Dynamic Emergence of Nanostructure and Transport Properties in Perfluorinated Sulfonic Acid Ionomers

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Abstract

Limitations in fuel cell electrode performance have motivated the development of ion-conducting binders (ionomers) with high gas permeability. Such ionomers have been achieved by copolymerization of perfluorinated sulfonic acid (PFSA) monomers with bulky and asymmetric monomers, leading to a glassy ionomer matrix with chemical and mechanical properties that differ substantially from common PFSA ionomers (e.g., Nafion\textsuperscript{TM}). In this study, we use perfluorodioxolane-based ionomers to provide fundamental insights into the role of the matrix chemical structure on the dynamics of structural and transport processes in ion-conducting polymers. Through \textit{in-situ} water uptake measurements, we demonstrate that ionomer water sorption kinetics depend strongly on the properties and mass fraction of the matrix. As the PFSA mass fraction was increased from 0.26 to 0.57, the Fickian swelling rate constant decreased from 0.8 s\textsuperscript{-1} to 0.2 s\textsuperscript{-1}, while the relaxation rate constant increased from 3.1\times10\textsuperscript{-3} s\textsuperscript{-1} to 4.0\times10\textsuperscript{-3}. The true swelling rate, in nm s\textsuperscript{-1}, was determined by the chemical nature of the matrix; all dioxolane-containing materials exhibited swelling rates ~1.5 - 2 nm s\textsuperscript{-1} compared to ~3 nm s\textsuperscript{-1} for Nafion. Likewise, Nafion underwent relaxation at twice the rate of the fastest-relaxing dioxolane ionomer. Reduced swelling and relaxation kinetics are due...
to limited matrix segmental mobility of the dioxolane-containing ionomers. We demonstrate that changes in conductivity are strongly tied to the polymer relaxation, revealing the decoupled roles of initial swelling and relaxation on hydration, nanostructure, and ion transport in perfluorinated ionomers.

Introduction

Perfluorinated sulfonic acid ionomers (PFSIs) have become ubiquitous to state-of-the-art electrochemical devices such as fuel cells, water electrolyzers, redox flow batteries, and CO2 reduction devices. Nafion™, the most widely-used PFSI, has historically been employed as the proton-exchange membrane (PEM) as well as a catalyst binder in fuel cells. Molecularly, Nafion consist of a perfluorocarbon backbone copolymerized with a strongly acidic sulfonic acid side chain; these phase separate at the nanoscale into acid-rich ionomer domains embedded in a hydrophobic matrix1-7. Insights over the past decades into the complex phase-separated nanostructure of Nafion1-7 and its resulting transport properties have revealed serious performance limitations as a catalyst binder8-11, due to nano-confinement and interfacial effects in Nafion thin films12-16. Specifically, non-Fickian oxygen transport resistance in the catalyst binder13,17-19 and poisoning of catalyst sites due to interactions between sulfonic acid groups in the binder and catalyst surfaces20-23 are motivating the development of alternative ionomers for catalyst layers24.

Crystallinity in Nafion’s polytetrafluoroethylene (PTFE) matrix reduces oxygen permeability25,26 contributing to mass-transport limitations in the electrode27,28. An emerging strategy to mitigate this is the implementation of perfluorinated ionomers with side-chain or backbone groups that reduce matrix crystallinity and/or increase fractional free volume (FFV). Recent investigations have demonstrated reduced transport resistance in catalyst layers employing dioxolane-containing ionomers with amorphous matrixes29,30. In these emerging ionomers, there is a trade-off between oxygen transport and ionic conductivity due to the limited ability of the ionomer domains to expand upon swelling due to their stiffer matrix30. While there is a wealth of literature detailing the complex structure-property relationships in perfluorinated ionomers with PTFE backbones, it is unknown how these relationships are affected by
chemical and structural changes of the matrix. Understanding the relationship between the physicochemical properties and transport characteristics of these materials is critical to informing catalyst layer formulations for the next generation of electrochemical devices.

In this work, we gain further insight into the role of matrix physicochemical properties on water transport properties in perfluorinated ionomer thin films by measuring transient swelling rates while varying both the chemistry of the matrix and its mass fraction. Specifically, we study the interplay between swelling rate and strain in Nafion, which has a semicrystalline PTFE matrix, and poly[perfluoro(2-methylene-4-methyl-1,3-dioxolane)-co-perfluoro(4-methyl-3,6-dioxaoct-7-ene) sulfonic acid] (PFMMD-co-PFSA), which has an amorphous dioxolane matrix and the same sulfonated side chain as Nafion. By varying the mass fraction of PFSA in the copolymer from 0.26 to 0.57 (an equivalent weight, EW, range of 1745 to 776 g mol⁻¹), we can separately resolve the impact of matrix composition and ionic strength on water transport and polymer relaxation in ionomer thin films. Furthermore, we study the transient evolution of ionic conductivity and nanostructure in these materials to gain new insights into the interplay between matrix stiffness and ionic strength on the structure and transport properties which dictate electrochemical performance in emerging perfluorinated ionomers.

Figure 1: PFSIs such as Nafion™ (top left) typically comprise a PTFE backbone with a sulfonic acid side chain. Polarity differences in these groups drive phase separation into acid-rich ionomer domains in a semicrystalline
hydrophobic matrix with the size and shape of ionomer domains dictated by the interplay between ionic strength, which drives water sorption, and mechanical deformation of the matrix. Emerging ionomers such as PFMMMD-co-PFSA (top right) introduce bulky dioxolane groups into the ionomer matrix, altering the phase separation behavior due to changes in matrix properties. In this study, we explore the role of matrix physicochemical properties and ionomer ionic strength in the evolution of transport properties and structure morphology of ionomer domains.

Results and Discussion

Swelling Kinetics in Ionomer Thin Films and Their Dependence on Matrix Chemistry and Mass Fraction

Steady-state water transport in Nafion is dictated by interfacial and diffusive mass transport. Transport rates for bulk Nafion at steady state have generally been shown to increase with increasing hydration (i.e., humidity or water activity) due to swelling of hydrated domains and increased concentration of unbound water molecules. Interfacial resistance is higher for water vapor than liquid water, likely due to structure of the water-ionomer interface changing with environmental water content.

The transient behavior of water sorption processes in ionomer thin films is not well understood for several reasons. Transient experiments simultaneously probe water transport (internal diffusion and interfacial resistance) and polymer physical processes which may include nanostructural evolution and matrix relaxations in response to the accumulated stress from swelling deformation. These considerations are especially convoluted in thin films which are subject to confinement- and substrate- driven stiffening, interfacial structure, and changes in hydration-nanostructure relationships. Transient water sorption in Nafion thin films under an imposed humidity change has been shown to be non-Fickian, and follows a biexponential swelling over time:

$$\frac{M(t) - M_0}{M_{\infty} - M_0} = 1 - Ae^{-k_1t} - (1 - A)e^{-k_2t}$$

(Equation 1)

where $M(t)$ is the transient ionomer film thickness, $M_0$ is the initial thickness, $M_{\infty}$ is the final thickness, $t$ is the time since the humidity change, and $A$, $k_1$, and $k_2$ are fitting parameters. The first exponential term is considered to represent Fickian mass-transport processes (i.e., internal diffusion and interfacial transport) and the second a polymer relaxation.
Significant discrepancies in mass-transport rates ($k_1$) and their scaling with water content have been reported for vapor-phase transient water sorption\textsuperscript{33,42,46,48–50}. As shown by Hallinan and Elabd, these discrepancies can likely be attributed to inconsistent boundary-layer control at the vapor-ionomer interface across different experimental setups, due to the high partition coefficient of water across the vapor/ionomer interface (\textit{c.a.} 10,000 for saturated water vapor at room temperature)\textsuperscript{44,45}. In our study, this measurement challenge is mitigated by the implementation of high flow rates (> 500 sccm) in small-volume cells (< 2 cm$^3$ per cm$^2$ of film), with the vapor stream directed incident to the ionomer film plane to enhance water convection to the film. With sufficient vapor flow rate, $k_1$ has generally been observed around 1-3 orders of magnitude higher than $k_2$, indicating relatively rapid water transport which is inhibited by a slower polymer relaxation that is observed at high swelling ratios. Swelling is further inhibited by backbone stiffening during deformation which mechanically opposes chemical-potential driven swelling and is exacerbated in thin films\textsuperscript{38,51}.

Overwhelmingly, thin-film transient water sorption has been studied for a single ionomer structure and composition (Nafion, 1100 EW or 0.4 PFSA mass fraction). Substitutions in matrix chemistry and sulfonic acid content may significantly alter the chemical-mechanical energy balance which dictates steady-state and transient swelling. Matrix stiffness is expected to oppose swelling and is directly correlated with the transition temperature of the matrix ($T_\beta$). Nafion has a PTFE backbone characterized by $T_\beta$ near -20 °C\textsuperscript{52–54}; the matrix of PFMMD-co-PFSA, poly(PFMMD) has a $T_g$ of 135 °C\textsuperscript{55}, and is thus expected to exhibit reduced swelling rates compared to Nafion. In varying sulfonic acid concentration, competing effects are expected. Lower PFSA mass fractions exhibit elevated $T_g$ and lower fractional swelling\textsuperscript{30}, suggesting reduced swelling kinetics. However, lower sulfonic acid content reduces the partition coefficient of water across the vapor-ionomer interface and thus the total swelling-induced deformation.

Figure 2 shows transient thickness changes measured by \textit{in-situ} ellipsometry for ~140 nm ionomer films under imposed humidity steps from 0 to 100% relative humidity (RH) in increments of 25% RH. At low humidity, all materials swelled similarly and reached equilibrium thickness at similar rates. With increasing humidity, the magnitude of swelling varied more between the materials, with higher PFSA
fractions exhibiting greater swelling and longer equilibration times. Increases in both factors that drive swelling magnitude (i.e., RH step and PFSA fraction) resulted in slower equilibration.

Figure 2: Transient swelling of 140 nm ionomer thin films on silicon at differential humidity steps for Nafion and a range of PFMMMD-co-PFSA compositions. Equilibration time increased with PFSA fraction and humidity. Measurements were collected every 2.5 s and are shown here averaged every 5 measurements. Swelling rate constants were obtained by fitting the transient swelling curves to Equation 1. Figure 3a shows swelling rate constant $k_1$ (correlated to mass transport resistance) decreased from 0.08 s$^{-1}$ to 0.02 s$^{-1}$ between 26% and 57% PFSA at high humidity. This decrease in swelling rate coincided with an increase in swelling fraction from 1.03 to 1.09. This suggests that the ionomer physical response to swelling deformation dictates swelling kinetics and is consistent with the hypothesis that slow ionomer physical processes (i.e., matrix relaxation and/or nanostructure evolution) are responsible for reducing water transport rates at high humidity. However, swelling rate constants are convoluted by differences in swelling magnitude; higher equilibrium swelling fraction $M_\infty$ may artificially deflate the normalized rate constant $k_1$. To account for the differences in swelling magnitude, the rate constant $k_1$ was scaled by the swelling deformation ($l_\infty - l_0$) at each humidity step to obtain a thin-film swelling rate (nm s$^{-1}$). The results (Figure 3b) feature two distinct regions defined by matrix type. Nafion, with a PTFE matrix, had a characteristically higher thin-film swelling rate than all PFMMMD-based ionomers; after rapid initial hydration these collapsed into a single region independent of PFSA mass fraction and humidity. This suggests that matrix properties dictate swelling kinetics, and that the dependence of kinetics on ionomer ionic strength (i.e., PFSA fraction) and swelling deformation is weak. This observation is obfuscated in strain-normalized swelling models.
which exaggerate the swelling rate in low-strain experiments (*i.e.* low humidity or low ionic strength ionomers).

Figure 3: (a) Mass transport rate constant $k_1$ extracted from transient swelling curves. Rate constants for all materials decreased with increasing relative humidity, and also decreased with increasing PFSA fraction. (b) Rate constants scaled by thickness change collapse into two distinct regions based on matrix type. Nafion (green triangles) exhibited higher swelling rates than PFMMMD-co-PFSA. When scaled by thickness change, PFMMMD swelling rate showed weak dependence on matrix volume fraction and humidity. Error bars indicate (a) 95% confidence interval (CI) of fitting to Equation 1 and (b) CI scaled by the thickness change.

High swelling strain appeared to result in slower mass transport, possibly due to stress accumulation in the matrix resisting further deformation. This accumulated matrix stress may drive polymer relaxation. In that case, polymer relaxation rate should scale with swelling strain, or the PFSA fraction. Figure 4 shows $k_1$ (mass transport rate) and $k_2$ (polymer relaxation rate) at the highest humidity step, for which both processes were readily resolved, for PFSA mass fractions ranging from 0.26 to 0.57. The $k_1$ data is the same as the high humidity step from Figure 3a and clearly shows swelling rate $k_1$ decreased with increasing PFSA mass fraction, due to increased swelling magnitude. Conversely, the relaxation rate $k_2$ scaled with PFSA fraction. This is consistent with stress accumulation in the matrix driving a polymer relaxation which enables further hydration; the cases which result in small deformations (low humidity or low PFSA content) yield a weak driving force for the stress-driven relaxation. Equilibrium swelling in these cases is reached more quickly than in cases with higher swelling deformation which have a strong driving force for relaxation but also depend on that relatively slow relaxation to fully hydrate. The highest PFSA-fraction
ionomer was thus the slowest in approaching its equilibrium swelling fraction, but exhibited the fastest relaxation. Nafion $k_1$ was 0.047 s$^{-1}$, falling within the range of mass-transport rates exhibited by the PFMM-co-PFSA ionomers. Nafion $k_2$, however, was 8×10$^{-3}$ s$^{-1}$, twice that of the fastest-relaxing PFMM-co-PFSA composition. Similar to the swelling rate presented in Figure 3b, this indicates that matrix chemistry has a strong influence on the swelling-induced relaxation rate. This is likely tied to the relative segmental mobility of the different backbone monomers that may dictate their ability to rearrange in response to stress.

![Figure 4: Mass transport rate ($k_1$, blue squares) and relaxation rate ($k_2$, orange triangles) of PFMM-co-PFSA ionomers during hydration from 75% RH to near 100% RH. Mass transport rate decreased with PFSA mass fraction, due to increased swelling magnitude. Relaxation rate exhibited the opposite behavior, increasing due to additional mechanical stress with large swelling deformation. Error bars indicate 95% CI of fit to Equation 1.]

**Thermal Transitions of Nafion and PFMM-co-PFSA**

Transient swelling kinetics indicate that physicochemical characteristics of the ionomer matrix strongly influence the swelling-induced relaxation. In general, polymer relaxations depend on segmental mobility which can impact thermal transitions. Segmental mobility in ionomer thin films is complex due to multiple thermal transitions in the matrix and ionomer domains which depend on film thickness, cation nature, hydration state, and substrate interactions$^{35,39,40}$. These interactions have been recently probed in thin films by *in-situ* heated ellipsometry, a technique which captures thermal transitions via changes in the linear thermal-expansion coefficient of the polymers$^{39,40}$. Matrix main-chain segmental motion in bulk
Nafion is characterized by the $\beta$-transition, observed between -40 and 20 °C, which is slightly higher than the $\beta$-transition of the mobile amorphous phase of PTFE. In thin films of more than 100 nm, a single thermal transition has been reported between 70 - 85 °C. This transition has been attributed to segmental mobility in ionomer domains which is reduced in thin films due to strong interactions between sulfonic acid and hydrophilic substrates. It was previously reported that, in the non-ionic sulfonyl fluoride form, the PFMMD-based ionomer had higher $T_g$ than Nafion which scaled inversely to PFSA mass fraction and approached the $T_g$ of poly(PFMMD) (135 °C). Similarly, reduced water sorption and polymer relaxation kinetics of the sulfonyl acid form indicate increased ionomer stiffness (i.e., lower segmental mobility in the matrix) upon incorporation of a PFMMD matrix. However, the impact of ionic strength on thermal transitions is unknown. Increased sulfonyl acid fraction may result in increased substrate-induced stiffening.

Figure 5a shows in-situ heated ellipsometry traces of varying PFMMD-co-PFSA compositions. A clear thermal transition was observed between 120 and 150 °C and shifted to lower temperatures with increasing matrix fractions. Figure 5b shows the transition temperature ($T_T$) for both the neutral perfluoro(4-methyl-3,6-dioxaoct-7-ene) sulfonyl fluoride (PFSF) and charged (PFSA) forms of PFMMD-co-PFSA. Typical $T_T$ of Nafion thin films (acid form, green squares) and its bulk PFSF precursor (green triangles) are lower by 30 – 90 °C than PFMMD with the same sulfonated group. For both classes of material, the introduction of a dioxolane matrix clearly reduced segmental mobility regardless of the ionic state. This reduction of segmental mobility upon incorporation of a higher $T_g$ monomer in the backbone also reduced the swelling and relaxation rate.

In the case of PFMMD, The PFSF form (orange triangles) exhibited reduced $T_T$ with increasing PFSF fraction, but the PFSA form (orange squares) showed the opposite behavior. Electrostatic interactions strongly impact the polymer mobility by inhibiting segmental motion of the ionomer domains, but the nature and strength of these interactions cannot be discerned. Any electrostatic interactions such as hydrogen bonding and sulfonate-substrate interactions likely change under hydration which is of significant consequence for high swelling cases under which strong polymer relaxation was observed. We consider the
PFSF form to be more relevant to the matrix swelling relaxation behavior given (i) the lack of interference from hydration-dependent ionic interactions and (ii) the fact that the polymer relaxation was dictated by the hydrophobic matrix backbone which is less susceptible to change under hydration. From the PFSF form, it is clear that higher side-chain fractions exhibited greater segmental mobility. These results show that the incorporation of PFMMD in the ionomer backbone stifled matrix segmental mobility and reduced the swelling and relaxation rate. This finding has implications for hydration-dependent properties including conductivity and nanostructure in dioxolane-based ionomers.

Figure 5: (a) *In-situ* heated ellipsometry traces of a range of PFMMD-co-PFSA films (140 nm) on silicon. Transition temperature ($T_T$) is defined by the intersect of the lower and upper linear thermal expansion regions. (b) PFMMD-co-PFSF $T_T$ decreased with increasing PFSF mass fraction, indicating greater mobility of the side chain than the dioxolane backbone. After conversion to the ionic form, this behavior changed likely due to ionic interactions.

**Transient Ionic Conductivity and Evolution of Nanostructure During Hydration**

Ionic conductivity is intimately related to hydration state in phase-separated perfluorinated ionomers, as water content impacts both the dissociation of ions and the size/shape of hydrated pathways. Structural models for Nafion suggest that initial hydration promotes swelling of isolated clusters of ionic groups which become increasingly interconnected with hydration. Conductivity is expected to change on the same timescale that swelling occurs; rapid increase with initial (low strain) hydration followed by a slower increase as the shape and interconnectedness of the ionomer domains develop. However, the
relationships between hydration, phase separation, and ionomer domain shape/percolation may lead to more complex transient behavior.

Transient conductivity measurements of 140 nm PFMMD-co-PFSA and Nafion during hydration from 75% RH to > 95% RH (Figure 6a) showed similar behavior to swelling experiments. Increasing PFSA fraction resulted in higher magnitude of conductivity but longer equilibration times. The reduced rates were especially evident when presented as normalized conductivity ($\frac{\sigma(t) - \sigma_0}{\sigma_\infty - \sigma_0}$, Figure 6b) and are consistent with the expected behavior for swelling-dependent conductivity. However, when fit to the same equation used to characterize swelling behavior, only a single rate constant for transient conductivity was observed (i.e., $k_{\text{cond}}^1 = k_{\text{cond}}^2 = k_{\text{cond}}$) and the behavior was better described by a one-term exponential function with rate constant $k_{\text{cond}}$. This rate constant decreased with increasing PFSA fraction, following a similar trend to the “fast” swelling process ($k_{\text{swell}}^1$). However, as shown in Figure 6c, the magnitude of the rate constant was of the same order of magnitude as the “slow” swelling process ($k_{\text{swell}}^2$) indicating a polymer relaxation dominated behavior. This suggests two decoupled physical processes which enable (i) rapid water sorption in ionomer hydrated domains and (ii) ion conduction in the same domains. Structural rearrangements in the polymer may be needed to achieve a highly interconnected network of conducting domains; these rearrangements being modulated by the polymer relaxation would lead to conductivity increases on the same time scale.

Figure 6: (a) Transient conductivity measurements of ionomer thin films during hydration from 75% to > 95% RH showed increased conductivity but decreased equilibration rates as PFSA fraction increased. (b) Transient conductivity of ionomer films normalized as the left hand side of Equation 1. Equilibration rate evidently decreased with increased
PFSA fraction. (c) Rate constants extracted by fitting transient conductivity (1-term exponential function) and swelling (Equation 1). The conductivity rate constant decreased with increasing PFSA fraction but proceeded on the same time scale as the polymer relaxation observed by swelling experiments. Error bars indicate 95% CI of fitting.

As was observed for swelling, the magnitude of the conductivity change scaled conversely to the normalized rate constant for different PFSA fractions. In this case, however, the differences were of orders of magnitude; 0.26 PFSA mass fraction underwent a change of 12 µS cm\(^{-1}\) compared to 15 mS cm\(^{-1}\) for 0.57 PFSA fraction. Such low PFSA fraction materials may not reach a fully percolated ionomer morphology, as previously shown in bulk\(^{30}\), causing a faster but less physically significant conductivity change. Higher ionic strength materials reach a high degree of percolation which may occur more slowly, on the timescale of the previously observed swelling relaxation. This is clearly observed in the conductivity change rate (mS cm\(^{-1}\) s\(^{-1}\)), calculated as \((\sigma_{\infty} - \sigma_0)k_{\text{cond}}\) and shown in Figure 7 alongside the analogous swelling rate \(((l_{\infty} - l_0)k_{i\text{swell}})\) for the fast (full triangles) and slow (empty triangles) swelling processes.

While the fast swelling process did not change significantly with ionomer ionic strength, the conductivity change rate and slow swelling process did. This indicates the physical decoupling of fast water sorption (\(i.e.,\) H\(_2\)O mass transport) and conductivity, the latter being clearly tied to a physical relaxation and structural rearrangement of the ionomer.

Figure 7: Conductivity change rate \((\sigma_{\infty} - \sigma_0)k_{\text{cond}}, \) blue squares) and swelling rate \(((l_{\infty} - l_0)k_{i\text{swell}}, \) orange triangles) for ionomer thin films with a range of PFSA mass fractions. Filled triangles indicate \(k_1\), and empty triangles \(k_2\). The fast swelling process was independent of ionomer ionic strength, while the swelling relaxation process and conductivity change rate both increased monotonically with PFSA fraction. This scaling, and the overlapping time constant for normalized conductivity change and swelling relaxation, suggest that conductivity and polymer relaxation
correlate to the same physical process. Error bars indicate 95% CI of fitting scaled by the respective conductivity or swelling change.

The correlation of ionic conductivity to structural rearrangement is consistent with the current understanding of hydration-dependent nanostructure and conductivity in Nafion. Relatively small changes in water content and ionomer domain spacing induce orders-of-magnitude changes in conductivity, both in bulk and thin-film ionomers\(^1,12,14,16,68\). Drastic conductivity changes arise from hydration-dependent evolution of the ionomer nanoscale morphology; ionomer clusters isolated within the matrix at low humidity become increasingly interconnected at higher humidity to enable cohesive ion transport\(^63–67\). Multiple structural rearrangements occur during this transition, encompassing the size, shape, and ordering of ionomer domains. The transient behavior of these transitions has been debated, but it is clear that structural evolution of bulk Nafion under hydration is characterized by multiple physical changes which may proceed at distinct rates\(^33,49,69\). While static hydration-nanostructure relationships in Nafion thin films are well established\(^12,14,16,36,70\), the kinetics of these processes are key to understanding the correlation of conductivity change to polymer relaxation in Nafion and PFMMMD-co-PFSA thin films and have not been investigated.

To probe this, Nafion and PFMMMD-co-PFSA (57% PFSA) films were characterized by grazing-incidence small-angle x-ray scattering (GISAXS) during hydration from near 0% RH to around 80% RH. Time constants were not extracted from these experiments because limitations in the experimental set-up required a larger humidity step compared to dynamic swelling and conductivity experiments. However, the experimental cell was designed to promote vapor stream convection at the film surface to promote sorption-limited kinetics. Figure 8a shows time-resolved scattering spectra (color indicates intensity) of Nafion collected every 15 s during hydration. Upon initial hydration, a broad scattering feature near 2 nm\(^{-1}\) (the ionomer peak, indicative of hydrated domains\(^4,6,63–66\)) appeared. Under continued hydration, the peak did not shift noticeably but did change in intensity. The ionomer domain-spacing \(d_{\text{space}} = 2\pi/q_{\text{peak}}\) of both Nafion and PFMMMD-co-PFSA, shown in panel b, did not vary significantly during hydration, suggesting that the size/spacing of hydrated domains did not change after initial hydration. However, the peak breadth
measured by the full-width at half maximum (FWHM, Figure 8c) decreased throughout the course of the experiment in both Nafion and PFMM-co-PFSA. FWHM is a measure of the dispersity of domain spacing (i.e., order of the phase-separated structure)\textsuperscript{14,16,37}. Decreasing FWHM suggests that under hydration, the domains became increasingly ordered over time. Simultaneously, the peak intensity increased, indicating the formation of more ionomer domains or an increase in phase contrast due to higher degrees of swelling (Figure 8d). Together, these results are consistent with two physical processes occurring in the ionomers under hydration; a rapid swelling of ionic clusters followed by a slower ordering in which the hydrated domains became increasingly interconnected. Both processes were resolved in transient swelling measurements as they are both accompanied by increased water uptake. Only the second process was observed in transient conductivity measurements because the ion transport is dependent on a highly interconnected internal morphology.

![Figure 8](image)

**Figure 8:** (a) Time resolved grazing-incidence small angle x-ray scattering of a Nafion (140 nm, on silicon) thin film during hydration, with scattering profiles collected every 15 s and averaged over 1 min intervals. Ionomer peak ($q \sim 2$ nm$^{-1}$) appeared immediately upon hydration and continued developing throughout the experiment. (b) Ionomer domain spacing of Nafion (blue squares) and PFMM-co-PFSA (57% PFSA) (orange triangles) did not vary significantly once the ionomer peak appeared. (c) Full-width at half-max (FWHM) of the ionomer peak decreased slowly during hydration, for Nafion and PFMM-co-PFSA. (d) Peak intensity (normalized by the intensity at 3 nm$^{-1}$) increased over the course of the experiment. This indicates the rapid formation of spatially-correlated domains which became increasingly interconnected over a longer time. The data in panels (b) – (d) is averaged in 60 s intervals, corresponding to 4 scattering profiles per data point. Error bars reflect the standard deviation over that interval.

**Conclusions**

This study explored the impact of matrix chemical composition and mass fraction on transient processes related to water sorption in perfluorinated ionomer thin films. Ionomers with PTFE and perfluorinated dioxolane backbones both exhibited non-Fickian water sorption with a fast (i.e., mass
transport) process that exhibited slower kinetics for larger swelling and a slow (i.e., polymer relaxation) process with kinetics that increased monotonically with swelling. Both processes were strongly tied to the chemical composition and mass fraction of the matrix domain. Transient conductivity measurements exhibited a single time-constant on the same order as the polymer relaxation and scaled similarly with ionomer ionic strength, suggesting that conductivity and polymer relaxation are driven by the same physical process. Transient GISAXS experiments revealed that, during hydration, ionomer films underwent rapid ionomer domain formation followed by a slower ordering of these domains. Together, these experiments provide strong evidence that ionomer thin films exhibit a slow coalescence of ionomer domains during hydration which enables proton conduction decoupled from the total water content. Matrix segmental mobility plays a key role in these transient processes, so ionomers should be designed with high-mobility matrixes while maintaining high FFV.

**Experimental**

**Materials**

All chemical reagents referenced below were purchased from Sigma Aldrich (St. Louis, MO) unless otherwise noted.

**Ionomer Synthesis**

PFMMD-co-PFSA was synthesized by free-radical copolymerization of perfluoro(2-methylene-4-methyl-1,3-dioxolane (PFMMD) and (perfluoro(4-methyl-3,6-dioxaoct-7-ene) sulfonyl fluoride (PFSVE) in hexafluorobenzene with perfluorobenzoyl peroxide as initiator. Reagents were added to a thick-walled glass ampoule (Chemglass Life Sciences), degassed by freeze-pump-thaw cycles in liquid nitrogen, sealed under vacuum, and heated to 60 °C to initiate polymerization. Reaction times were controlled to avoid compositional drift due to the higher reactivity of PFMMD. PFMMD is prone to self-polymerization and was stored as the potassium salt of perfluoro(2,4-methyl-1,3-dioxolane-2-carboxylate). Before use, PFMMD was prepared by thermal decomposition above 250 °C, distilled, and stored at -8 °C until use.
as-synthesized polymer was in the sulfonyl fluoride (-SO₂F) form and was converted to sulfonic acid by base-catalyzed hydrolysis followed by protonation with concentrated sulfuric acid. Polymer composition was determined by elemental analysis (Atlantic Microlab, Inc.) with ± 0.3% accuracy and precision. Expanded experimental details of PFMMD and PFMMD-co-PFSA synthesis can be found in references 30, 71, and 72.

**Transient Swelling Measurements**

PFMMD-co-PFSA was dissolved at 5% (w/w) in 70% IPA in DI water, sonicated for 2 hours at 50°C, filtered with 0.22 μm pore size PTFE syringe filters (Aura MT, 13 mm diameter) and spin-cast on 1 cm² silicon substrates for 1 min at 4000 rpm to yield uniform films with thicknesses between 120 and 140 nm. Nafion (1100 equivalent weight) dispersion D2021 was purchased from FuelCellStore and diluted to approximately 4% Nafion with 70% IPA in DI water before spin-casting to achieve 140 nm films. Prior to spin-casting, silicon substrates were cleaned by sonicating in acetone for 1 min, rinsing with IPA and DI water sequentially, and O₂ plasma treatment for 10 minutes (Harrick Plasma PDC-001). Films were annealed for 12 hours at 130°C after spin-casting. *In-situ* thickness measurements were taken with a J.A. Woollam Variable Angle Spectroscopic Ellipsometer and collected every 2.5 s. Relative humidity was controlled by mixing streams of dry- and vapor-saturated N₂ with the vapor-saturated stream generated by flowing dry N₂ through a stainless-steel bubbler filled with DI water. The combined flow rate was maintained at 800 sccm with the dry- and humid- streams varied to control humidity. Relative humidity was measured directly upstream of the ellipsometer stage. Humidity was maintained at each set point for at least 10 minutes prior to ramping.

**Thin-Film Thermo-Mechanical Analysis**

Ionomer thin films were cast on silicon substrates following the procedure outlined above. Temperature-dependent thickness was measured by variable angle spectroscopic ellipsometer (VASE) M-2000D model from J. A. Woollam with a heated-cell assembly. Films were cycled twice between room
temperature and 200 °C at a ramp rate of 1°C min⁻¹ and the second ramp-up cycle was used for analysis. During measurement, films were exposed to low flow of dry N₂ to prevent water sorption from the environment. \( T_T \) was determined by fitting lines to the lower (30 – 90°C) and upper (~150 – 200°C) thermal expansion regions on the thickness-temperature profile. \( T_T \) was defined as the temperature at which the two lines intersect.

**Transient Conductivity Measurements**

*In-situ* conductivity measurements were performed using planar platinum interdigitated microelectrode (IDE) arrays fabricated at the NYU Tandon Nanofab Cleanroom. 20 nm titanium adhesion layer followed by 200 nm platinum were deposited on 100 mm silicon wafer with a 250 nm thermally-grown oxide layer (UniversityWafer) in a Kurt Lesker physical vapor deposition cluster tool. Electrodes were patterned with AZ 5214 E photoresist (Microchemicals GmbH) and SÜSS Microtec MA 6 Contact Aligner followed by ion beam etching (IntlVac Nanoquest II) and then diced at the City University of New York Advanced Science Research Center (Disco DAD3320). Each electrode array was a 1 cm² square dice with 39 pairs of teeth with 3 mm overlap length, 5 um width, and 100 um spacing. Schematics of IDE geometry can be found in the supporting information of reference 73.

Ionomer films were prepared by the same method described above, using IDE substrates in place of bare Si. Films were loaded in a 3D-printed proprietary resin (Stratasys Objet) sealed flow-cell with embedded gold-coated spring-loaded pin contacts and barbed fittings for flow inlet/outlet. Humidity was controlled similarly to swelling measurements described above, with the humidified stream generated by passing dry N₂ through two midget impinger bubblers in series. Total flow rate was maintained at 800 sccm by two Sho-Rate™ series variable area flow meters (Brooks Instruments) and relative humidity immediately upstream of the sample cell was measured with an Adafruit DHT22 humidity sensor with ±3% accuracy. Temperature was measured simultaneously and varied between 21.9 and 23.0 °C.
Counter and working electrodes of the IDE array were connected to a Biologic VSP300 potentiostat via gold-coated spring-loaded pin contacts embedded in the flow cell. Electrochemical impedance spectra were collected every 50 s from 1 Hz to 7 MHz with 6 points per decade and 2 measurements per frequency. Film resistance was determined by fitting a semicircle to the high-frequency circular feature of the impedance spectrum, according to previous analysis of PFSI films on similar IDEs\textsuperscript{12,41,68,74}. Ionomer conductivity was calculated as:

$$\kappa_f = \frac{1}{R_f} \frac{d}{l(N-1)t}$$

where $\kappa_f$ is the film conductivity, $R_f$ is the resistance, $t$ is the film thickness, $d$ is the spacing between IDE teeth, $l$ is the length of the teeth, and $N$ is the number of teeth.

Transient GISAXS Experiments

\textit{In-situ} GISAXS measurements were performed at beamline 7.3.3 of the Advanced Light Source at Lawrence Berkeley National Lab. The X-ray energy was 10 keV with a monochromator resolution $E/dE$ of 100. Scattering patterns were acquired with a 2D Dectris Pilatus 1M CCD area detector (172 $\mu$m $\times$ 172 $\mu$m pixel size). Films were cast as described above, but on 2 cm $\times$ 1 cm silicon substrates to increase the path length and scattering contrast. Individual films were placed in a sealed 3D-printed (Stratasys Objet) chamber with polyimide windows for x-ray transmission and stainless-steel compression fittings for flow inlet/outlet. Humidity was controlled as described in the transient swelling measurements section and measured downstream of the sample chamber. Each film was dried under N\textsubscript{2} flow for at least 10 minutes before collecting scattering images. GISAXS images were collected at an incident angle of 0.16° and exposure time of 5 s. Images were collected every 15 s, and the sample stage was moved laterally 1 mm every 10 exposures to mitigate beam damage.

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Supporting Information: Conductivity and GISAXS Flow Cell Designs, Transient GISAXS Profiles

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References

(1) Kusoglu, A.; Weber, A. Z. New Insights into Perfluorinated Sulfonic-Acid Ionomers. *Chem. Rev.* 2017, 117 (3), 987–1104. https://doi.org/10.1021/acs.chemrev.6b00159.

(2) Mauritz, K. A.; Moore, R. B. State of Understanding of Nafion. *Chem. Rev.* 2004, 104 (10), 4535–4585. https://doi.org/10.1021/cr0207123.

(3) Kreuer, K. D.; Portale, G. A Critical Revision of the Nano-Morphology of Proton Conducting Ionomers and Polyelectrolytes for Fuel Cell Applications. *Adv. Funct. Mater.* 2013, 23 (43), 5390–5397. https://doi.org/10.1002/adfm.201300376.

(4) Rollet, A. L.; Diat, O.; Gebel, G. A New Insight into Nafion Structure. *J. Phys. Chem. B* 2002, 106 (12), 3033–3036. https://doi.org/10.1021/jp020245t.

(5) Grot, W. Discovery and Development of Nafion Perfluorinated Membranes. *Chem. Ind.* 1985, 647–649.

(6) Gebel, G.; Lambard, J. Small-Angle Scattering Study of Water-Swollen Perfluorinated Ionomer Membranes. *Macromolecules* 1997, 30 (25), 7914–7920. https://doi.org/10.1021/ma970801v.

(7) Allen, F. I.; Comolli, L. R.; Kusoglu, A.; Modestino, M. A.; Minor, A. M.; Weber, A. Z. Morphology of Hydrated As-Cast Nafion Revealed through Cryo Electron Tomography. *ACS Macro Lett.* 2015, 4 (1), 1–5. https://doi.org/10.1021/mz500606h.

(8) Weber, A. Z.; Kusoglu, A. Unexplained Transport Resistances for Low-Loaded Fuel-Cell Catalyst Layers. *J. Mater. Chem. A* 2014, 2 (41), 17207–17211. https://doi.org/10.1039/c4ta02952f.

(9) Kongkanand, A.; Mathias, M. F. The Priority and Challenge of High-Power Performance of Low-Platinum Proton-Exchange Membrane Fuel Cells. *J. Phys. Chem. Lett.* 2016, 7 (7), 1127–1137. https://doi.org/10.1021/acs.jpclett.6b00216.

(10) Holdcroft, S. Fuel Cell Catalyst Layers: A Polymer Science Perspective. *Chem. Mater.* 2014, 26 (1), 381–393. https://doi.org/10.1021/cm401445h.

(11) Karan, K. PEFC Catalyst Layer: Recent Advances in Materials, Microstructural Characterization, and Modeling. *Curr. Opin. Electrochem.* 2017, 5 (1), 27–35. https://doi.org/10.1016/j.coelec.2017.08.018.

(12) Modestino, M. A.; Paul, D. K.; Dishari, S.; Petrina, S. A.; Allen, F. I.; Hickner, M. A.; Karan, K.; Segalman, R. A.; Weber, A. Z. Self-Assembly and Transport Limitations in Confined Nafion Films. *Macromolecules* 2013, 46, 867–873. https://doi.org/10.1021/ma301999a.

(13) Suzuki, T.; Kudo, K.; Morimoto, Y. Model for Investigation of Oxygen Transport Limitation in a Polymer Electrolyte Fuel Cell. *J. Power Sources* 2013, 222, 379–389. https://doi.org/10.1016/j.jpowsour.2012.08.068.

(14) Kusoglu, A.; Dursch, T. J.; Weber, A. Z. Nanostructure/Swelling Relationships of Bulk and Thin-Film PFSA Ionomers. *Adv. Funct. Mater.* 2016, 26 (27), 4961–4975. https://doi.org/10.1002/adfm.201600861.

(15) Modestino, M. A.; Kusoglu, A.; Hexemer, A.; Weber, A. Z.; Segalman, R. A. Controlling Nafion Structure and Properties via Wetting Interactions. *Macromolecules* 2012, 45 (11), 4681–4688. https://doi.org/10.1021/ma300212f.

(16) Kusoglu, A.; Kushner, D.; Paul, D. K.; Karan, K.; Hickner, M. A.; Weber, A. Z. Impact of
Substrate and Processing on Confinement of Nafion Thin Films. *Adv. Funct. Mater.* **2014**, *24* (30), 4763–4774. https://doi.org/10.1002/adfm.201304311.

(17) Kudo, K.; Jinnouchi, R.; Morimoto, Y. Humidity and Temperature Dependences of Oxygen Transport Resistance of Nafion Thin Film on Platinum Electrode. *Electrochimica Acta.* **2016**, *209*, 682–690. https://doi.org/10.1016/j.electacta.2016.04.023.

(18) Novitski, D.; Holdcroft, S. Determination of O2 Mass Transport at the Pt | PFSA Ionomer Interface under Reduced Relative Humidity. *ACS Appl. Mater. Interfaces* **2015**, *7* (49), 27314–27323. https://doi.org/10.1021/acsami.5b08720.

(19) Freiberg, A. T. S.; Tucker, M. C.; Weber, A. Z. Polarization Loss Correction Derived from Hydrogen Local-Resistance Measurement in Low Pt-Loaded Polymer-Electrolyte Fuel Cells. *Electrochem. commun.* **2017**, *79* (April), 14–17. https://doi.org/10.1016/j.elecom.2017.04.008.

(20) Ohma, A.; Fushinobu, K.; Okazaki, K. Influence of Nafion® Film on Oxygen Reduction Reaction and Hydrogen Peroxide Formation on Pt Electrode for Proton Exchange Membrane Fuel Cell. *Electrochim. Acta* **2010**, *55* (28), 8829–8838. https://doi.org/10.1016/j.electacta.2010.08.005.

(21) Subbaraman, R.; Strmcnik, D.; Paulikas, A. P.; Stamenkovic, V. R.; Markovic, N. M. Oxygen Reduction Reaction at Three-Phase Interfaces. *ChemPhysChem* **2010**, *11* (13), 2825–2833. https://doi.org/10.1002/cphc.201000190.

(22) Subbaraman, R.; Strmcnik, D.; Stamenkovic, V.; Markovic, N. M. Three Phase Interfaces at Electrified Metal-Solid Electrolyte Systems 1. Study of the Pt(Hkl)-Nafion Interface. *J. Phys. Chem. C* **2010**, *114* (18), 8414–8422. https://doi.org/10.1021/jp100814x.

(23) Kodama, K.; Jinnouchi, R.; Suzuki, T.; Murata, H.; Hatanaka, T.; Morimoto, Y. Increase in Adsorptivity of Sulfonate Anions on Pt (111) Surface with Drying of Ionomer. *Electrochem. commun.* **2013**, *36*, 26–28. https://doi.org/10.1016/j.elecom.2013.09.005.

(24) Yandrasits, M. A.; Lindell, M. J.; Hamrock, S. J. New Directions in Perfluoroalkyl Sulfonic Acid-Based Proton-Exchange Membranes. *Curr. Opin. Electrochem.* **2019**, *18*, 90–98. 

https://doi.org/10.1016/j.coelec.2019.10.012.

(25) Mukaddam, M.; Litwiller, E.; Pinnau, I. Gas Sorption, Diffusion, and Permeation in Nafion. *Macromolecules* **2016**, *49* (1), 280–286. https://doi.org/10.1021/acs.macromol.5b02578.

(26) Evans, C. M.; Singh, M. R.; Lynd, N. A.; Segalman, R. A. Improving the Gas Barrier Properties of Nafion via Thermal Annealing: Evidence for Diffusion through Hydrophilic Channels and Matrix. *Macromolecules* **2015**, *48* (10), 3303–3309. https://doi.org/10.1021/acs.macromol.5b00579.

(27) Van Cleve, T.; Khandavalli, S.; Chowdhury, A.; Medina, S.; Pylypenko, S.; Wang, M.; More, K. L.; Kariuki, N.; Myers, D. J.; Weber, A. Z.; et al. Dictating Pt-Based Electrocatalyst Performance in Polymer Electrolyte Fuel Cells, from Formulation to Application. *ACS Appl. Mater. Interfaces* **2019**, *11*, 46953–46964. https://doi.org/10.1021/acsami.9b17614.

(28) Schuler, T.; Chowdhury, A.; Freiberg, A. T.; Sneed, B.; Spingler, F. B.; Tucker, M. C.; More, K. L.; Radke, C. J.; Weber, A. Z. Fuel-Cell Catalyst-Layer Resistance via Hydrogen Limiting-Current Measurements. *J. Electrochem. Soc.* **2019**, *166* (7), F3020–F3031. 

https://doi.org/10.1149/2.0031907jes.

(29) Rolfi, A.; Oldani, C.; Merlo, L.; Facchi, D.; Ruffo, R. New Perfluorinated Ionomer with Improved Oxygen Permeability for Application in Cathode Polymeric Electrolyte Membrane Fuel Cell. *J. Power Sources* **2018**, *396* (May), 95–101. https://doi.org/10.1016/j.jpowsour.2018.05.093.
Katzenberg, A.; Chowdhury, A.; Fang, M.; Weber, A. Z.; Okamoto, Y.; Kusoglu, A.; Modestino, M. A. Highly Permeable Perfluorinated Sulfonic Acid Ionomers for Improved Electrochemical Devices: Insights into Structure–Property Relationships. *J. Am. Chem. Soc.* **2020**, *142*(8), 3742–3752. https://doi.org/10.1021/jacs.9b09170.

Bass, M.; Berman, A.; Singh, A.; Konovalov, O.; Freger, V. Surface Structure of Nafion in Vapor and Liquid. *J. Phys. Chem. B* **2010**, *114*(11), 3784–3790. https://doi.org/10.1021/jp9113128.

Onishi, L. M.; Prausnitz, J. M.; Newman, J. Water-Nafion Equilibria. Absence of Schroeder’s Paradox. *J. Phys. Chem. B* **2007**, *111*(34), 10166–10173. https://doi.org/10.1021/jp073242v.

Gebel, G.; Lyonnard, S.; Mendil-Jakani, H.; Morin, A. The Kinetics of Water Sorption in Nafion Membranes: A Small-Angle Neutron Scattering Study. *J. Phys. Condens. Matter* **2011**, *23*(23). https://doi.org/10.1088/0953-8984/23/23/234107.

Monroe, C. W.; Romero, T.; Mérida, W.; Eikerling, M. A Vaporization-Exchange Model for Water Sorption and Flux in Nafion. *J. Memb. Sci.* **2008**, *324*(1–2), 1–6. https://doi.org/10.1016/j.memsci.2008.05.080.

Kushner, D. I.; Hickner, M. A. Substrate-Dependent Physical Aging of Confined Nafion Thin Films. *ACS Macro Lett.* **2018**, *7*(2), 223–227. https://doi.org/10.1021/acsmacrolett.7b01004.

Shrivastava, U. N.; Suetsugu, K.; Nagano, S.; Fritzche, H.; Nagao, Y.; Karan, K. Cross-Correlated Humidity-Dependent Structural Evolution of Nafion Thin Films Confined on a Platinum Substrate. *Soft Matter* **2020**, *16*(5), 1190–1200. https://doi.org/10.1039/c9sm01731c.

Eastman, S. A.; Kim, S.; Page, K. A.; Rowe, B. W.; Kang, S.; Soles, C. L.; Yager, K. G. Effect of Confinement on Structure, Water Solubility, and Water Transport in Nafion Thin Films. *Macromolecules* **2012**, *45*(19), 7920–7930. https://doi.org/10.1021/ma301289v.

Page, K. A.; Kusoglu, A.; Stafford, C. M.; Kim, S.; Kline, R. J.; Weber, A. Z. Confinement-Driven Increase in Ionomer Thin-Film Modulus. *Nano Lett.* **2014**, *14*(5), 2299–2304. https://doi.org/10.1021/nl501233g.

Zhang, C.; Davies, M.; Karan, K. Probing Interfacial Interactions of Nafion Ionomer: Thermal Expansion of Nafion Thin Films on Substrates of Different Hydrophilicity/Hydrophobicity. *J. Polym. Sci. Part B Polym. Phys.* **2019**, *57*(6), 343–352. https://doi.org/10.1002/polb.24792.

Tesfaye, M.; Kushner, D. I.; McCloskey, B. D.; Weber, A. Z.; Kusoglu, A. Thermal Transitions in Perfluorosulfonated Ionomer Thin-Films. *ACS Macro Lett.* **2018**, *7*, 1237–1242. https://doi.org/10.1021/acsmacrolett.8b00628.

Paul, D. K.; Karan, K.; Docoslis, A.; Giorgi, J. B.; Pearce, J. Characteristics of Self-Assembled Ultrathin Nafion Films. *Macromolecules* **2013**, *46*(9), 3461–3475. https://doi.org/10.1021/ma4002319.

Majsztik, P. W.; Satterfield, M. B.; Bocarsly, A. B.; Benziger, J. B. Water Sorption, Desorption and Transport in Nafion Membranes. *J. Memb. Sci.* **2007**, *301*(1–2), 93–106. https://doi.org/10.1016/j.memsci.2007.06.022.

Satterfield, M. B.; Benziger, J. B. Non-Fickian Water Vapor Sorption Dynamics by Nafion Membranes. *J. Phys. Chem. B* **2008**, *112*(12), 3693–3704. https://doi.org/10.1021/jp7103243.

Hallinan, D. T.; De Angelis, M. G.; Giacinti Baschetti, M.; Sarti, G. C.; Elabd, Y. A. Non-Fickian Diffusion of Water in Nafion. *Macromolecules* **2010**, *43*(10), 4667–4678. https://doi.org/10.1021/ma100047z.
[45] Hallinan, D. T.; Elabd, Y. A. Diffusion of Water in Nafion Using Time-Resolved Fourier Transform Infrared-Attenuated Total Reflectance Spectroscopy. *J. Phys. Chem. B* 2009, 113 (13), 4257–4266. https://doi.org/10.1021/jp811325v.

[46] Kongkanand, A. Interfacial Water Transport Measurements in Nafion Thin Films Using a Quartz-Crystal Microbalance. *J. Phys. Chem. C* 2011, 115 (22), 11318–11325. https://doi.org/10.1021/jp2028214.

[47] Kusoglu, A.; Weber, A. Z. Water Transport and Sorption in Nafion Membrane. In *Polymers for Energy Storage and Delivery: Polyelectrolytes for Batteries and Fuel Cells*; Society, A. C., Ed.; Washington, D.C., 2012; Vol. 1096, pp 175–199. https://doi.org/10.1021/bk-2012-1096.ch011.

[48] He, L.; Smith, H. L.; Majewski, J.; Fujimoto, C. H.; Cornelius, C. J.; Perahia, D. Interfacial Effects on Water Penetration into Ultrathin Ionomer Films: An in Situ Study Using Neutron Reflectometry. *Macromolecules* 2009, 42 (15), 5745–5751. https://doi.org/10.1021/ma900973f.

[49] Kusoglu, A.; Modestino, M. A.; Hexemer, A.; Segalman, R. A.; Weber, A. Z. Subsecond Morphological Changes in Nafion during Water Uptake Detected by Small-Angle X-Ray Scattering. *ACS Macro Lett.* 2012, 1 (1), 33–36. https://doi.org/10.1021/mz200015c.

[50] Davis, E. M.; Stafford, C. M.; Page, K. A. Elucidating Water Transport Mechanisms in Nafion Thin Films. *ACS Macro Lett.* 2014, 3 (10), 1029–1035. https://doi.org/10.1021/mz500515b.

[51] Kusoglu, A.; Savagatrup, S.; Clark, K. T.; Weber, A. Z. Role of Mechanical Factors in Controlling the Structure-Function Relationship of PFSA Ionomers. *Macromolecules* 2012, 45 (18), 7467–7476. https://doi.org/10.1021/ma301419s.

[52] Page, K. A.; Cable, K. M.; Moore, R. B. Molecular Origins of the Thermal Transitions and Dynamic Mechanical Relaxations in Perfluorosulfonate Ionomers. *Macromolecules* 2005, 38 (15), 6472–6484. https://doi.org/10.1021/ma0503559.

[53] Osborn, S. J.; Hassan, M. K.; Divoux, G. M.; Rhoades, D. W.; Mauritz, K. A.; Moore, R. B. Glass Transition Temperature of Perfluorosulfonic Acid Ionomers. *Macromolecules* 2007, 40 (10), 3886–3890. https://doi.org/10.1021/ma062029e.

[54] de Almeida, S. H.; Kawano, Y. Thermal Behavior of Nafion Membrane. *J. Therm. Anal. Calorim.* 1999, 58, 569–577. https://doi.org/10.1023/A:1010196226309.

[55] Yavari, M.; Fang, M.; Nguyen, H.; Merkel, T. C.; Lin, H.; Okamoto, Y. Dioxolane-Based Perfluoropolymers with Superior Membrane Gas Separation Properties. *Macromolecules* 2018, 51 (7), 2489–2497. https://doi.org/10.1021/acs.macromol.8b00273.

[56] Araki, Y. Thermal Expansion Coefficient of Polytetrafluoroethylene in the Vicinity of Its Glass Transition at about 400°C. *J. Appl. Polym. Sci.* 1965, 9 (2), 421–427. https://doi.org/10.1002/app.1965.070090203.

[57] Drubeck, G.; Sen Gupta, A.; Pionteck, J.; Häßler, R.; Krause-Rehberg, R.; Kaspar, H.; Lochhaas, K. H. Glass Transition and Free Volume in the Mobile (MAF) and Rigid (RAF) Amorphous Fractions of Semicrystalline PTFE: A Positron Lifetime and PVT Study. *Polymer (Guildf).* 2005, 46 (16), 6075–6089. https://doi.org/10.1016/j.polymer.2005.04.090.

[58] Calleja, G.; Jourdan, A.; Ameduri, B.; Habas, J. P. Where Is the Glass Transition Temperature of Poly(Tetrafluoroethylene)? A New Approach by Dynamic Rheometry and Mechanical Tests. *Eur. Polym. J.* 2013, 49 (8), 2214–2222. https://doi.org/10.1016/j.eurpolymj.2013.04.028.

[59] Nagao, Y. Highly Oriented Sulfonic Acid Groups in a Nafion Thin Film on Si Substrate. *J. Phys.*
Kim, J. H.; Jang, J.; Zin, W. C. Thickness Dependence of the Glass Transition Temperature in Thin Polymer Films. *Langmuir* **2000**, *16* (9), 4064–4067. https://doi.org/10.1021/la991618t.

Keddie, J. L.; Jones, R. A. L.; Cory, R. A. Size-Dependent Depression of the Glass Transition Temperature in Polymer Films. *Europhys. Lett.* **1994**, *59* (1), 59–64.

Hickner, M. A. Water-Mediated Transport in Ion-Containing Polymers. *J. Polym. Sci. Part B Polym. Phys.* **2012**, *50* (1), 9–20. https://doi.org/10.1002/polb.22381.

Kim, J. H.; Jang, J.; Zin, W. C. Thickness Dependence of the Glass Transition Temperature in Thin Polymer Films. *Langmuir* **2000**, *16* (9), 4064–4067. https://doi.org/10.1021/la991618t.

Keddie, J. L.; Jones, R. A. L.; Cory, R. A. Size-Dependent Depression of the Glass Transition Temperature in Polymer Films. *Europhys. Lett.* **1994**, *59* (1), 59–64.

Hickner, M. A. Water-Mediated Transport in Ion-Containing Polymers. *J. Polym. Sci. Part B Polym. Phys.* **2012**, *50* (1), 9–20. https://doi.org/10.1002/polb.22381.

Keddie, J. L.; Jones, R. A. L.; Cory, R. A. Size-Dependent Depression of the Glass Transition Temperature in Polymer Films. *Europhys. Lett.* **1994**, *59* (1), 59–64.

Hickner, M. A. Water-Mediated Transport in Ion-Containing Polymers. *J. Polym. Sci. Part B Polym. Phys.* **2012**, *50* (1), 9–20. https://doi.org/10.1002/polb.22381.
Paul, D. K.; Fraser, A.; Karan, K. Towards the Understanding of Proton Conduction Mechanism in PEMFC Catalyst Layer: Conductivity of Adsorbed Nafion Films. *Electrochem. commun.* **2011**, *13*(8), 774–777. https://doi.org/10.1016/j.elecom.2011.04.022.