Communication—Pt-Doped Thin Membranes for Gas Crossover Suppression in Polymer Electrolyte Water Electrolysis

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Hydrogen gas crossover is a major safety issue in polymer electrolyte water electrolyzers (PEWE) and a limiting factor for the use of thinner polymer electrolyte membranes for high voltage efficiency PEWE. This article outlines a simple impregnation method for a recombination catalyst, yielding high crossover suppression for thinner membranes at differential pressures without negative effects on the cell performance.

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A key concern for the safe operation of polymer electrolyte water electrolysis (PEWE) cells is the high hydrogen gas crossover that can lead to explosive hydrogen-oxygen gas mixtures. The safety aspect is especially important with thinner membranes and high differential pressures.1 So far, different approaches have been taken to suppress the hydrogen gas crossover or to reduce the content of hydrogen in the anode compartment. Grigoriev et al.2 introduced a hydrogen-oxygen recombination catalyst on the anode side. Ito et al.3 used a mixed catalyst of Pt and Ir on the oxygen side to suppress the hydrogen content. Schalenbach et al.4 implemented an additional electrode into the electrolyte to electrochemically reduce the permeating hydrogen. The concept of Pt-doping of the proton exchange membrane (PEM) followed by chemical reduction is well known from polymer electrolyte fuel cells (PEFCs), where it was used for electrode preparation and self-humidification.5,6 The Pt particles in such impregnated membranes serve as recombination catalyst and can be applied to reduce hydrogen crossover in PEWE.7 In this study, we present a new reduction method yielding thinner membranes with high crossover suppression, without a negative impact on the cell performance.

Experimental

Cell and test station.—Experiments were performed with the same electrolysis test bench described elsewhere.8 A PEWE cell with an active area of 25 cm² was employed to accommodate a commercial T10 sintered-Ti porous transport layer (PTL) from GKN on the anode and a SPECTRACARB 2050A-6060 carbon gas diffusion layer (GDL) with 1.5 mm thickness on the cathode. The same PTL was used for all experiments in this study to avoid changes in the PTL affecting the membrane performance. Ito et al.3 used a mixed catalyst of Pt and Ir on the oxygen side to suppress the hydrogen content. Schalenbach et al.4 implemented an additional electrode into the electrolyte to electrochemically reduce the permeating hydrogen. The concept of Pt-doping of the proton exchange membrane (PEM) followed by chemical reduction is well known from polymer electrolyte fuel cells (PEFCs), where it was used for electrode preparation and self-humidification.5,6 The Pt particles in such impregnated membranes serve as recombination catalyst and can be applied to reduce hydrogen crossover in PEWE.7 In this study, we present a new reduction method yielding thinner membranes with high crossover suppression, without a negative impact on the cell performance.

The PTL was circulated in one compartment to humidify the membrane and a hydrogen pressure of 5 bar was applied to the other compartment. The part of the membrane which was exposed to the hydrogen had an area of $A_{\text{H}_2} = 66.2$ cm². After 5 days the membranes were removed and rinsed with water. The modified membranes were placed in 50 mL of a 1 M HNO₃ solution, which was heated and kept at 60°C for one hour to leach out remaining Pt-ions. Used solutions were kept after each step and diluted in 1 M HNO₃ solution. Pt concentrations were determined by atomic absorption spectroscopy (AAS-OES, Varian 720-ES) measurements and the Pt loading in the membranes determined to be 0.1 mg cm⁻² (for detailed explanation see SM). As prepared membranes are referred to as Pt-N212.

Cross-section imaging.—The Pt-N212 membranes were embedded into an epoxy resin (Epon-812, Sigma-Aldrich), which was cured for 48 h at 60°C. The embedded samples were cut into about 100 mm thick slices using an ultra-microtome (FC6, Leica) equipped with a diamond knife (ultra 45°, Diatome). The sections were imaged with a transmission electron microscope (TEM, JEOL 1010) at an acceleration voltage of 200 kV. The surface of the particles was determined using an image processing software (ImageJ) and the diameter was calculated assuming spherical particles.

CCM preparation.—The anode catalyst ink was prepared by mixing 0.85 mL isopropanol, 2.7 mL miliQ water and 2.54 mL Nafion Solution (Aldrich, 5 wt% Nafion). The ink was sonicated for 15 minutes. 1 g of IrO₂/TiO₂ catalyst (Umicore Elcyt Ir75 0480) was added to the solution and the mixture was sonicated for an additional 30 min. The ink was then sprayed onto the membranes using an airbrush pen (Conrad Electronics Airbrush Pistol HP-200) and 2.5 mL of ink per CCM to achieve the desired loadings. The CCMs were dried for 12 h and subsequently weighed. The ink-spraying preparation method yielded anode loadings of 2.5 ± 0.1 mgPt cm⁻². A gas diffusion electrode (Johns4 Matthey ELE0244-0542 with HiSpec 9190 Pt/carbon 0.4 mgPt cm⁻²) was used as the cathode. The CCMs were assembled in the wet state after immersion in miliQ water for 12 h before testing.

Experimental conditions.—Cells were conditioned at 60°C by cycling the current density between 1 and 2 A cm⁻² until stable performance and uniform temperature in the system were achieved.
Hydrogen gas crossover measurements were performed at balanced (atmospheric) pressure and differential pressure with 5 and 10 bara at the cathode side, respectively, at eight galvanostatic steps between 2.0 A cm$^{-2}$ and 0.5 A cm$^{-2}$. The current densities were applied for 30 min and the hydrogen content in oxygen was averaged over the last 10 min. Polarization curves were recorded galvanostatically, while measuring the cell impedance at 10 kHz at each current step.

Results and Discussion

Membrane imaging.—Figure 1 shows two TEM images of a Pt-N212 membrane. Figure 1a shows a border area of the membrane and Figure 1b shows an area in the center of the membrane. There are lighter and darker areas on the image indicating deviations from the nominal cutting thickness of 100 nm. The particles seem to be distributed homogeneously over the whole cross-section of the membrane and vary in diameter between 1 and 100 nm with an average of about 15 nm. The part of the membrane into which the Pt is impregnated becomes brown (cf. Supplementary Material, Figure S1b), since Pt particles absorb in the visible range of light.9 Hagihara et al. report the impregnation of Pt into the membrane via ion exchange of Pt-ions and subsequent reduction in hydrazine.6 In their study the same Pt loading as in our study was determined and a uniform Pt distribution over the cross-section is claimed.

Hydrogen crossover.—Figure 2 shows the hydrogen content in oxygen in the anode compartment of PEWE cells using a Pt-N212 and a pristine membrane (N212) respectively at different current densities. The data shows a decreasing hydrogen fraction with increasing current density as the rate of the oxygen evolution reaction is increasing.2,10,11 Pressure increase on the cathode side leads to a higher hydrogen permeation and increases the fraction of hydrogen in oxygen. In comparison to pristine N212, the hydrogen content was significantly reduced for the Pt-N212 membranes over the whole current density range at all cathode pressures.

Turn-down ratio.—The PEWE polarization curves are shown in Figure 3. The Pt-N212 cell shows slightly lower performance. The different offsets and the faster increasing slope in the Tafel regime can be explained by slight variations in the anode catalyst layer loading and variations in the spraying procedure. The high frequency resistance (HFR) is similar for both samples (133 ± 6 mOhm cm$^2$ for N212 vs 135 ± 4 mOhm cm$^2$ for Pt-N212 at 1 A cm$^{-2}$ and 60°C).

The operational range of a PEWE cell stack in terms of current density, i.e. the turn-down ratio, is limited on the one hand by the voltage efficiency target and on the other hand by the hydrogen in oxygen safety limit.1 Thus, the current density range is limited between a minimum determined by gas crossover and a maximum by voltage efficiency value of 66.8% LHV (1.84 V, DOE value12). Increasing the cathode pressure reduces the operational range by an increase of the lower and higher current density limit.13 To obtain the turn-down ratio, the cathode pressure was increased to 10 bara and further to 15 bara. The results are shown in Figure 4. As expected, the turn-down ratio decreases with increasing cathode pressure.
Figure 4. Turn-down ratio (operational range) of N212 (black), and Pt-N212 (green) at 60°C and 1, 5 and 10 bar cathode pressure (anode: 1 bar). Down ratio for the modified samples, the cell potential was corrected for the ohmic contribution of electronic contacts/cell housing using the procedure described by Suermann et al. and the 2% hydrogen in oxygen content was taken for the lower limit (Figure 4). Both, polarization curves and hydrogen in oxygen curves were extrapolated for the missing data points (cf. Supplementary Material, Table S1 and Figure S2). The benefit of suppressed crossover becomes evident at elevated differential pressures, where the Pt-N212 retained ∼80% of the operational range at \( p_{\text{cat}}^{\text{H}_2} = 10 \) bar.

Conclusions

Reducing the hydrogen content in the anode compartment of a PEWE cell and avoiding explosive mixtures is necessary when using thinner membranes and high cathodic pressures. Suppressing crossover by doping the PEM with Pt particles is a straightforward method to mitigate this problem. Our new approach of Pt impregnation and reduction in the PEM by hydrogen permeation reduces hydrogen crossover significantly and enables the use of thinner membranes in differential pressure PEWE cells.

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References

Supplementary Material: Pt-doped thin membranes for hydrogen cross-over suppression in proton electrolyte water electrolysis

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Membrane Pt loading. - The platinum loading \(L_{Pt}\) in the PEM can be determined as follows:

\[
L_{Pt} = \frac{n_{Pt} M_{Pt}}{A_{red}} \tag{1}
\]

where \(n_{Pt}\) is the number of Pt species, \(M_{Pt}\) is the molar mass of platinum, and \(A_{red}\) the exposed membrane area. \(n_{Pt}\) can be determined as follows:

\[
n_{Pt} = n_d - n_a - n_l \tag{2}
\]

where \(n_d\) is the number of doped platinum ions, \(n_a\) the number of Pt- ions in the doping solution after removal of the membrane and \(n_l\) the number of platinum ions leached from the membrane all to be determined by ICP-OES. The concentration of Pt-ions in the solution after removal of the membrane was below the detection limit of the ICP (< 50 µg/L) and is therefore assumed to be \(n_a < 50 \mu\text{g/L}\). This suggests an uptake of \(\sim 100\%\) of \((\text{NH}_3)_4\text{PtCl}_2\) into the membrane, which is reasonable in the concentration ranges used in this study (1) meaning that \(n_a\) can be neglected in [2] and holds for an exposed area of the membrane of 100%. In partially exposed membranes as by the hydrogen permeation reduced membranes, \(n_l\) is calculated as follows:

\[
n_l = n_d \frac{A_{tot} - A_{red}}{A_{tot}} + (n_d - n_{Pt}) \frac{A_{red}}{A_{tot}} \tag{3}
\]

Rearrangement gives:

\[
n_{Pt} = n_d (A_{tot} - A_{red}) - n_l A_{tot} + n_d \tag{4}
\]

For all numbers of Pt-atoms/ions \(n_x\) the following holds:

\[
n_x = c_x V_x \tag{5}
\]

where \(c_x\) is the concentration of solution \(x\) and \(V_x\) is the volume of solution \(x\). The \((\text{NH}_3)_4\text{Pt}^{2+}\) ions, provided for the doping solution, were completely taken up into the PEM and correspond to 11% sulfonic acid group occupation.

Hydrogen permeation. – By neglecting the diffusion of oxygen to the cathode side the permeating flux of hydrogen through the membrane to the anode side can be determined with (2):

\[
\dot{N}^{\text{perm}}_{\text{H}_2} = \frac{i}{4F} \frac{X_{\text{H}_2\text{in O}_2}}{1 - X_{\text{H}_2\text{in O}_2}} \tag{6}
\]
where $X_{H_2 \text{in } O_2}$ the percentage of hydrogen in oxygen on the anode side is, $i$ the current density and $F$ the Faraday constant. Rearrangement gives

$$N_{H_2}^{\text{perm}} = m \cdot i + c$$  \[7\]

The permeating hydrogen flux through the membrane increases linearly with the current density (Figure S2) (2) and the values for hydrogen permeation rate through the membrane at 0.5 A cm$^{-2}$ and 2.0 A cm$^{-2}$ are listed in the Table SI. At ambient pressure the hydrogen permeation rate is about two times higher for a pristine membrane than for a doped membrane, and at 10 bar$_a$ cathodic pressure it increases by a factor of five for low current densities and by a factor of four for high current densities. Trinke et al. (2) report a two times lower value for a pristine EF-40 (FuMa-Tech GmbH) CCM with a membrane thickness of 240 µm at 60°C and 11 bar$_a$ cathodic pressure. Through linear extrapolation of the hydrogen permeation rate in Figure S2, the slope $m$ and the intercept with the y-axis $c$ can be determined:

$$i = \frac{4F \cdot c (1 - X_{H_2 \text{in } O_2})}{X_{H_2 \text{in } O_2}} - \frac{c}{m}$$  \[8\]

The linear regression parameters are listed in Table SI. The increase of the hydrogen permeation rate with current density for all cathodic pressures is about two times higher for the pristine membranes than for the doped membranes. By substituting [7] into [6] and solving the equation for $i$ one obtains:

The lower operational limit (LOL) for the turndown ratio is set by the current density value for a concentration of 2% hydrogen in oxygen and can be determined by solving [8]. The experimentally obtained values for the LOL and the values obtained by solving [8] with the linear regression parameters from Table SI at differential pressures and membrane types are listed in Table SI. The lower values for the LOL from fitting than from the experiment could be due to neglecting the permeation of oxygen to the anode side in [6].

TABLE SI. **Top:** Hydrogen permeation rate $\dot{N}$ at 0.5 A cm$^{-2}$ and 2.0 A cm$^{-2}$ of N212 and Pt-N212 at 60°C and 1, 5 and 10 bar$_a$ cathode pressure (anode: 1 bar$_a$). **Middle:** Linear regression parameters (slope $m$, y-axis intercept $c$) extracted from the hydrogen permeation rate in Figure S2 of N212, and Pt-N212 at 60°C and 1, 5 and 10 bar$_a$ cathode pressure (anode: 1 bar$_a$). **Bottom:** Fitted and experimental (if accessible through Figure 4) lower operational limit (LOL) of N212, and Pt-N212 at 60°C and 1, 5 and 10 bar$_a$ cathode pressure (anode: 1 bar$_a$).

<table>
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<th>Pt-N212</th>
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<td>$\dot{N}$ (2.0A cm$^{-2}$)</td>
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<tr>
<td>1 bar$_a$</td>
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<td></td>
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<td>$c$ [mmol s$^{-1}$ m$^{-2}$]</td>
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<td>Fitted LOL</td>
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**Figure S1a.** Schematic representation of the Pt impregnation procedure used in this study. **S1b.** Photo of a Pt impregnated Nafion NR212 by the hydrogen reduction procedure introduced in this study. The brown area represents the Pt impregnated area.

**Figure S2.** Hydrogen permeation rate from anode to cathode side in a PEWE cell using pristine NR212 (N212, black), and a Pt doped NR212 obtained by reduction with hydrogen (Pt-N212, green) at ambient cathodic pressures, 5 bar, and 10 bar, respectively, and 60°C (anode: 1 bar). The lines represent a linear fit through the points calculated by [8]. The linear regression parameters are listed in Table SI.

**References**