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Solvation and Ionic Transport in Polymer Electrolyte Membranes

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Abstract

We developed a general theoretical framework to study the problem of proton solvation and transport in Nafion® and related materials.

Background and Research Objectives

Solvation and ionic transport underlies an enormous range of physical processes. Understanding the thermodynamics, structure, and dynamics of aqueous salt solutions is one of the oldest problems in physical chemistry. The understanding of these processes near interfaces is comparatively under-developed. Nevertheless, such interfacial effects are critical to the performance of a wide variety of applied and fundamental processes involving heterogeneous structures.

One situation in which these types of structures are found is in polymer electrolytes of mixed hydrophobic/hydrophilic character, such as membranes used for polymer electrolyte fuel cells (PEFCs). As the name implies, the central component of a PEFC is the polymer electrolyte. The polymer electrolyte provides protonic conductivity to complete the electrical circuit in the fuel cell. A multitude of electrochemical processes and devices utilize polymer electrolyte membranes. Nafion®, a poly(perfluorosulfonic acid) is the prototypical polymer electrolyte membrane. It exhibits favorable chemical, mechanical and thermal properties as well as high electrical conductivity when sufficiently hydrated. While Nafion® initially found extensive application in chlor-alkali cells as a cation-exchange membrane, Nafion® and closely related materials have recently taken center stage as a primary class of polymer electrolytes for fuel cells. However, these materials are presently rather costly. A variety of different sulfonated polymers, primarily sulfonated aromatics, are now under development worldwide.

With the central importance of water management in PEFCs, a substantial body of experimental work in ours and other laboratories has focused on water and ion transport in the hydrated Nafion® membrane. A brief outline of the water management problem will remind the reader of the key parameters which must be understood and, if possible, controlled. In a PEFC,

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water is carried into the fuel cell by the humidified gas fed through gas diffusion electrodes and is produced at the cathode. A mixture of vapor and liquid phase water passes through the gas diffusion backing and catalyst layers to the electrode/membrane interfaces to hydrate the membrane. Water in the membrane is transported via two primary mechanisms: electro-osmotic drag of water by protons transported from anode to cathode and back-diffusion of water from cathode to anode. In a PEFC, these two mechanisms balance to produce the water distribution in the membranes: electro-osmotic drag and the oxidation reaction tend to create an excess of water in the vicinity of the cathode, while back-diffusion tends to flatten the water concentration profile in the membrane. Generally, one wants to maximize proton conduction at all water concentrations and minimize electroosmotic drag.

Thus, to understand water management and the conductance of a fuel cell membrane, one needs to determine the protonic conductivity, water diffusion coefficient and electroosmotic drag coefficient all as functions of water content in the membrane. We used isopiestic equilibration of membranes to control water content and published a series of papers (1–3) detailing water uptake and transport properties of the membranes. The key conclusions from these studies were (a) the water self diffusion coefficient increases with increasing water content in the membrane; (b) the proton conductivity increases with increasing hydration of the membrane; and (c) the electroosmotic drag coefficient, the number of waters transported by coupling to a protonic flux, remains a constant value of 1 for membranes equilibrated with water vapor and, at room temperature, jumps to values of between 2 and 3 for membranes immersed in liquid water. At elevated temperature, the electroosmotic drag coefficient increases still further for membranes exposed to liquid water but remains constant for lower water content.

These measured transport coefficients for Nafion were used in our model of water and proton transport in fuel cells. That work identified critical gaps in our understanding of the molecular mechanisms of proton mobility in polymer electrolyte membranes. Of particular interest is *electroosmotic drag*. Electroosmotic drag measurements gave the same results for several types of sulfonated membranes in contact with liquid water. This suggested to us that wall effects dominated proton transport, *i.e.* the structural element controlling proton transport in these materials is the tethered sulfonic acid group and its associated tightly bound water. At the outset of this project, there was simply had been no attempt at a molecular level understanding of proton conduction or electroosmosis. We hoped that our work toward gaining such a molecular picture would point towards a rational modification of the membrane material to achieve improved performance.

Morphological features influencing transport in these membranes and have been extensively studied. In addition to transport measurements, Nafion® has been studied by a host of experimental techniques, including the following: small and wide angle x-ray scattering (4,5),

dielectric relaxation (6), and a number of microscopic (7-9) and spectroscopic (10-14) studies. The emerging picture of the morphology of hydrated Nafion® is that of a two-phase system made up of a water-containing ion cluster network surrounded by a hydrophobic polytetrafluoroethylene (PTFE) medium. The integrity and structural stability of the membrane is provided by a PTFE backbone and the hydrophilic clusters facilitate the transport of ions and water in the membrane. These clusters or pores are conceptually described as lined by an interfacial region of hydrated, sulfonate-terminated perfluoroether side chains surrounding a central region of 'bulk-like' water. Counterions such as H^+ , Li^+ *etc.* are found in the vicinity of the sulfonates (15,16).

Upon uptake of water, the dimension and shape of the clusters are determined by osmotic equilibrium and the elasticity of the organic matrix (17). There is, however, no consensus on the structure of the electrolyte-containing clusters. Gierke et al (5,18,19) proposed that the clusters were spherical inverted micelles of 40-50 Å diameter, interconnected by channels with characteristic dimensions of 10-20 Å. On the basis of their small angle X-ray data they concluded that the pores (hydrated with water vapor) contained approximately 70 side chains and 1000 water molecules. Although this model has gained fairly wide acceptance, others have suggested that the spherical shape and uniform spacing of the clusters are oversimplifications. On the basis of an infrared study, Falk (11) concluded that the hydrated clusters are non-spherical with frequent fluorocarbon intrusions. Falk (11) also suggested that a significant fraction of the water interacts with the fluorocarbon material. Additional X-ray diffraction and differential scanning calorimetry measurements by Starkweather (20) led him to propose a lamellar hexagonal structure of the fluorocarbon backbones with the side chains extending perpendicular to the alignment of the PTFE backbones and into the ionic cluster domains. More recently, Litt (21) reexamined the data of Gierke et al (5,18,19) and proposed a lamellar morphology for Nafion® where the side chains are located in planar domains. With hydration of the membrane, the water simply collects in the polar domains pushing the non-polar domains (PTFE backbones) further apart subject to extensions of disordered backbone segments. Similar lamellar micelle structures were observed by Rebrov et al (22) for Nafion® solubilized in DMF and by Zoppi et al (8) for Nafion® with incorporated silicon oxide.

A number of physical models have been developed to understand the mechanisms of water and ion transport in ionomer membranes. Breslau and Miller (24) used a hydrodynamic approach and were able to predict electroosmotic coefficients within 5% of experimental values except for the case of the proton. Capeci et al. (25) constructed solubility and transport models based on phenomenological equations and, based on these models, suggested that narrow pores dominate transport in the membrane. Pintauro and coworkers (26,27) derived a partition coefficient model treating effects of hydration, electrostatic interactions, and solvent dipole alignment due to fixed

wall charges. Eikerling *et al.* (28) developed a random network model of a microporous PEM, showing the importance of the connectivity of the pores and coordination of H_2O , to the overall conductivity of the PEM. Recently, Din and Michaelides (29) reported results of molecular dynamics simulations of water and protons in micropores with uniform charge density on the walls and concluded that the classic Poisson-Boltzmann theory did not accurately predict the distribution of protons within the pores.

As noted above, a key element missing from the modeling work is a consideration of the chemistry of the ionogenic groups of the polymer electrolyte. The recent results of Din and Michaelides (29), however, point to the importance of understanding the acid group and its immediate solvation sphere, our starting point. Complete description of this region of the solvated ionomer will improve on the simple model of an ionomer as a collection of hydrated pores lined with point charges.

Importance to LANL's Science and Technology Base and National R&D Needs

Under a proposed carbon management scenario, methane produced at a wellhead will be converted to H_2 and CO_2 . The latter will be re-injected into the well while the hydrogen will be piped away and converted to electricity where needed. This strategy allows the tapping of large domestic reserves of methane for energy production without evolving CO_2 . Polymer electrolyte fuel cells (PEFCs) are a central component of such strategies for carbon management. PEFCs are advanced, high efficiency, high power, energy conversion devices. In addition to their implication for the carbon management scheme mentioned above, the improved efficiency and low emissions resulting from implementation of fuel cells will also serve carbon reduction goals. Intense international development of PEFCs for automotive and residential utility use is presently underway. LANL is a central player in that development. Other polymer electrolyte-based electrochemical devices are also being investigated for increased efficiency and environmental friendliness.

Scientific Approach and Accomplishments

At an early stage in this project, we developed a simple picture to rationalize experimental results and indicate directions for further study. This picture begins with a consideration of the implications of isopiestic equilibration data for the membranes exposed to water. This data, shown in Figure 1, gives us a direct measure of the water activity (a_w) in the membrane for any given water content. There are two distinct regions of water uptake. At $a_w < 0.7$, a small and nearly constant H_2O content (λ) is achieved. This corresponds to H_2O of solvation of the fixed ionic sites and protons. At higher a_w , the polymer is swollen with water. Various spectroscopic

and other probes have shown that solvation water is less mobile, yielding lower H^+ conductivity. Activation energies and volumes for transport processes are also higher for lower water content. Water uptake decreases above room temperature at high a_w but not at low a_w .

Figure 1: Isopiestic uptake of water

Recasting this data to indicate the free energy of H_2O uptake, shown in Figure 2, we see that water is much more loosely bound into the membrane at high water contents. The differential free energy of uptake per H_2O molecule decreases substantially at higher water contents. This suggests that 5-6 waters per sulfonic acid site form the hydration shell around the fixed site and the proton. The H_2O in the membrane at high H_2O contents is typically thought of as more like liquid H_2O in an acid solution.

Figure 2: Free energy of uptake of water

The impact of the water content on the membrane protonic conductivity is shown for several closely related membranes in Figure 3. Conductivity decreases sharply as the H_2O content approaches 5 waters per sulfonate for some of the membranes. On the other hand, the sharpest change in activation energy associated with conduction or water diffusion occurs at somewhat lower water content, 2-3 waters per sulfonate. Measures of water mobility such as diffusion

coefficient or ^2H relaxation time indicate higher water mobility at higher water content. We (3) and Kreuer (23) have shown that the calculated proton and water diffusion coefficients are similar at low water contents but diverge (with $D(\text{H}^+)$ higher) at higher water contents. This is considered an indicator of Grøtthuss-like hopping of protons at high water contents. As the water becomes more 'bulk-like', conduction can occur by proton 'hand-off' between H_2O molecules and H_2O and proton motions are more decoupled. However, the electroosmotic drag coefficient, the coupling between H^+ and H_2O fluxes in the membrane, increases with increasing H_2O content. We discussed this apparent paradox previously (3).

Figure 3: Membrane Conductivity as a function of water content

A qualitative, descriptive picture of the transport phenomena (to be published) is illustrated in Figure 4. We developed this picture as a point of departure defining key issues for theoretical study. At the lowest H_2O contents, few waters are available to allow dissociation of the sulfonic acid and solvate the sulfonate and proton. Conduction requires charge separation between hydronium ion and sulfonate and most likely must involve a motion of the side chain to occur, as evidenced by the experimentally observed high values of activation energy and volume for conduction. At higher H_2O content, more water is available in the vicinity of the fixed site and the Debye length increases so each H_2O progressively enhances conduction. Furthermore, enough water is present to 'screen' the charged sites and proton-bearing groups, with complete acid dissociation, facilitating conduction and water diffusion processes. Nonetheless, the 'complex' in the vicinity of the fixed site is tightly enough bound that H_2O is difficult to displace by moving hydronium ions (or other proton/water complexes). Thus, electroosmotic drag does not increase in this hydration regime. Finally, enough 'loosely bound' H_2O is present that the H_2O drag increases. This last fraction of water lowers the average free energy of uptake per H_2O to roughly kT at room temperature. Thus, electroosmotic drag increases with temperature under complete hydration conditions.

Figure 4: Factors controlling water/ion transport

This 'cartoon'-level picture illustrates key structures and dynamics that must be understood to allow membrane development on a rational basis. To develop a framework in which we could explain transport phenomena, we carried out calculations on various portions of the structure shown in Figure 4.

The strategy was to build a comprehensive picture of transport processes in these materials via a stepwise process: (a) understanding properties of key active molecular fragments in the polymer electrolyte, most notably the sulfonic acid (or other acid!) moiety; (b) understanding water solvation and proton dissociation phenomena at the fixed acid site; (c) coupling the understanding from (a) and (b) to descriptions of transport processes in short segments of polymer electrolyte 'pores'; and finally (d) elaboration of a complete model of macroscopic transport by integrating (c) into a random network model taking account of variations of pore sizes, shapes and connectivity. Note that each lower stage in the hierarchy (a)-(d) contributes as well to our qualitative understanding of the behavior of these membranes. Thus, for example, a computational survey of various acid groups and their solvation can stand alone in assisting our interpretation of related experimental data.

The first steps in our recipe for constructing a complete picture of transport involve calculations of several types, yielding several pieces of the overall puzzle. These include quantum mechanical (QM) molecular electronic structure calculations, calculations including a continuum dielectric solvation environment around the optimized structures obtained from the QM calculations, and a new method for studying solvation energetics, quasichemical solvation theory.

We began with a study of trifluoromethanesulfonic (triflic) acid. We reported theoretical calculations on the triflic acid with and without an additional water molecule. The optimized geometry determined for the isolated triflic acid molecule, obtained from *ab initio* molecular orbital calculations, agrees with previous studies. In order to characterize side chain flexibility and accessibility of the acid proton, potential energy and free energy surfaces for rotation about both carbon-sulfur and sulfur-oxygen(hydroxyl) bonds are presented. We carried out additional *ab initio* electronic structure calculations with a probe water molecule interacting with the triflic acid. The minimum energy structures found here for the triflic acid molecule with the probe water revise results reported previously. To investigate the reaction path for extraction of a proton from triflic acid, we found minimum energy structures and energies for isolated molecular fragments, and solvation free energies for: (a) a docked configuration of triflate anion and hydronium cation and (b) a transition state for proton interchange between triflic acid and a water molecule. Those configurations are structurally similar but energetically substantially different. The activation free energy for that proton interchange is predicted to be 4.7 kcal/mol above the reaction end-points.

Such calculations yield gas phase information on water/acid adducts. An additional step performed is shown in Figure 6. In this work, we 'immersed' the molecule in a dielectric continuum. This was carried out in an investigation of rotational barriers in triflic acid but has not been applied to date to hydrated triflic acid.

Figure 5: Idealization of dielectric continuum model

Electrostatic solvation is predicted to reduce the free energy barrier to rotation about the F_3C-SO_3 bond from 3.5 kcal/mol to about 2.7 kcal/mol. This electrostatic effect is associated with slight additional polarization of the CF bond in the eclipsed conformation. The energetic barrier to rotation of the acid hydroxyl group away from the sulfonic acid oxygen plane, out into the solvent is substantially flattened by electrostatic solvation effects. The maximum free energy for those solvent accessible proton conformations is about 1.0 kcal/mol

The 'sidechain' of Nafion was studied in several steps. Optimized geometries for the acid side chain $CF_3OCF_2CF(CF_3)O(CF_2)_2SO_3H$ and the side chain with backbone attachment $CF(CF_2CF_3)_2-OCF_2CF(CF_3)OCF_2CF_2SO_3H$ were determined with electronic structure techniques exclusive of hydration effects. The minimum energy structures are folded with the two ether oxygen atoms in a *gauche* conformation. Rotation about the outermost ether group

provides natural transition path to the partial unfolding of the side chain. The potential energy surface for this rotation was determined and the results show that the staggered fluorine conformation of the head group is unchanged with rotation. This rotation produced conformations approximately 40% longer (8.5 Å) and about 3.5 kcal/mol higher in energy after surmounting a barrier of about 4.6 kcal/mol. Additional searching for stretched conformations of the side chain led to the discovery of an even longer (9.8 Å) minimum energy conformation that was entirely unfolded with the ether oxygen atoms located *trans* relative to one other. This unfolded conformation is essentially isoenergetic (+0.1 kcal/mol) with the (folded) minimum energy conformation. The existence of a small number of well-defined "short" and "long" side chain conformations, with substantially similar head-group chemistry, suggests the speculative view that hydration-dependent equilibria between these conformations should be a significant feature in physical models of the function of Nafion®. Equilibrium geometries were also obtained for both the folded and the unfolded acid side chains, each with an associated single water molecule. Water was found to interact very little with sidechain components other than the sulfonic acid. Thus, the acidic functionality of Nafion was subsequently represented as triflic acid.

To develop more sophisticated treatments of solvation in Nafion®, we have extended our theoretical studies of the water surrounding ionic groups in sulfonic acid membranes. The computational work described above has suggested that this simple system is an appropriate model capturing the needed properties to describe solvation of the side chain of Nafion® since the initial solvation is primarily in the vicinity of the sulfonic acid site. The first several water molecules interacting with the sulfonic acid site, which we term the 'interfacial waters,' turn out to be a key element missing in existing continuum-based simulations of water dynamics in Nafion®. Triflic acid/water clusters were the next target of study. Quantum mechanical calculations were carried out to determine optimized geometries for water complexes with the triflate anion and triflate hydronium ion pair.

Minimum energy structures found for the clusters $CF_3SO_3H(H_2O)_n$ with $n=1,2,3$ and $n=4,5,6$ are shown in Figures 7 and 8, respectively. The foremost point is that the acid proton remains associated with the sulfonic acid moiety for $n=1$ and 2. Three water molecules are required before a definitely dissociated acid proton is recognized in the lowest energy structure. For the simpler case of HCl (31), and also for polystyrenesulfonic acid (32), the first water of hydration is not sufficient to stabilize an ion pair configuration. The experimental results for polystyrenesulfonic acid (32) indicate that the second water of hydration is sufficient to dissociate the acid proton. The polystyrenesulfonic acid results also point to the importance of the $H_5O_2^+$ structure, the "Zundel" cation, for this proton dissociation mechanism. The present results

suggest that the sufficiency of the second water molecule need not be universal. However, we emphasize that the results of Figure 7 do not include any affects of a condensed phase environment (33). This could be due to the presence of the three sulfonate oxygen atoms in this particular special case.

Figure 6: Minimum energy structures found for $CF_3SO_3H(H_2O)_n$ clusters for $n=1$ (top), $n=2$ (middle), and $n=3$ (bottom). Note that the acid proton doesn't dissociate from the sulfonic acid for $n=1$ and 2 but does dissociate for $n=3$. In the latter case, the ball and labeled arrows on the right show the distances of near neighbor oxygen atoms to the oxygen atom that bears the additional proton.

Figure 7: Minimum energy structures found for $CF_3SO_3H(H_2O)_n$ clusters for $n=4$ (top), $n=5$ (middle), and $n=6$ (bottom). The ball and labeled arrows on the right show the distances between interesting oxygen atom neighbors. The $n=4$ and 6 structures are “Eigen”-like and the $n=5$ structure is “Zundel”-like.

In our results (Figure 6), when the proton does separate from the acid with the third water molecule, the structure formed is highly suggestive of the “Eigen” cation, $H_9O_4^+$. The larger clusters (Figure 7) show both “Eigen” ($n=4$ and 6) and “Zundel” ($n=5$) structural patterns associated with the additional proton. Thus, we anticipate that both of these structures should be involved in the fuller molecular description of acid dissociation in these materials.

One particularly important result is highlighted in Figure 8. There we show the optimized structures for triflate anion plus hydronium ion with 4 and 5 waters. An important transition in the structure of the system takes place between these two calculations: the hydronium ion is displaced from intimate interaction with the triflate anion by the addition of the fifth water molecule (or sixth if one counts from the sulfonic acid). This is evidenced by dramatic changes in the hydronium-H to sulfonate-O bond distance. Also note that the hydronium ion is only coordinated to two water molecules until 5 water molecules are added to the system. Then the hydronium coordinates with the water molecules as opposed to the triflate anion.

Figure 8: Displacement of hydronium ion through addition of a single water molecule.

Recently proposed quasi-chemical theories (34-36) establish a format in which to exploit such chemical electronic structure computations to study solution chemistry. The idea is to use electronic structure computational tools to determine the equilibrium coefficients K_n for the formation of precisely defined complexes as

The K_n are familiar forms:

$$K_n = \frac{\rho_{CF_3SO_3H(H_2O)_n}}{\rho_{CF_3SO_3H} (\rho_{H_2O})^n} \quad [2]$$

The ρ_α are number densities for α -molecules. The quasi-chemical approximations require these coefficients in the circumstances of an ideal gas, so that

$$K_n = K_n(T) = \frac{(q_{CF_3SO_3H(H_2O)_n} / V)}{(q_{CF_3SO_3H} / V) (q_{H_2O} / V)^n} \quad [3]$$

where the q_α are molecule (or cluster) partition functions (37). Standard electronic structure packages such as the Gaussian package can produce these coefficients within the harmonic approximation because they can compute molecular vibrational frequencies for the structures obtained. Moreover, the interactions involved in formation of these complexes are genuinely chemical. Electronic structure methods are appropriate and classical force-field models are currently not available. The adequacy of the harmonic approximation for these purposes has yet to be directly tested and the development of these approaches is in an early stage.

The fundamental thermodynamic parameter addressed by the quasi-chemical approximations is the chemical potential of the solute, here triflic acid. The interaction part of that chemical potential, the part due to interactions of the solute with hydrating water molecules, is then given by

$$\Delta\mu_{CF_3SO_3H} = -RT \ln \left[p_0 \sum_{n=0} \tilde{K}_n (\rho_{H_2O})^n \right] \quad [4]$$

The $\tilde{K}_n$ indicates that extra-cluster contributions, due to the environment more distant than the near neighbor water molecules, must be eventually considered (36,48). The notational convention is $K_0 = 1$. p_0 is a probability describing the free energy required to prepare for the cluster, a cavity in the medium. This contribution is associated with packing effects and is expected from an external theory addressing these features (39-44). Again, we emphasize that the practical adequacy of the current understanding of these additional features has not been directly tested in the present context and subsequent developments will have to focus on these requirements.

We also emphasize that this approach is constructive in style. Only a small number of terms in the series in Eq. [3] are expected to be significant; and the various contributions are well defined and physically natural. Therefore, we can take the attitude that several clear contributions need to be studied and effective descriptions of each contribution need to be secured. Note also that this methodology can be readily extended to other acids and solvents by performing the relatively simple QM electronic structure calculations. Furthermore this method is intuitively related to directly measurable thermodynamic quantities such as the free energy of formation of solvated acid groups.

Our modeling efforts directed at studying transport occurring over a longer range have thus far involved two primary thrusts: (a) a statistical mechanical approach to the calculation of the molar conductivity; and (b) a molecular dynamics simulation resulting in the computation of the protonic current. These models focus on the coupled transport of protons and water in an arbitrary hydrated pore of Nafion®. Once again, the extensions to other membranes and pore fluids are fairly straightforward with incorporation of membrane and solvent specific structural parameters.

In this model the hydrated PEM pore is assumed to have cylindrical geometry. The fixed anionic charge sites (due to the pendant side chains) are modeled as a periodic array of charges that exert a periodic potential within the pore on the inside surface. Molecular information from the earlier quantum mechanical calculations is incorporated into the periodic potential. The total Hamiltonian is derived for a hydronium ion as it moves through the hydrated pore and is affected by the following four potentials: (a) the interaction potential between the hydronium ion and the

solvent – modeled as an ion-dipole interaction; (b) the interaction potential experienced by the hydronium ion due to the presence of the pendant chains; (c) the solvent-solvent interaction potential – modeled as a dipole-dipole interaction; and (d) the interaction potential of the solvent in the presence of the pendant chains. From an analytical expression for the total energy of the hydronium ion in the pore, we derive the corresponding probability density through solution of the Liouville equation. This probability density is then used to compute the friction tensor for the hydronium ion. Two types of contributions are obtained: (a) the solvent-ion interactions for which the conventional continuum model is adopted; and (b) the interaction between the pendant charges and the hydronium ion. Preliminary results (45,46) look promising: predicted short-range hydronium ion mobilities are on the same order of magnitude of experimentally derived quantities without invoking full detail of proton hopping.

As in the statistical mechanical model, our molecular dynamics approach (46) assumes anionic charge distributed in a periodic fashion on the inside of the pore walls. Temporally averaged ion conductivity is obtained at constant temperature and with a constant field by considering various levels of molecular modeling (47) and details of the water molecules and pore geometry obtained through our electronic structure calculations. The simulations are carried out using periodic boundary conditions (48) in the direction of the externally applied field. The proton conductivity in the pore is computed as a function of water content, ion type, temperature, and pore wall geometry.

To summarize the state of completion of the various theoretical studies, we are presently poised on the cusp of developing a unified model of conduction in Nafion®. Reasonably straightforward extensions of this work will lead to results for other transport parameters such as electroosmosis and water diffusion. We can then begin to wrestle with the problem of polymer morphology and a more sophisticated treatment of inter-side chain interactions.

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