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Crosslinked sulfonated polyphenylenes:
overcoming the performance–gas permeation–
stability trilemma in water electrolyzers†Clara Schare,^{‡a} Giorgi Titvinidze,^{‡b} Noortje Platenburg,^a Marco Viviani,^{ac}
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Thermal crosslinking of Pemion®, a highly sulfonated polyphenylene membrane, is used as a viable route to combine high proton conductivity, low gas permeability and mechanical robustness. Crosslinked Pemion® not only outperforms any other membrane reported so far, as a PFAS-free membrane, it is also considered to be environmentally more benign.

The prospect of high voltage efficiency and dynamic load operation renders proton exchange membrane (PEM) electrolysis highly attractive for future green hydrogen production. To meet the U.S. Department of Energy (DOE) cost target of only \$1 per kg of green hydrogen, an efficiency of 3 A cm^{-2} at 1.6 V must be reached. Decreasing the area specific resistance (ASR) of the membrane is a major lever for achieving this goal.

State-of-the-art PEM water electrolyzers utilize PFSA-membranes, which are well established for other electrochemical technologies such as PEM fuel cells and chlorine-alkaline electrolysis. Unfortunately, in the presence of high gas partial pressure gradients (for hydrogen and oxygen) that are characteristic of electrolyzer operation, high inherent gas crossover leads to severe safety issues.¹ Increasing the membrane thickness diminishes this hazard by reducing the gas crossover but also increases the ASR and with that, reduces performance. Other mitigation strategies like recombination catalysts² are discussed controversially, as they are expensive, do not improve faradaic efficiency³ and might accelerate degradation.⁴ Moreover, there is a global aspiration to substitute so-called ‘forever chemicals’ such as PFASs.

Hydrocarbon membranes offer a promising alternative since first, they characteristically exhibit a higher ionic conductivity to gas permeability ratio compared to PFASs^{5,6} and second, they are not subject to potential restrictions for per- and polyfluoroalkyl substances (PFAS). However, severe swelling up to disintegration of these membranes under electrolysis conditions negatively affects durability.

So far, remediation measures like introducing a mechanical reinforcement have not been able to resolve the issue entirely. For instance, Qelibari *et al.* reduced in-plane swelling of a sulfonated polyphenylene sulfone (sPPS) membrane by introducing a PEEK mesh (Fig. 1 PEEK sPPS). Thereby a stable voltage (dV/dt : $80 \mu\text{V h}^{-1}$) over more than 600 h at 1 A cm^{-2} and 80°C was reached. Nevertheless, using such type of reinforcement layer comes with restrictions in terms of minimum viable membrane thickness and hence resistance.⁷ Recently, Noh *et al.*⁸ and Kang *et al.*⁹ successfully introduced other reinforcements (expanded polytetrafluoroethylene, Fig. 1 5L-5/S50 and

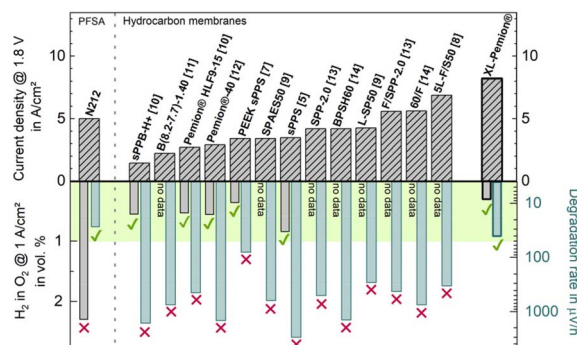


Fig. 1 Overview of current densities at 1.8 V, hydrogen in oxygen contents in the anode gas stream at 1 A cm^{-2} and degradation rates achieved with hydrocarbon membranes in PEM water electrolyzers. A H_2 in O_2 content below 1% (25% of lower explosion limit) and a degradation rate below $50 \mu\text{V h}^{-1}$ were defined as acceptable and highlighted in green. Apart from Klose *et al.*⁶ PFSA was used as the ionomer binder in the catalyst layer.^{7–14} For more details see ESI (Table S1).†

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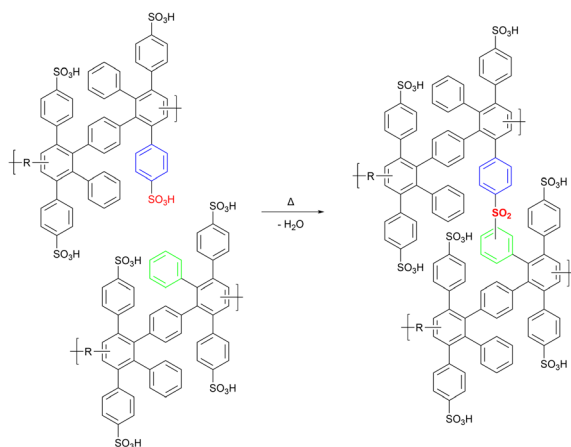
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Scheme 1 Schematic of the presumed crosslinking reaction of sulfonated phenylated polyphenylenes during the heat treatment step.

liquid crystal polymer fabric, Fig. 1 L-SP50) into hydrocarbon based ionomers, realizing high performance ($\sim 6.9 \text{ A cm}^{-2}$ and $\sim 4.25 \text{ A cm}^{-2}$ at 1.8 V , loading $> 2 \text{ mg cm}^{-2}$) but still falling short of state-of-the-art degradation rates ($330 \mu\text{V h}^{-1}$ and $290 \mu\text{V h}^{-1}$ @ 2 A cm^{-2}).

A promising alternative to integrating reinforcements into the membrane is molecular modification of the ionomer by thermal crosslinking. Di Vona *et al.*^{15,16} demonstrated thermal formation of sulfone (SO_2) bridges from sulfonic acid groups. The onset of this reaction depends on the reactivity of the sulfonic acid groups and the nature of the polymer backbone,¹⁷ but once crosslinking occurs, swelling decreases as a direct consequence of an increased mechanical strength.^{15,17}

Despite its high proton conductivity, low gas crossover and chemical stability, the sulfonated phenylated polyphenylene Pemion®¹⁸ is limited by its mechanical weakness under electrolyzer conditions,¹⁰ which makes it a good candidate for applying thermal crosslinking. In the following, we explain how this simple and economically feasible treatment enables stable electrolyzer operation with low gas crossover while virtually meeting the DOE performance target.

According to the reaction suggested by Di Vona *et al.*,¹⁶ the formation of each crosslink from a sulfonic group and an unsulfonated phenyl ring eliminates one fixed ionic group (Scheme 1). Therefore, the density of SO_2 -crosslinks is estimated to be around 0.4 per repeat unit. Since each SO_2 -group connects two repeat units, almost every repeat unit is involved in cross-linking.^{16,19}

At high water content in the membrane, which is typical under electrolyzer conditions, conductivity remains relatively

unaffected by the number of water molecules per sulfonic acid group (λ) because the mobility of charge carriers and dilution effects almost compensate each other. However, gas permeability, exclusively taking place within the aqueous phase of hydrocarbon ionomers,²⁰ strongly increases with the membrane's water content. Therefore, reducing λ is crucial for achieving a high ionic conductivity to gas permeability ratio. Hydrocarbon membranes generally have high ion exchange capacities (IEC) compared to PFSA in order to reach similar specific conductivities. For a given value of λ , this automatically leads to a higher uptake of water. Beyond this expected effect, hydrocarbon membranes in contact with water take up even more water per sulfonic acid group (*i.e.* higher λ). In the case of Pemion® with an IEC of 3.1 meq. g^{-1} , water uptake is as high as 225 wt% corresponding to $\lambda = 40$ at $T = 80^\circ\text{C}$.

Heat treatment of a $20 \pm 5 \mu\text{m}$ thick Pemion® membrane reduces the water uptake by a factor of two, which translates into a decrease of λ by 40% compared to the water uptake before the heat treatment. At the same time, the IEC of the treated membrane (further named XL-Pemion®) is reduced by only 10% (Table 1).

A natural consequence of crosslinking is an increase of mechanical strength (Table 1 and Fig. S1†) leading to a higher internal swelling pressure corresponding to a lower value for λ .²¹ While the emerging insolubility of XL-Pemion® in the corresponding solvents (dimethyl sulfoxide or ethanol) provides qualitative evidence for the formation of sulfone crosslinks, their characteristic symmetric and asymmetric $\text{S}=\text{O}$ stretching signals can be observed in FTIR (Fig. S2†).

For electrochemical characterization, catalyst coated membranes (CCMs) were fabricated by ultrasonic spray-coating electrodes onto a Nafion N212 and a self-cast Pemion® membrane using Nafion as the binding ionomer with an IrO_2 anode (1 mgIr cm^{-2}) and a Pt/C cathode (0.5 mgPt cm^{-2}). The Pemion® containing CCM (Pemion®-CCM) was heat-treated for 1 h at 175°C under vacuum to thermally crosslink the ionomer. The electrolysis cell setup includes on the anode side platinized titanium fiber felts (Bekaert), and on the cathode side a carbon fibre gas diffusion layer with a micro porous layer on top from Freudenberg (H24C5). More details can be found in the ESI.†

The two key-metrics of performance are ohmic losses and hydrogen crossover. The former is closely related to the ASR of the membrane material while the latter to its gas permeability. Since the dependence of both key-metrics on membrane thickness is just opposite, *i.e.* ohmic losses increase with membrane thickness while gas crossover decreases, the thickness of each membrane is chosen to optimize the overall

Table 1 IEC, water uptake, number of water molecules per sulfonic acid group λ (at 80°C) and Young's modulus E (wet samples, at 25°C) for Pemion® and crosslinked Pemion® (XL-Pemion®)

	IEC in meq. g^{-1}	Water uptake @ 80°C in %	λ @ 80°C	E @ 25°C , from water in MPa
Pemion®	3.1 ± 0.1	225 ± 15	~ 40	79
XL-Pemion®	2.8 ± 0.1	120 ± 5	~ 24	222



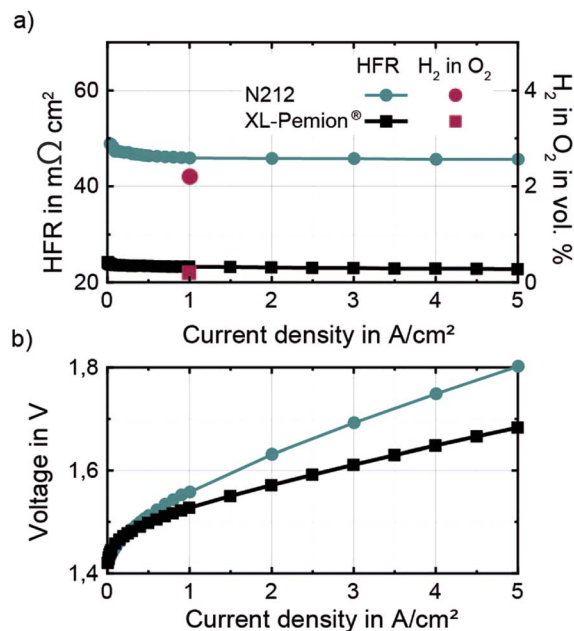


Fig. 2 (a) HFR over current density and H_2 in O_2 -concentration in the anode gas stream at 1 A cm^{-2} (red) for XL-Pemion®- (squares) and N212-CCM (circles). (b) Cell polarization for XL-Pemion®- (squares) and N212-CCM (circles). The measurements were conducted at 80°C .

performance profile. Of course, this is only possible within the limits of sufficient mechanical robustness.

Therefore, the thickness of the Nafion reference membrane was chosen to be $50 \mu\text{m}$, more than double the thickness of XL-Pemion ($20 \pm 5 \mu\text{m}$). For Nafion, this thickness yields a hydrogen concentration close to the lower explosion limit in the anode compartment even at 1 A cm^{-2} (Fig. 2a).

The data for a Nafion N212-CCM (blue circles) and XL-Pemion®-CCM (black squares) recorded under electrolyzer conditions impressively demonstrate that for the chosen thicknesses, all relevant key figures are significantly better for the latter: ohmic losses are lower by a factor of about 2 with a corresponding decrease of high-frequency resistance (HFR) while the hydrogen (H_2) in oxygen (O_2) concentration is lower by more than a factor of 7 (Fig. 2a). In numbers, this gives a noteworthy low H_2 -concentration measured in the anode O_2 stream of only 0.3% (red square) compared to 2.2% (red circle) for the thicker N212-CCM at a current density of 1 A cm^{-2} (Fig. 2a). Lower gas permeation of hydrocarbon vs. PFSA membranes is reported throughout the literature,^{6,11,20} but the permeation ratios are generally smaller than observed in the present work. A possible reason could be the relatively low water uptake of XL-Pemion® ($\lambda = 24$ at $T = 80^\circ \text{C}$) compared to other hydrocarbon membranes. Note that in hydrocarbon membranes residual gas permeation is constrained to the aqueous ionic domain.²⁰

Additionally, the XL-Pemion®-CCM shows the highest voltage efficiency for hydrocarbon CCMs, reported so far (Fig. 1). Almost identical iR -free voltages and comparable Tafel slopes for the XL-Pemion®- and N212-CCM (Fig. S3†) indicate that the high voltage efficiency is the immediate consequence of the low HFR of $23 \text{ m}\Omega \text{ cm}^2$ vs. $46 \text{ m}\Omega \text{ cm}^2$. The low HFR

reflects the high specific conductivity of XL-Pemion®, the low membrane thickness and good contact between the membrane and electrodes. Apparently, the heat treatment neither negatively affects the membrane-electrode contact, nor kinetics and gas transport within the electrodes.

As a side note, it is worth mentioning that the presented H_2 in O_2 contents are in line with values reported in the literature for non-optimized catalyst layers^{22,23} or cell configurations²⁴ on the cathode side (for details see ESI†).

During a 100 hour constant current hold at 1 A cm^{-2} , the XL-Pemion®-CCM and N212-CCM show stable performance with degradation rates of $40 \mu\text{V h}^{-1}$ and $27 \mu\text{V h}^{-1}$ (Fig. 3a). These degradation rates are within the lower range of degradation rates reported in the literature for Nafion-CCMs with N212 membranes,²⁵ and the degradation rate for the XL-Pemion®-CCM appears to be the lowest reported for hydrocarbon CCMs, so far (Fig. 1). The polarization curves at the beginning and end of the test can be found in the ESI (Fig. S4).† The virtually constant H_2 -crossover over time (Fig. 3b) underlines the stability of both CCMs, furthermore supported by no changes in the IEC and thickness of the XL-Pemion® membrane before and after the 100 h operation (see Fig. S5†).

For the XL-Pemion®-CCM, stable performance is observed only after heat treatment. An untreated Pemion membrane with similar thickness showed only a stable performance for the first two hours and disintegrated during the following 6 hours under electrolysis conditions (Fig. S6†). This can be underlined by the results from Wang *et al.*,¹⁰ reporting a lifetime of less than 86 hours for an untreated sulfonated phenylated polyphenylene membrane that is accompanied by an increase in H_2 in O_2 -content from 0.55% to 1.17% during the first 40 hours of the test.¹⁰

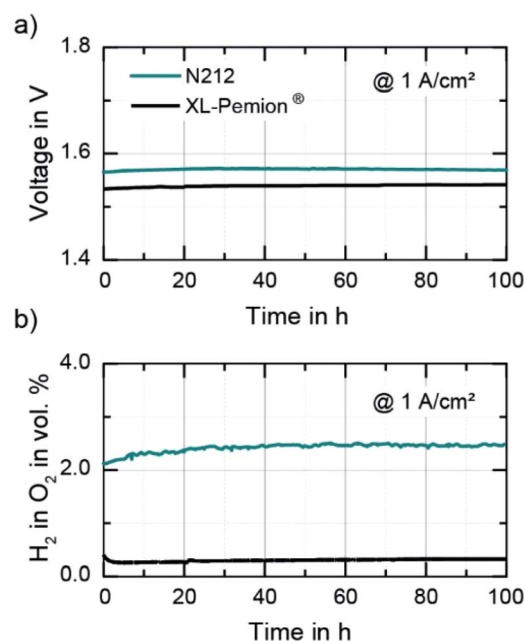


Fig. 3 (a) Voltage evolution and (b) H_2 in O_2 -concentration in the anode gas stream during a constant current hold at 1 A cm^{-2} and 80°C of the XL-Pemion®-CCM (black) and N212-CCM (green).



Thermal crosslinking of highly sulfonated polyphenylene Pemion® membranes leads to a combination of properties, which is outstanding for application in PEM water electrolysis. Swelling and gas permeability are significantly reduced while conductivity remains high. The easy treatment also improves membrane durability. In electrolyzer tests, these properties translate into very high voltage and faradaic efficiencies: at a voltage of only 1.61 V, the current density reaches 3 A cm^{-2} , exceeding state-of-the-art voltage efficiency for any type of membrane. At a current density of 1 A cm^{-2} , a stable hydrogen concentration in the oxygen stream of 0.3%, well below the explosion limit, is recorded. Stable performance over 100 h is demonstrated with a degradation rate of $<50 \mu\text{V h}^{-1}$. These results are obtained without any PFAS in the membrane. Considering the possibility that PFASs may fall under a future PFAS ban, the suggested approach gains further relevance for the next generation of PEM electrolyzers. Extending the approach to larger areas, longer testing times under various conditions and high pressures are next obvious steps for implementing thermally crosslinked sulfonated polyphenylene membranes in commercial PEM electrolyzers.

Data availability

All data generated or analysed during this study are included in this article and its ESI.†

Author contributions

C. S., G. T., A. M. and C. K. conceptualized the study and wrote the initial draft. C. S., G. T., M. V., A. M., N. P., conducted the experimental work. C. K., K.-D. K. and S. V. acquired project funding. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There are no conflicts to declare.

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