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Delineating Confinement Regimes for Nafion Thin Films via Simultaneous QCM-D and Spectroscopic Ellipsometry

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Keywords: Ionomer, Interfaces, Density, Hydration, Swelling, Kinetics

ABSTRACT: Proton-conducting ionomers used in electrodes of electrochemical devices form nanometer-scale films covering metallic catalyst surfaces, wherein they experience confinement and interfacial effects absent in the bulk polymer. This confinement alters the physical properties of the ionomer film, which is postulated to increase density and is attributed to the transport limitations observed in fuel cell electrodes. Despite studies showing reduced swelling, no systematic measurement has validated this phenomenon by demonstrating both densification and stiffening as the film gets thinner. This study aims to fill this gap by reporting the humidity-driven changes in swelling, mass uptake, and density of Nafion ionomer films cast at varying thicknesses (10 – 320 nm) onto a gold-plated sensor. The films were simultaneously probed during humidification using spectroscopic ellipsometry (SE) and a quartz crystal microbalance with dissipation (QCM-D), which allowed for determination of density and shear stiffness. The effects of confinement were prominently observed below ~30 nm, with films showing increased density along with decreased swelling and mass uptake during hydration. In addition, the confined films showed negative excess volume upon initial water sorption, implying a larger proportion of absorbed water bound to sulfonic acid groups in accord with local densification.

1. Introduction

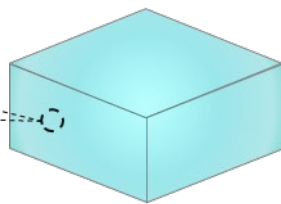
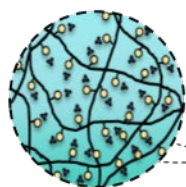
Ionomers – or ion conducting polymers – are commonly used as a solid electrolytes between electrodes in electrochemical technologies, such as fuel cells and electrolyzers. Perfluorosulfonic acids (PFSA)s are a subclass of ionomers oftentimes employed in proton exchange membrane (PEM) fuel cells and water electrolyzers for not only their chemical and mechanical stability, but their desirable transport properties.¹ Their primary role is to enable protons to traverse between electrodes, and this functionality is enabled by their multi-phasic structure of distinct water-filled nano-domains interwoven throughout the polymer matrix. These functional domains serve as the veins of the electrochemical system by enabling transport of ions and water while also impeding the flow of electrons. Protons in particular rely on water-ion complexes formed throughout the hydrophilic network to traverse gradients in potential, amplified by the Grotthuss hopping mechanism across the hydrogen-bonded molecular network.²

PFSA ionomers not only exist as membranes but also as nanometer-thick films in the catalyst layers of these devices, wherein they form thin coatings over electrocatalyst nanoparticles, often comprised of a platinum alloy plated on a carbon-based support.³ In this electrode structure, the ionomer provides conductivity to shuttle protons from catalyst sites to the membrane. But unlike in membrane, the transport of gasses to the catalyst is essential in catalyst thin-film ionomer, and any resistance impedes performance. An ionomer's ability to transport ionic and gaseous species is critical for the performance of the electrodes and overall fuel cell system. The performance limitations observed in fuel-cell cathodes, for example, have been attributed to the thin films of ionomer, which exhibit reduced swelling and proton conductivity compared to their bulk membrane analogue.⁴⁻⁶ Literature studies have provided evidence for increased stiffness and domain-orientation as the ionomer films get thinner (< 100 nm).⁶⁻⁹ In addition, it has been postulated, though not explicitly demonstrated, that the ionomer gets denser as it gets thinner.^{10, 11} This densification occurs in tandem with other changes in other properties measured, such as thermal-transition temperature¹² and swelling kinetics.¹³ Since in polymers there exists a linkage between free volume, density and stiffness,¹⁴ it is plausible to assume the origins of observed transport resistances in ionomer thin films could lie in increased density and reduced mobility, which are expected to manifest themselves as reduced swelling and conductivity. Due to the challenges associated with measuring such properties at nm length scales, demonstrations of these linkages – in particular of density and stiffness with ionomer thickness – has been scarce, but nascent.

The length scales of an ionomer film in a catalyst layer suggest intermolecular forces between the metallic catalyst particles and the ionomer are pertinent in these systems. In the thin film regime, significant physical changes in the ionomer's structure are expected due to interactions with the substrate that would be inapplicable when considering the bulk material. The polymer domains rearrange themselves in response to these forces, resulting in a conformational change near the catalyst interface. For ionomers comprised of polymer aggregates, confinement manifest by orienting individual aggregates parallel to the substrate as the thickness is reduced.⁴⁻⁶ This change in structure at the interface is synonymous with confinement, intensify the ionomer-metal interactions, and is therefore attributed to many shortcomings in ionomer function resulting in electrode performance in terms of mass activity and resistance.

During confinement, the water domains are less effective at facilitating proton transport away from the substrate, as the stacking of polymer domains leads to higher tortuosity in the perpendicular direction. This concept is illustrated in Figure 1. The increased transport limitation due to interfacial confinement is a critical issue to consider when investigating improvements to devices that use PFSA ionomers, and thus effort has been expanded over the past decade into better understanding this phenomenon and mitigating its negative impacts to transport function and device performance.^{15, 16} This study aims to contribute to this effort and expand the understanding of mechanical-swelling effects and densification by exploring the thickness dependence of properties of confined films of Nafion – a well-known PFSA ionomer by Chemours. Thin films were probed simultaneously with spectroscopic ellipsometry (SE) and a quartz crystal microbalance that reports energy dissipation (QCM-D). Others have used these tools independently to measure properties of thin ionomers, but there are few instances¹⁷ where both are used simultaneously, yet still without a mechanical analysis. Almost all previous works that utilize a QCM for a PFSA

Non-oriented nanodomains

Bulk ionomer
(Free standing)

Parallel nanodomains

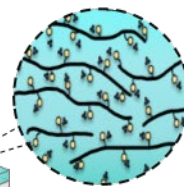
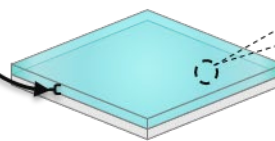
Confined
to interfaceIonomer film on
metallic substrate

Figure 1. The bulk ionomer (membrane) structure has no preferential orientation for its functional hydrophilic nanodomains. This is contrary to when the ionomer is cast as a thin film on a substrate, wherein interfacial effects under confinement cause these domains to align parallel to the substrate. This structural change is accompanied by changes in physical, mechanical and transport properties.

ionomer do so by assuming a value for density and neglecting stress transport in the film.^{5, 7, 16, 18} In contrast, this work directly measures density as a function of thickness for films between 10 and 350 nanometers while fitting the shear-elastic and shear-loss modulus to the Kelvin-Voigt relationship using the Cauchy momentum equation. Finally, swelling, water uptake, and volume effects are also reported as functions of thickness and humidity, which are then analyzed within the context of thermodynamics applied to a thin film system.

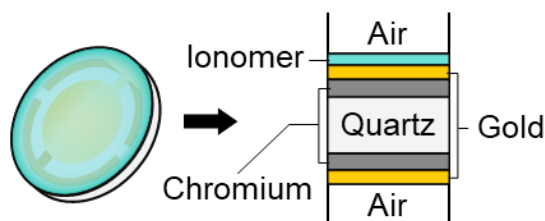


Figure 2. Geometry for the one-dimensional Quartz-crystal microbalance with Dissipation (QCM-D) configuration and material model.

Flat plates of gold (yellow), chromium (dark gray), and quartz (light gray) are stacked on top of one another. The polymer film (blue) is the topmost plate. Infinite reservoirs of air are above and below the plate stack.

2. Experimental Procedure

2.1 Using a Quartz Crystal Microbalance

A QCM-D measures resonance frequencies of an oscillating quartz sensor as well as the energy dissipated from the sensor at those frequencies. There are infinitely many resonance frequencies, and so a given machine may be designed to probe a select subset of them. This work utilizes a QSense Explorer by Biolin Scientific, which is capable of probing seven resonance frequencies – referred to as overtones.

Using a QCM-D requires a model to convert the frequency and dissipation measurements into physically relevant properties. The model used in this work is similar to the one proposed by Voinova et. al.,¹⁹ with the primary difference being the quartz is not treated as a dampened harmonic oscillator. Instead, the sensor is modelled as several solid slabs stacked on top of one another as shown in Figure 2. The Cauchy momentum equation is solved in each slab and two boundary conditions are enforced at each interface: Newton’s third law and the no-slip condition. Since continuum mechanics are used in all slabs (including the quartz), this model more closely mirrors that of Gagnon et. al.,²⁰ with some minor additions. For one, the gold and chromium layers that are present on the real QCM-D sensor are included in the model. In addition, the model adjusts the dissipation measurements for electrical energy losses. A detailed description of the model, as well as a comparison to Voinova et. al.’s harmonic oscillator approach, is provided in the Supporting Information (SI), but the final expressions for frequency and mechanical energy dissipation are reproduced in Equations 1 and 2 for convenience.

$$\omega_n = \frac{\pi n}{h_Q} c_Q - \frac{\left(\text{Arg}(R_Q^+) + \text{Arg}(R_Q^-)\right)}{2h_Q} c_Q \quad 3$$

$$D_{\text{mech}} = \frac{2\pi}{k'_Q h_Q} \frac{\left(1 - |R_Q^+|^2 |R_Q^-|^2\right)}{\left(1 + |R_Q^+|^2\right)} \quad 4$$

In Equations 1 and 2, ω is the angular resonant frequency, $n \in \mathbb{N}$ is the overtone number, h is a slab’s thickness, Q as a subscript refers to the quartz slab specifically, c is the speed of the stress wave in a medium, $R \in \mathbb{C}$ is the reflection coefficient at an interface (the $+$ superscript referring to the interface on the positive- y side and $-$ referring to the interface on the negative- y side), k is the wave vector for the stress wave, a prime mark refers to the real part of a complex number, and the Arg operator returns the argument (angle) of a complex number. The important input in these equations are the two reflection coefficients, which depend on everything in the stacked slab system. It is not entirely obvious as presented in these equations, but when there are only two slabs in a vacuum – the quartz and a film infinitely thinner than the wavelength of the stress wave passing through it – the magnitudes of these reflection coefficients become unity, the negative side’s argument becomes null, and the positive side’s argument causes Equation 1 to collapse into the much more famous Sauerbrey equation.²¹

For this work, only five overtones are used – colloquially the 3rd, 5th, 7th, 9th, and 11th. Since each overtone provides two scalar measurements, the system is described by a 10th dimensional vector equation. Nonlinear regression (via SciPy’s least squares module) is used to fit the density, storage modulus, and loss modulus to this vector equation by way of R^+ and R^- .

2.2 Using Spectroscopic Ellipsometry

The tools used for SE are the Alpha-SE by J.A. Woolam and its commercial software *CompleteEase*. This technique works by measuring how the relative phase and amplitude of two different polarizations of visible light change upon reflecting off the sample. In particular, one can discern the thickness of a flat coating from this information, provided the refractive index – or equivalently, the permittivity – is known. As such, using the SE requires

a model to describe the optical response of the materials being probed as a function of the light's frequency. For gold, the model proposed by Echegoin et. al.²² is utilized. For the polymer, a model representing a two-component mixture of water and some unknown material was derived in a fashion similar to Kushner et. al.²³ This latter model is detailed in the supporting information and can be input into *CompleteEase* using the “User Defined” capability in the software.

2.3 Materials and Thin Film Fabrication

The results of any study on ionomer films will be highly dependent on the standardization of process variables during fabrication. From annealing temperature to solvent composition and choice of substrate, care must be taken to ensure the independent variable – thickness – is isolated and as decoupled as possible from other process effects. For this experiment, we used Nafion ionomer by Chemours in dispersion form of 1100 g/mol equivalent weight (EW). The stock dispersion Nafion D521 was used if the solids weight percent of the final dilution was intended to be below 1.25 wt%, and the dispersion Nafion D2021 was used for more concentrated dilutions. Each dilution was prepared such that the liquid phase was 85% by mass n-propyl alcohol (nPA) and 15% by mass water. All water used was Millipore-grade water (18.2 M Ω -cm). Stock solutions of Nafion D521 off-the-shelf were presumed to contain 50% by mass n-propanol, 45% by mass water, and 5% by mass solids, as per the manufacturer's technical data sheet. Stock solutions of Nafion D2021 were presumed to contain 46% by mass n-propyl alcohol, 33% by mass water, and 21% by mass solids. Dilutions were performed in a 5-milliliter glass vial. All glassware was cleaned with acetone prior to use and allowed to evaporate for 15 minutes. Dilutions of D2021 were filtered using a 0.20 micrometer PTFE syringe filter by way of a 5 mL syringe with rubber stopper. All dilutions were labelled and allowed to settle for 24 hours or more. Afterwards, a dilution was prepared for coating by placing its vial in a Branson 5510 sonication tool for one hour. A chiller set to 15°C and a pump were used to maintain the temperature of the sonication bath during this time.

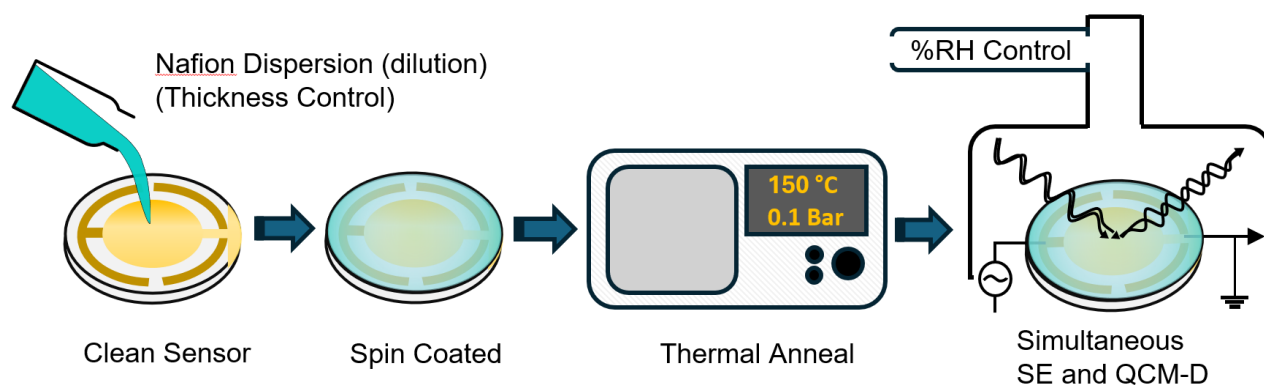


Figure 3. Illustration depicting thin film fabrication. A QCM-D sensor is prepped via a cleaning process before being coated by a Nafion dispersion. It is spin coated at 3000 RPM and annealed in a vacuum oven. Experiments proceed in a humidity-controlled module that allows for simultaneous measurements using a QCM-D and an SE.

The sensor was first inspected to ensure there were no visible defects near the active areas on both sides. Acetone was brought in a clean, glass jar to roughly 40 °C and the sensor was submerged and washed for between two and four minutes. The QCM-D sensor was always handled with graphite-tipped forceps with care taken not to touch the active sensing area. After washing in acetone, the sensor was submerged in water at approximately 85 °C and similarly agitated by hand for between 2 and 4 minutes. Whenever the sensor was removed from a cleaning bath, care was taken such that no fluid droplets stuck to the active area where it may have evaporated and left debris. After washing, the sensor was dried with a stream of clean nitrogen across the substrate surface for one to two minutes. The sensor was then placed in the ellipsometry module by Biolin Scientific for use in the QSense QCM-D to protect it from airborne contaminants. The module was transported to the Alpha SE by J.A. Woolam outfitted with the QSense QCM-D and placed in the fixture. A calibration measurement was taken on both the ellipsometer and the QCM-D tool and saved for data analysis.

The sensor was then transported inside the module to a Laurell spin coater and kept inside the module until coating was to be performed. In the meantime, a glass plate was washed thoroughly in isopropyl alcohol, dried with nitrogen and placed in a Binder vacuum oven, held at 150 °C. The spin coater was wiped with a dry lab wipe to remove dust. Then, the sensor was placed on a central chuck with an O-ring approximately 1 cm in diameter connecting the back end of the sensor to vacuum. The vacuum was turned on and the spin coater program checked as to spin at 3000 RPM for 1 minute. The acceleration parameter was set to 1200 RPM per second. Afterwards, the Nafion dilution was removed from the sonication bath at the one-hour mark and a pipette used to cover the sensor in dispersion. Within ten seconds of wetting the sensor, the spin coater program was started.

After spinning was complete, the coated sensor was inspected to ensure it was fully coated and free of debris. Any visible marks on the sensor at this stage represented a defect and the full fabrication process was restarted. If the sensor successfully completed inspection, it was placed in the vacuum oven on the clean, glass plate and vacuum pulled until the pressure was 100 millibar. The film on the sensor was left to anneal for 60 minutes at 150 °C and then removed from the oven to cool on a glass plate for 1 minute before assembly into the fixture.

After annealing, the sensor was removed from the still-hot oven and placed in the QSense ellipsometry module to protect it from contamination. The module was then carried to the combined ellipsometer and QCM-D tool and mounted in the fixture. The humidity control system – consisting of custom plumbing connecting to house nitrogen, a glass vessel of Millipore-grade water, a bubbler tube, a humidity sensor, and two mass flow controllers – was hooked up to the Qsense ellipsometry module. The humidity system was programmed to maintain the chamber at various relative humidities throughout the experiment. First, the humidity was brought as high as possible for fifteen minutes, brought back down to zero for fifteen minutes, and this process repeated once. This humidity priming step was to allow the ionomer coating to solvent anneal in the water vapor briefly and remove any built-in stress due to variability caused by processing and environmental history. The experiment then proceeded by increasing humidity in a stepwise fashion, with target humidities set to 20%, 50%, 70%, and 90% RH. A typical humidity cycle, along with typical raw data is shown in Figure 4.

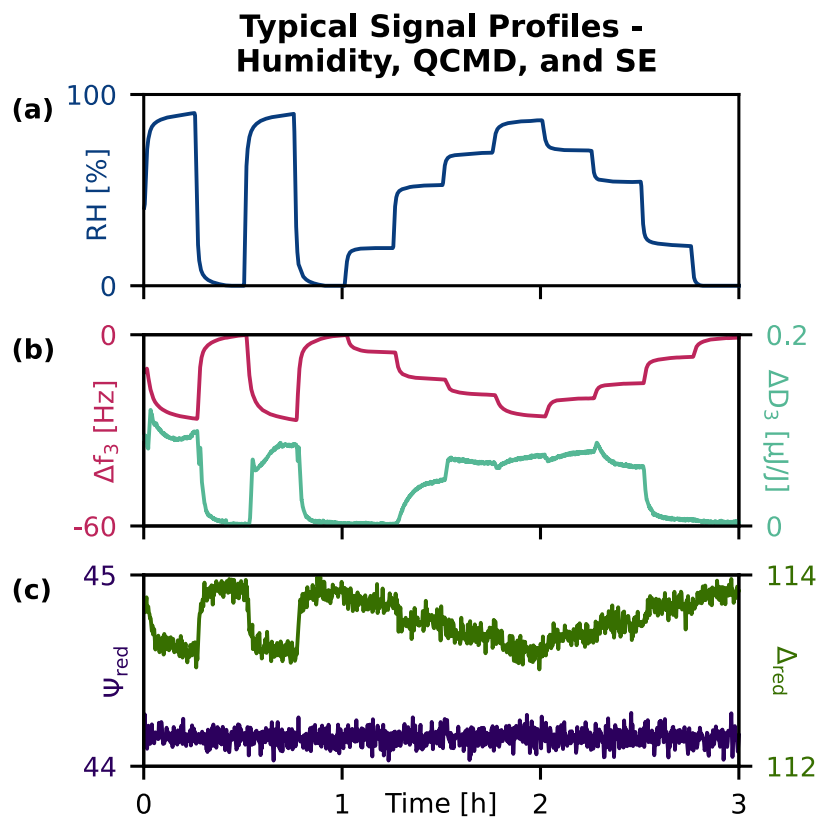


Figure 4: Each sample is cycled through stepwise changes in relative humidity (a), with each step lasting 15 minutes. The response is detected by the QCMD-D via the change in resonance frequency and dissipation (b) and SE via changes in optical parameters (c). The third overtone is shown for the QCMD-D signals in (b) and the optical parameters in (c) are for red light, but material properties are determined by best fit to five overtones and the entire visible light spectrum.

3. Results and Discussion

3.1 Density and Volume Effects

The densities of the Nafion films are plotted in Figure 5(a), and the results agree with those reported by Oberbroeckling et. al.²⁴ Thicker films had a density between 1.85 and 2.02 g/cm³, depending on relative humidity. For all samples, the density decreased with increasing relative humidity. This is intuitive by rule of mixtures, as water is less dense than the dry polymer. As sample thickness reduced, the dry film density gradually increased from 2.01 g/cm³ at 76 nm to 2.06 g/cm³ at 33 nm. Films thinner than 25 nm exhibited dry densities between 2.12 and 2.25 g/cm³ – 10% greater than bulk values.

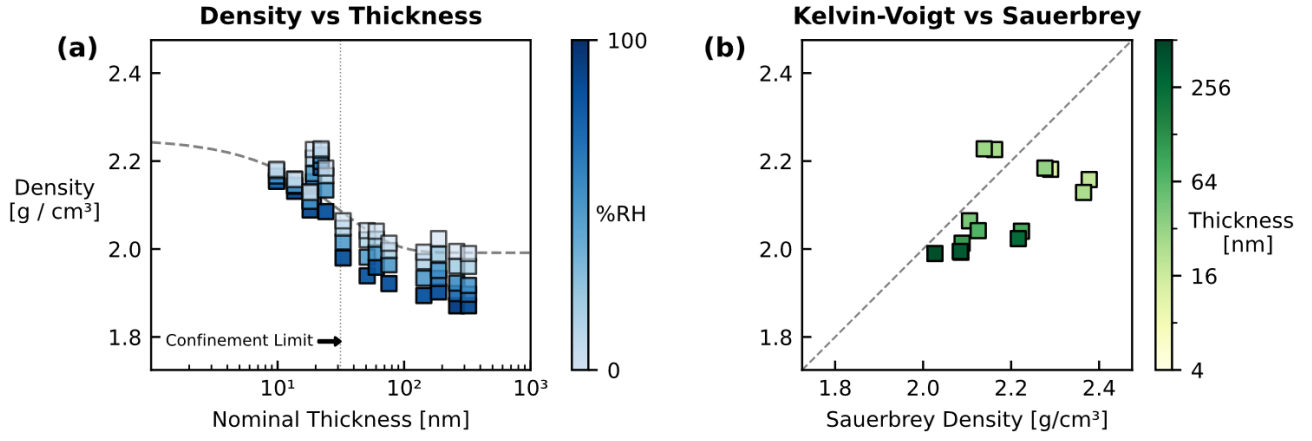


Figure 5. The density of the Nafion films is plotted against their nominal thickness in (a). This density is acquired using the model mentioned in Section 2.1. Relative humidity is plotted using a blue, linear color axis with target humidities of 0%, 20%, 50%, 70%, and 90%, ranging from light to dark blue. The dashed line in (a) is the empirical relation expressed in Equation 3. Below a threshold of 31 nm (labeled as the confinement limit and expressed as h_c in Equation 3), films measured up to 10% denser than their thicker counterparts. In (b), the density acquired using the model in Section 2.1 is compared to what one would acquire using the classical Sauerbrey equation. On this plot, the dashed line marks $y = x$ and the thickness is plotted using a green, logarithmic color axis. The Sauerbrey equation returns higher densities in most cases and does not produce a coherent trend against thickness.

Molecular dynamic simulations predict the ionomer's density is only impacted within the first nanometer from the substrate,¹¹ but these data suggest a gradual increase that becomes pronounced as film thickness falls below 30 nm. The reported values represent an average density of the film, implying if density can be presumed continuous with depth and a density gradient exists through the film's thickness, then local density near the substrate would be even higher than the average.

The density will likely reach some value ρ_c at a small thickness limit and decrease monotonically as thickness increases, approaching some value ρ_∞ – the density of bulk Nafion. The dependence of dry film density on dry thickness, h_0 , can be fit to an exponential function as captured in Equation 3:

$$\rho_{\text{dry}} = (\rho_\infty - \rho_c) \left(1 - e^{-\frac{h_0}{h_c}} \right) + \rho_0 \quad 3$$

When the data was fit to this relation, the bulk density was returned as 1.99 g/cm³ and the value for ρ_c was best fit to 2.25 g/cm³. These fits imply that the density of a thin Nafion film is on par with that of highly crystalline PTFE.²⁵ There is a notion, evinced both by mechanical⁸ and structural²⁶ investigations, that PFSA's undergo stiffening when preferentially orienting crystallites parallel to a substrate. These data are in line with this concept, as the increased density could suggest elevated crystallinity. Moreover, the fit reveals a characteristic thickness, h_c , of 31 nm. Herein, h_c is referred to as the *confinement limit* – the point under which densification is prominent (Figure

5(a)). The exact value of the confinement limit is expected to vary between films cast on different substrates,^{4, 23} as polymer-substrate interactions depend strongly on substrate permittivity.²⁷

Figure 5(b) shows how the Sauerbrey analysis compares to fitting the Kelvin-Voigt parameters with nonlinear regression. For most samples, the Sauerbrey equation yielded a larger density than the Kelvin-Voigt fit. There are two outliers to this observation, but both of these outliers fit the appropriate equations indiscernibly from other samples. An assessment of outliers can be found in the supporting information (SI).

The Sauerbrey equation deviated from the Kelvin-Voigt fit by between 3 and 10%, which is comparable in magnitude to the categorical increase in density observed in films below the confinement limit. Ergo, concluding confinement-induced densification hinges on the accuracy of the model presented in Section 2. Still, the fact that returned densities for the thicker films are comparable to literature values of bulk Nafion builds a compelling case for this choice of analysis.

The water content in an ionomer is traditionally discussed by normalizing the moles of water present by the moles of fixed ionic groups. This quantity, denoted λ , can be calculated from the measured masses (m) given the equivalent weight (E_w) of the ionomer and the molecular weight (M_w) of water. λ is discussed in more detail in Section 3.3, but its definition is presented in Equation 4.

$$\lambda = \frac{\text{mol H}_2\text{O}}{\text{mol SO}_3^-} = \frac{E_w}{M_{w,\text{H}_2\text{O}}} \times \frac{m_{\text{H}_2\text{O}}}{m_{\text{dry}}} \quad 6$$

During humidification of the air, water enters the film and λ changes by $\Delta\lambda$. The volume is expected to rise by 1 cm^3 per gram of water sorbed – or 18 cm^3 on a molar basis. The difference between the true increase in ionomer volume and this expected increase is known as the excess volume. The average specific excess volume is defined as:

$$\Delta\hat{V}^{\text{Ex}} = \frac{\Delta V_{\text{tot}}}{\Delta m_{\text{tot}}} - 1 \left[\frac{\text{cm}^3}{\text{g}} \right] \quad 5$$

In Equation 5, V_{tot} is the film's volume and m_{tot} is the film's mass. The excess volume is plotted in Figure 6 as a function of $\Delta\lambda$ during sorption. Desorption measurements are present in the supporting information for completeness, but the difference between sorption and desorption was insignificant. Herein, all discussion will focus on sorption against elevated humidity.

The excess volumes measured were generally less than or equal to 0, and approached 0 only for the thickest films in the dataset at high relative humidity. This general trend matches the one observed by Bai. et al.²⁸ and is due to water molecules that are loosely bound by partial ionic interactions near sulfonic acid groups taking up significantly less space than the free water molecules that comprise the liquid nanodomains.^{29, 30} At low water content, there are plenty of partially charged sites for new water entering the ionomer to occupy, serving functionally as a source of free volume. These sites may be enthalpically favorable, but entropy demands water be distributed between the bound and unbound state. At high water content, the bound sites approach saturation, and new water entering the system is more likely to contribute to the volume by becoming free water and expanding the film by 1 cm^3/g .

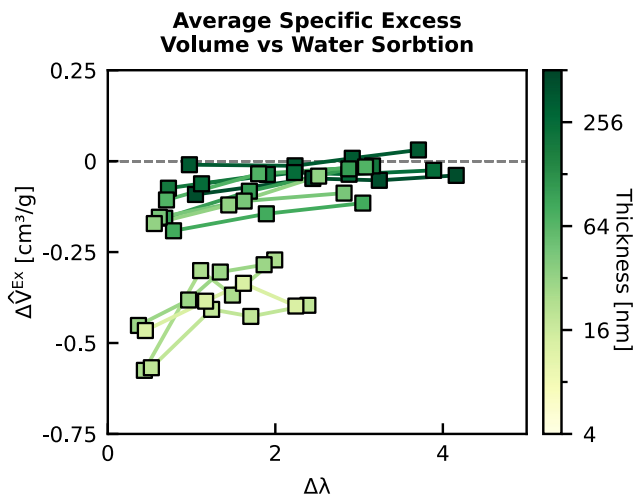


Figure 6. The excess volume of mixing per mass of sorbed water is plotted against change in water content for Nafion on gold. There are two categories of films apparent: those below roughly 22 nanometers where water molecules appear to contribute less specific volume to the system, and thicker films that approach conservation of volume as they approach some maximum $\Delta\lambda$ at higher relative humidity. The negative excess volumes are attributed to water that is loosely bound by charged sulfonic acid groups. The thinnest films are in the ultra-thin film regime where the parallelized lamellae structure extends to the air interface. Ultra-thin films absorbed less water into the free state, leaving dryer liquid-phase domains.

Ultra-thin films less than 22 nm had categorically different excess volumes than thicker films – a slightly lower limiting thickness than the 31 nm confinement limit detected via density measurements. These thickness thresholds bound a thickness regime that agrees closely with the birefringence transition limit, where ionomer chain orientations shift to a more ordered structure.²³ At high humidity, these sub-22 nm films were able to reach an average excess volume between -0.5 and -0.25 cm^3/g , but never 0 (ideal mixing). It is likely that the parallelized lamella structure in these ultra-thin films extends to the air-ionomer interface, as reported by Decaluwe et. al.³¹ In the ultra thin-film regime, ionic groups are more accessible to water molecules from the vapor phase. This accessibility increases the fraction of water that adsorbs as bound water, resulting in less free water than films thicker than the confinement limit, where the ionomer-air interface is slightly less ordered.

The findings in Figure 6 and subsequent conclusions are consistent with prior studies^{23, 31-33}, suggesting transport limitations at ionomer-electrocatalyst interfaces are due in part to a structural change accompanied by diminished water uptake. Furthermore, the trend in density is consistent with the densification inferred from Jinnouchi et. al.'s molecular dynamic simulation study.¹¹ Such densification is associated with increasing oxygen and proton transport resistance at the device level, which are not trivial properties to measure in the ultra-thin-film regime due to arising anisotropy. This anisotropy itself is reported in a recent study³⁴ to reduce ionic conductivity in films below 100 nm, but its specific effect on oxygen transport has been inconclusive. With this in mind, our investigation sheds light into change in density (and by proxy, oxygen transport) of ultra-thin ionomer films as thin as 10 nm – a thickness regime inaccessible by most techniques.

3.2 Kelvin-Voigt Parameters

The Kelvin-Voigt shear storage and loss moduli can be analyzed to determine the influence of confinement on mechanical properties. The former is a measure of the film's stiffness in shear-mode displacement while the latter is a measure of molecular mobility and propensity for creep. The storage modulus is a static value, but the loss modulus is proportional to the frequency of oscillation, ω . It is convenient to divide out the frequency dependence of the loss modulus to obtain the retardation time, τ_r , defined below:

$$\tau_r = \frac{G''}{\omega G'} = \frac{1}{\omega} \tan(\delta) \quad 6$$

The retardation time is independent of frequency in the Kelvin-Voigt model, and is scaled by the storage modulus. In an oscillatory mode, it represents a characteristic period needed for a vibration to induce viscoelastic flow in the ionomer, and is functionally equivalent to the $\tan(\delta)$ commonly probed by dynamic mechanical analysis (DMA) in bulk ionomer membranes.¹ In a linear deformation mode, the retardation time represents a characteristic time delay for a viscoelastic material to impart a reactionary force to an input stress. A high retardation time implies little external energy is needed to induce flow, and such a material may flow under its own weight. A retardation time of zero ($\tau_r = 0$), therefore, implies the material is perfectly elastic.

The Kelvin-Voigt parameters – specifically in the direction tangent to the substrate – are reported in Figure 7. Films greater than 100 nm exhibit reasonably expected values for shear storage modulus, generally measuring between 250 and 500 MPa at most humidities. These values agree with Page et. al.⁸ provided the material is transversely isotropic, and the moduli under oscillatory and static conditions can be compared. All thinner films within the estimated resolution range measured less stiff in shear mode. Considering that, in the confinement regime for this ionomer, the Young's modulus is expected to increase as thickness decreases,⁸ these data suggest that films less than 75 nm are likely orthotropic – a realistic conclusion considering the expected structural change in this regime based on previous studies.^{7, 23, 31, 35-37} When the polymer domains form morphologies parallel to the substrate, the material's structure loses its axial rotational symmetry, resulting in an orthotropic structure. The water in the adjacent liquid domains acts as a plasticizer, allowing the solid domains to slide against one another in shear-mode displacement more readily than in a structure interconnected in a random manner. This phenomenon occurs even at 0% relative humidity, as the ionomer retains some amount of water due to its charged sulfonic acid groups remaining solvated to maintain an energetically favored structure. Because of this effect, films thinner than 75 nm exhibit little impact to their shear modulus upon humidification, as it would seem an increase in water content does not equate to a significant increase in plasticization for the confined morphology. Conversely, films greater than 100 nm softened as humidity increased and water domains expanded, resulting in a net decrease in stiffness and load-bearing capability of the film. Thus, these results collectively highlight the combination of confinement (thickness) effect and hydration (humidity) effects on film's mechanical response.

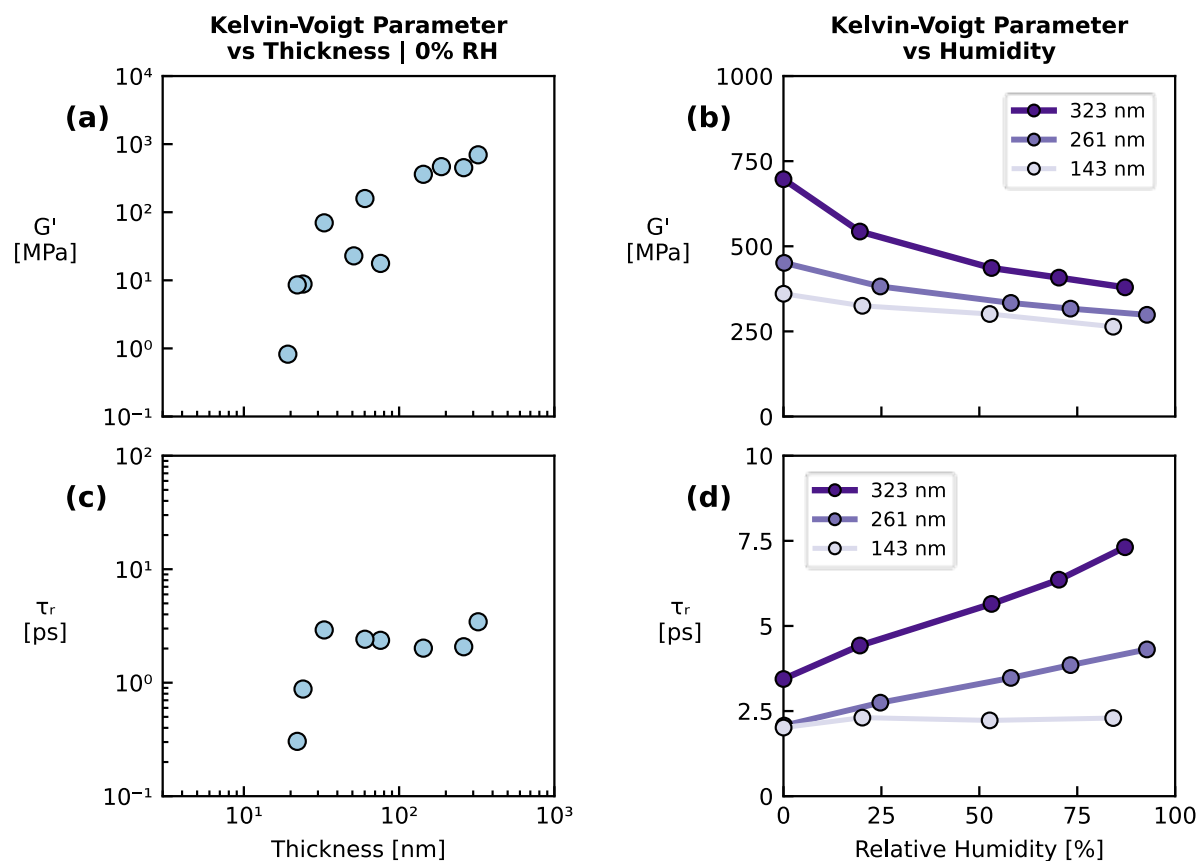


Figure 7. The shear modulus – (a) and (b) – and retardation time – (c) and (d) – are plotted against either dry thickness, or humidity at select thicknesses. The shear modulus is greater than bulk values for thicker films, but decreases for smaller films. Since the Young’s modulus is expected to have the opposite trend, these data suggest Nafion becomes orthotropic after its structure shifts towards parallelized lamella. Retardation time values remain roughly similar until the confinement limit, but are so incredibly low the film cannot be considered viscoelastic. Modulus is expected to reduce with humidity (b), and retardation time is expected to increase with humidity (d), but this was only observed for the thicker films. Kelvin-Voigt values are interpreted from energy dissipation measurements which reached a resolution limit below 20 nm.

The measured retardation time values were incredibly small – in the range of 2 to 4 picoseconds for thicker films. Considering hydrogels can expect to have retardation times of the order of 100 milliseconds under 1 hertz oscillations,³⁸ the films in this study were highly immobile by contrast. Interestingly, these retardation times are in the same time scale (ps) reported for proton mobility in Nafion ionomer systems.¹ It is likely that the retardation time at small frequencies is not directly comparable to what is measured at tens of megahertz, as in this study. Other QCM-D studies for thin polymers have measured retardation times on the order of nanoseconds, but scaling arguments using nanometer length scales predict characteristic times on the order of tens of picoseconds.^{39–41} Still, our picosecond-order measurements imply thin films of Nafion are predominantly elastic and the viscous component is insignificant – at least when coated on a gold substrate. Hence, these mechanical insights could be interpreted as

the strength of binding between the ionomer domains and the gold substrate, in that ultra-thin films forming a strong adhesion experience a more restricted flow and elastic response, in accord with their higher density. Films greater than 100 nm showed an increase in retardation time upon humidification, implying a higher propensity for flow when wet, but still a value too insignificant to change the phase angle of the complex modulus. Similar to shear storage modulus, the impact of humidification on retardation time fell off below 75 nm.

3.3 Hydration Thermodynamics for Thin Films

The change in thickness, h , during hydration normalized by the dry film thickness, h_0 , is referred to as the film's swelling. Due to the high ratio of surface area to thickness, swelling can be assumed to occur in one dimension. Thus, thickness swelling can be considered equivalent to volumetric swelling. In the same fashion, the normalized change in mass (m) with respect to the dry mass at 0% RH is the gravimetric water uptake. Equations 7 and 8 depict these definitions in mathematical form:

$$\text{Swelling} = \frac{h - h_0}{h_0} \quad 7$$

$$\text{Uptake} = \frac{m - m_0}{m_0} \quad 8$$

These quantities are proxies for understanding more relevant properties when the ionomer is in a device; in particular they relate to ionic conductivity and internal strain during varied operating conditions. Swelling and uptake for the sorption isotherm generated during humidification are plotted in Figure 8. These data agree with Kusoglu et. al,⁴ but additionally reveal clearly that swelling and uptake decrease incrementally as thickness is reduced.

What is interesting about Figure 8 is that both swelling and uptake are approximately linear with humidity for annealed films on gold substrates – a contrast to known behavior for bulk-phase ionomers, or even thin films on silicon substrates.^{1, 42, 43} Because these plots are pseudolinear, their slopes can approximate their terminal value. With this in mind, the extent of hydration, $\Delta\lambda$, at a fixed water activity, a_w , serves as a tangible metric for comparing films of different thicknesses. Under dry conditions, the ionomer has a water content of λ_0 , representing the strongly bound water within the primary solvation shell. Upon hydrating via an increase in RH, the water content increases by $\Delta\lambda$ – which, shown previously in Equation 4, is directly proportional to gravimetric water uptake. The slope of $\Delta\lambda$ at any point against a_w is then approximately the extent of hydration in saturated vapor, $\Delta\lambda_{\text{max}}$ ($a_w = 1$). This metric is plotted in Figure 9(a), revealing the following empirical relation between the extent of hydration and thickness:

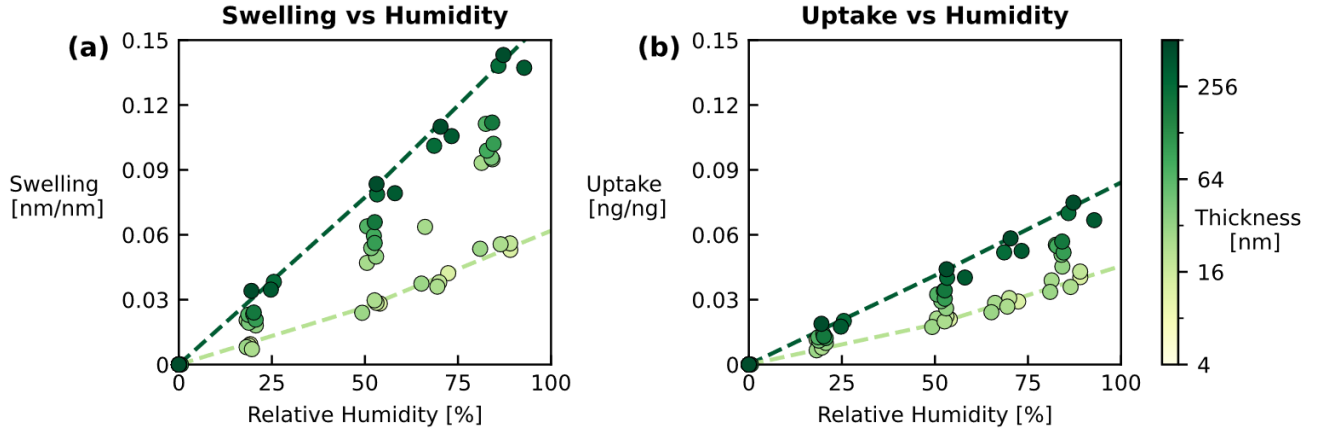


Figure 8. The normalized change in thickness (a) and normalized change in mass (b) plotted against relative humidity for Nafion on gold. The dry film thickness is shown using a color axis. Thicker films, shown in dark green, swell more and take up more relative mass than thinner films, shown in light green. Two fitted curves following the same color scheme serve as a visual aid to show the color gradient between them. At a fixed relative humidity, gradual increase in thickness appears to correlate strongly with an increase in swelling and uptake. Not all samples were measured at all 5 humidity setpoints, which is why the region close to 70% RH is scarce in points.

$$\Delta\lambda_{\max} \approx \frac{\Delta\lambda}{a_w} = \alpha_\lambda \log_{10} \frac{h_0}{\beta_\lambda} \quad ;$$

In Equation 9, a_w is the water activity in vapor phase (taken as the RH divided by 100) and h_0 is the film's dry thickness. The parameters α_λ and β_λ are then likely to be dependent on substrate and process variables, but for this study were found to be 1.475 and 0.268 nm respectively. β_λ represents the projected, physically-limiting thickness where an ionomer film cannot sorb water against a humidity gradient. The fitted value is interesting, as it is of the order of the size of a simple molecule, such as water. It is possible, then, that the characteristic length scale governing sorption physics for thin ionomers in general is simply the average size of a monolayer of sorbed water.

Figure 9(b) mirrors Figure 9(a) to depict maximum swelling. When juxtaposed, it is clear that the interfacial transition that occurs in the ultrathin regime more dramatically impacts volume change as opposed to the extent of hydration. While mass-based water content (λ) is continuous with thickness, the swelling shows a first-order transition. Moreover, there is a region – and not a specific thickness value – where the transition is expected. Maximum swelling can be described in a similar manner as Equation 9, but different values for fitting parameters are needed for ultra-thin films versus thicker films to account for the change in excess volume. For completeness and convenience, this linear relationship between thickness change and humidity for each film can be generalized with a logarithmic dependence on the initial film thickness:

$$\frac{\Delta h_{\max}}{h_0} \approx \frac{\Delta h(a_w)}{h_0} \times \frac{1}{a_w} = \alpha_h \log_{10} \frac{h_0}{\beta_h} \quad 32$$

In Equation 10, (α_h, β_h) fits to the data as (0.0180, 4.67 pm) for ultra-thin films, and (0.0437, 76.8 pm) for thicker films. These characteristic lengths are shorter than that of a covalent bond, and so may carry little physical meaning

other than their fit to the data. Still, it is useful to have an empirical fit for the ionomer's swelling, considering the thickness variation of catalyst ionomer films in the electrochemical systems.

Equations 3, 9 and 10 can be combined to arrive at an empirical expression for the terminal excess volume:

$$\Delta \hat{V}_f^{\text{Ex}} = \frac{\Delta h_{\text{max}}/h_0}{\Delta \lambda_{\text{max}}} \frac{E_w}{\rho_{\text{dry}} M_{w, \text{H}_2\text{O}}} - 1 \left[\frac{\text{cm}^3}{\text{g}} \right] \quad 33$$

From a mass balance, the density for all points along the hydration isotherm can be determined if both the swelling and the uptake are known. This is expressed in Equation 12:

$$\frac{1}{\rho} - \frac{1}{\rho_{\text{dry}}} = \frac{\Delta \lambda}{\Delta \lambda + \frac{E_w}{M_{w, \text{H}_2\text{O}}}} \left(\Delta \hat{V}_f^{\text{Ex}} - \frac{1}{\rho_{\text{dry}}} + 1 \left[\frac{\text{cm}^3}{\text{g}} \right] \right) \quad 34$$

The result in Equation 12 for the hydrated films is plotted in Figure 9(c) along with the result from Equation 3 for comparison. As a whole, Figure 9 highlights several thickness dependent trends for hydration thermodynamics and how they are impacted by confinement and the ultra-thin transition.

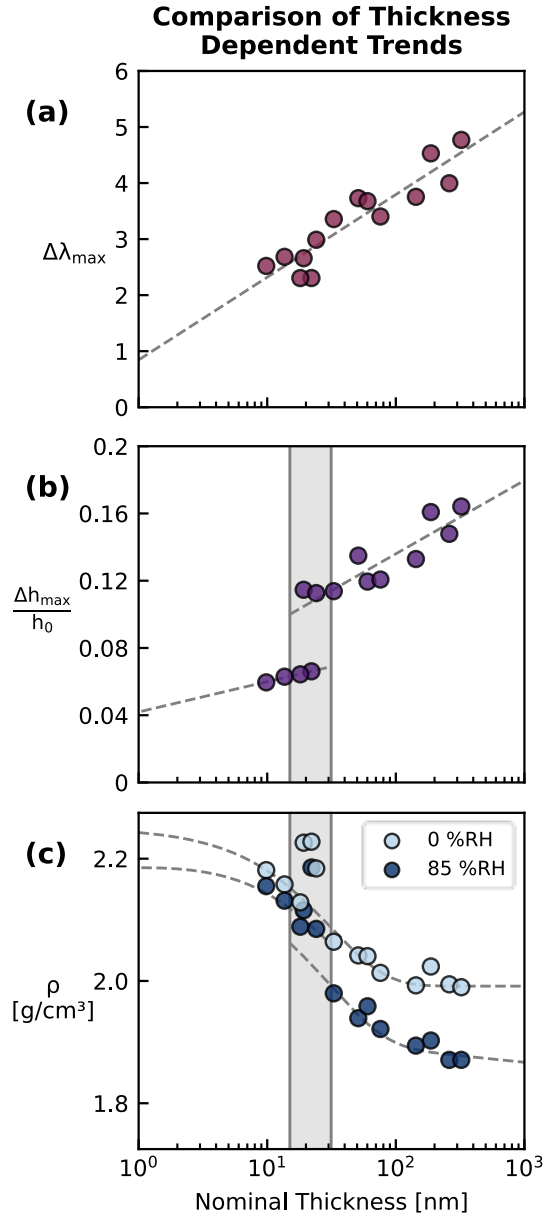


Figure 9. Trends in hydration (a), swelling (b), and density (c) plotted against film thickness at high humidity. Empirical relations are represented by dashed lines and are presented in Equations 9, 10, 3 and 12. In (b), there is an observed region – bound from above by the confinement limit – where films transition to the ultra-thin film regime. The lower bound for this region is only an approximation. These bounds are marked in (b) and (c) with vertical lines.

The thermodynamics of ionomer hydration are in general nontrivial, but have been investigated for bulk membranes.⁴² The lack of complexity in Equation 9 suggests that hydration of thin films may be described in a less complex fashion, owing to their one dimensional swelling and somewhat layered structure, especially for thinner films. Consider the absolute simplest of cases: a set of N locally-flat polymer domains, all functionally identical and stacked parallel on one another, as shown in Figure 10. There would be $N - 1$ gaps in between these flat plates.

For k objects (water molecules), there are k^{N-1} ways of sorting into these gaps. If each assortment has equal probability of occurring, the entropy, S , can be calculated as:

$$S = (N - 1)k_b \ln(N_w) \quad 35$$

In Equation 13, N_w is the number of water molecules. By taking the dry state as a reference, the change in entropy of swelling can then be approximated as:

$$\Delta S^{\text{Swell}} = (N - 1)k_b \ln\left(1 + \frac{\Delta\lambda}{\lambda_0}\right) \quad 36$$

Equations 13 and 14 can be built upon by adding contributions to entropy due to partitioning of bound and free water, but useful conclusions can be drawn from their simplest forms. The swelling entropy can be used to express the Gibbs free energy. From there, the chemical potential (μ) of water in the ionomer is the partial derivative of the free energy with respect to the amount of water. At quasi-equilibrium with humid air, the chemical potential of the water in the ionomer film equals the chemical potential of the water in the external vapor. This is summarized in Equations 15(a) through 15(d):

$$\mu_{\text{H}_2\text{O}}^{\text{Inmr}} = \mu_{\text{H}_2\text{O}}^{\text{Vapor}} \quad 37^*c+$$

$$\mu_{\text{H}_2\text{O}}^{\text{Inmr}} = \partial_n(\Delta H^{\text{Swell}} - T\Delta S^{\text{Swell}}) \quad 15(b)$$

$$\mu_{\text{H}_2\text{O}}^{\text{Vapor}} = \partial_n(-T\Delta S^{\text{Humidify}}) \quad 15(c)$$

$$\int \Delta H^{\text{Swell}} dn = T \int (\Delta S^{\text{Swell}} - \Delta S^{\text{Humidify}}) dn \quad 15(d)$$

The result is an expression for the enthalpy (H) of hydration for a thin film:

$$\frac{\Delta \bar{H}^{\text{Swell}}}{RT} = \frac{BE_w}{\rho_0 \Delta \lambda} \ln\left(1 + \frac{\Delta \lambda}{\lambda_0}\right) + \ln\left(a_w \frac{P^{\text{sat}}}{P^{\text{atm}}}\right) \quad 38$$

In Equation 16, $\bar{H}$ is the average enthalpy per mole of water, B is the moles of flat polymer domains per volume while in dry air, E_w is the equivalent weight of the ionomer, ρ_0 is the dry film density, P^{atm} is the ambient pressure, and P^{sat} is the saturated vapor pressure of water in air. The latter two parameters come about because the chosen reference state was the dry air and not saturated vapor, despite a_w being defined as the RH over one hundred. Equation 16 requires input of parameters B and λ_0 to learn about the swelling enthalpy, but the relation between a_w and $\Delta \lambda$ is known empirically from Equation 9.

Figure 11 plots Equation 16 against thickness as well as along an isotherm. For these plots, λ_0 is set to 2 and several values are input for B , with the naive assumption that B is irreverent of humidity or thickness. Recall this model is idealized, ignoring entropic contributions from ionic groups and partitioning of free and bound water – considerations others have described in detail when investigating bulk membranes.^{42, 44, 45} Still, this analysis suggests enthalpy of hydration monotonically increases with decreasing thickness in the lamellae structure, meaning thinner films experience a heightened enthalpy burden to reach equilibrium swelling. In order to induce swelling,

the incoming water molecules must perform work to increase the hydrophilic domain size between polymer blocks. This work will expand the film, but also elastically compress the hydrophobic domains to induce a swelling pressure, providing further resistance to swelling.⁴⁴ Using standard thermodynamic relations, the swelling enthalpy relates to the swelling pressure as:

$$\Delta \bar{H}^{\text{Swell}} = -Q^L + \bar{V}_{\text{H}_2\text{O}} \Delta P^{\text{Swell}} \quad 39$$

In Equation 17, Q^L is the (positive) latent heat of desorption and $\bar{V}$ is molar volume. Since swelling enthalpy depends on two terms, there are two potential conclusion that may be drawn. It is possible the change in swelling pressure increases as film thickness is reduced – or at least to a greater extent than the molar volume of sorbed water reduces. The increased density is due to heightened crystallinity within the hydrophobic domains,²⁶ and an increase in crystallinity implies increased stiffness. If solid domains are stiffer, or denser, a higher osmotic pressure is required to compress them and induce swelling.

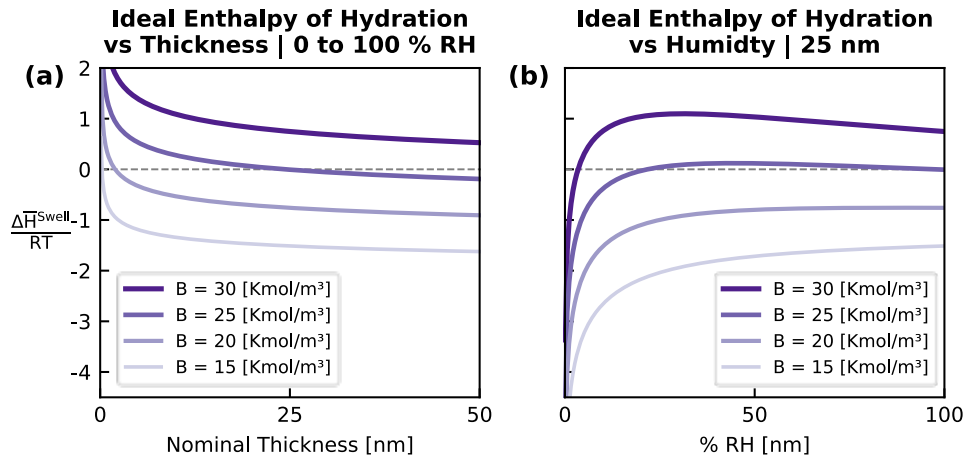


Figure 10. The average molar enthalpy of hydration for an ideal parallel lamellae system is plotted for 4 values of B – the number density of polymer domains in the film – and plotted against film thickness (a) and relative humidity at 25 nm (b). This is done using the relation in Equation 9 with the model from Figure 10. The plots are the result from Equation 16 with $\lambda_0 = 2$. The exact value of the enthalpy depends on B , but thinner films see an increased enthalpy burden when sorbing water.

The other possibility to explain the increased entropy burden is a reduction in the latent heat of sorption as films reduce in thickness. The change in internal energy is associated with water binding to ionic sites, a phenomenon that should remain consistent regardless of substrate proximity. As per the first law of thermodynamics, this means the sum of heat and work performed by sorbed water can be presumed invariant of thickness. A reduction in latent heat is therefore a symptom of an increase in work due to expansion against additional force. This force on the stacked plates atop the metal substrate is resultant of the Casimir effect, or synonymously the Van der Waals, London, or Hamaker force.⁴⁶ The Casimir pressure pushes each lamella towards the substrate, causing additional resistance to vertical displacement that bulk ionomer would not encounter. This pressure decays smoothly with distance from the substrate, which is why films see a gradual reduction in uptake with reduced thickness even above the confinement limit.

Lastly, it is worth noting that the flat plate model describing Equation 13 has translational symmetry for plates moving horizontally. That is, the sorting arrangement of water molecules between gaps is invariant to a single plate's horizontal displacement. If the state does not change, the displacement is necessarily isenthalpic. In contrast, a vertical displacement of a plate will force water to flow, limiting the final state to one with less water in the displaced gap. Hence, vertical displacement is an endergonic process, and the model system is expected to exert a spontaneous restoring force after compression. Put plainly, the idealized system has no shear modulus, but can expect to have a Young's modulus. As previously observed in Figure 7(a), the films in this study exhibited reduced shear modulus with reducing thickness, suggesting a gradual transition to a structure of similar thermodynamics. While the flat-plate model oversimplifies the ionomer films, it may be consistent enough with observations to serve as a starting point for understanding of thermodynamics of swelling of supported ionomer thin films under confinement.

3.4 Kinetics of Sorption in Thin Films

In this, study, the kinetics of water sorption in the films was implicitly measured during humidification from 0% to 100% RH in addition to the pseudo-steady state values at set humidities mentioned in prior sections. Because the mass and volume changes were measured simultaneously, it is possible to examine the rate at which swelling and uptake occur. A double exponential function, shown in Equation 18, is used to model the kinetics of thickness swelling and uptake over time (t).

$$f(t) = 1 - A \exp\left(-\frac{t}{\tau_1}\right) - (1 - A) \exp\left(-\frac{t}{\tau_2}\right) \quad 3:$$

In Equation 18, the first exponential is associated with the initial (fast) kinetics of hydration whereas the second (slower) exponential term is linked to the polymer mobility and relaxation accommodating additional water molecules over time.^{1,4} The faster time constants for each film is plotted in Figure 12, and the results imply the dynamics of volume change and mass change are comparable at short time scales. Furthermore, these data suggest three groups of films (thickness regions) are present based off kinetics alone. Ultra-thin films have a swelling time constant close to 1 min. The second group of films extends perhaps up to 75 nm, where films swell with a characteristic time between 2 and 3 min. The final group covers the thicker films in the data set, which exhibit higher variation in hydration kinetics. One explanation for these classifications could be the inherent role of entropy on the film structure in each category. Films thicker than 75 nm have a wider distribution of polymer domain orientations after fabrication. At the air-ionomer interface, this distribution impacts the concentration of accessible ionic groups at the surface. Two different films of similar thicknesses in this regime could see variability in this surface orientation distribution, and thus a variability in hydration rates.

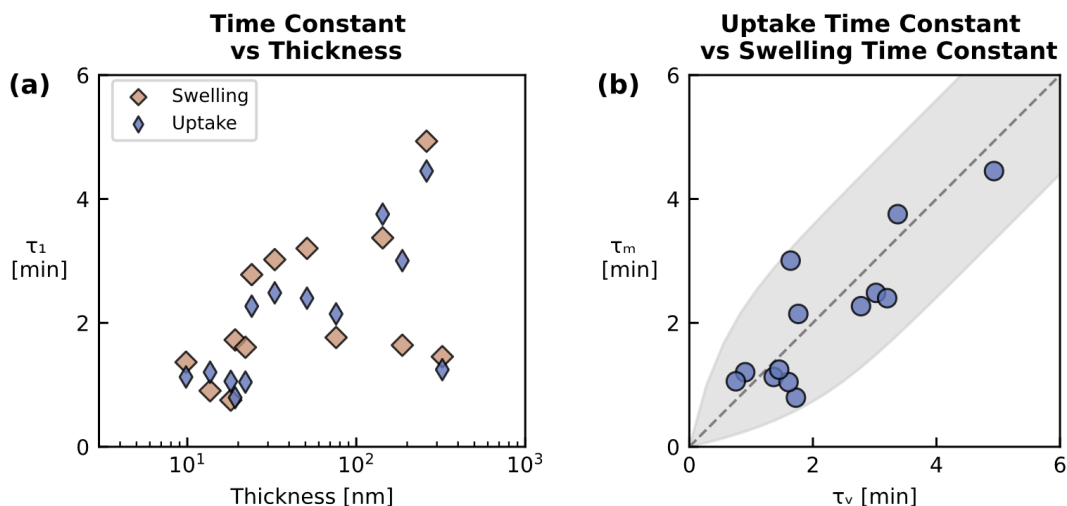


Figure 11. The time constant for initial hydration is plotted against thickness on the left (a), and the time constant specifically for uptake is plotted against the comparable time constant for swelling on the right (b). The two different time constants are relatively comparable to each other for each sample, as shown by the visual aid envelope. Three categories of films are apparent from the dynamics based on thickness: 1) Films greater than 75 nm with highly variable dynamics due to an entropy driven ensemble; 2) Films between 22 and 75 nm where confinement begins to impact structure, leading to more consistent hydration behavior; 3) Films thinner than 22 nm, or ultra-thin films, where the domains are parallelized and the air-ionomer interface is densely populated by sulfonic acid groups.

A thicker film approaching the confinement limit, on the other hand, has its structure imposed on it by substrate interactions. The surface orientation distributions may still have some variance, but are more likely to be comparable between two different films due to the increasing role of enthalpic interactions on morphology. In addition, mechanisms by which swelling occurs in much of these films' volumes are limited, involving mostly unidirectional movement as the parallelized polymer domains are pushed directly apart by the penetrating water molecules. Since the possible pathways of swelling are limited, there is little room for variation in hydration rates.

In the ultra-thin film regime, the parallelized domain geometry is present throughout the whole volume of the film. In addition to having a predictable mechanism of swelling in the inner volume, these films have a façade of ionic groups layering the air-polymer interface. This surface effect leads to higher wettability, and therefore less interfacial resistance to diffusion. The result is as the data depicts: significantly faster hydration rates than films in the next thickest regime – an observation that agrees with the contact angle measurements by Paul et. al.⁴⁷

4. Conclusion

This systematic study of thickness-dependent properties for thin Nafion films leveraged simultaneous measurements from a QCM-D and spectroscopy ellipsometry (SE). Three general categories (thickness regimes) of thin films arise from the data, dictated by the relative impact of substrate effects on the film's structure. These classifications of films based on their structure has been delineated by thickness thresholds in prior studies, but the combined QCM-D and SE data has served well to provide additional clarity of these regimes and understanding on their impact on film function and response.

Films greater than 75 nm are expected to fit the first regime and have similar densities to that of a bulk membrane, but are stiffer and swell less. Films below 75 nm begin to experience the initial effects of confinement and substrate interaction. They show evidence of orthotropy, implying a significant portion of their volume takes on a parallelized domain structure. A characteristic distance is reached at the confinement limit – found to be 31 nm in this study – where significant densification begins to occur and films transition to fit into the third and final category, known as ultra-thin films. This is where the biggest effects of confinement occur and the polymer domains become almost entirely parallelized, with the confined structure present through to the air-polymer interface. The front-facing ionic groups afford these films faster hydration dynamics, as the increased wettability of the surface accelerates water sorption. In addition, these highly confined films see significant excess volume effects due to a higher propensity to bind water to ionic groups as they swell. Because of this propensity, films in the ultra-thin film regime are expected to have much less ionic conductivity, as bound water cannot aid in proton transport via Grotthuss hopping as does free water. In addition, vehicular diffusion of any species may be impeded if the primary paths for flow are filled with densely packed bound water molecules.

The behaviors of films approaching the confinement limit and within the ultra-thin film regime are resultant of an enthalpic burden imparted by substrate interactions, observable by way of a consistent decrease in the extent of hydration with decreasing thickness. By likening a confined film's structure to a stack of flat, parallel plates, it becomes apparent that this enthalpic burden is the result of an increase in internal swelling pressure, as well as a decrease in the latent heat of sorption – indirectly caused by an elevated Casimir pressure. While this model is a pure idealization, it serves as a good starting point for recognizing why the properties of the thinnest films deviate from bulk. Simultaneous measurements of swelling, mass uptake and viscoelastic properties as a function of humidity unraveled previously-unexplored intercorrelations between confinement and hydration governing film's behavior. Confinement-driven densification in thinner films along with the mechanical insights gleaned from the dissipation measurements help establish a consistent framework enriched by a thermodynamic analysis to elucidate how in thinner films, the reduction in swelling and increased in hydration enthalpy and density are interrelated at a fundamental level. The dissipation analysis from QCM-D also provide insights into how ultra-thin films could form a stronger adhesion on metallic substrates thereby restricting their viscous flow – a phenomenon quantified by retardation time – in accord with their higher density.

This study sought fundamental understanding of thin ionomer films and the effects of confinement, but also justifies a practical hypothesis that affects modern design of electrochemical catalyst layers. The phase separated nanodomains only create desirable proton conductivity when entropy is allowed to dictate the ionomer's structure, else enthalpy will limit the amount of free water available for proton hopping. Since the latter is the case at catalytic interfaces, engineers must contend with confined films inhibiting their devices.

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Author Contributions

K.E.: Primary contributor to writing, created final illustrations, collected data, programmed fitting algorithm for data analysis, developed and applied the theory used in the analysis of the data.

D.K.: Edited, provided insight on data interpretation, provided training on equipment use and methods, set up and performed troubleshooting on equipment.

A.K.: Supervised work, developed scope, contributed to writing and editing, performed data analysis and data visualization.

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ABBREVIATIONS

QCM-D, Quartz Crystal Microbalance with Dissipation; SE, Spectroscopic Ellipsometer(-ry); PFSA, Perfluorosulphonic Acid; PTFE, Polytetrafluoroethylene; PEM, Polymer Electrolyte Membrane; RH, Relative Humidity; RPM, Revolutions Per Minute; k_b Boltzmann Constant;

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