of the fluoride release rate (FRR) below the value obtained with an undoped Nafion™ membrane, which indicates concurrent reduction of gas crossover and radical scavenging.

However, given the short lifetime of HO• in the proton exchange membrane (PEM) in the range of microseconds, it is necessary to position the cerium-zirconium oxide close to the Pt sites where radicals are catalytically produced, for effective radical scavenging. To address this issue, a bi-functional catalyst Pt/$Ce_xZr_{1-x}O_2$ has been synthesized, where Pt particles are anchored on the $Ce_xZr_{1-x}O_2$ support. Pt/$Ce_xZr_{1-x}O_2$ catalysts were synthesized with Ce contents of x = 0.25, 0.5, 0.75 and 1, and two Pt-to-oxide loadings of 0.5 and 5 wt.%. A HAADF-STEM image of the obtained Pt-CZO bifunctional catalyst and elemental analysis of Pt is shown in Figure 3b.

Two selected compositions, namely 0.5-Pt/$Ce_{0.5}Zr_{0.5}O_2$ and 5-Pt/$Ce_{0.5}Zr_{0.5}O_2$, were incorporated at a loading of the oxide of 0.8 mg/cm^2 into a Nafion™ membrane with a thickness of 50 to 60 μm by solution casting. CCMs were assembled into single cells and characterized for performance and durability. The effect of the gas recombination catalyst is assessed by measuring the content of hydrogen in the oxygen product stream on the anode side (Figure 4a). In general, the H_2-in-O_2% decreases with increasing current density, because of increasing dilution of H_2 by the produced O_2. It is observed that with the low Pt content of 0.5 wt.% on CZO, corresponding to a Pt loading of 4 μg/cm^2, the H_2 content is not significantly reduced compared to the blank membrane without additive. With the higher Pt content of 5 wt.% and a Pt loading of 40 μg/cm^2 an effective gas recombination performance is obtained, which reduces the H_2 content by a factor of ~2.

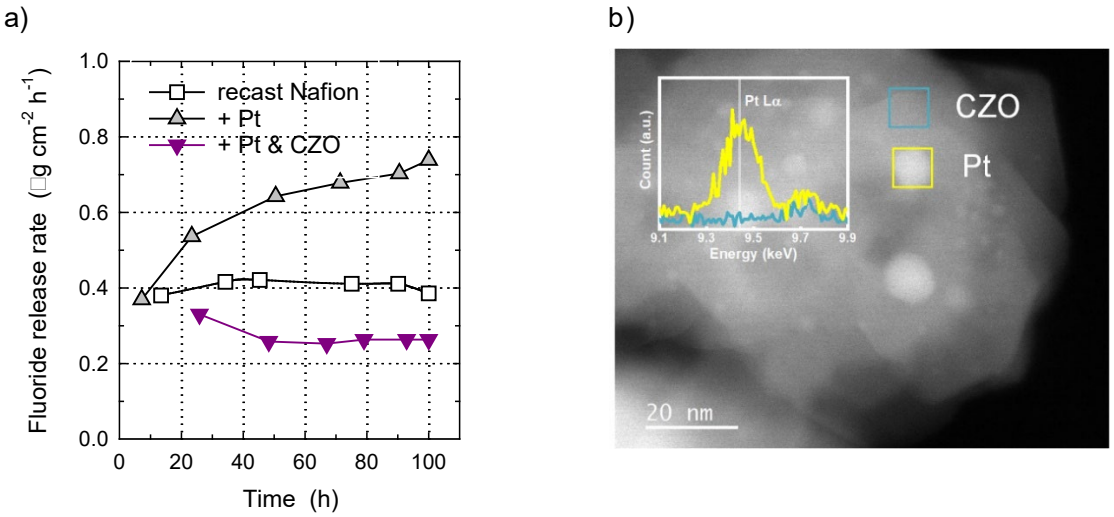

Figure 3: (a) Fluoride release rate measured in the cathode effluent from single cell experiments at a current density of 2 A/cm^2 over 100 h at a cell temperature of 80°C. (b) HAADF-STEM image of the bi-functional catalyst Pt/$Ce_{0.5}Zr_{0.5}O_2$, with comparison of EDX spectra measured on the selected areas of Pt and cerium-zirconium oxide support.

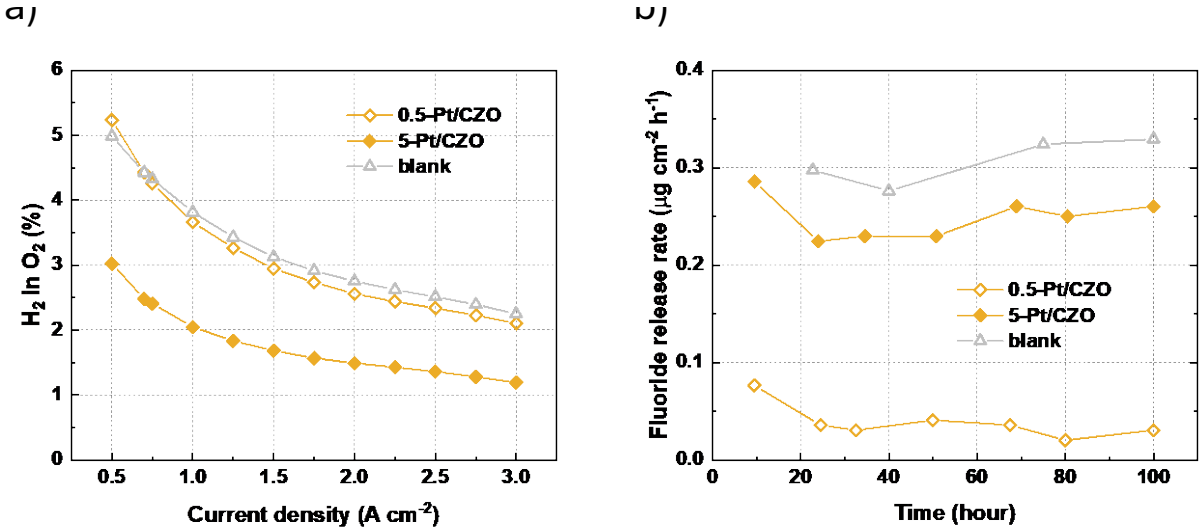

Figure 4: (a) Anode H_2-in-O_2% recorded at a range of current densities at a cathode pressure of 11 bar, and (b) fluoride release rate determined during the 100-hour constant current test at a cathode pressure of 3 bar. The cell temperature is 80°C, the anode pressure is kept at ambient.

The radical scavenging performance is evaluated by measuring the FRR from the membrane. With the use of the bifunctional catalyst with lower Pt content, 0.5-Pt/CZO, a reduction of FRR by a factor of ~10 was obtained, which indicates a significant mitigation of membrane degradation. For the catalyst with higher Pt loading, 5-Pt/CZO, FRR was reduced by only ~20% compared to the blank. This confirms what was mentioned above (Figure 3a) that the presence of Pt in the membrane promotes the formation of radicals.

The results show that through a careful choice of the composition of the bifunctional catalyst Pt/CZO, a concurrent reduction of gas crossover and a mitigation of membrane degradation can be achieved. In these experiments the additive was dispersed throughout the membrane. It is likely that the confinement

of catalysts in specific locations of the membrane can improve their performance, because they can be placed in regions where they are most effective. A detailed study is reported in the following section.

2.2.3. Catalyst coated membranes with interlayer architecture

In this study, the location of catalytic additives for gas recombination and radical scavenging in different layers close to the anode and close to the cathode was investigated. Nafion™ 212 (thickness: 50 µm) was used as a membrane, onto which layers of CZO, Pt, or Pt-CZO catalyst and ionomer were spray-coated, on one side or both sides, in different configurations (Figure 5). To avoid the exposure of the deposited particles to the electrode potential of the anode or cathode, a Nafion™ top-coat was added by spray-coating on top of the layer containing the membrane additives. In configuration a), CZO and Pt were deposited in two layers onto the Nafion™ 212 membrane facing the cathode catalyst layer (CL_C). In configuration b), the Pt-layer was placed near the anode catalyst layer (CL_A). For configuration c), a bifunctional catalyst, Pt/CZO, was used on the anode side of the membrane. The background of this particular CCM design is based on the finding that radicals seem to be predominantly formed in the cathode catalyst layer of a PEM water electrolysis cell [4]. Therefore, the radical scavenger should ideally be placed near the cathode. Regarding the gas recombination catalyst, it has been reported in the literature that locating it near the anode is much more effective in reducing the H_2 content in the anode, owing to being close to the stoichiometric amount of O_2 at this location [5].

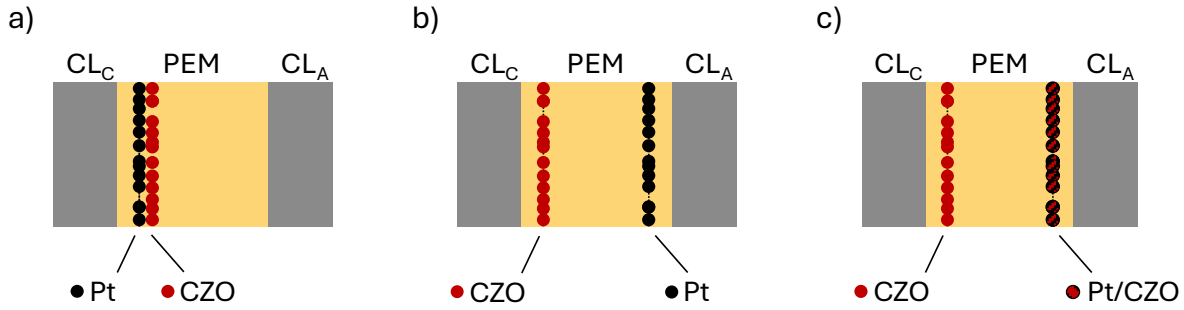

Figure 5: Configuration of catalyst coated membranes with different interlayer structure containing Pt recombination catalyst, CZO radical scavenger, and Pt/CZO bifunctional catalyst. The PEM used here was a Nafion™ 212 membrane with 50 µm dry thickness.

For the study reported here, CZO with the composition $Ce_{0.25}Zr_{0.75}O_2$ was used, as it has shown the best radical scavenging performance in *ex situ* Fenton tests, as described in the Interim Report 2023. The gas recombination performance of the Pt catalyst according to the 3 configurations a)-c) was evaluated by measuring the H_2 content in the anode product gas as a function of current density (Figure 6a). In agreement with the literature, it was found that Pt was more effective as a gas recombination catalyst when placed near the anode (configuration b) than when located near the cathode (configuration a). An even better gas recombination performance was achieved when CZO supported Pt was used (configuration c). This is likely related to the better dispersion of the Pt particles on the CZO and a concomitantly higher specific surface area compared to the use of unsupported Pt-black in configurations a) and b). Compared to the H_2-in-O_2 content at i = 0.5 A/cm^2 using a pristine, undoped membrane of 7.0 %, the preferred configuration c) leads to a reduction of H_2 content of a factor of 4.5.

The radical scavenging performance of the CZO layer(s) was evaluated by measuring the FRR over a test duration of 100 h (Figure 6b). The highest FRR was measured for configuration b), where the Pt recombination layer was located near the anode. The FRR was lower when the recombination layer is located next the cathode (configuration a), probably owing to the proximity to the CZO layer acting as a radical scavenger. The lowest FRR was obtained when a supported bifunctional Pt/CZO catalyst was located near the anode (configuration c), because in this case radicals formed on the Pt are effectively scavenged by the CZO support. The FRR of 0.023 µg·cm^{-2}·h^{-1} with this optimum configuration after 100 h constitutes an improvement compared to a blank Nafion™ recast membrane (FRR of 0.17 ± 0.01 µg·cm^{-2}·h^{-1}) of a factor of ~7.

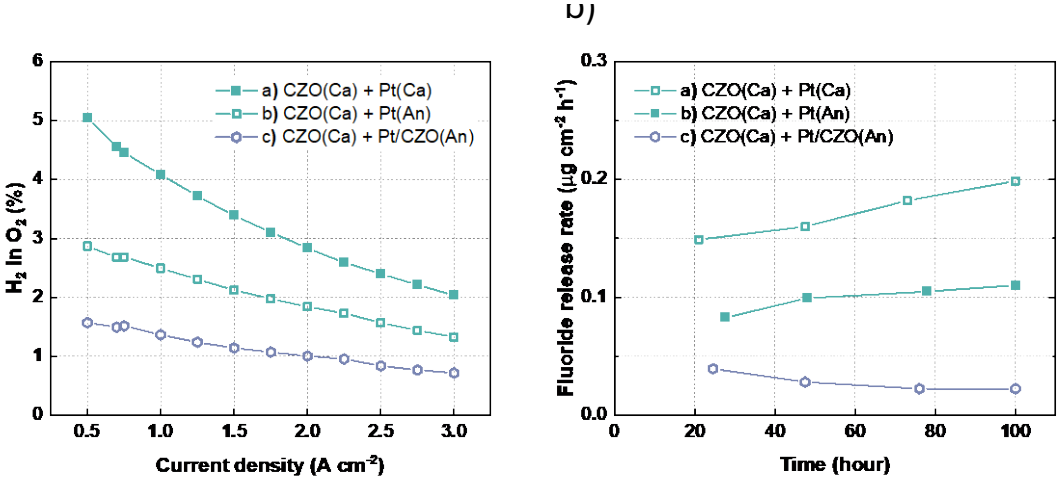

Figure 6: (a) Content of H_2 in the anode exhaust, (b) fluoride release rate in the cathode effluent during a 100 h constant current test at a current density of 2 A/cm^2. Cell temperature: 90°C, cathode pressure: 11 bar, anode pressure: ambient.

Based on the experimental results obtained, the preferred CCM design is configuration c), where the CZO radical scavenging layer is located near the cathode and the Pt recombination layer is placed near the anode. For the latter Pt supported on CZO is used, which ensures that the radicals produced on the Pt are scavenged by the Ce(III) in the oxide support. The FRR of 0.023 $\mu g \cdot cm^{-2} \cdot h^{-1}$ allows us to estimate a lifetime of the membrane with thickness of 50 μm of approximately 30'000 h at 90°C, assuming that the end-of-life criterion is reached when 10% of the fluorine inventory of the membrane is lost [6]. Membrane lifetime at today's more common and mild operating temperature of 80°C can be estimated assuming an activation energy for membrane degradation of 58 kJ/mol [6,7], yielding a value of 50'000 h, and 90'000 h at 70°C.

2.2.4. Chemical stability of catalysts

The stability of the oxide catalyst under the acidic conditions in the ionomer is essential to ensure a sustained radical scavenging activity and prevent the release of Ce and Zr ions into the membrane, which could block exchange sites and impair cell performance. Ceria (CeO_2) is thermodynamically unstable in acid and is slowly digested according to:

$$2\ CeO_2 + 6\ H^+ \rightarrow 2\ Ce^{3+} + 3\ H_2O + ½\ O_2$$

The instability of CeO_2 in the membrane was reported in the Interim Report 2022. We used the synchrotron X-ray beam at PSI for an accelerated degradation experiment. The degradation of CeO2 was negligible if the membrane was exchanged into the Na^+-form (Table 1). Further experiments with mixed cerium-zirconium oxide (CZO) showed those mixed-metal oxides to be more stable than pure ceria. The presence of Pt in Pt/CZO particles seems to slightly increase the rate of oxide digestion. It is therefore concluded that Zr stabilizes the oxide against degradation. Considering that the preferred CZO has a low Ce content of 25% (see previous section), oxide stability is expected to be significantly higher than that of pure ceria, making it a promising membrane additive for long-term use in the electrolyzer. For validation, actual extended durability experiments in the cell over thousands of hours would be required. This, however, is beyond the scope of this project.

Table 1: Stability of oxides in a Nafion™ membrane exposed to high-intensity X-ray radiation at the materials science beamline (MS - X04SA) of SLS at PSI (https://www.psi.ch/en/sls/ms) (measurement campaign in November 2022).

Particle		Nafion membrane	Cell condition	Dissolution after 80-min beam exposure	
CeO_2	Sigma-Aldrich	H^+	80 °C and 100% RH	81%	
CeO_2	Sigma-Aldrich	Na^+ form	80 °C and 100% RH	3%	
$Ce_{0.5}Zr_{0.5}O_2$	Sigma-Aldrich	H^+	80 °C and 100% RH	52%	Ce-rich $(Ce:Zr)O_2$ phase
				13%	Zr-rich $(Ce:Zr)O_2$ phase
$Ce_{0.5}Zr_{0.5}O_2$	500 °C, 3 hrs in air	H^+	80 °C and 100% RH	12%	
$Ce_{0.5}Zr_{0.5}O_2$	500 °C, 3 hrs in air	H^+	120 °C and 24% RH	14%	
Pt-$Ce_{0.5}Zr_{0.5}O_2$	900 °C, 3 hrs in air	H^+	120 °C and 24% RH	22%	Ce-rich $(Ce:Zr)O_2$ phase
				16%	Zr-rich $(Ce:Zr)O_2$ phase
				3%	Pt phase

In addition, the stability of $Ce_{0.5}Zr_{0.5}O_{2-\delta}$ particles was investigated *ex situ* in an acid bath of 2 M sulfuric acid at a temperature of 80°C (see interim Report 2023) to mimic the conditions in the cell. Based on the accumulation of Zr and Ce measured in the solution as a result of oxide digestion, the lifetime, corresponding to the complete dissolution of the particles, was estimated. With a concentration of ~0.9–1 mg_{CZO}/mL, for particles calcined at 500°C for 3 h, a projected lifetime of only 210 h is obtained, for particles calcined at 900°C for 3 h the projected lifetime is 3'200 h. This is much shorter than the target lifetime of water electrolyzers of ≫10'000 h. At this point, the transfer factor from *ex situ* to *in situ* is unknown. It is, however, likely that the digestion of the oxide particles in the membrane during cell operation is significantly slower, otherwise a much stronger increase in high-frequency resistance would have been observed in the 100 h tests, owing to the release of Ce and Zr ions into the membrane ionomer and the concomitant decrease in membrane ionic conductivity. Nevertheless, chemical stability of the oxides under the acidic operating conditions of the PEM water electrolyzer cell is crucial and, as shown, depends strongly on the synthesis and thermal treatment conditions of the material.

3 Conclusions and outlook

Water electrolysis is an anticipated core technology to produce green hydrogen from renewable energy sources for power-to-X processes. Among the different electrochemical water splitting technologies for hydrogen production, PEM water electrolysis is well suited for the integration with intermittent renewable energy sources, providing dynamical response, high electrochemical performance and gas purity. Employing thinner membranes in PEM water electrolysis cells for improved performance is faced with challenges, including increased hydrogen crossover and limited membrane lifetimes. These obstacles were addressed in this project through investigations into design strategies of catalyst coated PEMs.

For the assessment of performance improvement, we assume that a membrane with a (dry) thickness of 130 μm, such as Nafion™ 115, represents the state of the art. Figure 7 shows polarization curves for Nafion™ standards and two selected composite membranes from this project as representative examples. The main change in performance with Nafion™ 212 and membranes designed and prepared within this project, all with a thickness of ~50 μm, compared to Nafion™ 115 is a result of the reduction in ohmic resistance related to the use of thinner membranes. At the technically relevant current density of 2 A/cm^2, this leads to a decrease of the cell voltage of around 0.1 V, concomitant with an increase in

conversion efficiency (based on the lower heating value of hydrogen) of up to 4.7 %. An alternative performance analysis at a constant cell voltage of 1.8 V, corresponding to a conversion efficiency of 69%, shows that an increase in current density of up to 66 % is achieved with the use of thinner membranes.

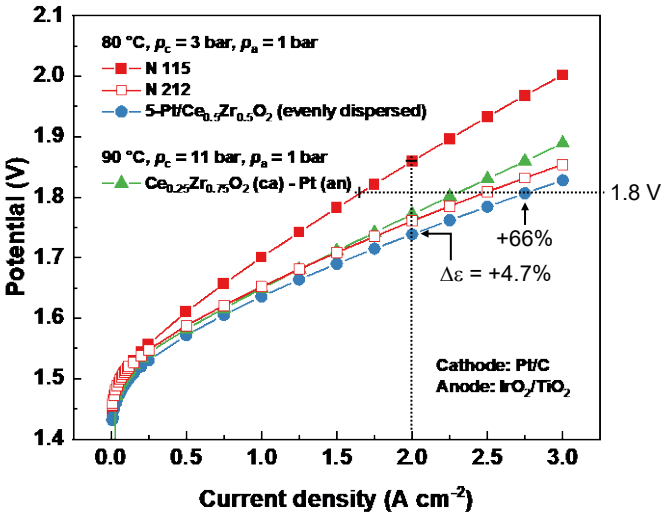

Figure 7: Cell performance comparison (polarization curves) of selected composite membranes prepared within the ELY-MAT project (thickness: ~50 μm), compared to Nafion™ 115 (130 μm) as state of the art and Nafion™ 212 with a similar thickness (50 μm). Improvements over the state of the art at a constant current of 2 A/cm^2 and a constant voltage of 1.8 V, respectively, are indicated. Δε indicates the change in conversion efficiency.

The addition of nanoparticle catalysts to membranes in the framework of this project served two functions. Pt acts as a H_2-O_2 recombination catalyst, which reduces the crossover of H_2 from the cathode to the anode side and therefore enlarges the current density range of the cell for safe operation. In the optimized composite membrane configuration, the Pt nanoparticle catalyst supported on CZO synthesized in-house and placed near the anode side of the membrane, showed the highest activity for gas recombination and a reduction of the H_2 content by a factor of 4.5 compared to an undoped membrane with similar thickness. The second catalyst, CZO, serves as an antioxidant and reduces membrane degradation, characterized by the fluoride release rate, thus increasing the projected membrane lifetime. The CZO catalyst is the most effective when placed near the cathode, as this is where the reactive oxygen species that attack the membrane are predominantly formed. In the optimum configuration, a 7.5-fold reduction in the FRR compared to an undoped membrane has been achieved. It has furthermore been shown that the use of CZO supported Pt for gas recombination instead of Pt-black is essential for two reasons. First, it yields a better dispersion of Pt nanoparticles. Second, the proximity of CZO and Pt allows for effective scavenging of radicals created on the Pt surface as a side product of the H_2-O_2 recombination reaction, thus reducing membrane exposure to reactive intermediates.

The potential lack of thermodynamic stability of CZO in the acidic environment of the membrane was identified as a potential concern for long-term stability of membranes. Digestion of CZO in a model sulfuric acid solution at 80°C was observed within several hundred hours. In the membrane, a lower rate of degradation is expected, yet the transfer factor between *ex situ* and *in situ* test is unknown at this point. This clearly represents an area of future work. In particular, a suitable method to characterize the stability of CZO or other dopants in the membrane using *ex situ* techniques ought to be developed, which should allow to assess whether the catalyst material is expected to be stable over the target electrolyzer component lifetime of 80'000 h.

A very rough estimate of H_2 production cost can help us to judge the techno-economic implications of the use of next-generation composite membranes as demonstrated in the ELY-MAT project. We select an operating point with constant cell voltage of 1.8 V, which corresponds to a conversion efficiency of

69% based on the lower heating value of hydrogen. The electricity cost, assuming an electricity price of 0.05 CHF/kWh, is 2.41 CHF/kg(H_2) at the chosen operating voltage. The capex cost, using the parameters given in Appendix A for calculation, is estimated at 0.76 CHF/kg(H_2) for the state-of-the-art technology. Owing to the higher current density obtainable with thinner membranes (cf. Figure 7), the required cell active area for a given target hydrogen output can be reduced accordingly, which leads to a reduction of investment cost by 40% to 0.46 CHF/kg(H_2). The total cost for hydrogen production thus decreases from 3.17 to 2.87 CH/kg(H_2). We also have to account for the increase of cost of the catalyst coated membrane, owing to the use of additional catalytic materials (Pt, CZO) and the more elaborate membrane design (multilayer composite membrane). Since the catalyst coated membrane only accounts for around 10% of the total electrolyzer installation cost, an increase in cost of 20% of the membrane would only lead to a capex increase of 2 %. However, from a circular economy point of view, the use of additional elements in the cell (such as cerium and zirconium) would render the recycling of electrochemically active materials more cumbersome. Typically, recycling costs are not accounted for in cost estimates for electrolyzers. Clearly, the community has to adapt appropriate techno-economic methods in the interest of a more holistic analysis of cost and reuse of critical raw materials.

4 National and international cooperation

The work performed at PSI in the group of J. Herranz on advanced porous transport layers for water electrolysis cells, funded by BFE (Project no. SI/502629) is of particular interest for the use of thin membranes. In the follow project of ELY-MAT, called ELY-MEM (project no. SI/502849), we plan to exploit this synergy and use the novel materials (NovElyTi™) in combination with new, thin membranes to be developed in the framework of the project.

An SNF funded project focusing on radical stability of anion exchange membranes (AEMs) was been started in December 2023. In particular AEM water electrolyzers (AEMWEs) have been receiving considerable attention in the past few years, as they offer the prospect of the use of fluorine-free membranes and non-noble metal catalysts. In the follow-up project ELY-MEM we plan to translate key design principles using gas recombination catalysts and radical scavengers from the PEM to the AEM water electrolyzer technology.

PSI has negotiated a 2 year project (1 postdoctoral research fellow) with Bosch (Linz, Austria) on the topic of metal-ion contamination of PEMs in water electrolyzers. This builds upon expertise going back to the ELY-DEG project funded by BFE (SI/501198-01)

Unfortunately, to this date the group has not succeeded in joining a project consortium of a Horizon 2020 project on the topic of water electrolysis. The PSI is a member of Hydrogen Europe[1], which offers the opportunity of networking within the European community on hydrogen and water electrolysis research and development.

[1] https://hydrogeneurope.eu

5 Publications and other communications

Peer-reviewed articles

Z. Zhang, M. Sirim, A. Testino, L. Gubler, "Composite Proton Exchange Membranes with Interlayer Structure containing Functional Catalyst Particles for Water Electrolysis ", ACS Appl. Mater. Interfaces 17 (2025) 54656-54667 (DOI: 10.1021/acsami.5c08461)

Z. Zhang, F. Pilger, I. Alxneit, A. Carino, M. Tarik, E. Müller, A. Cervellino, A. Mühlmann, C. Ludwig, L. Gubler, A. Testino, "Pt/$Ce_xZr_{1-x}O_2$ Bi-Functional Catalyst for Gas Recombination and Radical Scavenging in PEM Water Electrolysis Cells", ACS Catal. 15 (2025) 5577–5588 (DOI: 10.1021/acscatal.4c07426)

Z. Zhang, A. Baudy, A. Testino, L. Gubler, "Cathode Catalyst Layer Design in PEM Water Electrolysis towards Reduced Pt Loading and Hydrogen Crossover", ACS Appl. Mater. Interfaces 16 (2024) 23265-23277 (DOI: 10.1021/acsami.4c01827)

Z. Zhang, Z. Han, A. Testino, L. Gubler, "Platinum and Cerium-Zirconium Oxide Co-Doped Membrane for Mitigated H_2 Crossover and Ionomer Degradation in PEWE", Journal of The Electrochemical Society 169(10) (2022) 104501 (DOI: 10.1149/1945-7111/ac94a3)

Talks at Conferences

Z. Zhang, A. Baudy, Z. Han, A. Testino, L. Gubler, "Towards Next-Generation Catalyst Coated Membranes for Polymer Electrolyte Water Electrolyzers", 4th International Conference on Electrolysis (ICE), Sun City, South Africa, Aug 27 – Sept 1, 2023 (https://engineering.nwu.ac.za/hysa/ice-2023)

Z. Zhang, Z. Han, A. Testino, L. Gubler, "Suppressing Hydrogen Crossover and Scavenging Radicals By Incorporation of Pt and Cerium-Zirconium Oxide for Polymer Electrolyte Water Electrolyzers", 241st Electrochemical Society Meeting, Vancouver, Canada, May 28 – June 2, 2022 (https://ecs.confex.com/ecs/241/meetingapp.cgi/Paper/156928)

Posters at Conferences

Z. Zhang, A. Mühlmann, A. Testino, L. Gubler, "Pt-Doped Ceria-Zirconia as a Bi-Functional Catalyst for Gas Recombination and Radical Scavenging in PEM Water Electrolysis Cells", 20th Symposium on Modeling and Experimental Validation of Electrochemical Energy Technologies (ModVal 2024), Baden, Switzerland, March 13-14, 2024 (Poster #49) (DOI: 10.3929/ethz-b-000662523)

Patent Application

Z. Zhang, L. Gubler, A. Testino, “Electrochemical cell comprising a composite proton exchange membranes with interlayer structure”, Paul Scherrer Institut, EP25168162, April 3, 2025

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2. Z. Zhang, A. Baudy, A. Testino, L. Gubler, ACS Appl. Mater. Interfaces 16 (2024) 23265 (DOI: 10.1021/acsami.4c01827)
3. Z. Zhang, Z. Han, A. Testino, L. Gubler, Journal of The Electrochemical Society 169 (2022) 104501 (DOI: 10.1149/1945-7111/ac94a3)
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7 Appendix A: Techno-Economic Analysis

Parameters for the estimation of hydrogen production cost:

Parameter	**Value**	**Unit**
Investment cost per active area	1.2	CHF/cm^2
Electrolyzer utilization	60	%
Debt period	5	years
Electricity cost	0.05	CHF/kWh