Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information:

Crosslinked Sulfonated Polyphenylenes:

Overcoming the Performance – Gas Permeation – Stability Trilemma in Water Electrolyzers

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Introduction

Table S1 Comparison of current densities at 1.8 V, hydrogen in oxygen contents at 1 A/cm^2 and degradation rates (dv/dt) achieved with hydrocarbon membranes in PEM water electrolyzers. Apart from Klose et al.[1] PFSA (Nafion) was used as ionomer binder in the catalyst layer.[2–9]

Membrane	Reinforcement	Thickness dry in µm	Anode iridium loading in mg_{Ir}/cm^2	Temperature in°C	Current density @ 1.8 V in A/cm^2	H_2 in O_2 in vol. %	Current density during Chronoamperometry in A/cm^2 /AST	Time duration in h	dV/dt in µV/h	Source
N212	no	50	1	80	5	2.3	1	100	27	This work
sPPB-H^+	no	50	3.5 ± 0.6	70	1.45	0.55	1	46	1630	[2]
B(8.2-7.7)-1.40	no	50	2	80	2.23	-	AST*	90	745	[3]
Pemion® PF1-HLF9-15	ePTFE	15	3.5 ± 0.6	70	2.7	0.53	1	27	440	[2]
Pemion-15	ePTFE	15	3 ± 0.4	70	2.91	0.56	1	10	20	[4]
Pemion-40	ePTFE	40	3 ± 0.4	70	2.89	0.56	1	100	1460	[4]
PEEK sPPS	PEEK	74	0.5	80	3.4	0.36	1	433	80	[5]
sPPS	no	115	1.5	80	3.48	0.84	1	58	3000	[1]
BPSH60	no	50	2	80	4.19	-	AST*	90	1421	[3]
SPP-2.0	no	50	1.7±0.17	80	4.19	-	2	100	500	[6]
SPAES50	no	47	2.4	80	3.41	-	2	100	620	[7]
L-SP50	LCP	33	2.0±0.17	80	4.25	-	2	100	290	[7]
SPAES60	no	32	1.7±0.26	80	5.37	-	2	100	1140	[8]
F/SPP-2.0	2x PTFE	20	1.7±0.17	80	5.62	-	2	100	420	[6]
60/F	PTFE	31	1.7±0.26	80	5.63	-	2	100	744	[8]
3L-F/s50	1x PTFE	20	1.7±0.17	80	6.18	-	2	100	710	[9]
5L-F/S50	2x PTFE	20	1.7±0.17	80	6.87	-	2	100	330	[9]
Pemion®	**no**	**25**	**1**	**80**	**8.11**	**0.3**	**1**	**6**	**-**	**This work**
XL-Pemion®	**no**	**25**	**1**	**80**	**8.21**	**0.3**	**1**	**100**	**40**	**This work**

*cycling between 3 and 0.02 A/cm^2

Results and discussion

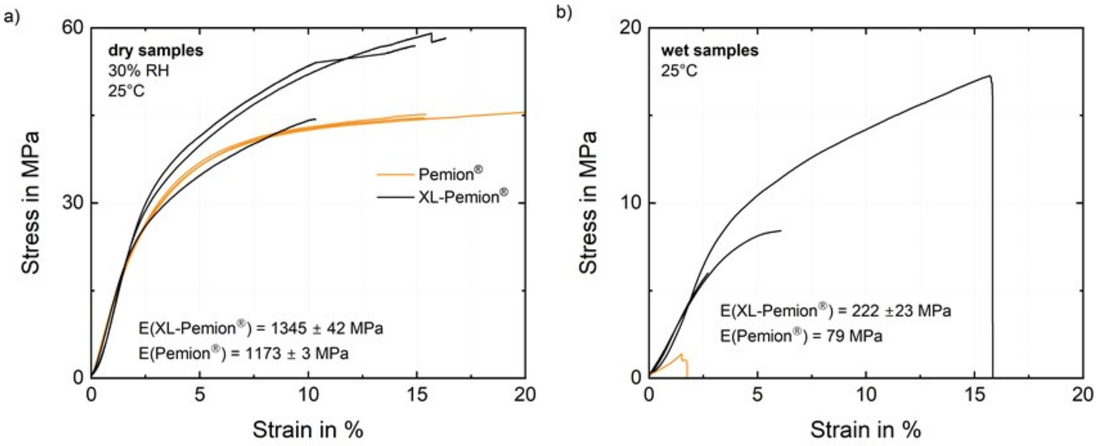

Fig. S1 Stress-strain data at 30% relative humidity (RH) and 25 °C for a) dry and b) wet crosslinked (black) and non crosslinked (orange) Pemion® membranes. The wet samples were soaked in water for 24h, assembled in the wet state and measured within 30 seconds under ambient conditions. The crosslinked (XL-Pemion®) samples demonstrate higher mechanical robustness under both conditions compared to the non-crosslinked (Pemion®) counterparts. Notably, four out of five pre-swollen non-crosslinked samples failed during mounting in the tester due to mechanical weakness.

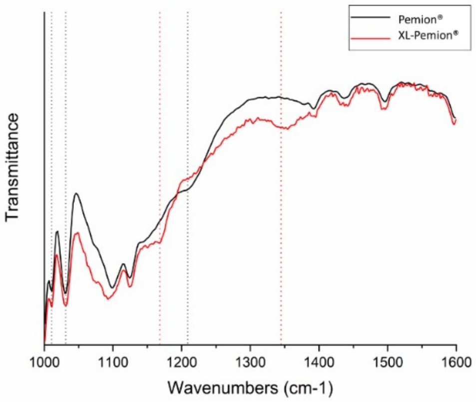

Fig. S2 In the IR spectra of Pemion, the bands at 1012 cm⁻¹, 1031 cm⁻¹, and 1210 cm⁻¹ are assigned to the SO_3H group. After thermal treatment, two additional bands appear at 1168 cm⁻¹ and 1346 cm⁻¹, which are characteristic of the symmetric and asymmetric S=O stretching vibrations, respectively, indicating that crosslinking occurs via $Ph–SO_2–Ph$ linkages. However, since the intensity of the SO_3H signals depends strongly on hydration, and the water uptake of crosslinked and non-crosslinked Pemion differs by nearly a factor of two, it is challenging to rely on band intensity as evidence of crosslinking. At the same time, it should be noted that the decrease in IEC is relatively small – from 3.1 down to 2.8 mequiv/g.

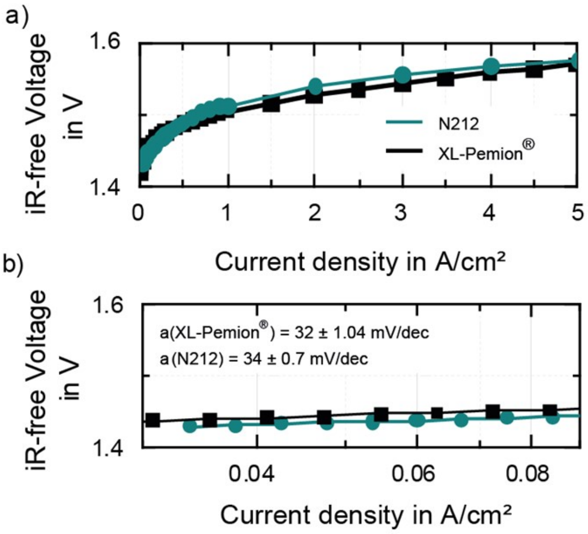

Fig. S3 The iR-free voltage was calculated by subtracting the ohmic losses from the cell voltage and is here plotted against the current density for a N212- (green circles) and a XL-Pemion- (black squares) CCM (a). Based on the similar Tafel slopes (32±1,04 mV/dec for XL-Pemion® vs. 34±0,7 mV/dec for N212) it is safe to assume, that both cells present similar kinetic related losses (b). The only minor difference in iR-free voltage of approximately 8 mV at 3 A/cm² can be attributed to other losses like mass transport losses. Therefore, the excellent performance of XL-Pemion® can be mostly attributed to the membrane and not to significant differences in the catalyst layers.

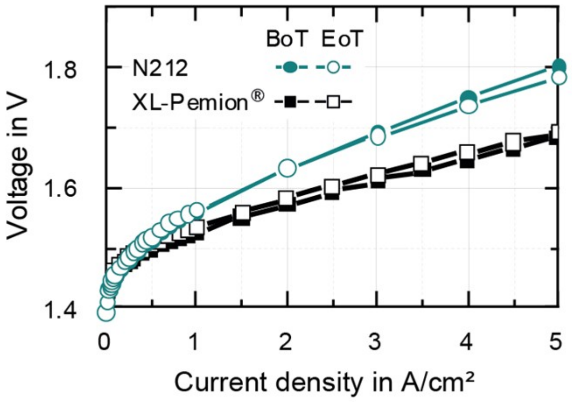

Fig. S4 Polarization curves were conducted before- (BoT: filled symbols) and end-of-test (EoT: empty symbols). The similarity between these after 100 h operation at 1 A/cm² and 80 °C demonstrates the good stability of both N212- (green circle) and XL-Pemion®-CCM (black squares).

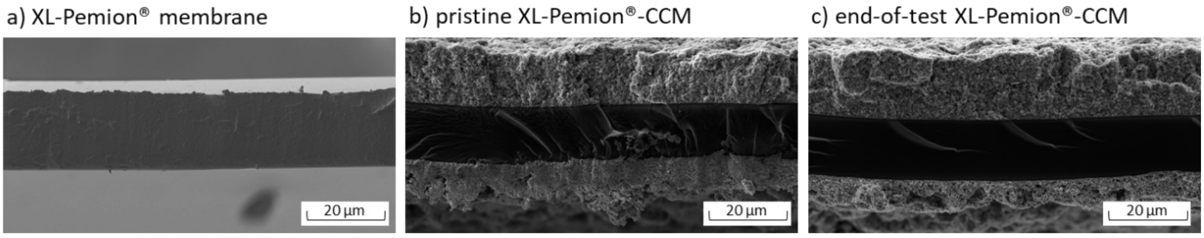
a) XL-Pemion® membrane
b) pristine XL-Pemion®-CCM
c) end-of-test XL-Pemion®-CCM

Fig. S5 Cross sections of a Pemion® membrane after crosslinking (a), a pristine XL-Pemion®-CCM (b) and a XL-Pemion®-CCM after a constant current hold at 1 A/cm² and 80°C for 100 h (c). There is a difference of roughly 5 µm in thickness between the uncoated (19.8±0.5) and catalyst coated membrane (14.4±0.3 µm). Reduced membrane thickness after CCM production may be attributed to partial membrane redissolution during the spraycoating process. The average membrane thickness for the pristine XL-Pemion®-CCM (14.4±0.3 µm) is similar to the end-of-test XL-Pemion®-CCM (15.1±0.4 µm) indicating no membrane thinning due to chemical or mechanical membrane degradation. Furthermore the unchanged IEC after operation confirms the chemical stability of at least the aryl-sulfonic bond between the phenyl ring and sulfonic acid group.

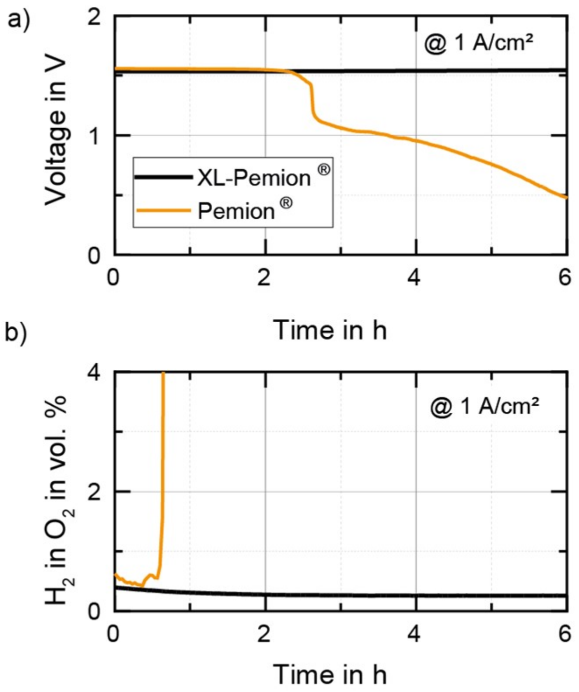

Fig. S6 Comparing the voltage evolutions (a) and H_2 in O_2 contents (b) during a constant current hold at 1 A/cm² and 80 °C for a heat treated XL-Pemion® (black) and non-treated Pemion® (orange). The XL-Pemion®-CCM clearly shows, that heat treatment enables the use of Pemion® as membrane for water electrolyzers. The measured voltage for the non-treated Pemion® was stable during the first two hours, followed by a continuous voltage decrease until the membrane completely disintegrated (S3a blue line). Furthermore, the rapid increase of H_2 in O_2 % during the first hour underlines the poor stability of non-treated Pemion® under electrolyzer conditions at 80 °C (b).

Gas crossover

As mentioned in the main text, the H_2 in O_2 contents reported in the present work are relatively high compared to optimized cathode catalyst layers in literature.[10] Due to a high ionomer content in the catalyst layer (28 wt%) and the utilization of a microporous layer in addition to a substantially compressed gas diffusion layer (H24C5) on the cathode side the hydrogen partial pressure in the cathode compartment increases along with the hydrogen crossover.[11] Nevertheless, since the same setup is used for measuring the XL-Pemion®- and N212-CCM, internal comparison is valid.

Experimental details

Membrane fabrication

For membrane fabrication, a 10 wt% polymer solution was prepared. Initially, Pemion® HNN8 (titrated IEC: 3.1 meq/g) was dissolved in dimethyl sulfoxide (DMSO), while stirring at 80 °C. The solution was then filtered (syringe filter, Whatman GDX, 2.7 µm, 6888-2527) and degassed (30 min under vacuum). Subsequently, the solution was evenly distributed with a knife coater (BYK Instruments) onto a glass plate. The glas plate was pretreated in a base bath solution (1 M KOH in IPA:H2O at a ratio of 4:1) to prevent dewetting. By adjusting the wet film thickness to 254 µm (10 mils), a dry membrane thickness of about 25 µm was aimed. The cast membrane was then dried in a vacuum oven at 80 °C and 1 mbar for a minimum of 12 hours to enable solvent evaporation. Following drying, the membrane was washed in a 5 wt% hydrochloric acid (HCl) solution at room temperature for 10 minutes, followed by rinsing with deionized water. Finally, the membrane was dried under ambient conditions, while being pressed between tissues to prevent wrinkling. The thickness of the membrane under ambient conditions was 20±5 µm, measured with a micrometer gauge.

CCM fabrication

Two CCMs were prepared by spraycoating catalyst layers directly onto a commercial N212 (50 µm) and a self-cast Pemion® Membrane (20±5 µm), respectively. Nafion served as ionomer binder in the catalyst layers, and a content of 10 wt% were aimed for the anode side and 28 wt% for the cathode side. IrO_2 powder (H2EL, 79 wt%, Hereaus) and Pt/C (46,9 wt%, Umicore Elyst Pt50 0550) powder were used as catalyst for the anode and cathode, respectively. The catalyst layers were directly deposited onto the membrane with a loading of 1.0 mg/cm² Iridium and 0.5 mg/cm² Platinum for the anode and cathode respectively, while tracking the deposition rate gravimetrically. The ink preparation and spray coating parameters can be taken from Klose et. al.[1].

After spraycoating, the Pemion® containing CCM underwent heat treatment at 175 °C for one hour under vacuum. During heat treatment, the CCM was pressed between tissues to prevent wrinkling. This step represents the sole production difference between the two CCMs. In parallel, an uncoated Pemion® membrane piece was treated in the oven along with the CCM for measuring properties of the crosslinked membrane (XL-Pemion®). After crosslinking the membrane thickness was determined using SEM cross sections. The uncoated membrane (19.8±0.5 µm) was roughly 5 µm thicker than the coated one (14.4±0.3 µm).

Cell Set-Up

For the anode side a titanium fiber felt (Bekaert), with a thickness of 250 µm were used as porous transport layer (PTL). The titanium fiber felts were sputtered with a 300 nm platinum layer on both sides, under clean room conditions. As PTL on the cathode side, 5 cm^2 carbon fiber papers with micro-porous layer by Freudenberg (H24C5, 270 µm uncompressed thickness) were used. The GDL were placed within PTFE frames, which at the same time acted as hard-stops, setting the compression of the PTLs. Since the titanium fiber felts are assumed to be uncompressible a hard-stop with a similar thickness was chosen (260 µm) on the anode side. For the cathode side a PTL compression of around 40 % was yield by using a 150 µm tick PTFE sheet.

In addition to the PTFE frames 7 µm thick Kapton sheets with an open area of 1 cm^2 were used and thus partly covers the 4 cm^2 sprayed CCM area. Thus reduces mechanical stress to the edges of the sprayed area, which were seen to be the most likely area for the formation of pinholes or cracks in previous studies. This way the active area was defined to be 1 cm².

Electrochemical testing

All electrochemical measurements were performed using a BioLogic VSP-300 with two 10 A/5 V amplifiers in a single cell setup. The customized cell fixtures consist of PEEK end plates and titanium flow fields with a parallel flow pattern that are aligned perpendicular to each other. The flow fields were contacted directly and sputtered with a thin gold layer, to keep the cell resistance as low as possible. The cell was heated to 80 °C using heating elements inside the flow fields. Additionally, preheated DI water was pumped on both sides to the cell with a flow rate of 40 ml/s.

FT-IR analysis

Infrared spectra were recorded on a Bruker Alpha II FT-IR spectrophotometer with ZnSe-ATR. All spectra were recorded in transmission mode in the range of 600-4000 cm-1 (200 scans, 2 cm-1 resolution). After casting, the membranes were washed with deionized water at least for 72 hours. Washing step was implemented to remove residual DMSO or low-molecular-weight sulfoxide-containing compounds, thereby avoiding overlap of S=O signals. In some studies, this step is ignored, which in turn can lead to misleading conclusions. Prior the analysis, the membranes were dried in vacuum oven for 24 h.

IEC and λ determination

Membrane samples in H$^+$ form were kept for 24 h in water at respective temperature (RT and 80 °C), then quenched in water at RT and weighed before being dried overnight (@ 80 °C, vac.) and weighed again. They were then immersed in 1 M NaCl for at least 24 h. The solution was titrated with 0.01 M NaOH and an Eco Titrator from Metrohm GmbH equipped with a pH sensor to an end point of pH=7.0.

CCM samples after 100 h electrolysis operation were removed from their catalyst layers, before IEC determination.

Tensile strength measurement

Tensile strength measurements were carried out using a Shimadzu stress-strain tester at room conditions (25 C and 30 % RH) at a constant strain rate of 5 mm/min. The membranes were punched into rectangular pieces with a sample size of 10 x 40 mm. For the wet measurements, the membranes were removed from deionized water in which they were soaked for 24 hours at room temperature. Before mounting the sample, excess water droplets were removed by briefly blotting both sides of the sample with dry paper towels. The membrane thickness for the wet and dry samples was measured at three different points along the entire membrane length using a micrometer gauge.

Test protocol

Before the electrochemical characterization started a Voltage of 1.2 V for 2 minutes was applied to exclude electrical shortage. An initial polarization curve was recorded by holding a current constant for 120 s on each step. Each current step was followed by a full impedance spectra, which were performed with an amplitude of 10 % of the applied current density and a frequency between 10 Hz and 100 kHz. The high frequency resistance (HFR) was determined at the intersection of the x-axis (real part of impedance) in the Nyquist plot. After the electrochemical characterization a constant current of 1 A/cm² was applied for 100 hours and the cell potential as well as the hydrogen gas content in the anode compartment were monitored. A gas chromathograph (Agilent Micro GC 990) was used to measure the anode gas outlet inline every 3 minutes while the constant current hold was running. Finally, a second polarization curve under equal conditions was measured, followed by a constant Voltage of 1.2 V for 2 minutes.

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