#### ECS Transactions, 80 (8) 619-632 (2017) 10.1149/08008.0619ecst ©The Electrochemical Society

# Finite Thickness Effects on Nafion Water Uptake and Ionic Conductivity at Hydrophilic Substrate Interfaces, and Implications for PEMFC Performance

S. C. DeCaluwe<sup>a</sup>, J. A. Dura<sup>b</sup>

<sup>a</sup> Department of Mechanical Engineering, Colorado School of Mines, Golden, Colorado 80401, USA

<sup>b</sup> NIST Center for Neutron Research, Gaithersburg, Maryland, 20899, USA

The effect of film thickness on water uptake in Nafion films is probed via neutron reflectometry for a series of 10 samples with thicknesses ranging from 7–103 nm, and the resulting effects on ionic conductivity. The water uptake in the lamellae and the bulklike layer varies non-monotonically, decreasing as the equivalent Nafion thickness increases from 7 nm to 12 nm, increasing with increasing film thickness for equivalent Nafion thicknesses ranging from 12 nm—60 nm, and then constant for films with equivalent thickness  $\geq$  60 nm. Composition depth profiles are used to predict the anisotropic ionic conductivities, which are used in a floodedagglomerate model of PEMFC catalyst layers to predict the effect of lamellar structure transport properties on PEMFC performance.

# Introduction

Due to its high ionic conductivity and chemical, mechanical, and thermal stability, Nafion(1) is the state-of-the-art polymer electrolyte material for a range of electrochemical energy and separation devices, including polymer electrolyte membrane fuel cells (PEMFCs),(2–6) batteries,(7,8) water electrolyzers,(9,10) and chemical sensors.(11–13) For PEMFCs, most attention has focused on bulk membrane properties.(14–23) Only recently has attention turned to thin film properties, which more closely reflects the Nafion found in the catalyst layer (CL), the complex heterogeneous region where limiting charge-transfer processes occur in the PEMFC (Figure 1). Recent work suggests that high transport resistance in CL Nafion contributes to poor PEMFC performance with low Pt loading,(4,24–27) but the limitations' specific causes and how to address via PEMFC design are not fully understood.(26–28) Understanding is hindered by the complex microstructure of the CL, where thin Nafion layers coat ionomer-flooded agglomerates of carbon-supported Pt catalyst nanoparticles, and by the influence of multiple material interfaces and operating conditions on the thin-film Nafion properties.

Studies therefore typically use planar thin-films as a model to understand CL Nafion properties. Previous studies show deleterious changes in stiffness,(29) water uptake(2,25,30–33) water mobility,(2,30) and proton conductivity(24,27,34,35) with decreasing film thickness below ca. 60 nm. Studies also show that water uptake is influenced by substrate interfaces,(2,25,31) thermal processing(24,25) and deposition method.(25) However, most of these studies report the average sample properties. Because transport is driven by *local* gradients in species free energy and is closely tied to the polymer structure in Nafion, *in situ* depth-profiles are required to correlate the thin film Nafion structure with the resulting transport properties. properties in PEMFC CLs



Figure 1. Illustration of PEMFC catalyst layer limiting processes associated with the flooded agglomerates, as highlighted in the call-out.

In this work, we report the influence of Nafion thickness on the water uptake and anisotropic ionic conductivity for ultrathin Nafion films (ranging from 7–103 nm) coated onto SiO<sub>2</sub> substrates. Neutron reflectometry (NR) is used as an *in situ* probe of the Nafion thickness and 1-D composition depth profiles. Hydrophilic substrates such as SiO<sub>2</sub> lead to alternating water-rich and water-poor lamellae in the Nafion at the substrate interface.(30–33) While the more technologically relevant Pt substrate has fewer lamellae,(36–38) several factors motivate the focus on SiO<sub>2</sub>: (*i*) comparison to previous studies with SiO<sub>2</sub> as a support,(20,25,27,30–32,39) (*ii*) greater sensitivity to the lamellae is achieved in the multi-lamellar structure on SiO<sub>2</sub>, which may yield insights into structures on Pt; and (*iii*) chemical treatments to improve Pt dispersion or PEMFC CL durability may also generate multi-lamellar Nafion structures at Pt and carbon interfaces.

Using these results, we calculate effective ionic conductivities for Nafion thin films with interfacial lamellae. Results show how the Nafion thickness, structure, and water uptake influence conductivity in the PEMFC CL. We then construct a 1D, continuum-level PEMFC CL simulation (anode and cathode) to predict the PEMFC performance with varying thickness of the Nafion layer coating CL agglomerates. These simulations demonstrate how complex interactions between the Nafion thickness, structure, and water uptake influence PEMFC performance in ways that are sometimes non-intuitive. While not intended to be fully predictive, they demonstrate that varying Nafion properties within the thickness range of 5-60 nm can have important effects on PEMFC performance, and thus motivate the need for additional accurate measurements of Nafion transport properties and structure-property relationships as a function of thickness, substrate, and chemical environment in relevant PEMFC operating environments.

# Methods

# Sample Fabrication and NR Measurement

A detailed explanation of the NR data collection and fitting process is given in our previous publication,(32) but briefly: a series of Nafion thin-films were deposited onto

polished Si wafers. The Si wafers were cleaned via detergent scrub and UV-ozone treatment prior to deposition, and films were deposited via spin coating, from a commercial dispersion diluted with ethanol. The concentration of the dispersion and, in some cases, the spin speed were used to control the thickness of the resulting Nafion film. Spin-coat recipes are provided in Table I. Samples were subsequently heated for  $\geq 1$  hr at 60°C under vacuum to ensure solvent removal, adhesion to the substrate and consistent thermal history. Subsequently, samples were installed in the controlled RH chamber, as described previously,(32) and NR was measured under 92.1 ± 1.5% RH and at  $T = 29.6 \pm 0.2^{\circ}$ C, with dry Ar vapor humidified by H<sub>2</sub>O. Error bars throughout the manuscript represent plus or minus one standard deviation. For select samples, NR was also measured under 92.0% RH humidified by D<sub>2</sub>O and/or under 0% RH (dry Ar vapor).

NR measures the intensity of a reflected neutron beam as a function of grazing angle from the surface. Fitting NR data determines the 1-D depth profile (averaged in the plane of the film) of the scattering length density (SLD), which is the linear combination of the known bound coherent scattering lengths  $b_k$  [nm] of all isotopes k in the layer, multiplied by their number density  $n_k$ [1/nm<sup>3</sup>]:

$$SLD = \sum_{k} b_{k} n_{k}$$
<sup>[1]</sup>

Unlike x-ray probes, the neutron SLD can be highly sensitive to light elements, and  $b_k$  varies greatly with the isotopes of certain elements. In particular, the contrast between water ( $SLD_{H2O} = -5.6 \times 10^{-5} \text{ nm}^{-2}$ ) and dry Nafion ( $SLD_{Nafion} = 4.16 \times 10^{-4} \text{ nm}^{-2}$ ) makes NR very sensitive to water content fluctuations through the Nafion film thickness, while the large SLD contrast between H<sub>2</sub>O and D<sub>2</sub>O ( $SLD_{D2O} = 6.36 \times 10^{-4} \text{ nm}^{-2}$ ) allows for precise, accurate determination of the water concentration profile, as described previously.(32)

In this study, humidified Nafion is modeled as a mixture of water and dried Nafion, where the SLD of the two-phase mixture at any given depth z is equal to a linear combination of the individual phase SLDs, weighted by their volume fractions:

$$SLD(z) = V_{\text{water}}(z)SLD_{\text{water}} + (1 - V_{\text{water}}(z))SLD_{\text{Nation}}$$
[2]

In the second term,  $(1-V_{water}(z))$  is used because the volume fraction of the two phases sums to one. In this manner, the SLD profile determined from fitting the NR data provides the depth profile of the water volume fraction,  $V_{water}$ .

Sample $t_{Naf}$ (nm)	% volume Nafion in dilution	Stage 1 spin speed (RPM or	Stage 1 time (s)	Stage 2 spin speed (RPM or	Stage 2 time (s)
		$Hz \times 60)$		$Hz \times 60)$	
7	0.72	3500	60		
12	1.74	3500	60		
20	1.50	3500	60		
42	5.01	3500	60		
60	7.52	500	3	3500	60
103	11.11	550	4	3500	60

Table I. Nafion-Ethanol dilutions and spin-coat recipes for all samples in the study.

NR data was fit using Refl1D,(40) using the "individual layer" model described previously,(32) which models the SLD profile as a series of slabs with finite thickness, interfacial width (i.e. "roughness") and SLD. For all fits, reduced  $\chi^2$  values  $\leq 1.26$  were obtained, signifying excellent fits.

# Estimating Transport Properties in Thin-film Nafion and Lamellae

Estimating the transport properties of CL Nafion remains a challenge, due to the complex microstructure of the CL and to a limited number of measurements in thin-film Nafion. To provide a first-order approximation of CL Nafion transport parameters, a few basic assumptions are made. Because there have been no studies to calculate transport properties in Nafion lamellae as a function of water uptake or ionic domain structure, our *a priori* assumption is that the local ionic conductivity for thin-film Nafion obeys the dependence on  $\lambda$  that has been previously-determined for bulk-like samples:(19)

$$\sigma_{io} = (0.5139\lambda - 0.326) \exp\left(1268\left(\frac{1}{303} - \frac{1}{T}\right)\right),$$
[3]

where T is the temperature (302.75 K, here) and  $\lambda$  is the molar ratio of water to sulfonic acid. For "well mixed" Nafion, this is a function of the local water content:

$$\lambda = \frac{V_{\text{water}}}{1 - V_{\text{water}}} \frac{\rho_{\text{H2O}}}{\rho_{\text{Nafion}}} \frac{EW_{\text{Nafion}}}{MW_{\text{H2O}}}$$
[4]

where  $\rho$  is the mass density (g/cm<sup>3</sup>),  $EW_{Nafion}$  is the Nafion equivalent weight (mass of polymer per mole of sulfonate; 1100 g/mol in this study), and where  $MW_{\rm H2O}$  is the molecular weight of water (g/mol). In bulk Nafion, the isotropic phase segregation implies a constant ratio of sulfonate to backbone groups, which allows for direct calculation of  $\lambda$  from  $V_{\text{water}}$ , as in Eq. 4. For all layers other than the two adjacent to the SiO<sub>2</sub>, Equations 2, 3, and 4 are used to calculate the conductivity for each layer, where the fitted layer SLD is used in Equation 2. Equation 3 is also used to calculate  $\sigma$  as a function of  $\lambda$  for the two layers adjacent to the SiO<sub>2</sub>, but different approaches are used to calculate  $\lambda$  for these two layers, depending on the sample thickness. For  $t_{\text{Naf}} < 60$  nm, phase segregation of the Nafion moieties between the two lamellae closest to the SiO<sub>2</sub> implies that Eq. 4 is invalid. For these samples,  $\lambda$  for the two layers adjacent to the SiO<sub>2</sub> are derived directly from the moles of H<sub>2</sub>O and SO<sub>3</sub>H in the 'atomistic profile' in our previous publication.(32) For the two layers closest to the SiO<sub>2</sub> for  $t_{\text{Naf}} \ge 60$  nm, large interface widths cause the SLDs of the actual profiles to deviate from the layer SLD values fit within the slab model. Rather than using those fit parameters, the layer SLD used for eq. 2 is taken as the average minimum (first layer) or average maximum (second layer) from the SLD profiles, averaged over all samples in the thick-film regime ( $t_{\text{Naf}} \ge 60$ nm). The resulting  $\lambda$  are then used in Equation 3 to determine layer conductivities.

We further assume that reactant species  $O_2$  and  $H_2$  diffuse through the Nafion as dissolved species in the absorbed water. To first order, then, the local diffusion coefficients for these species are approximated as proportional to the local water content:

$$D_k = \frac{V_{\text{water}}}{V_{\text{water}}^o} D_k^o, \qquad [5]$$

where  $V_{\rm w}$  is the actual local water volume fraction and where  $V_{\rm water}^o$  and  $D_k^o$  are the water volume fraction and diffusion coefficient measured for bulk Nafion samples, respectively.

Again, these assumptions are intended as a first-order approximation, to assess the potential impact of finite thickness effects and interfacial lamellae on CL transport processes. They are most likely accurate for the bulk-like layers on samples with  $t_{\text{Naf}} \ge 60$  nm, where the ionic domain morphology is similar to that for bulk Nafion. For thinner layers, and regions with lambda well outside the normal range, factors other than  $\lambda$  no doubt influence the value of  $\sigma$ . More accurate functional relationships can and should be developed, in future studies, for enhanced predictive capabilities.

Because of the significant uncertainty of the CL transport parameters, we restrict our calculations to estimating the effective ionic conductivity for a series of planar thin films. The ionic conductivity (Eqs. 3 and 4) is a non-linear function of the water content, so the conductivity of the stack of layers is non-isotropic. For each sample we calculate effective conductivities in the surface normal ( $\sigma_{normal}$ ) and parallel ( $\sigma_{parallel}$ ) directions, relative to the film surface, for a range of expected conductivities with varying Nafion thickness. In the surface normal direction, transport is in series across the layers *j* in a film, resulting in a net effective conductivity of:

$$\sigma_{\text{normal}} = \frac{t_j}{\sum_j \frac{t_j}{\sigma_j}},$$
[6]

while the individual layers contribute in parallel in the surface-parallel direction:

$$\sigma_{\text{parallel}} = \frac{\sum_{j} \sigma_{j} t_{j}}{t_{\text{film}}},$$
[7]

summed over all *j* layers in the film, where  $t_{\text{film}}$  is the total thickness of the, and where the individual layer conductivities  $\sigma_j$  are calculated according to Equation 3. In the absence of better estimates, layer conductivities are assumed to be isotropic. Given the significant uncertainties, the effective conductivities in Eqs. 6 and 7 establish a range of possible variations with varying thickness and interfacial structure. More accurate relationships can and should be developed, going forward.

# PEMFC Catalyst Layer Simulations: "Flooded Agglomerate" Model

Correlated with decreasing water uptake and decreasing species mobility, competing transport effects come into play as the Nafion coating thickness decreases: conductivity generally decreases, but decreasing thickness also enables quicker transport into and out of the CL agglomerates. To estimate the magnitude of finite thickness effects on CL transport and PEMFC performance, a numerical simulation of the PEMFC CLs (anode

and cathode) is constructed to calculate the CL overpotentials as a function of current density. The CL processes are illustrated in Figure 1, for a PEMFC cathode. In the model presented herein, we employ a "flooded agglomerate" approach, and focus on limiting processes within the agglomerates. As such, the simulation neglects losses due to reactant and product transport in the electrode pores (so-called "concentration overpotentials"), neglects transport within the bulk Nafion membrane, and considers the Nafion water content in the CL to be in equilibrium with a vapor at the same RH as the measurements described above (92%). Instead, the simulation focuses on the following three phenomena, as highlighted by the call-out in Figure 1:

- Absorption and diffusion of H<sub>2</sub> and O<sub>2</sub> into and through the agglomerate;
- Proton  $(H_3O^+)$  transport between the Nafion membrane and the catalytic sites; and
- Charge-transfer reactions at the Nafion-Pt interface.

Models based on physical conservation laws derived as continuum partial differential and algebraic equations (DAE) were discretized in 1D with a finite-volume method and implemented in MATLAB. The flooded agglomerates are also discretized spherically, to enable calculation of diffusion rates to and from the active catalyst surfaces. By integrating out to a long time span with constant boundary conditions, the model calculates the steady-state catalyst layer overpotential ( $\eta = \text{OCV} - V_{\text{cell}}$ ) as a function of current density. Electrochemical models require a complex multi-physics approach, and numerous detailed descriptions are found in the literature.(5,19,26,42–44) The description for many of the DAEs are therefore common throughout the literature, but are summarized, below, for completeness.

<u>Charge Conservation</u>: Conservation of charge determines the electric potential profiles in the electrode and ionomer phases. In any given volume, the model assumes charge neutrality within each phase interior in the volume (Nafion and carbon), as well as the volume as a whole. The buildup of the charged double-layer at the ionomerelectrode interface is used to calculate the electric potential difference at the phase boundary. Charge balance equations therefore incorporate the sources and sinks due to the faradaic current  $i_{Far}$  and current densities due to electric potential gradients:

$$C_{\rm dl} \frac{\partial \Delta \Phi_{\rm el}}{\partial t} = i_{\rm Far} \pm \frac{\partial}{\partial y} \left( \sigma_m^{\rm eff} \frac{\partial \Phi_m}{\partial} \right).$$
[8]

The difference between the electrode phase (anode or cathode carbon supports) electric potential  $\Phi_{\text{electrode}}$  and the electrolyte/ionomer phase (Nafion thin film) electric potential  $\Phi_{\text{ionomer}}$  is defined as  $\Delta \Phi_{\text{el}} \equiv \Phi_{\text{electrode}} - \Phi_{\text{ionomer}}$ . The effective conductivity of phase *m* (carbon or Nafion) per unit geometric area is  $\sigma_m^{\text{eff}}$ . The double-layer capacitance per unit total volume  $C_{\text{dl}}$  can be extracted from equivalent-circuit modeling of experimental data. However, the value of  $C_{\text{dl}}$  only impacts transient calculations, and as such estimated values of  $C_{\text{dl}}$  are sufficient for the steady-state overpotentials in this study. The  $\pm$  sign on the right-hand side of eq. 8 depends on the phase *m* (+ for the carbon electrode phase, and – for the Nafion electrolyte phase). The faradaic current density, *i*<sub>Far</sub>, is defined such that it is positive when positive charge is delivered to the carbon phase. Two versions of Eq. 8 can be written, once for the carbon phase and once for the Nafion. However, because

there is only one value of the left-hand side derivative at any given time, setting the two equal to one another provides the charge-neutrality condition for the volume as a whole:

$$\frac{\partial}{\partial y} \left( \sigma_{\text{electrode}}^{\text{eff}} \frac{\partial \Phi_{\text{electrode}}}{\partial y} \right) + \frac{\partial}{\partial y} \left( \sigma_{\text{ionomer}}^{\text{eff}} \frac{\partial \Phi_{\text{ionomer}}}{\partial y} \right) = 0, \qquad [9]$$

which is equivalent to requiring that the ionic and electronic currents, summed over all boundaries of a given finite volume, sum to zero. Eqs. 8 and 9 constitute a set of differential and algebraic equations which, taken together, determine the electric potential profiles of the electrode and Nafion phases at any given point in time.

<u>Mass and Species Conservation Inside the Agglomerate</u>: The model assumes spherical agglomerates, which are at all times in equilibrium with the RH in the vapor phase. As the local  $H_3O^+$  hydronium ion concentration is fixed (due to the assumption of local charge neutrality) by the ionomer equivalent weight, the only species concentrations tracked by the model are of absorbed  $H_2$  (anode) and  $O_2$  (cathode) diffusing between the vapor and the catalyst surface. In spherical coordinates, the conservation equation for  $C_{k,agg}$ , the concentration of dissolved species k in the agglomerate interior is written as:

$$\frac{dC_k}{dt} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_{k,\text{agg}}^{\text{eff}} \frac{\partial C_{k,\text{agg}}}{\partial r} \right) + \dot{s}_{k,\text{agg}} \,.$$
[10]

Within the interior of the agglomerate,  $\dot{s}_{k,agg}$  terms reflect the influence of the faradaic current density, while the effective diffusion coefficient:

$$D_{k,\text{agg}}^{\text{eff}} = \frac{\phi_{\text{Naf,agg}}}{\tau_{\text{Naf,agg}}^2} D_k$$
[11]

incorporates water content artifacts (i.e.  $D_k$  in eq. 11 is calculated via eq. 5) as well as microstructural impacts (the ionomer phase volume fraction  $\phi_{\text{Naf,agg}}$  and tortuosity  $\tau_{\text{Naf,agg}}$ within the agglomerate). In the ionomer layer that coats the agglomerate, reaction rates at the vapor interface (absorption and desorption) are incorporated into  $\dot{s}_{k,\text{agg}}$ , but there is no faradaic current density and the species diffusion coefficients are not impacted by microstructural impacts (i.e., the coefficient from eq. 5 is used directly).

Species production rates due to chemical and electrochemical reactions are calculated as the linear combination of net stoichiometric coefficients  $v_{k,j}$  and net rates of progress  $\dot{q}_i$ , summed over all *j* reactions:

$$\dot{s}_{k,agg} = \sum_{j} v_{k,j} \dot{q}_{j} , \qquad [12]$$

where the  $v_{k,j}$  for species k in reaction j is the difference between reverse and forward stoichiometric coefficients:  $v_{k,j} = v_{k,j}^{\text{rev}} - v_{k,j}^{\text{fwd}}$ . Rates of progress  $\dot{q}_j$  for a reaction j are calculated by mass action kinetics. For strictly chemical reactions (absorption/desorption at the Nafion/vapor interface), this takes the typical form:

$$\dot{q}_{j,\text{chem}} = k_{j,\text{fwd}} \Pi_k \left[ C_k \right]^{v_{k,j}^{\text{fwd}}} - k_{j,\text{rev}} \Pi_k \left[ C_k \right]^{v_{k,j}^{\text{rev}}},$$
[13]

where  $k_{j,\text{fwd/rev}}$  are the forward and reverse rate parameters, and where  $[C_k]$  is the activity concentration of species k. For electrochemical charge-transfer reactions, an extra electric potential term is added to the forward and reverse rates:

$$\dot{q}_{j,\text{echem}} = k_{j,\text{fwd}} \Pi_k \left[ C_k \right]^{v_{k,j}^{\text{fwd}}} \exp\left(-\frac{a_{j,\text{fwd}} n_j F \Delta \Phi_{\text{el}}}{RT}\right) - k_{j,\text{rev}} \Pi_k \left[ C_k \right]^{v_{k,j}^{\text{rev}}} \exp\left(\frac{a_{j,\text{rev}} n_j F \Delta \Phi_{\text{el}}}{RT}\right), \quad [14]$$

where  $\alpha_{j,\text{fwd/rev}}$  are the forward and reverse charge transfer coefficients and  $n_j$  elementary charge transferred from the ionomer to the electrode phase by reaction *j*. *F* is is the net Faraday's constant, *R* the universal gas constant, and *T* the temperature. All chemical reactions are written as thermodynamically reversible, with rates and species thermodynamic calculations handled by Cantera.(45)

# **Results and Discussion**

# Water content of ultrathin Nafion films

The Nafion water uptake can be analyzed in terms of three different regions of the sample: (i)  $V_{\text{water,lamellae}}$ : the lamellar region, (ii)  $V_{\text{water,bulk-like}}$ : the bulk-like layer plus surface layer (when present), and (iii)  $V_{\text{water,average}}$  the entire sample (i.e. regions *i* and *ii*). In sample names 'tXX', the number XX is the sample's equivalent Nafion thickness,  $t_{\text{Naf}}$ , i.e. the resulting thickness if all water were removed:

$$t_{Naf} = \sum_{i} (1 - V_{\text{water},i}) t_i, \qquad [15]$$

As detailed in our previous publication,(41) the thickness trends fall into three regimes:

<u>Truncated Regime</u>: For t7, the film consists entirely of lamellae, since the film is 'truncated' before it reaches a thickness where the bulk-like layer forms. The lamellae are on average more water rich than for the subsequent "thin-film" regime, mainly due to a high water volume fraction in the water rich layers.

<u>Thin-film Regime</u>: For 7 nm  $< t_{Naf} < 60$  nm, a thin bulk-like layer (which increases its water uptake with thickness) is present between the lamellae and the vapor environment. The lamellar region contains 6 layers with a relatively constant thickness. The lamellar water uptake is lower than for the truncated regime, but also increases with thickness, remaining slightly higher than  $V_{water,bulk-like}$ .

<u>Thick-film Regime</u>: For  $t_{\text{Naf}} \ge 60$  nm, both  $V_{\text{water,lamellae}}$  and  $V_{\text{water,bulk-like}}$  increase significantly, relative to the values in the other two regimes.  $V_{\text{water,bulk-like}}$  is relatively constant in this regime, and equals that expected for bulk Nafion 1100 membranes.

Results demonstrate that the lamellae are influenced by interactions with the substrate and the bulk-like layer (or the vapor interface). In the truncated regime,  $V_{\text{water,lamellae}}$  ranges from 21–24%. When the bulk-like layer forms, this drops to 16.7%, and then

 $V_{\text{water,lamellae}}$  and  $V_{\text{water,bulk-like}}$  both increase with increasing bulk-like layer thickness. In the thick-film regime,  $V_{\text{water,bulk-like}}$  increases to a relatively constant 25.1±0.7%, but  $V_{\text{water,lamellae}}$  increases by a greater amount, and ranges from 31.1–40.9%. The large non-monotonic and discontinuous shifts lamellar water uptake—despite a constant substrate, temperature, and vapor RH—demonstrate the influence of the bulk-like on the lamellae.

#### Ionic Conductivity of Thin-film Nafion

These results emphasize the importance of *in situ* depth profiles in revealing not just *how much* water is in the film, but *how it is distributed*. For example, in the in-plane direction, where layer conductivities add in parallel, water uptake variations in the structure produce a different total in-plane conductivity than that estimated assuming a single layer with average water uptake. However, the assumption that the dependence of conductivity on  $\lambda$  in thin films follows that established for bulk membranes is not valid. In the interfacial lamellae, the tortuosity and likely the internal structure of the ionic domains differ from bulk-like material, giving rise to a different dependence of conductivity on lambda than represented in Equation 3. Even in layers where the ionic domain morphology is similar to bulk samples, confinement effects play a role.

Predicted conductivities from the NR profiles are shown in Figure 2.  $\sigma_{\text{average}}$  is the conductivity predicted if  $V_{\text{water,average}}$  were measured and used to calculate the conductivity via Equations 3 and 4. The dashed line is the conductivity of bulk Nafion at these conditions.(19,46) Predictions show two trends: (i) for  $t_{\text{Naf}} \le 42$  nm, the conductivities decrease upon formation of the dry bulk-like layer (at t12), and then increase as the water content of the bulk-like layer increases with increasing thickness; (ii) the decreases (i.e.  $\sigma_{\text{parallel}}$  and  $\sigma_{\text{normal}}$  become more similar) with increasing thickness, due to the increasing contribution from the well mixed, isotropic bulk-like layer. There is an interesting increase in anisotropy for sample t60, due to the significant increase in the lamellae water content between samples t42 and t60; this anisotropy mostly disappears for sample t103, as the thick, isotropic bulk-like layer dominates the conductivity. We also see that, for samples with no bulk-like layer, knowing the concentration depth profile is essential to correctly predict the conductivity: the conductivity calculated using the average water is significantly different from both content ( $\sigma_{average}$ )  $\sigma_{\rm narallel}$ and  $\sigma_{\rm normal}$ .



Figure 2. Predicted effective ion conductivities with varying thickness. ' $\sigma_{parallel}$ ' and ' $\sigma_{normal}$ ' correspond to transport direction, relative to agglomerate surface. ' $\sigma_{average}$ ' is based on the average water content of the film, ignoring through-plane variations. Dashed line shows the conductivity of bulk Nafion at 29.6 °C and 92% RH.



Figure 3. Catalyst layer overpotentials for flooded spherical agglomerates of radius  $r_{agg} = 500$  nm. Ionic conductivities in Nafion use the a) normal and b) parallel conductivities from Figure 2.

#### PEMFC Catalyst Layer Simulations

PEMFC CL simulation restults for agglomerates with radius  $r_{agg} = 500$  nm are shown in Figure 3, with simulation parameters in Table II. As shown schematically in Figure 1, transport in the CL Nafion includes processes parallel to and normal to the plane of the agglomerate shell. As such, the 'normal' and 'parallel' conductivities serve as limiting cases. As one would expect from the conductivities in Figure 2, if 'parallel' transport processes dominate in the PEMFC CL, simulations generally predict better PEMFC performance. As the Nafion phase becomes thicker and transport becomes more isotropic, the differences between the 'parallel' and 'normal' predictions decrease, and are mostly negligible for  $t_{\text{Naf}} \ge 60$  nm. For both transport directions, sample t7 (7 nm Nafion shell around the agglomerates) gives the best performance, given the low thickness and high conductivity. In general, simulations predict better performance for thinner Nafion films, with a few interesting exceptions: in the 'normal' direction, sample t20 gives better performance than t12. The increase in conductivity is more than enough to compensate for the increase in the shell thickness. Additionally, in the 'normal' and 'parallel' directions, simulations predict better performance for t60 than for t42, correlated with the increase in water uptake. However, we also see transport-limited currents for t60 (the sharp upturn in overpotential at i = 1.5 A/cm<sup>2</sup>), which become severe for t103 (limiting current  $i_{\text{lim}} = 0.55 \text{ A/cm}^2$ .

The simulations have two important implications. First, predicted conductivities in Figure 2, the ionomer shell coating the CL agglomerates should be as thin as possible. For any coating thickness over roughly 50 nm, absorbed species transport ( $O_2$  and  $H_2$ ) become performance limiting. Second, in the thickness range 10—60 nm, non-monotonic variations in PEMFC performance with varying ionomer thickness are possible, due to the correlation between film thickness and water uptake for films > 10 nm thick. Note that the predictions assume that the only transport limitations in thin-film Nafion < 60 nm thickness are due to reduced water uptake. In reality, additional limitations due to confinement and substrate bonding are likely. While the work here provides a first-order estimate of transport limitations in PEMFC CLs, additional study is required to determine transport properties of thin-film Nafion with greater accuracy.

Parameter	Value/Equation	
$H_{\rm H2(Naf)}$ Henry's Law Constant for $H_{2(Naf)}$	0.6 (47)	
Anode H <sub>2</sub> absorption reaction	$H_2 \leftrightarrow H_{2(Naf)}$	
Anode H <sub>2</sub> absorption reaction rate constant	$2*10^{18}$ (m)	
Anode charge-transfer reaction	$2 \text{ H}^+_{(\text{Naf})} + 2 e^- \leftrightarrow \text{H}_{2(\text{Naf})}$	
Anode charge-transfer reaction rate constant	$2.5*10^{-11} (m^4/mol)$	
Anode charge-transfer reaction coefficient $\alpha_{\text{fwd}}$	0.5	
Anode charge-transfer reaction activation energy	13.683 (kJ/mol)	
$H_{O2(Naf)}$ Henry's Law Constant for $O_{2(Naf)}$	0.1 (48)	
Cathode O <sub>2</sub> absorption reaction	$0_2 \leftrightarrow 0_{2(Naf)}$	
Cathode O <sub>2</sub> absorption reaction rate constant	$2*10^{18}$ (m)	
Cathode charge-transfer reaction	$4 \operatorname{H}^{+}_{(\operatorname{Naf})} + \operatorname{O}_{2(\operatorname{Naf})} + 4 e^{-} \leftrightarrow \operatorname{H}_{2}\operatorname{O}_{(\operatorname{Naf})}$	
Cathode charge-transfer reaction rate constant	$7.5*10^{28} (m^{13}/mol^4)$	
Cathode charge-transfer reaction coefficient $\alpha_{fwd}$	0.5	
Anode charge-transfer reaction activation energy	23.0 (kJ/mol) (49)	
$r_{\text{agg}}$ , agglomerate radius	500 (nm)	
Gas phase volume fraction in CL, $\phi_{g}$	0.1	
Nafion ionomer phase volume fraction in CL, $\phi_{\text{Naf}}$	0.5	
Gas phase tortuosity in CL, $\tau_{g,CL}$	1.6	
Specific surface area of agglomerate $A_{\text{surf,agg}}$ , per unit volume of CL	6*10 <sup>5</sup> (1/m)	
Specific Pt surface area A <sub>surf,cat</sub> , per unit volume of CL	$2.5*10^{5} (1/m)$	
Double layer capacitance $C_{dl}$	$1.5*10^{-6} (F/m^2)$	
Catalyst layer thickness $H_{CL}$	20 (µm)	
Bulk $O_2$ diffusion coefficient in Nafion, $D_{O2(Naf)}^{o}$	$8*10^{-10} (m^2/s) (44)$	
Bulk H <sub>2</sub> diffusion coefficient in Nafion, $D_{H2(Naf)}^{o}$	$5*10^{-9} (m^2/s) (47)$	

#### Table II. PEMFC CL simulation parameters.

#### Conclusions

In situ NR of ultra-thin Nafion films with an equivalent thickness ranging from 7–103 nm was collected at  $T = 29.6 \pm 0.2^{\circ}$ C and RH = 92.1 ± 1.5%, and demonstrates the variation in the water uptake and lamellar structure with film thickness. For films with equivalent thickness < 12 nm, the entire sample consists of lamellae. For thicker films a non-lamellar, bulk-like layer is added. For the samples with equivalent thickness, due to confinement effects. For films with equivalent thickness  $\geq 60$  nm, the bulk-like layer absorbs the same amount of water as in bulk membranes ( $\lambda = 10$ ). Results demonstrate that the lamellar water uptake is influenced by interactions with both the SiO<sub>2</sub> substrate and the bulk-like layer (or vapor interface). On some samples a surface layer was observed at the interface between the bulk-like layer and the vapor reservoir, which is consistent with the hydrophobic, fluorocarbon rich skin reported in the literature.(50–52)

These NR-fitted depth profiles are used to predict ionic conductivities for the thinfilm samples, using previously established relationships to relate water uptake and conductivity. Results reveal anisotropic conductivities for films in the 'truncated' regime, and demonstrate that at length scales relevant to PEMFC CL agglomerates, the lamellae can have a significant impact on transport limitations, such that small changes in ionomer thickness lead to significant variations in the ionic conductivity. Incorporating these transport properties into a flooded agglomerate model of the PEMFC CLs predicts that, in general, thinner ionomer films in the CL yield better PEMFC performance, and that nonmonotonic performance variations with increasing CL ionomer thickness are possible.

#### Acknowledgments

The authors are grateful for the generous financial support of the National Academies' NRC Research Associateship Program.

#### References

- 1. Certain commercial equipment, instruments, materials, suppliers, or software are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.
- 2. A. Kusoglu, A. Kwong, K. T. Clark, H. P. Gunterman, and A. Z. Weber, *J. Electrochem. Soc.*, **159**, F530–F535 (2012).
- J. D. Fairweather, D. Spernjak, A. Z. Weber, D. Harvey, S. Wessel, D. S. Hussey, D. L. Jacobson, K. Aryushkova, R. Mukundan, R. L. Borup, *J. Electrochem. Soc.*, 160, F980–F993 (2013).
- 4. D. K. Paul, A. Fraser, and K. Karan, *Electrochem. commun.*, 13, 774–777 (2011).
- 5. M. Secanell, K. Karan, A. Suleman, and N. Djilali, *Electrochim. Acta*, **52**, 6318–6337 (2007).
- 6. A. Z. Weber and A. Kusoglu, J. Mater. Chem. A, 2, 17207–17211 (2014).
- 7. I. Bauer, S. Thieme, J. Brückner, H. Althues, and S. Kaskel, *J. Power Sources*, **251**, 417–422 (2014).
- R. M. Darling, A. Z. Weber, M. C. Tucker, and M. L. Perry, J. Electrochem. Soc., 163, A5014–A5022 (2015).
- 9. P. Millet, R. Ngameni, S. A. Grigoriev, N. Mbemba, F. Brisset, A. Ranjbari, C. Etiévant, *Int. J. Hydrogen Energy*, **35**, 5043–5052 (2010).
- 10. C. Rozain and P. Millet, *Electrochim. Acta*, 131, 160–167 (2014).
- 11. S. M. Ayyadurai, A. D. Worrall, J. A. Bernstein, and A. P. Angelopoulos, *Anal. Chem.*, **82**, 6265–6272 (2010).
- 12. Y. Lin, Q. Zhou, Y. Lin, D. Tang, G. Chen, D. Tang, *Biosens. Bioelectron.*, **74**, 680–686 (2015).
- 13. J. Zavazalova, M. E. Ghica, K. Schwarzova-Peckova, J. Barek, and C. M. A. Brett, *Electroanalysis*, **27**, 1556–1564 (2015).
- 14. J. A. Elliott, D. Wu, S. J. Paddison, and R. B. Moore, Soft Matter, 7, 6820 (2011).
- 15. F. Xu, O. Diat, G. Gebel, and A. Morin, J. Electrochem. Soc., 154, B1389 (2007).
- G. Gebel, O. Diat, S. Escribano, and R. Mosdale, *J. Power Sources*, **179**, 132–139 (2008).
- 17. T. D. Gierke, G. E. Munn, and F. C. Wilson, *J. Polym. Sci. Polym. Phys. Ed.*, **19**, 1687–1704 (1981).
- M. Lopez-Haro, L. Guétaz, T. Printemps, A. Morin, S. Escribano, P.-H. Jouneau, P. Bayle-Guillemaud, F. Chandezon, G. Gebel, *Nat. Commun.*, 5, 5229 (2014).
- 19. T. E. Springer, T. A. Zawodzinski, and S. Gottesfeld, J. Electrochem. Soc., 138, 2334 (1991).
- 20. T. A. Zawodzinski, C. Derouin, S. Radzinkai, R. J. Sherman, V. T. Smith, T. E. Springer, S. Gottesfeld, *J. Electrochem. Soc.*, **140**, 1041 (1993).
- 21. K. Schmidt-Rohr and Q. Chen, Nat. Mater., 7, 75-83 (2008).

- 22. K. A. Mauritz and R. B. Moore, Chem. Rev., 104, 4535-4586 (2004).
- 23. K.-D. Kreuer and G. Portale, Adv. Funct. Mater., 23, 5390-5397 (2013).
- 24. D. K. Paul, R. Mccreery, and K. Karan, J. Electrochem. Soc., 161, 1395–1402 (2014).
- 25. A. Kusoglu, D. Kushner, D. K. Paul, K. Karan, M. A. Hickner, A. Z. Weber, *Adv. Funct. Mater.*, **24**, 4763–4774 (2014).
- 26. A. Z. Weber, R. L. Borup, R. M. Darling, P. K. Das, T. J. Dursch, W. Gu, D. Harvey, A. Kusoglu, S. Litster, M. M. Mench, R. Mukundan, J. P. Owejan, J. G. Pharoah, M. Secanell, I. V. Zenyuk, *J. Electrochem. Soc.*, **161**, F1254–F1299 (2014).
- 27. M. A. Modestino, D. K. Paul, S. Dishari, S. A. Petrina, F. I. Allen, M. A. Hickner, K. Karan, R. A. Segalman, A. Z. Weber, *Macromolecules*, 46, 867–873 (2013).
- 28. C.-Y. Jung and S.-C. Yi, Electrochem. commun., 35, 34-37 (2013).
- 29. K. A. Page, A. Kusoglu, C. M. Stafford, S. Kim, R. J. Kline, A. Z. Weber, *Nano Lett.*, 14, 2299–2304 (2014).
- 30. S. A. Eastman, S. Kim, K. A. Page, B. W. Rowe, S. Kang, S. C. DeCaluwe, J. A. Dura, C. L. Soles, K. G. Yager, *Macromolecules*, 46, 571–571 (2013).
- J. A. Dura, V. S. Murthi, M. Hartman, S. K. Satija, and C. F. Majkrzak, *Macromolecules*, 42, 4769–4774 (2009).
- 32. S. C. DeCaluwe, P. A. Kienzle, P. Bhargava, A. M. Baker, and J. A. Dura, *Soft Matter*, 10, 5763 (2014).
- 33. S. Kim, J. A. Dura, K. A. Page, B. W. Rowe, K. G. Yager, H.-J. Lee, C. L. Soles, *Macromolecules*, 46, 5630–5637 (2013).
- 34. D. Paul, A. Fraser, J. Pearce, and K. Karan, ECS Trans., 41, 1393–1406 (2011).
- 35. D. K. Paul and K. Karan, J. Phys. Chem. C, 118, 1828–1835 (2014).
- 36. D. D. Borges, G. Gebel, A. A. Franco, K. Malek, and S. Mossa, *J. Phys. Chem. C*, **119**, 1201–1216 (2015).
- D. Damasceno Borges, A. A. Franco, K. Malek, G. Gebel, and S. Mossa, *ACS Nano*, 7, 6767–6773 (2013).
- 38. V. S. Murthi, J. Dura, S. Satija, and C. Majkrzak, in *ECS Transactions*, vol. 16, p. 1471–1485, ECS (2008).
- 39. M. A. Modestino, A. Kusoglu, A. Hexemer, A. Z. Weber, and R. A. Segalman, *Macromolecules*, **45**, 4681–4688 (2012).
- 40. P. A. Kienzle, J. A. Krycka, and N. Patel, "Refl1D: Interactive depth profile modeler," can be found under http://www.reflectometry.org/danse/software .
- 41. S. C. Decaluwe, A. M. Baker, P. Bhargava, J. E. Fischer, and J. A. Dura, *Submitted for publication; currently under review.* (2017).
- 42. A. Z. Weber and J. Newman, J. Electrochem. Soc., 151, A311-A325 (2004).
- 43. Y. Wang, S. C. Cho, and P. P. Mukherjee, *Multi-physics, Multi-scale Modeling in Polymer Electrolyte Fuel Cells*, p. 1-14, Proceedings of the ASME International Mechanical Engineering Congress and Exposition 2010, Vol 11, (2012).
- 44. W. Sun, B. A. Peppley, and K. Karan, *Electrochim. Acta*, 50, 3359–3374 (2005).
- 45. D. G. Goodwin, H. K. Moffatt, and R. L. Speth, "Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes," can be found under: http://cantera.org (2016).
- 46. T. Zawodzinski Jr, T. Springer, F. Uribe, and S. Gottesfeld, *Solid State Ionics*, **60**, 199–211 (1993).
- 47. A. A. Shah, G.-S. Kim, P. C. Sui, and D. Harvey, *J. Power Sources*, **163**, 793–806 (2007).
- 48. S. Kamarajugadda and S. Mazumder, J. Power Sources, 208, 328-339 (2012).
- 49. A. B. Anderson, J. Roques, S. Mukerjee, V. S. Murthi, N. M. Markovic, V.

Stamenkovic, J. Phys. Chem. B, 109, 1198–1203 (2005).

- 50. K. B. Daly, J. B. Benziger, A. Z. Panagiotopoulos, and P. G. Debenedetti, J. Phys. Chem. B, 118, 8798–8807 (2014).
- 51. A. Kongkanand, J. Phys. Chem. C, 115, 11318-11325 (2011).
- 52. P. W. Majsztrik, M. B. Satterfield, A. B. Bocarsly, and J. B. Benziger, *J. Memb. Sci.*, **301**, 93–106 (2007).