Localized Ionomer Degradation Analysis of Sulfonated Poly(phenylene sulfones) in Fuel Cell Applications using Confocal Raman Microscopy

Supporting Information

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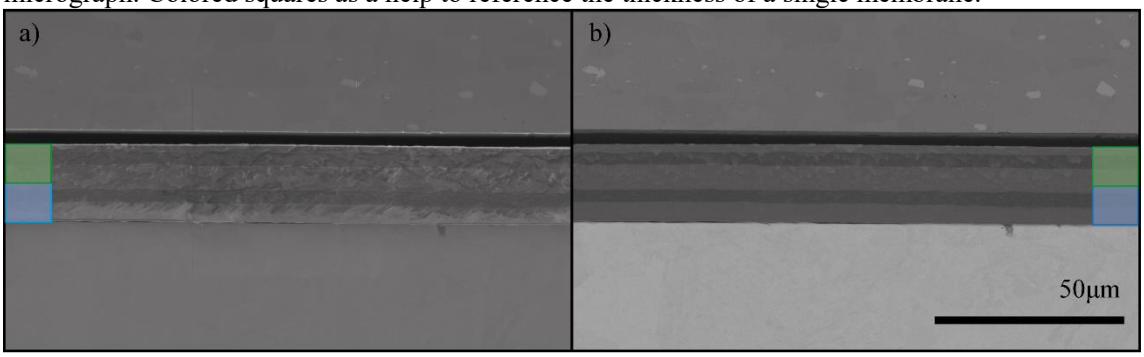
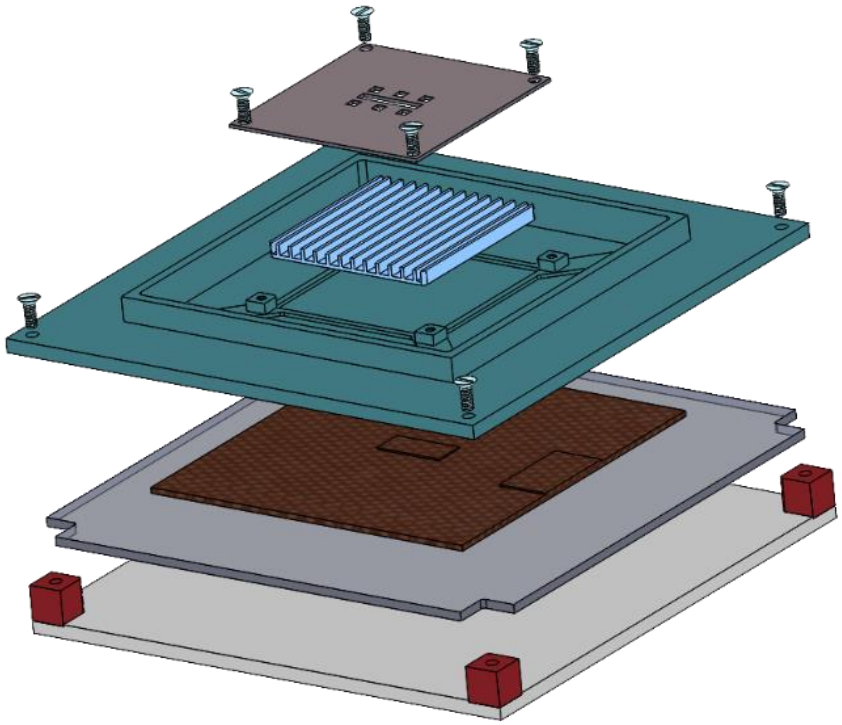
S1. SEM cross-section of 2-layer membrane

SEM cross-section of the 2-layer membrane. a) Secondary electron micrograph; b) Backscattered electrons micrograph. Colored squares as a help to reference the thickness of a single membrane.

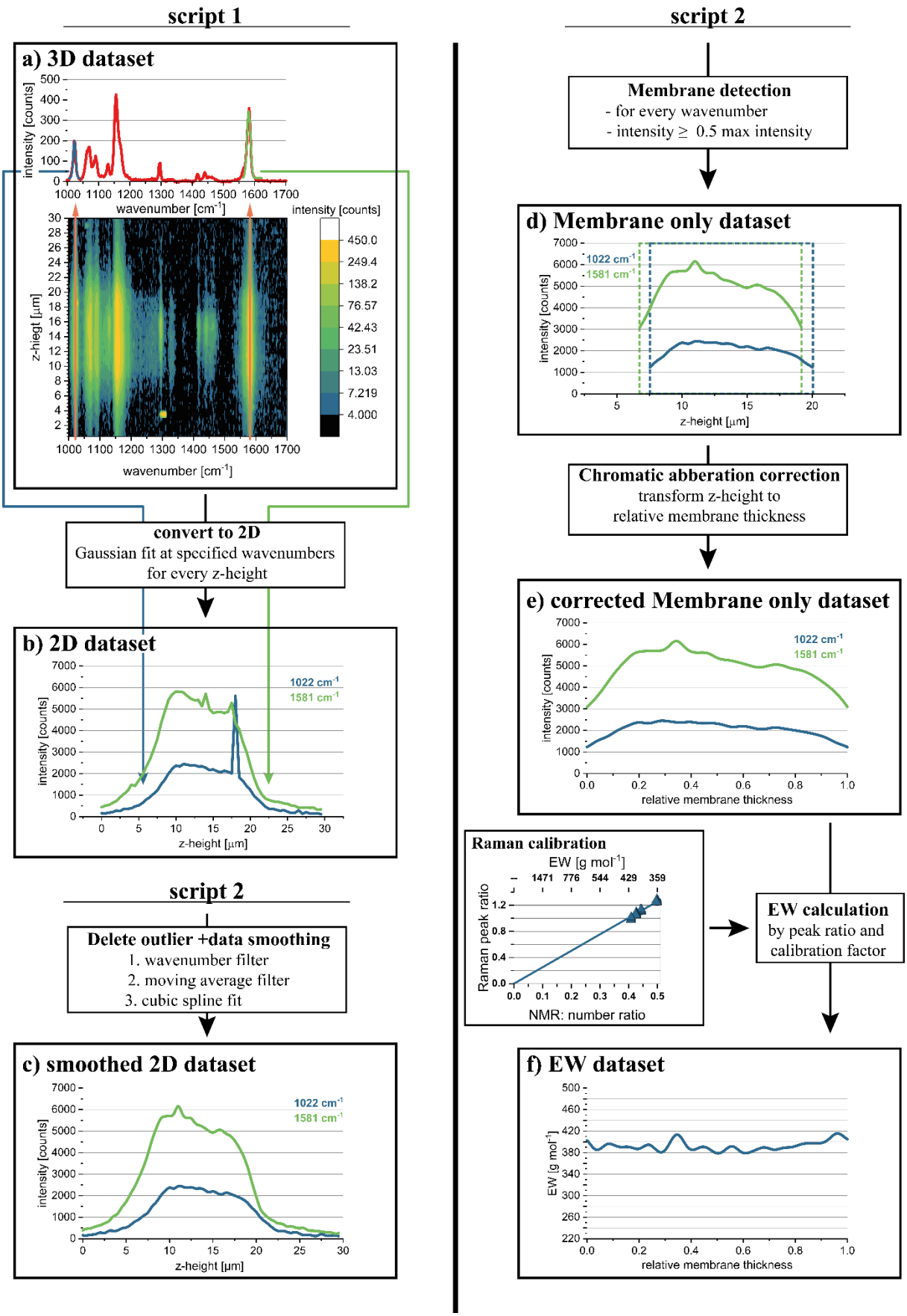


S2. Custom Raman sample holder for water immersion measurements

A custom sample holder was designed for submerged confocal Raman measurements. The main unit is a PMMA (polymethyl methacrylate) water bath (100×100 mm inner dimensions) with a channel structure that supports the sample, enabling hydration from below. The sample is secured by a PET (polyethylene terephthalate) plate with small cutouts (3×3 mm and 3×19 mm) that allow for hydration from above while also accommodating the Raman measurement. Beneath the sample, a silicone heating mat is placed on insulating foam to minimize heat transfer to the sample stage. The water bath is attached to the baseplate with standoffs to stabilize the setup and reduce movement caused by the foam.

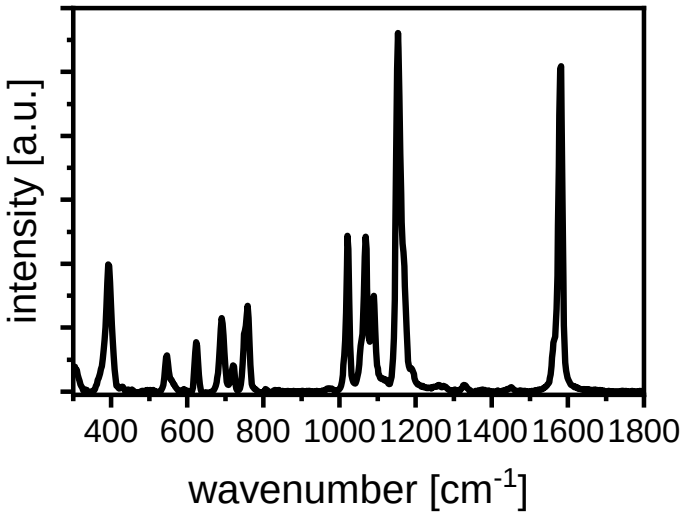


S3. Visual Guide for data processing programming

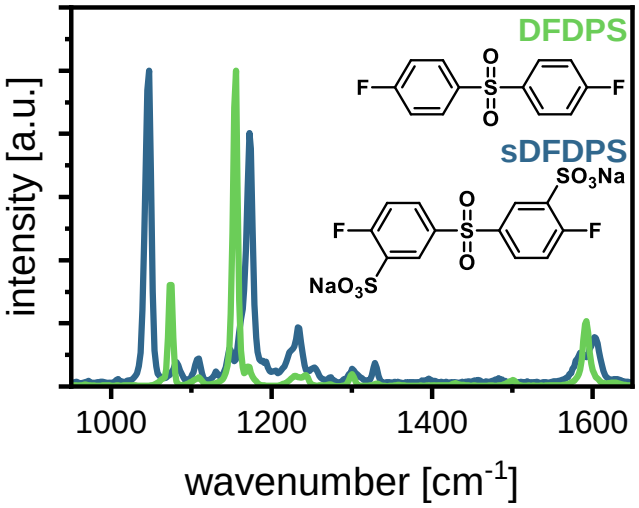


S4. Raman spectra of sPPS

a) Full Raman spectra of pristine sPPS-390 submerged in water.



b) Spectra of monomers. 4,4′-difluorodiphenyl sulfone (DFDPS) and 3,3′-disulfonated-4,4′-difluorodiphenyl sulfone (sDFDPS)

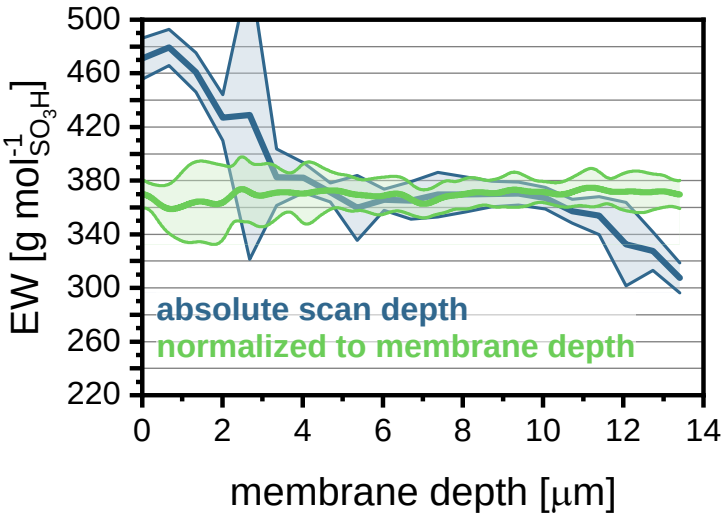


S5. Slopes and coefficient of determination for the linear correlation between Raman peak ratios and number ratio of sulfonic acid to backbone, determined by NMR

Wavenumber [cm^{-1}]	*Slope: linear correlation*	*Coefficient of determination*
1090	2.517	R^2=0.99966
1155	0.702	R^2=0.9977
1581	0.923	R^2=0.99816

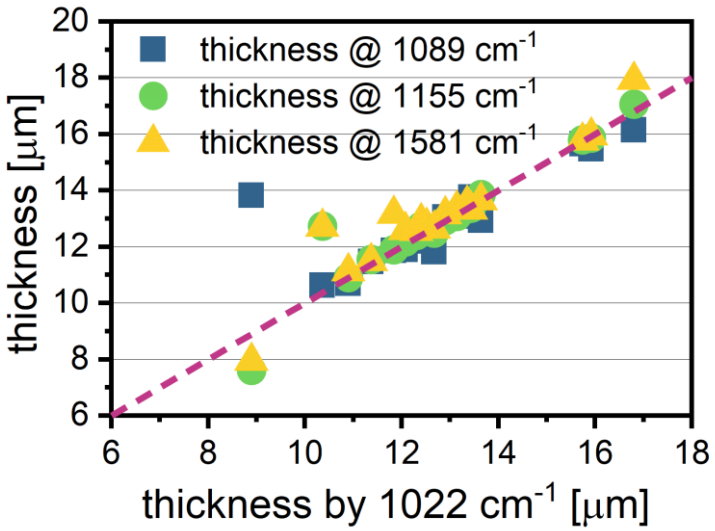
S6. Comparison of EW evaluation by absolute scan position and relative membrane depth

Comparison of two evaluation methods: Blue: EW evaluation by absolute scan position. Green: EW evaluation by relative membrane position. In the middle of the membrane, there is a good match between both methods. The problem is at the edges of the membrane where chromatic aberration drastically changes the measured peak intensity.



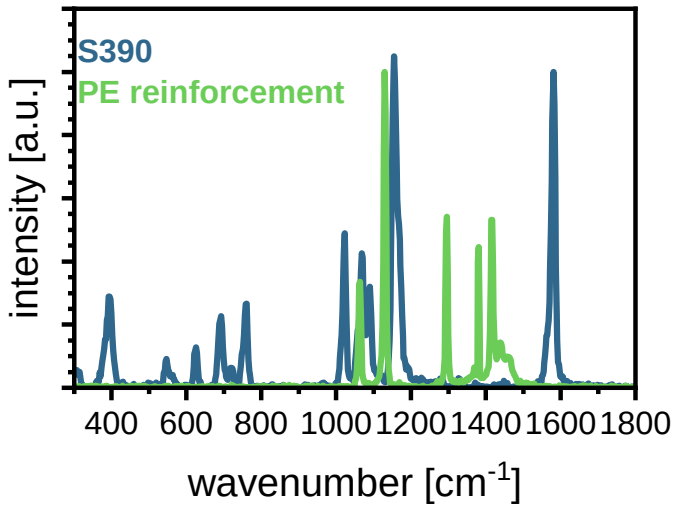
S7. Comparison of measured thickness in dependency of used Raman signal

Comparison of thickness measured by three different backbone peaks (1089 cm^{-1}, 1155 cm^{-1} and 1581 cm^{-1}) in comparison to the thickness measured by the sulfonic acid peak signal (1022.0 cm^{-1}). The dashed line (y=x)is added as guide to the eye.

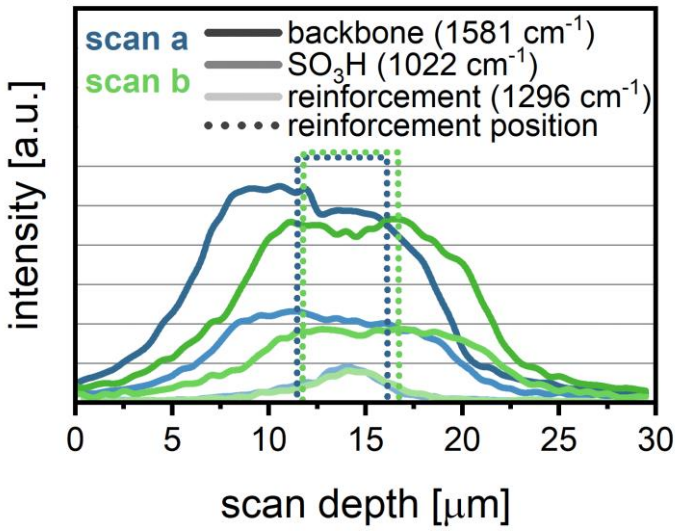


S8. Evaluation of reinforced sPPS membranes

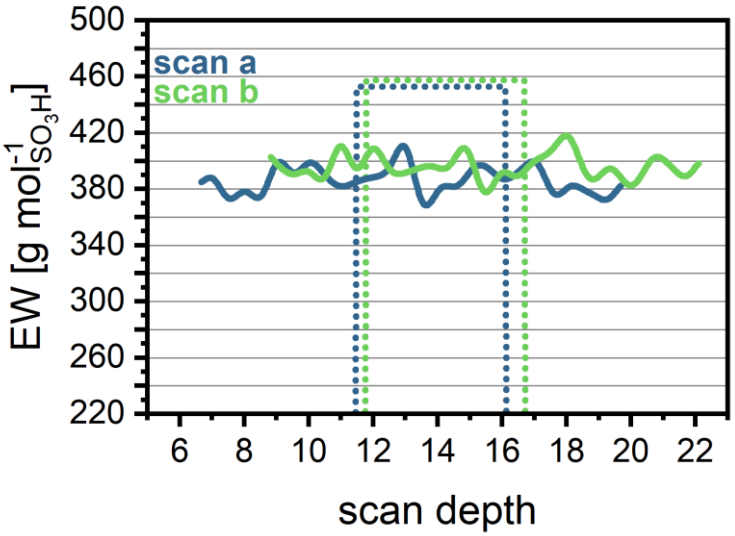
a) Raman spectra of S390 (blue) and polyethylene of the reinforcement (green).



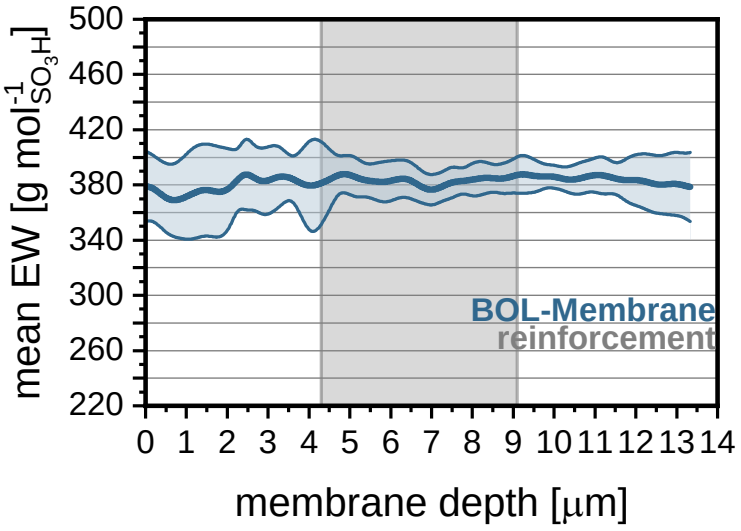
b) Two exemplary depth-scan for reinforced S390 (BOL). Dark lines represent the signal intensity for the CC bond (1581 cm^{-1}), medium lines represent the signal intensity of the sulfonic acid peak and light lines represent the signal intensity for the reinforcement signal at 1296 cm^{-1}. Dotted lines: scan-depth where reinforcement is detected (50% of max intensity for the signal at 1296 cm^{-1}).



c) Two exemplary EW-depth-scan for reinforced S390 (BOL; same scans as in b): Solid lines are the EW depending on absolute scan depth for all areas where the membrane is detected. Dotted lines: scan-depth where reinforcement is detected (50% of max intensity for the signal at 1296 cm^{-1}).

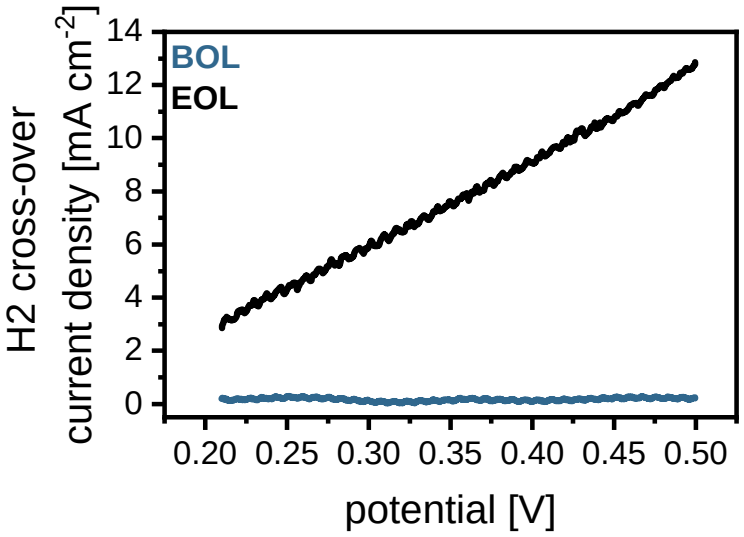


d) Mean EW vs membrane depth and reinforcement position vs membrane depth-averaged over all S390 (BOL) samples.

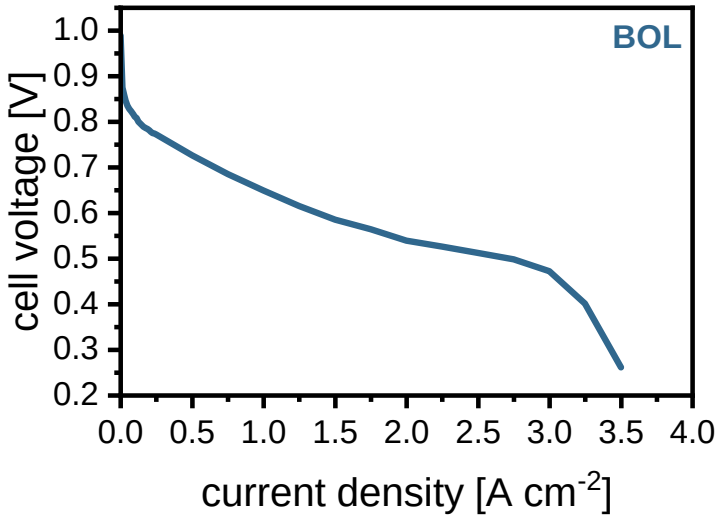


S9. Additional in situ cell data

a) Linear sweep voltammetry (LSV) measurement of the cell. LSV was measured at: at 80 ° 100 % RH under H_2 /N_2 conditions with a flow of 0.2 / 0.2 nlpm. The cell voltage was swept from 0.20 to 0.50 V at 2 mV/s.



b) Polarization curve of the cell at BOL, EOL could not be measured due to excessive H_2-crossover. Polarizatoin urve was measured at: 80 °C, 100 % RH at 150 kPa_g. Reactant flows were fixed to a stoichiometry of 1.5 / 1.5 (H_2 / O_2) with a minimum flow of 0.2 / 0.2 nlpm



S10. HFR-thickness relation

The measured HFR change of -11 mΩ cm^2 can be set in relation to a thickness change of the membrane, assuming that the entire HFR change is due solely to a reduction in membrane thickness. This relationship is described by the following equation:

$$\Delta HFR = \frac{1}{\sigma}(t_2 - t_1) = \frac{1}{\sigma}\Delta t$$
$$\Delta HFR \cdot \sigma = \Delta t$$

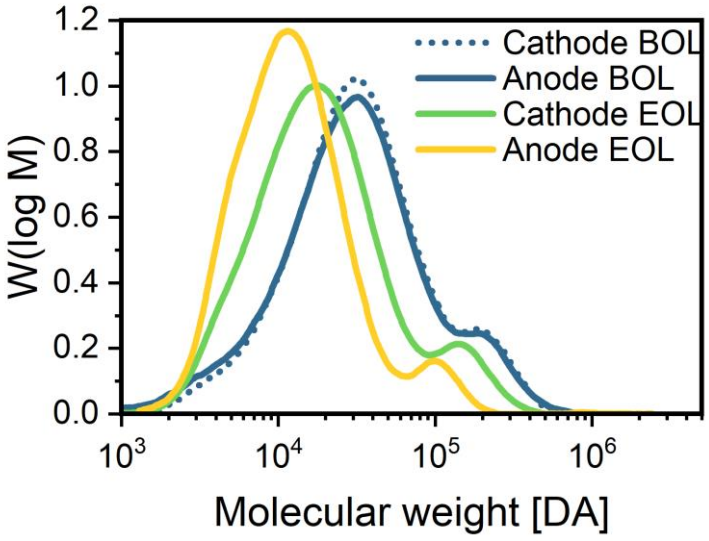
With σ being the membrane conductivity, t_1 and t_2 being BOT and EOT membrane thickness, and Δt being the change in membrane thickness

Using sPPS conductivities published by Piesold et. al,[1] of 90 mS cm^{-1} and 70 mS cm^{-1}, for similar polymers of varied IEC, a change in membrane thickness of -9.9 µm (for σ = 90 mS cm^{-1}) and -7.7 µm (for σ = 70 mS cm^{-1}) is calculated, which is rather close to the measured thickness change of about 12 µm.

It is important to note that the protonic conductivities used for this calculation were measured at 25 °C. It is to be assumed that the conductivity of the material used in our experiments would be slightly higher, as our aging experiments were performed at 80 °C. A higher conductivity would also result in a bigger calculated thickness change. Additionally, this is only a rough estimate, as the HFR is also affected by electrical resistances in the cell's catalyst layer and interface resistances between different layers, all of which may change during aging.

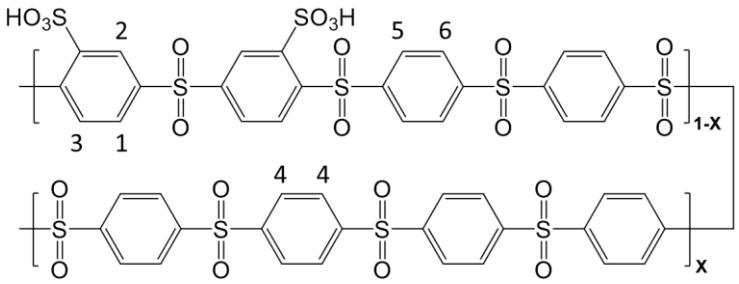
S11. Full GPC data

Molar mass distribution w(logM) (mass portion of material of a given molar mass) of the BOL and EOL samples.

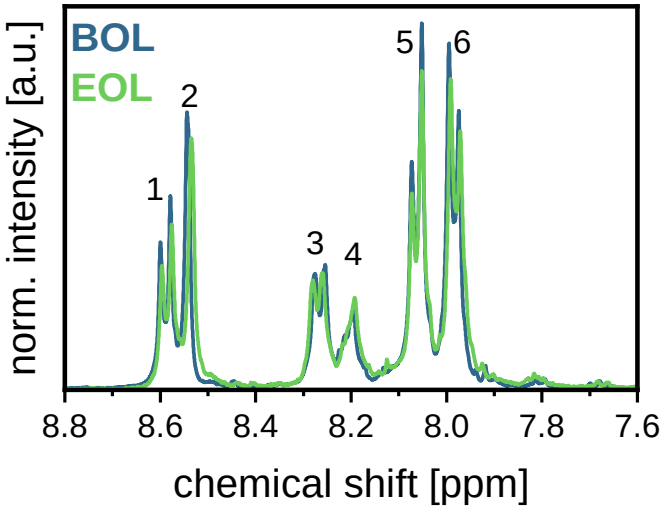


S12. NMR comparison of BOL and EOL sample

a) Chemical structure of sPPS for reference. All protons are labeled with numbers and the corresponding number can be found in Figure S9b.



b) NMR of BOL and EOL samples. Spectra were normalized to the integral of Proton 1 and 2. The numbers on the peak correspond to the protons marked in the chemical structure in Figure S9a.



References

1 C. Piesold, C. Schare, C. Klose, M. Viviani and G. Titvinidze, Novel branched sulfonated poly(phenylene sulfone)s for PEM- water electrolysis application, *Polymer Bulletin*, 2025, Accepted not yet published.