All-Hydrocarbon MEA for PEM Water Electrolysis
Combining Low Hydrogen Crossover and High Efficiency

Carolin Klose, Torben Saatkamp, Andreas Münchinger, Luca Bohn, Giorgi Titvinidze, Matthias Breitwieser, Klaus-Dieter Kreuer,* and Severin Vierrath*

Hydrocarbon ionomers bear the potential to significantly lower the material cost and increase the efficiency of proton-exchange membrane water electrolyzers (PEMWE). However, no fully hydrocarbon membrane electrode assembly (MEA) with a performance comparable to Nafion-MEAs has been reported. PEMWE-MEAs are presented comprising sPPS as membrane and electrode binder reaching 3.5 A cm\(^{-2}\) at 1.8 V and thus clearly outperforming state-of-the-art Nafion-MEAs (N115 as membrane, 1.5 A cm\(^{-2}\) at 1.8 V) due to a significantly lower high frequency resistance (57 ± 4 mΩ cm\(^{-2}\) vs 161 ± 7 mΩ cm\(^{-2}\)). Additionally, pure sPPS-membranes show a three times lower gas crossover (<0.3 mA cm\(^{-2}\)) than Nafion N115-membranes (>1.1 mA cm\(^{-2}\)) in a fully humidified surrogate test. Furthermore, more than 80 h of continuous operation is shown for sPPS-MEAs in a preliminary durability test (constant current hold at 1 A cm\(^{-2}\) at 80 °C). These results rely on the unique transport properties of sulfonated poly(phenylene sulfone) (sPPS) that combines high proton conductivity with low gas crossover.

1. Introduction

The most commonly used polymer membranes for proton-exchange membrane (PEM) water electrolysis are perfluorosulfonated acids (PFSAs). Apart from their high proton conductivity and mechanical and chemical robustness,[1] this is mainly due to the fact that this membrane type is already well established in PEM fuel cell technology and readily available. However, high cost and environmental issues associated with PFSAs' fluorine chemistry[2] and their significant gas (especially H\(_2\)) permeability and poor mechanical stability at high temperature (T > 80 °C) drive the ongoing search for alternative membrane materials.[3] A particularly promising alternative to PFSAs are hydrocarbon membranes. Their distinctly different properties from those of PFSAs are still preventing them from being used in PEM fuel cells, but substantially lower gas crossover as a consequence of their particular morphology, similar conductivity especially when fully hydrated, better thermal stability, lower production cost, and the fact that they are fluorine free should make them ideally suited for PEM water electrolysis.[4–6]

While for PEM fuel cells there is extensive literature on hydrocarbon membranes[7–12] and hydrocarbon electrodes[13] similar studies in the field of PEM water electrolyzers (PEMWEs) are still missing despite the aforementioned advantages. Especially their gas tightness is of high importance, since PEMWEs are often operated at high pressures[14] and critical contents of hydrogen in oxygen can be easily reached, forcing a system to shut down.[15] In state-of-the-art PEM water electrolysis systems this issue is circumvented by using recombination catalysts or thick PFSA membranes (>100 µm),[16] which lower the efficiency of the electrolyzer.[15] Hydrocarbon membranes therefore are a very attractive solution, as they exhibit a lower gas crossover without sacrificing performance.

Among the PEMWE studies so far, hydrocarbon membranes are often paired with pure metal electrodes, leading to a low catalyst utilization: Nolte et al. fabricated cells based on sulfonated poly(arylene ether sulfone)s with platinum as anode and cathode catalyst achieving a cell voltage of 30 mA cm\(^{-2}\) at 1.8 V and 25 °C.[17] Linkous et al. published data of a PEMWE cell with sulfonated poly(ether ether ketone) (sPEEK) as membrane material, reaching the same current density of 30 mA cm\(^{-2}\) at 1.8 V (60 °C).[18] Jang et al. tested PEM water electrolyzers with...
membranes based on sulfonated polysulfone) and poly(ether ether ketone) with platinum deposited as anode as well as cathode catalyst and reported a current density of 1 A cm⁻² at 1.8 V for the polysulfone-based membrane electrode assembly (MEA).

Albert et al. performed preliminary electrolysis tests with a radation grafted membrane and iridium oxide and platinum black as electrodes reaching 0.6 A cm⁻² at 1.8 V. While in the lower current density region, their hydrocarbon MEA showed better performance than a commercial MEA, at higher current densities (>0.5 A cm⁻²) a strong increase of voltage, related to mass transport was observed. This observation could be explained by an unfavorable constitution of the electrodes. In general, studies that demonstrate the feasibility of hydrocarbon materials not only as membranes but also as proton-conducting binder in the electrode are scarce. Only Wei et al. fabricated MEAs using sPEEK as the ionomer in the electrode and sPEEK blended with poly(ether sulfone) as membrane material and reported a cell performance of 1 A cm⁻² at 1.8 V.

Apart from these pure hydrocarbon MEA studies, promising efficiencies were reported for hydrocarbon membranes combined with PFSA in the electrodes: Skulimowska et al. presented a MEA consisting of a sulfonated polybenzimidazole (sPBI) membrane coated with iridium and platinum catalysts that contain Nafion as ionomer binder. Despite severe losses in the kinetic region, a current density of 1.6 A cm⁻² at 1.8 V was demonstrated. The losses in the kinetic region were explained by dimensional changes of the sPBI membrane during the process of spray coating the electrodes onto the membrane, which harmed uniform deposition. MEAs fabricated by spray coating iridium and platinum catalysts with Nafion as ionomer binder onto a sulfonated polysulfone membrane, presented by Siracusano et al., reached a current density of 1.1 A cm⁻² at 1.8 V.

Even though these results are encouraging to further explore the benefits of hydrocarbon membranes in PEM water electrolysis, chemical stability during operation still needs to be investigated: on the one side, PFSA membranes are expected to be more stable as they make use of the systematically stronger carbon-fluorine bond compared to the carbon-hydrogen bond. On the other side, hydrocarbon membranes allow for less gas crossover, which in turn reduces radical formation and thereby chemical degradation.

So far, only very few studies report on the stability of hydrocarbon membranes under PEMWE operation. Nolte et al. reported a hydrocarbon membrane lifetime of 300 h at a constant current hold of 1 A cm⁻²; however, the test was conducted at 25 °C, which makes a prediction of the stability at relevant temperatures difficult. Only Siracusano et al. performed chronocoulometric measurements for 32 h at 80°C and reported an improvement of the cell polarization of the sulfonated polysulfone membrane after the test.

In this work, we used sulfonated poly(phenylene sulfone) (sPPS) with an equivalent weight of 360 g eq⁻¹ (ion-exchange capacity (IEC): IEC = 2.78 meq g⁻¹, Figure 1) prepared according to ref. [28] to build fully hydrocarbon-based, fluorine-free MEAs with sPPS as membrane material as well as ionomer binder in the electrodes. The hydrocarbon membrane material, which was first presented in 2007, exhibits the highest IEC of any water insoluble crosslinked random copolymer combining very high conductivity and low gas crossover. The latter is supposed to be the direct consequence of the ionomer’s distinct morphology with a relatively small correlation length even at high degrees of hydration. While sPPS shows exceptionally high hydrolytical, oxidative, and thermal stability, pure sPPS membranes suffer from brittleness in the dry state and significant swelling when submerged in water. In the current study we therefore are interested in the feasibility of sulfonated poly(phenylene sulfone) for PEM water electrolysis application and the overall potential this type of hydrocarbon has, while accepting the viscoelastic shortcomings of pure unoptimized sPPS at this stage.

With sPPS, we show fully hydrocarbon MEAs that, for the first time, reach higher voltage efficiencies and lower gas crossover than state-of-the-art PFSA-MEAs. For a first look onto durability, an initial stability test (constant current hold at 1 A cm⁻²) exceeding 80 h at 80 °C is conducted.

2. Results and Discussion

Four MEAs were fabricated, two sPPS-MEAs with a sPPS-membrane and sPPS as electrode binder and two Nafion-MEAs with a Nafion N115-membrane and Nafion as electrode binder. As shown in Figure 2a, the cross-section of the sPPS-MEAs revealed a membrane thickness of (115 ± 12) µm, which is comparable to the nominal thickness of the reference Nafion N115 (125 µm, Figure 2b). Thickness variations of sPPS-membranes stem from the manual casting and could in the future be eliminated by, e.g., utilizing a spray coating system for micrometer-precise membrane fabrication. The electrodes of the Nafion-MEAs comprised 8 wt% Nafion on the anode and 28 wt% Nafion on the cathode side. Based on preliminary experiments comparing a 2, 4, and 8 wt% sPPS-containing anode and taking into account an increased water volume fraction in fully humidified sPPS of ΦₓsPPS = 0.7 compared to Nafion (ΦₓN115 = 0.4), a significantly lower ionomer content was chosen for the sPPS-electrodes (4 wt% on the anode and 10 wt% on the cathode side).

Scanning electron microscope (SEM) images of focused ion beam (FIB)-prepared cross-sections, shown in Figure 7 in the Appendix A.1, revealed no visible differences of the electrode morphology between the electrodes with sPPS-ionomer and with Nafion-ionomer. While this work does not entail a systematic optimization of sPPS-based electrodes, a more in-depth look at the effect the ionomer content and type of ionomer has on (proton, water, and gas) transport in the electrodes will be subject of future studies.

2.1. Performance

Figure 3a shows the cell polarization of the two sPPS-MEAs (purple) and the two Nafion-MEAs (green), where the error

![Figure 1](https://example.com/figure1.png)

Figure 1. Chemical structure of the used sulfonated poly(phenylene sulfone) with an equivalent weight of 360 g eq⁻¹.
bars correspond to the standard deviation between the individual measurements. The performance of the herein reported Nafion-MEAs (1.49 ± 0.01 A cm⁻² at 1.8 V) is in line with current state-of-the-art performance in literature, despite lower catalyst loading than the majority of the reports[30–35] and therefore a suitable benchmark.

The pure hydrocarbon sPPS-MEAs exhibit substantially higher current densities than the Nafion-MEAs (3.48 ± 0.03 A cm⁻² at 1.8 V). This remarkable difference in current density at 1.8 V is due to the more than 60% lower high frequency resistance (HFR) for sPPS compared to Nafion, shown in Figure 3b. Most probably this low HFR is partly stemming from the higher specific protonic conductivity of sPPS compared to Nafion under the given conditions. Subtracting the voltage loss contribution of this resistance from the cell polarization yields the iR-free voltages (Figure 3c). The similarity between the iR-free voltages of the Nafion- and the sPPS-MEAs shows that the main difference in cell polarization stems from the membrane with no additional losses from the electrodes due to mass transport or kinetics. This is a highly encouraging result, since hydrocarbon electrodes for fuel cells typically suffer from reduced gas transport to the catalyst particles and poor electrical connectivity for high ionomer contents or poor proton conductivity in the electrode for low ionomer contents.[13]

The highest performance so far for a PEMWE cell with a hydrocarbon PEM (1.6 A cm⁻² at 1.8 V) was reported with Nafion as the ionomer binder in the electrodes.[22] There, it was stated that the performance was hampered by poor kinetics, related to membrane swelling during the electrode deposition and associated inhomogeneities. Such inhomogeneities were not observed in our study, which is most likely related to
the low flow rate chosen for spray coating which minimized swelling and allowed uniform deposition of the electrodes.

2.2. Crossover

Hydrogen crossover data for sPPS- and Nafion-membranes (N115) were obtained by linear sweep voltammetry (LSV) in a fuel cell setup as suggested in ref. [20]. The voltammograms can be found in Figure 8 in the Appendix A.2. Figure 4 shows the crossover rates along with literature values from Albert et al.[20] measured with radiation grafted hydrocarbon membranes (purple circles) and a Nafion-membrane (N115). The hydrogen crossover was measured at 100% relative humidity (RH, filled symbols) to allow comparison to the values measured by Albert et al. and oversaturated conditions (empty symbols). It is important to note that the membrane thickness has a major impact on the hydrogen crossover,[16] which can be accounted for by plotting the crossover over the HFR. For Nafion-membranes (EW 1100), this trade-off is visualized by the dashed green line (adapted from Albert et al.). Thus, data points for membranes featuring ideal properties (low crossover as well as a low HFR) lie in the lower left corner of Figure 4.

The hydrogen crossover current density of the Nafion-membrane from this work (green diamond) and obtained by Albert et al. (green circle) are in good agreement. However, the HFR deviates due to the different measurement conditions (96% RH, ambient pressure vs 100% RH, 2.5 bar) and electric contributions from the measurement setup. Our measurement conditions yield a lower RH and with that a higher HFR, as can be seen for the Nafion-MEAs. Thus, for correct comparison our data need to be shifted more to the left as indicated by the gray arrows, which brings them even closer to the ideal region of low crossover and low resistance (Figure 4). The hydrogen crossover current densities of all hydrocarbon membranes (purple) are lower than that of the Nafion-membranes (green). This is in accordance with other reports in literature and one of the major advantages of hydrocarbon membranes over PFSA.[37] The hydrogen crossover current densities of sPPS-membranes (purple diamonds) are not only lower than for N115-membranes but also lower than for the hydrocarbon membranes used by Albert et al. (purple circles)—despite a lower HFR. This may be explained by structural inhomogeneities that could result from the grafting process in the membranes by Albert et al., which might lead to additional aqueous pathways that allow for extra gas transport. Compared to the Nafion-membranes measured in this work (green diamonds), the hydrogen crossover current density of the sPPS-membranes is less than one third (at 100% RH), while the HFR is less than half.

Going from 100% RH (filled symbols) to oversaturated conditions (empty symbols), which is closer to PEMWE operating conditions in liquid water, the hydrogen crossover current density increases due to a significantly increased water content of the membrane.[38,39] This increase is mainly explained by the softening effect water (as opposed to water vapor) has on the membrane surface. This reduces the counter-pressure provided by the polymeric network compensating for the osmotic pressure generated by the aqueous ion domain.[40] The latter is particularly high when the membrane is submerged in deionized water. Despite a stronger increase of gas crossover with rising water uptake for the sPPS-membrane, the crossover is still substantially lower than that of the Nafion-membrane. Future mitigation strategies for further reducing the gas crossover must therefore be the reduction of water uptake of the membrane in contact with liquid water.

In summary, sPPS-MEAs for PEMWE combine low gas crossover and high efficiency better than any other material discussed so far. Further development of this unique hydrocarbon ionomer could be a significant contribution to the current state of PEMWEs.

2.3. Operational Current Density Range

Combining performance and hydrogen crossover data allows for an estimation of the operational current density range of a theoretical sPPS-based (purple) electrolyzer and a N115-based (green) electrolyzer (Figure 5). The limits were defined according to Babic et al. with the lower limit resulting from the safety limit of 2% hydrogen in oxygen and the upper limit deriving from a minimum voltage efficiency of 74%, corresponding to 2 V operation voltage.[15] For industrial relevance, the operational window is given for 30 bar balanced operation by extrapolating the experimental hydrogen crossover data obtained for the sPPS- and Nafion-MEA at 1, 1.5, 2, and 2.5 bar (Figure 9a). The upper limit was directly derived from Figure 3, since effects of pressure on the cell polarization were found to cancel each other out (for balanced pressures).[41] A detailed description of the calculation can be found in Appendix A.3.
As can be seen from Figure 5, both limits strongly constrain the operational range of a PEMWE system. However, for the sPPS-MEA (purple) we find a more than five times larger operation window than for the Nafion-MEA. This larger operation window is due to both beneficial properties of the sPPS-MEA: the lower gas crossover, which enables lower current densities, and the higher efficiency, enabling higher current densities. This significantly enlarged window of operation is a highly relevant finding for industrial application which emphasizes the beneficial properties of the herein reported hydrocarbon membrane material.

2.4. Durability

The voltage evolution of one Nafion-MEA (green) and two sPPS-MEAs (purple and blue) during a 100 h constant current hold at 1 A cm$^{-2}$ is displayed in Figure 6a. The voltage of the Nafion-MEA increased by $\approx 300$ µV h$^{-1}$. For these moderate testing conditions, this increase rate is slightly higher than reported literature data, with values up to 260 µV h$^{-1}$.[42–45] The slightly higher degradation rate could be related to the fact that the test bench has no deionizer and potential iron-ion contamination was only countered by exchanging the reservoir water every 20 h. The sPPS-I-MEA showed a voltage increase rate of 850 µV h$^{-1}$, considering only the time frame with no electrical shorting (<60 h). This rate is significantly higher than that of Nafion. Associated, the performance of the sPPS-I-MEA at the “end of test” (EOT) (blue empty upward facing triangles) deteriorated compared to the performance at “beginning of the test” (BOT) (blue filled upward facing triangles, Figure 6b). Due to the similar iR-free voltages of the sPPS-I-MEA for BOT and EOT (Figure 6c), membrane degradation is the most likely reason for the performance loss.

The degradation rate and performance of the sPPS-II-MEA are dominated by electrical shorts concealing an opposing voltage increase (details on the effect of electrical shorts on the electrolysis voltage can be found in ref. [46]). Since both sPPS-MEAs showed similar performance at BOT (Figure 6b, filled triangles) and failed at about the same time of test, assembly errors can be excluded.
In general, this initial durability test points out two issues: first, the lack of mechanical robustness of a pure sPPS membrane—which we assume to be the most likely reason for the electrical shorts—and second, that formation of radicals and radical degradation of the membrane—potentially enhanced by iron-ion contamination—may be a more critical issue to solve for sPPS and hydrocarbon materials in general than for Nafion.

As mentioned above, the reduction of water uptake of a sPPS-based membrane by, e.g., blending or copolymerization could be a mitigation strategy that potentially resolves both, the lack of mechanical robustness and helps to reduce gas crossover and thus radical formation. While these findings show clear room for improvement, one should note that this is the longest operation ever reported for hydrocarbon membranes. Considering the remarkably low HFR, the high performance of the hydrocarbon electrodes and the very low hydrogen crossover current density reported here gives a bright perspective for sPPS-based cells for PEMWEs.

3. Conclusion

Fluorine-free MEAs with sPPS, a hydrocarbon polymer with unique transport properties, were evaluated as membrane and ionomer in the electrodes in a polymer electrolyte membrane water electrolyzer. The performance of the sPPS-MEAs was substantially better than that of state-of-the-art Nafion N115-MEAs (3.5 A cm$^{-2}$ vs 1.5 A cm$^{-2}$ at 1.8 V) with identical catalyst loading and comparable membrane thickness. Compared to other hydrocarbon-based MEAs the here presented fully hydrocarbon sPPS-MEAs possess the highest efficiency published to date. The cause for the excellent cell performance is a significantly lower high frequency resistance of the sPPS-MEAs (compared to Nafion-MEAs). Furthermore, electrodes with sPPS-ionomer showed similar kinetics as conventional Nafion-electrodes at significantly reduced ionomer content, which is another benefit as material cost can potentially be further reduced.

The hydrogen crossover was found to be three times lower for sPPS-membranes (0.3 mA cm$^{-2}$) compared to Nafion N115-membranes (1.1 mA cm$^{-2}$). These findings confirm that sulfonated poly(phenylene sulfone) combines low hydrogen crossover with high conductivity. An important consequence is a wider operational window of a sPPS-based PEMWE due to the high efficiency and low gas crossover the operational window is expected to be larger by a factor of 5 compared to that of a Nafion–MEA.

An initial long-term stability test of sPPS-MEAs performed as constant current hold at 1 A cm$^{-2}$ for 100 h showed lower durability for two sPPS-MEAs compared to the Nafion reference. It is theorized that the observed degradation partially originates from the high water content in the sPPS-membranes yielding a softening of the membrane and an increase of the gas crossover and thus, degradation via radical attack. Future mitigation strategies should therefore focus on the reduction of the water uptake of sPPS-membranes and other measures to enhance the durability of hydrocarbon membranes for water electrolysis.

4. Experimental Section

Membrane Fabrication: Membranes were prepared by dissolving 0.8–0.9 g of sPPS (previously exchanged to H$^+$-form and dried at 120 °C in vacuum) in 11 ml DMAC under constant stirring at 80 °C overnight. The clear yellow solution was then filtered using a Whatman 3.2 µm glass-fiber syringe filter and poured onto a glass plate that was previously cleaned in a KOH-bath. The solvent was evaporated in a vacuum oven at 65 °C at 12 mbar for 14 h. The dry membrane was then submerged in a 10 wt% aqueous sulfuric acid solution at room temperature and released off the glass plate. The sulfuric acid solution was exchanged after 2 h. After 4 h the membrane was washed in deionized water at room temperature until pH-neutrality of the washing water was reached. The membrane was subsequently stored in water. Prior to spray coating, the sPPS-membranes were dried at ambient conditions while pressed between tissues to avoid wrinkling for at least 2 d.

Water Uptake: Water uptake in sPPS membranes in terms of water molecules per ionic group (λ) was measured at room temperature using a membrane sample that was stored in deionized water for at least 1 d. The sample was taken out of the water, excess water droplets removed by briefly dabbing the sample with dry, dust-free paper towels from both sides, and weighed. The sample was then transferred into an oven and dried for 2 d at 120 °C under vacuum. The dried membrane was quickly weighed and the water uptake in terms of λ (water molecules per ionic group) calculated according to: \( \lambda = (m_{\text{sample, dry}} - m_{\text{sample, wet}})/\text{IEC} \) with λ (m$_{\text{PPS}}$ = 28), the water volume fraction Φ calculated using the dry polymer’s density \( \rho_{\text{dry}} \) and IEC (IEC$_{\text{PPS}}$ = 2.78 mequiv g$^{-1}$) as well as molecular weight and density of water, according to Φ$_{\text{PPS}}$ = \( \frac{\text{IEC} \times \lambda \times (\text{H}_2\text{O})}{1000} \left( \frac{\rho_{\text{water}}}{\rho_{\text{PPS}}} + \text{IEC} \times \lambda \times (\text{H}_2\text{O}) \right) \).

MEA Fabrication: The MEAs were fabricated by spray coating on the membranes. By this, the electrodes were directly deposited onto the membrane foils. To do so, four different inks were mixed to get Nafion- and sPPS-based inks for the anode and cathode side of the MEAs each. MEAs were fabricated with a loading of 1.5 mg cm$^{-2}$ IrO$_2$ at the anode and 0.5 mg cm$^{-2}$ Pt at the cathode.

The inks for the cathode electrodes were fabricated by mixing Pt/C (60 wt%, HiSPEC 9100, VWR International GmbH) powder at first with water and afterward with 2-propanol (IPA) in a H$_2$O:IPA ratio of 1:1 yielding 1.6 wt% Pt/C in liquids. For the Nafion containing ink, D520 ionomer was added subsequently, in order to obtain an ionomer content of 28 wt% Nafion in solids, equivalent to an I/C ratio of 1. For the cathode catalyst ink, sPPS ionomer was added from a 5 wt% solution of DMAc in order to obtain a 10 wt% content of sPPS in solids, equivalent to an I/C ratio of 0.28.

The inks for the anode electrodes were fabricated by mixing IrO$_2$ powder (Premion, 99.99%, Alfa Aesar) at first with water and afterward with in a H$_2$O:IPA ratio of 1:1 yielding 1 wt% IrO$_2$ in liquids. Subsequently, for the Nafion containing ink, Nafion was added by feeding DS20 ionomer into the IrO$_2$ dispersion to get an ionomer content of 8 wt% (0.22 I/C ratio). Similarly, for the sPPS-containing electrode, sPPS from a 5 wt% DMAc solution was added until an ionomer content of 4 wt% (0.1 I/C ratio) was obtained.

Prior to spray coating, all inks were sonicated for at least 30 min in an ice bath to prevent overheating and agglomeration. For spray coating, the membranes were framed by 1 mm thick polymethylmethacrylat sheets leaving two superimposed openings of 4 cm$^2$ on each side of the membrane.

Spray coating was performed with an ultrasonic spray coater (SNR-300, Sonocell), where the inks were atomized and deposited by a 130 kHz ultrasonic nozzle (Sonaei NS130K50531). The flow rate was set to 0.1 ml min$^{-1}$, the heating plate temperature to 40 °C and the robot axis speed to 140 mm s$^{-1}$. The spraying path consisted of a serpentine pattern with 3 mm spacing. To ensure uniform deposition, each pattern was sprayed with a shift of 1.5 mm and then tilted by 90° again with and without 1.5 mm shift. To obtain the desired loading, a thin metal pad of 2.5 cm$^2$ area was placed next to the membranes in the coating area and weighted before and after the spraying process.
This measure is very important to rule out significant weighing errors stemming from humidity uptake and not Pt-loading increase (which is, e.g., the case for a gas diffusion layer substrate or membrane).

As porous transport layers on the anode side, sintered titanium fiber felts (2GDL40-1,0, Bekacart) were used. The titanium fiber felts had a thickness of 1 mm. As cathodic porous transport layer, 4 cm² carbon fiber papers with microporous layer by Freudenberg (H24CS, 270 µm uncompressed thickness) were used.

**Material Characterization:** Cross-sections of the MEAs as well as the electrodes were imaged with a scanning electron microscope (Vega3, Tescan) at a voltage of 10 kV and a working distance of 5 mm. Prior to imaging, a thin layer of gold was sputtered onto the samples to reduce charging effects. The enlarged images of the catalyst layers were recorded with a FIB-SEM (Scios2 HiVac, Thermo Scientific). The sample was milled by Gallium-ions at 30 kV, using declining milling currents of 3 nA, 0.5 nA, and 50 pA for sample preparation. Images were taken at a voltage of 5 kV, a working distance of 7 mm, and a tilt of the stage of 52° using an in-lens T2 detector.

**Electrochemical Measurements:** The MEAs in dry state including the PTLs were assembled in a 4 cm² cell setup using 1 and 0.05 mm Teflon sheets (Hightechflon), as hard stop for compression of the anode and cathode side, respectively. Electrochemical measurements were performed with a potentiostat (857, Scribner) at 80 °C, ambient pressure, and flow rates of deionized water of 40 mL min⁻¹ at the anodic and cathodic compartment.

The measurement sequence consisted of conditioning voltage sweeps, polarization curves, and electrochemical impedance measurements. Conditioning voltage sweeps were conducted by scanning the voltage from 1.4 to 2.2 V in steps of 200 mV, while holding each step for 30 s. Polarization curves were conducted by scanning current from 0 to 0.04 A in steps of 20 mA, from 0.05 to 1 A in steps of 50 mA, from 1.25 to 3 A in steps of 250 mA, from 3.5 to 5 A in steps of 500 mA, and from 6 to 20 A in steps of 1000 mA while holding each step for 2 min. Polarization curves were always followed by electrochemical impedance spectroscopy (EIS) measurements at 0.1, 0.5, 1, 3, and 4 A cm⁻² whereby each current was held for 3 min before each EIS measurement. EIS measurements were subsequently performed by scanning the frequency from 20 kHz to 0.1 Hz.

The measurement procedure consisted of a polarization curve, followed by EIS, 20 conditioning voltage sweeps, 1 polarization curve followed by EIS, 12 h of an open circuit voltage hold to ensure proper hydration, and subsequently again 1 polarization curve followed by EIS. The latter polarization curve is in the following the polarization curve referred to.

**Stability Testing:** Stability was tested by a moderate constant current hold at 1 A cm⁻² and 80 °C for a time frame of 100 h. Every 20 h polarization curves were recorded and EIS measurements conducted, followed by draining and refilling the deionized water in the gas–water interface.

Figure 7. FIB-SEM images of anode (top) and cathode (bottom) catalyst layers with sPPS (left) and Nafion (right) as ionomer binder in the stated weight concentrations in respect to solids.

Figure 8. Linear sweep voltammograms of MEAs with Nafion- (green) and sPPS-membrane (purple) at 100% RH (solid lines) and in oversaturated conditions (dashed lines). The shown graphs display the mean value obtained by two individual measurements of two identical samples each. The error bands display the standard deviation of these measurements.
separation tanks. To avoid stressing the MEAs, the water in the tubing and the cell fixture was not exchanged.

**Crossover Measurements**: Crossover measurements were conducted as suggested by Albert et al. \[20\] by using a Fuel Cell test bench (Scribner 850e) at 80 °C, with H\(_2\)/N\(_2\) flows fixed at 0.2/0.2 L min\(^{-1}\) and 2.5 bar absolute pressure in the anode and cathode compartment. Membrane thicknesses of the MEAs measured in this test were comparable to those used in the electrolysis measurements. LSV measurements were performed by increasing the voltage in steps of 1 mV s\(^{-1}\) from 0 to 0.6 V. The hydrogen crossover current density was obtained by the y-axis intercept of a linear fit of the LSV between 0.25 and 0.35 V to exclude the influence of the hydrogen desorption peak and ohmic contributions. Measurements were performed at 100% RH and at oversaturated conditions, by setting the fuel temperature to 90 °C dew point.

The HFR for the crossover measurements was measured in the same setup with H\(_2\)/air fixed at 0.1/0.2 L min\(^{-1}\) at ambient pressure and 96% RH. The slightly lower RH was chosen to prevent flooding due to limited back diffusion through the thick PEMs. The HFR value was measured at 3.2 kHz at a current of 250 mA cm\(^{-2}\).

**Appendix**

A.1 Electrode Morphology (Figure 7)

A.2 Linear Sweep Voltammetry (Figure 8)

A.3 Approximation of the Operation Window

The hydrogen crossover was measured by linear sweep voltammetry, in a proton-exchange membrane fuel cell system. To do so, humidified hydrogen was supplied at the anode and nitrogen at the cathode. To get results as close as possible to the operation conditions in a PEMWE, oversaturated conditions were chosen by setting the dew point of the gases to 90 °C. LSV measurements were performed at ambient pressure and at 1.5, 2.5, 3, and 3.5 bar absolute pressure for MEAs with sPPS- (purple diamonds) and with Nafion N115-membrane (green circles) (Figure 9a). PEMWE systems, however, are operated at much higher pressures in the range of tens of bars. Operation in this higher pressure range causes an increase of gas crossover and with that critical hydrogen in oxygen contents. A linear fit of the measured crossover current densities in the low pressure range yields an average crossover current density for the MEA with sPPS-membrane of 9 mA cm\(^{-2}\) and with N115-membrane of 17 mA cm\(^{-2}\) at 30 bar. Deviations from the linear fit especially for the high partial pressure points might be explained by insufficient humidification at the beginning of the measurement sequence, which was conducted from low to high pressures. Therefore, the crossover current densities for small partial pressures are most likely underestimated and the extrapolated pressure values should be seen more as conservative estimates.

If treating the gas crossover as independent of the applied current density, the hydrogen in oxygen content increases in the low current density range, when only little oxygen is produced. The hydrogen in oxygen content in the anode compartment at 30 bar, extracted from the approximated crossover current densities for MEAs with sPPS (purple) and N115 (green) membrane, is displayed in Figure 9b. The current density, at which a PEMWE system has to be shutdown, is set at 2% hydrogen in oxygen to leave a safety margin to the explosion limit. The shutdown limit is displayed by the dashed black line and applies at 0.9 and 1.7 A cm\(^{-2}\) for the MEAs with sPPS- and Nafion-membrane, respectively.

**Acknowledgements**

C.K. and T.S. contributed equally to this work. The authors gratefully acknowledge the financial support by the Federal Ministry of Education and Research of Germany in the framework of PSUMEA 3 (Project No. 03EK3045), Robert Bosch GmbH, Siemens AG, and FUMATECH BWT GmbH.

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

electrolysis, hydrocarbons, membrane electrode assembly, sulfonated poly(phenylene sulfone), water electrolysis

Received: December 4, 2019
Revised: February 3, 2020
Published online: February 25, 2020
[1] F. D. Coms, ECS Trans. 2008, 16, 235.
[2] M. Feng, R. Qu, Z. Wei, L. Wang, P. Sun, Z. Wang, Sci. Rep. 2015, 5, 9859.
[3] Fuel Cell Technical Team Roadmap, United States Driving Research and Innovation for Vehicle efficiency and Energy sustainability, table 4, 2017, p. 9.
[4] K. D. Kreuer, in Handbook of Fuel Cells: Fundamentals Technology and Applications (Eds: W. Vielstich, A. Lamm, H. A. Gasteiger), John Wiley and Sons Ltd., New York 2003.
[5] K. D. Kreuer, J. Membr. Sci. 2001, 185, 29.
[6] K. D. Kreuer, S. J. Paddison, E. Spohr, M. Schuster, Chem. Rev. 2004, 104, 4637.
[7] K. H. Lee, S. Y. Lee, D. W. Shin, C. Wang, S.-H. Ahn, K.-J. Lee, M. D. Guiver, Y. M. Lee, Spec. Issue Polym. Membr. 2014, 55, 1317.
[8] K.-H. Oh, I. Bae, ACS Appl. Nano Mater. 2019, 2, 3857.
[9] C. H. Park, S. Y. Lee, D. S. Hwang, D. W. Shin, D. H. Cho, K. H. Lee, T.-W. Kim, T.-W. Kim, M. Lee, D.-S. Kim, C. M. Hoherty, A. W. Thornton, A. J. Hill, M. D. Guiver, Y. M. Lee, Nature 2016, 532, 480.
[10] D. W. Shin, S. Y. Lee, C. H. Lee, K.-S. Lee, C. H. Park, J. E. McGrath, M. Zhang, R. B. Moore, M. D. Lingwood, L. A. Madsen, Y. T. Kim, I. Hwang, Y. M. Lee, Macromolecules 2013, 46, 7797.
[11] S. Y. So, Y. J. Yoon, T.-H. Kim, K. Yoon, Y. T. Hong, J. Membr. Sci. 2011, 381, 204.
[12] S. Tian, Y. Meng, A. S. Hay, Macromolecules 2009, 42, 1153.
[13] J. Peron, Z. Shi, S. Holdcroft, Energy Environ. Sci. 2011, 4, 1575.
[14] K. E. Ayers, E. B. Anderson, C. Capuano, B. Carter, L. Dalton, G. Hanlon, J. Manco, M. Niedzwiecki, in 218th ECS Meeting, ECS, Transactions, Las Vegas, Nevada, USA 2010, p. 3.
[15] U. Babic, M. Suermann, F. N. Büchi, L. Gubler, T. J. Schmidt, J. Electrochem. Soc. 2017, 164, F387.
[16] D. Bessarabov, H. Wang, H. Li, N. Zhao, PEM Electrolysis for Hydrogen Production: Principles and Applications, CRC Press, Boca Raton, Florida, USA 2016.
[17] R. Nolte, K. Ledjef, M. Bauer, R. Mühlaupt, J. Membr. Sci. 1993, 83, 211.
[18] C. A. Linkous, H. R. Anderson, R. W. Kopitzke, G. L. Nelson, Int. J. Hydrogen Energy 1998, 23, 525.
[19] I.-Y. Jang, O.-H. Kweon, K.-E. Kim, G.-J. Hwang, S.-B. Moon, A.-S. Kang, J. Membr. Sci. 2008, 322, 154.
[20] A. Albert, A. O. Barnett, M. S. Thomsassen, T. J. Schmidt, L. Gubler, ACS Appl. Mater. Interfaces 2015, 7, 22203.
[21] G. Wei, L. Xu, C. Huang, Y. Wang, Int. J. Hydrogen Energy 2010, 35, 7778.
[22] A. Skulimowska, M. Dupont, M. Zaton, S. Sunde, L. Merlo, D. J. Jones, J. Rozière, Int. J. Hydrogen Energy 2014, 39, 6307.
[23] S. Siracusano, V. Baglio, F. Lufrano, P. Staiti, A. S. Aricò, J. Membr. Sci. 2013, 448, 209.
[24] G. Hübner, E. Roduner, J. Mater. Chem. 1999, 9, 409.
[25] R. Shimizu, J. Tsuji, N. Sato, J. Takano, S. Itami, M. Kusakabe, K. Miyatake, A. Iiyama, M. Uchida, J. Power Sources 2017, 367, 63.
[26] F. N. Büchi, B. Gupta, O. Haas, G. G. Scherer, Polym. Electrolyte Fuel Cells 1995, 40, 345.
[27] T. Holmes, T. J. G. Skalski, M. Adamski, S. Holdcroft, Chem. Mater. 2019, 31, 1441.
[28] M. Schuster, K. D. Kreuer, H. T. Andersen, J. Maier, Macromolecules 2007, 40, 598.
[29] C. de Araujo, K. D. Kreuer, M. Schuster, G. Portale, H. Mendil-Jakani, G. Gebel, J. Maier, Phys. Chem. Chem. Phys. 2009, 11, 3305.
[30] V. K. Puthiyapura, M. Mamlouk, S. Pasupathi, B. G. Pollet, K. Scott, J. Power Sources 2014, 269, 451.
[31] V. K. Puthiyapura, S. Pasupathi, H. Su, X. Liu, B. Pollet, K. Scott, Int. J. Hydrogen Energy 2014, 39, 1905.
[32] M. G. Chourashiya, A. Urakawa, J. Mater. Chem. A 2017, 5, 4774.
[33] J. W. D. Ng, T. R. Hellstern, J. Kibsgaard, A. C. Hinckley, J. D. Benck, T. F. Jaramillo, ChemSusChem 2015, 8, 3512.
[34] S. Siracusano, V. Baglio, A. Stassi, L. Merlo, E. Moukheiber, A. S. Aricò, J. Membr. Sci. 2014, 466, 1.
[35] X. Wang, Z.-G. Shao, G. Li, L. Zhang, Y. Zhao, W. Lu, B. Yi, Int. J. Hydrogen Energy 2013, 38, 9057.
[36] L. Gubler, Membranes for Water Electrolysis: Target-Oriented Choice and Design of Materials, Second International Workshop on Durability and Degradation Issues in PEM Electrolysis Cells and its Components, Fraunhofer ISE, Freiburg, Germany 2016.
[37] K. D. Kreuer, Membr. Fuel Cells 2001, 185, 29.
[38] M. J. Cheah, I. G. Kevrekidis, J. Benziger, J. Phys. Chem. B 2011, 115, 10239.
[39] M. Bass, A. Berman, A. Singh, O. Konovalov, V. Freger, J. Phys. Chem. B 2010, 114, 3784.
[40] K. D. Kreuer, Solid State Ionics 2013, 252, 93.
[41] M. Suermann, A. Pátru, T. J. Schmidt, F. N. Büchi, Int. J. Hydrogen Energy 2017, 42, 12076.
[42] C. Rakousky, U. Reimer, K. Wippermann, S. Kuhri, M. Carmo, W. Lueke, D. Stolten, J. Power Sources 2017, 342, 38.
[43] C. Rozain, E. Mayousse, N. Guillet, P. Millet, Appl. Catal., B 2016, 182, 123.
[44] H. Su, V. Linkov, B. J. Bladergroen, Int. J. Hydrogen Energy 2013, 38, 9601.
[45] C. Klose, P. Trinke, T. Böhm, B. Bensmann, S. Vierrath, R. Hanke-Rauschenbach, S. Thiele, J. Electrochem. Soc. 2018, 165, F1271.
[46] S. P. S. Badwal, S. Giddey, F. T. Ciacchi, Ionics 2006, 12, 7.