Supporting Information

Highly Permeable Perfluorinated Sulfonic Acid Ionomers for Improved Electrochemical Devices: Insights into Structure – Property Relationships

Adlai Katzenberg\textsuperscript{1,2}, Anamika Chowdhury\textsuperscript{2,3}, Minfeng Fang\textsuperscript{1}, Adam Z. Weber\textsuperscript{2}, Yoshiyuki Okamoto\textsuperscript{1}, Ahmet Kusoglu\textsuperscript{2}, and Miguel A. Modestino\textsuperscript{1}

\textsuperscript{1}Tandon School of Engineering, New York University, Brooklyn, 11201, NY
\textsuperscript{2}Lawrence Berkeley National Laboratory, Berkeley, 94720, CA
\textsuperscript{3}Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720, United States
Conversion of Sulfonyl Fluoride to Sulfonic Acid in as-prepared PFMMD-co-PFSA

PFMMD-co-PFSA was prepared by free radical polymerization of PFMMD and PFSVE in a sealed reaction ampoule with a fluorinated initiator. After free-radical polymerization, the sulfonated side-chain remained in the sulfonyl fluoride (−SO₂F) form and was converted to sulfonic acid (−SO₃H) form by base hydrolysis followed by protonation. As presented in the main text, this was performed by sequential dispersion of the as-prepared polymer in concentrated base and acid at 85°C. The conversion of -SO₂F to SO₃H was assessed by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). Hydrolysis resulted in a loss of the S-F absorbance peak at 1468 cm⁻¹ as these bonds were converted to S-O Bonds (Figure S1). The presence of the PFSVE repeat unit after hydrolysis was confirmed by the split ester peak near 1000 cm⁻¹, indicating that the loss of the S-F peak was not due to washing of unreacted PFSVE monomer in the base slurry.

Figure S1: (a) ATR-FTIR spectra of the as-synthesized PFMMD-PFSVE copolymers. Absorbance peak at 1468 cm⁻¹ was assigned to the sulfur-fluorine bond of the side chain. The magnitude of absorbance was clearly correlated to PFSVE mole fraction. (b) ATR-FTIR spectra of as-synthesized (orange) and base-hydrolyzed (blue) polymer. The hydrolyzed (salt-form) ionomer had no peak at 1468 cm⁻¹, indicating quantitative conversion of sulfonyl fluoride group.

Thermal Stability of PFMMD-co-PFSA Ionomers
Thermal stability is a key feature of ionomers owing to the aggressive oxidizing environment during fuel cell operation (elevated temperatures in the presence of oxygen and oxidative potentials) and high temperature processing of fuel cell MEAs. Thermal and oxidative stability in ionomers is enhanced by the use of fluorinated materials. PFMMMD-co-PFSA stability was measured by thermogravimetric analysis (TGA) to determine the decomposition temperature ($T_d$) in $\text{N}_2$ and air environment for a range of PFSA fractions (Figure S2). $T_d$ decreased with increasing PFSA fraction, suggesting that the sulfonated side chain decomposes at a lower temperature than the dioxolane monomer. This is consistent with thermal decomposition in Nafion, in which sulfonic acid is the first functional group to decompose. $T_d$ of the PFMMMD homopolymer has previously been reported above 370°C.

![Image](image.png)

**Figure S2:** Decomposition temperature of PFMMMD-co-PFSA for a range of PFSA fractions, in air and $\text{N}_2$. $T_d$ is defined by inflection point in the TGA trace during decomposition, where the second derivative of mass with respect to temperature is zero.

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**Swelling Behavior at Variable Humidity**

As stated in the main text, equilibrium swelling fraction in soft materials is dictated by the chemical/mechanical energy balance where the chemical potential of water in the external reservoir is in equilibrium with the water in the ionic domains of the polymer, and considers the change in the free energy.
induced in the polymer by swelling. Increasing the sulfonic-acid concentration or increasing the humidity shifts this equilibrium toward higher hydration states. Figure S3 shows the humidity- and chemistry-dependence of swelling in PFMM-co-PFSA and Nafion.

![Figure S3: Swelling of PFMM-co-PFSA ionomers showed sensitivity to environmental humidity and PFSA fraction. The humidity response was consistent with that of Nafion (green triangles).]

Confinement Considerations in Thin-Film Measurements

The ionomer binder in MEA catalyst layers is confined to length scales below 100 nm on metal/carbon substrates. Water sorption, proton conductivity, and nanostructure of ionomers are well-documented to vary with film thickness and substrate as the relative contribution of interfacial effects on internal structure change under confinement. In this study, water sorption, proton conductivity, and density were studied for films cast on Si and metallic substrates but on length scales above 100 nm, for which confinement is not expected to significantly alter the observed physical properties. To confirm that the thicknesses were large enough to mitigate confinement effects, water sorption and conductivity were measured for films of 57% PFSA at lengths ranging from 140 nm to 670 nm (Figure S4). These material properties were unchanged across this length scale, suggesting that confinement effects did not impact the measurements presented here.
Figure S4: Ionomer properties are well known to change under nanoscale confinement. The length scale on which confinement effects become significant is not well defined for Nafion or other ionomers. Swelling (via ellipsometry) and conductivity (via EIS on Pt microelectrodes) measurements were performed for film thicknesses ranging from 140 to 670 nm. No significant changes in material properties occurred over this range, confirming that the transport properties were not altered by confinement.

Through-Plane Ionic Conductivity

The complex morphology of PTFE-based PFSAs suggests the possibility of anisotropic charge transport, and differences have been reported between in-plane and through-plane proton conductivity. To measure through-plane conductivity of PFMM-co-PFSA, sample reservoirs were prepared from laser-etched polyimide adhesive placed on conductive Veeco AFM mounting disks. Reservoirs were 60 μm deep and approximately 500 μm in diameter. The area of each reservoir was measured by pixel count in ImageJ. Ionomers were drop-cast from solution in 70% IPA in water to fill the volume of the reservoir, and after drying were then hydrated in liquid water for 30 minutes. After removal of excess water with dry N₂ flow, the top (open) side of the reservoir was compressed against another clean AFM disk for ohmic connection to external electronics. Resistance of the ionomer was determined by the x-intercept of EIS spectra collected from 7 MHz to 10 Hz with a Biologic VSP-300 potentiostat and was used to calculate ionomer conductivity as
\[ K = \frac{l}{A \ast R} \]  
(Equation S1)

where \( l \) is the depth of the ionomer reservoir, \( A \) is the reservoir area, and \( R \) is the measured resistance. The through-plane conductivity values (blue squares) generally agreed with the in-plane values presented in the main text (orange triangles) with some deviation. The possibility of anisotropy in conductivity is obfuscated by key differences in the measurement techniques. For example, it is unknown if proton conduction in these materials is sensitive to mechanical stress, as has been suggested for Nafion\(^\text{10}\), induced during sample compression. Processing differences (i.e. spin-casting or drop-casting) may also influence conductivity.

Furthermore, the humidity in the through-plane measurements was not precisely controlled, where in-plane measurements shown here were at an imposed relative humidity of 97%. Therefore, it is difficult to draw meaningful conclusions from this comparison, but these measurements show no evidence of anisotropy in proton conduction in PFMMMD-co-PFSA.

Figure S5: Through-plane (blue squares) and in-plane (orange triangles) ionic conductivity of PFMMMD-co-PFSA showed similar values and similar dependence on PFSA mass fraction. No clear anisotropy in charge transport was observed, given differences in environmental and mechanical factors between the two measurement techniques.

Small-Angle X-Ray Scattering of Humidified Nafion
Scattering profiles of Nafion were collected with PFMMD-co-PFSA at the same conditions and beamline parameters as outlined in the experimental section of the main text. For reference, the scattering profile of Nafion is shown in Figure S5. The matrix knee (0.5-1 nm\(^{-1}\)) and ionomer peak (1.3 – 2 nm\(^{-1}\)) were observed at \(q\)-values consistent with the literature.

Figure S6: The scattering profile of humidified Nafion shows a clear matrix knee (0.5-1 nm\(^{-1}\)) and ionomer peak (1.3 – 2 nm\(^{-1}\)). Scattering profiles of PFMMD-co-PFSA presented in the main text show a clear ionomer peak and no matrix knee.

Wide-Angle X-Ray Scattering of Humidified PFMMD-co-PFSA

Ionomer nanostructure is highly sensitive to environmental humidity. Humidity dependence is most clear in the size and spacing of ionomer domains, resolved by SAXS with scattering vectors on the order of 0.8 – 3 nm\(^{-1}\). Chain-packing distance and degree of crystallinity are generally independent of humidity and are resolved by WAXS at \(q\)-values on the order of 10 nm\(^{-1}\). In the main text, WAXS profiles of PFMMD-co-PFSA at ambient humidity demonstrated chain packing similar to the PFMMD homopolymer (with broad peaks at 5.7 and 11 nm\(^{-1}\)) and with a different structure than Nafion (Figure 6c). WAXS profiles of humidified PFMMD-co-PFSA (Figure S6) showed a markedly different structure. Scattering on the WAXS range was negligible, with only a very small and broad feature with a nominal peak at 14 nm\(^{-1}\), independent of PFSA fraction. This shift in chain-packing upon hydration is not typical of state-of-the-art
PFSA ionomers, as evident in the similarity between ambient (Figure 6c) and humidified (Figure S6) Nafion WAXS traces. The significant change in chain-packing structure should influence ionomer permeability; any disruption in the matrix structure will influence the free volume distribution and in turn gas diffusivity. Permeability of state-of-the-art ionomers already depends on humidity, owing to different mechanisms of gas transport in the dry and wet state. Combining these effects with structural changes in the matrix likely leads to even stronger dependence of permeability on humidity.

Figure S7: WAXS profiles of PFMM-co-PFSA for a range of PFSA mass fractions and Nafion, hydrated with water. While Nafion displays similar structure to its dry morphology, the chain-packing features of PFMM-co-PFSA are changed upon hydration. The distinct peaks at 5.7 and 11 nm\(^{-1}\) were not present, replaced with a single weak feature with a peak at 14 nm\(^{-1}\). This hydration-dependent matrix structure likely induces a strong dependence of permeability on ionomer hydration.

WAXS profiles were obtained by drop-casting PFMM-co-PFSA from dispersion in IPA/H\(_2\)O into PTFE washers sealed with Kapton tape. Prior to sealing, a small amount of deionized water was added to each washer to hydrate the ionomer. WAXS profiles were obtained on beamline CMS at the National Synchrotron Light Source II at Brookhaven National Laboratory. The X-ray energy was 13.5 keV with 0.7% resolution. Scattering patterns were acquired with a 2D Dectris Pilatus 800K CCD area detector (172 µm x 172 µm pixel size) at a sample-detector-distance of 0.371 meters and 30 second exposure time.

Measurement of ECSA in MEAs
ECSA was estimated from CO monolayer adsorption of Pt by CO stripping voltammetry\textsuperscript{11}. The WE and CE were flushed with Ar for 5 mins, after which the CE feed was switched to 2\% H\textsubscript{2} (Ar balance). 20 cleaning cycles were performed at scan rate of 50 mV s\textsuperscript{-1} followed by another 20 cycles at scan rate of 100 mV s\textsuperscript{-1} from 0.08 V to 0.95 V. After CVs, a constant potential of 0.1 V was applied on WE and the gas was switched to 1\% CO (Ar balance) for 6 – 7 mins. Unadsorbed CO was then purged with Ar for 15 mins while holding the potential at 0.1 V to achieve a monolayer. Finally, three CVs were recorded by sweeping the WE potential between 0.08 to 0.95 V at 100 mV s\textsuperscript{-1}. ECSA was calculated from the charge integration of the CO peak and was normalized by the geometric area. The second and third CVs served as a baseline for charge integration of the CO peak. A CO-monolayer oxidation charge of 420 mC cm\textsuperscript{-2} was assumed in all the calculations\textsuperscript{12}. The results of CO stripping are shown in Table S1. ECSA of the PFMMMD-co-PFSA electrode was 27\% lower than the Nafion-containing electrode. This is likely due to differences in the MEA fabrication, which has inherent error in prepared inks at low loading.

\begin{center}
\begin{tabular}{|c|c|}
\hline
WE Binder & Normalized ECSA (cm\textsuperscript{2} Pt cm\textsuperscript{-2}) \\
\hline
Nafion & 64.12 ± 2.02 \\
PFMMMD-co-PFSA & 46.95 ± 1.47 \\
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\end{tabular}
\end{center}

Table S1: Normalized ECSA of the WE containing Nafion and PFMMMD-co-PFSA in MEA experiments. The PFMMMD-co-PFSA WE had significantly lower ECSA representing reduced catalyst loading compared to the Nafion-containing WE. This difference will inhibit fuel cell performance and is not accounted for in the measured current densities.

Catalyst loading has a strong impact on fuel cell performance, especially for low-loading devices. The low ECSA measured in the PFMMMD-co-PFSA electrode represents a significant reduction in effective loading, which should exacerbate ohmic and transport resistances. The raw polarization curves (Figure S7a) showed reduced current density (defined by geometric electrode area) but do not account for the differences in effective loading or ECSA. To attempt to correct for the reduction in ECSA, polarization curve current densities were normalized by ECSA rather than geometric area (Figure S7b).
Figure S8: Polarization curves of MEAs constructed with PFMM-co-PFSA, 0.57 mass fraction PFSA (blue squares) and Nafion (orange triangles) as the binder at the working electrode. (a) Geometric current density showed reduced performance in the PFMM-co-PFSA MEA but does not account for differences in loading/ECSA. (b) Polarization curves normalized by the ECSA show improved performance per cm² Pt in the PFMM-co-PFSA device.

References


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