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Proton Conduction in Exchange Membranes across Multiple Length Scales

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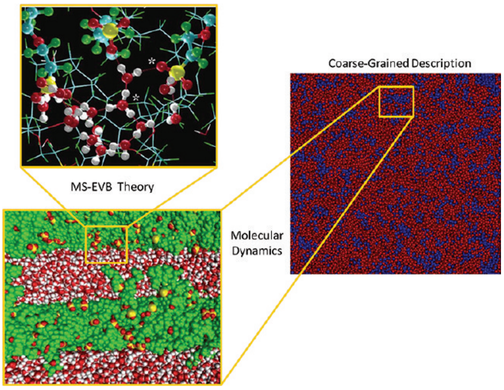

Concerns over global climate change associated with fossil-fuel consumption continue to drive the development of electrochemical alternatives for energy technology. Proton exchange fuel cells are a particularly promising technology for stationary power generation, mobile electronics, and hybrid engines in automobiles. For these devices to work efficiently, direct electrical contacts between the anode and cathode must be avoided; hence, the separator material must be electronically insulating but highly proton conductive. As a result, researchers have examined a variety of polymer electrolyte materials for use as membranes in these systems.

In the optimization of the membrane, researchers are seeking high proton conductivity, low electronic conduction, and mechanical stability with the inclusion of water in the polymer matrix. A considerable number of potential polymer backbone and side chain combinations have been synthesized to meet these requirements, and computational studies can assist in the challenge of designing the next generation of technologically relevant membranes. Such studies can also be integrated in a feedback loop with experiment to improve fuel cell performance. However, to accurately simulate the currently favored class of membranes, perfluorosulfonic acid containing moieties, several difficulties must be addressed including a proper treatment of the proton-hopping mechanism through the membrane and the formation of nanophase-separated water networks.

We discuss our recent efforts to address these difficulties using methods that push the limits of computer simulation and expand on previous theoretical developments. We describe recent advances in the multistate empirical valence bond (MS-EVB) method that can probe proton diffusion at the nanometer-length scale and accurately model the so-called Grotthuss shuttling mechanism for proton diffusion in water. Using both classical molecular dynamics and coarse-grained descriptions that replace atomistic representations with collective coordinates, we investigated the proton conductivity of polymer membrane structure as a function of hydration level. Nanometer-sized water channels form torturous pathways that are traversed by the charges during fuel cell operation. Using a combination of coarse-grained membrane structure and novel multiscale methods, we demonstrate emerging approaches to treat proton motion at the mesoscale in these complex materials.

I. Introduction

Concerns over global climate change associated with fossil-fuel consumption continue to drive the development of electrochemical alternatives for energy technology. Proton exchange fuel cells in particular are a promising technology for stationary power generation, mobile electronics, and hybrid engines in automobiles.[1] In their simplest form, proton exchange systems depend on oxidizing hydrogen gas at an anode assembly via an embedded catalyst layer to generate electrons, which traverse an external circuit to provide a current to the load, and protons, which migrate to the cathode via a separator material. Clearly, for the device to work efficiently, direct electrical contacts between the anode and cathode must be avoided; hence, the separator must be electronically insulating but highly proton conductive. While a variety of separator materials exist,

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perfluorosulfonic acid (PFSA) moieties have recently been utilized for polymer membranes in fuel cells because of their stability and desirable physical properties.[1−3] Numerous approaches have been proposed for designing PFSA membranes; yet DuPont's Nafion continues to hold a place of prominence in the field because of its high proton conductivity and thus it provides a useful standard with which other PFSA candidate membranes are often compared.[3]

The quest to understand the origin of Nafion's proton conduction mechanism has extended over five decades, in part because of its unresolved morphology as a function of water uptake. The efficient conduction of protons through PFSA membranes in general relies on water exposure, which drives phase segregation between the hydrophobic, fluorinated backbone polymer and its hydrophilic, sulfonic acid side chains to form extensive water networks.[3] The size of the water channels formed within the membrane is dictated by the amount of water absorbed and the swelling behavior of the hydrophilic domains. While the conductivity of Nafion has been analyzed by using percolation theory to capture the dependence of conductivity on water content,[4] the precise shape of the water clusters remains a mystery.

Scattering experiments performed to date have elucidated the relevant length scale for the size and spacing of the separated domains to be on the order of nanometers, but relatively few details beyond this estimate are available. Several model structures for the water channels can be found in the literature[3] including nanoscale spheres of water embedded in polymer and connected by thin channels, lamellar sheets of polymer and water, cylinders of water surrounded by polymer, and fibril aggregates of polymer surrounded by water (see ref 3 and references therein).

Computer simulation of proton conduction in PFSA membranes is challenging, not only because of their amorphous morphology, but also because of the subtleties associated with proton transport within the confined water regions.[1,2,5,6] It is well-known that protons diffuse in bulk water markedly faster than do water itself and other cations. The anomalous proton mobility is accounted for by the presence of an additional transport mechanism known as Grotthuss shuttling.[5,7] Not only can the excess proton and associated waters diffuse via the thermal motion common to any solute in liquid, the so-called vehicular motion, but protons can also be chemically exchanged between waters, resulting in facile transport of the excess charge. Accounting for both vehicular and Grotthuss transport of protons thus requires theoretical methods that can describe changes in chemical bonding topology on the fly during the simulation. As discussed in the following sections, this requirement presents a fundamental challenge to traditional simulation methods in the context of the length scales representative of pore dimensions in PFSA membranes. Thus, the challenge for computational methods seeking to describe proton conduction in polyelectrolyte membranes remains the accurate incorporation of the fundamental transport mechanisms at the angstrom-length scale within the context of a structure possessing the correct mesoscale heterogeneity.[4]

Recent computational investigations of PFSA membranes are discussed subsequently, particular emphasis on proton dynamics in Nafion, given its central role in ongoing research and its utility as a prototype membrane. Modeling efforts also are highlighted, which range from the atomistic-length scale to tens of nanometers and hundreds of nanosecond trajectories, with the ultimate goal of connecting atomistic information to macroscopic quantities relevant to device engineering. Given the extent of recent reviews on the topic,[1,2] we focus here on the most recent advances in the field; the interested reader is referred to the cited literature for further background. The initial discussion describes methods to account for Grotthuss shuttling of protons in the confined environments of PFSA membranes. Also discussed are the advantages of the multistate empirical valence bond (MS-EVB) method, followed by an examination of previous attempts to study the morphology of Nafion as a function of water content. A recently developed approach is then presented that models both conduction and morphology by uniting coarse-grained modeling for the membrane structure and information from atomistic simulations with nonequilibrium thermodynamics. This multiscale approach allows us to describe proton fluxes and concentration dynamics at the scale of tens of nanometers, with ready extension to even longer length scales. Most importantly, this approach enables us to use atomistic information to connect to measured conductivities. Ongoing work and future directions regarding these methods conclude this topical overview.

II. Accounting for Proton Hopping in Membranes

The most natural choice for modeling proton hopping via bond rearrangements involves ab initio methods in which the electronic structure of the system is treated explicitly. Previous studies have focused on the equilibrated structure of the sulfonic acid side chains as well as a thorough examination of the first solvation shell of water molecules surrounding the side chains.[2] The threshold for the dissociation of the sulfonate proton as a function of hydration was determined to be three waters, in good agreement with experimental measurements for the onset of conductivity through Nafion.[8] More recently, the dynamics of proton transport upon dissociation have been investigated by using ab initio molecular dynamics (AIMD) and metadynamics to investigate the complex interplay between vehicular transport and Grotthuss shuttling as a function of water content along with the acid/base equilibrium for the proton dissociation.[9,10] It was found that the continuity of the hydrogen bonding network within the water clusters is crucial to the efficiency of proton hopping and was significantly disrupted at low hydration levels. The effects of side chain mobility and pore structure have also been examined by using small simplified model systems in which the sulfonate groups are bound to carbons immobilized in a plane[11] or on the walls of a cylindrical pore.[12]

While useful for studying the proton dynamics surrounding individual side chains, scaling ab initio methods up to the level of individual pores with nanometer dimensions is currently computationally intractable. In response to this challenge, our group has focused on the development of MS-EVB methods to model proton transport in confined environments.[5,6,13−16] This method assumes that the electronic degrees of freedom can be captured by a finite number of valence bond basis states, which consist of atoms arranged in the same positions but with different bonding topologies. Both ab initio and empirical data can be used to parametrize the coupling between states, and the force field in the simulation describes the energy of each basis state. A Hamiltonian for the system is thus constructed and the eigenvectors obtained to describe the state of the excess proton complex.

An advance pertinent to the simulation of proton transport in Nafion is the development of self-consistent iterative MS-EVB, also known as SCI-MS-EVB, which allows for multiple excess protons in a system. Given the concentrated acidic environment of PFSA membranes, such an extension is critical to allow for multiple reactive EVB complexes. While capable of describing proton conduction at the level of pores, however, the method is still too expensive to scale to sample the full mesoscopic heterogeneity of PFSA membranes and requires bridging to more coarse-grained methods, as discussed later.

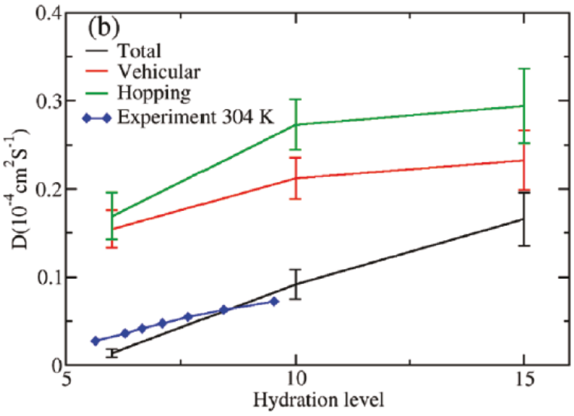

FIGURE 1. Decomposition of the proton diffusion coefficient in Nafion into the vehicular (red) and hopping (green) components. The total diffusion coefficient (black) allowing for both contributions is compared with the experiments of ref 13. (blue). Reprinted with permission from ref 16. Copyright 2011 American Chemical Society.

We have demonstrated the utility of the SCI-MS-EVB method to extend the length and time scales well beyond those of AIMD by simulations consisting of multiple polymer chains comprising ten monomer plus side chain units each.[14,16] This is nearly the same simulation size used in the standard molecular dynamics (MD) studies discussed below to investigate the morphology of the hydrated domains. The major qualitative finding of these simulations relates to the interplay of proton hopping and vehicular diffusion as a function of water content, as demonstrated in Figure 1.

For all hydration levels, the sum of the hopping and vehicular diffusion coefficients is greater than the total proton diffusion constants, with the hopping coefficient being larger than the vehicular component. This result clearly indicates anticorrelation of the hopping and vehicular motions of the excess protons in Nafion, which is an unexpected result compared with bulk water where these components are additive. Analysis of experimental results has indicated that structural diffusion was negligible at low and intermediate hydration levels.[3] As Figure 1 shows, however, structural diffusion is still an important transport mechanism even at low hydration levels, but the opposing vehicular diffusive motion masks this reality. Comparisons of experimental results with the proton diffusion coefficients obtained from these simulations show good agreement, with improvements over the classical MD results (which neglect hopping transport) being most dramatic at higher hydration levels. This observation agrees with the previous hypothesis that structural diffusion becomes increasingly important at higher hydration levels.[17] It was shown that the forward rate of hydrogen bond switching in water exhibits the same long time decay as does proton hopping,[15] identifying the dependence of the hopping process on the breaking of hydrogen bonds in the water surrounding the excess proton. The impact of the lower hydration level on the ability of the hydrogen bond network in Nafion to reorient has also been shown experimentally,[18] and the impact is clear in the proton-hopping rates in lower hydration levels of Nafion.

Beyond the fundamental behavior of vehicular and hopping motions within proton transport, the detailed local properties of the proton motion within the hydrophilic regions of the membrane were also examined. The directionality of the proton hopping was investigated as a function of distance from the closest sulfonate group and the analysis indicated that protons close to the sulfonate group preferable hopped back toward the sulfonate.[14,16] At further distances, however, the probability was roughly the same for a hop backward or a hop away from the side chain. Important structural features were also gleaned from the results, especially of the proton complex around the sulfonate group. It was shown that the sulfonate groups stabilize the formation of the $[H_5O_2]^+$ Zundel cation for protons in its first solvation shell, compared with farther away from the sulfonate groups, where the $[H_9O_4]^+$ Eigen cation was more stable. It was also noted that at higher temperatures the protonic charge moves closer to the sulfonate group and the Zundel cation is further stabilized. This slightly unintuitive result was explained by the water moving farther from the sulfonate group at higher temperature, resulting in less effective screening between the charged side chain group. Another structural feature noticeable in MS-EVB simulations is the amphiphilic nature of the excess proton.[19] The lower coordination level of the hydronium ion compared with that of water results in a region of reduced density in the vicinity of the hydronium lone pair, which is entropically unfavorable in the bulk. Thus, the hydronium lone pair is actually preferably oriented toward the hydrophobic interface of the hydrophilic region of the membrane,[14] a feature that is seen in the restricted radial distribution of the hydronium oxygen around the polymer backbone.

III. Structure from MD to Mesoscale

Classical molecular dynamics, which neglects the proton hopping mechanism, has provided access to the nanometer-length scale in PFSA membranes to capture the formation of individual pores. MD simulations have revealed more information on Nafion than can be addressed here; the salient features include qualitative agreement with experimental observations of swelling and proton diffusivity with increasing water content, elucidation of the local solvation structure of the sulfonate group, and investigation of the solvent separation of the proton as a function of hydration level.[1,2] Recent work has continued to focus on the characteristics of the water clusters formed within the membrane as well as drawing comparisons between Nafion and other candidate PFSA membranes such as Hyflon, also known as the short-side chain (SSC) PFSA.[20−23] Studies combining molecular dynamics and Fourier transform infrared spectroscopy have shown that the fractions of slowly diffusing water surrounding the sulfonates and those resembling a more bulklike environment within the membrane experience an inversion with increasing hydration around $\lambda = 7$,[20] where λ corresponds to the number of waters per sulfonate group in the membrane. The finding of significant changes near this water content can be correlated with the estimated percolation threshold between $\lambda = 5$ and 6 from MD studies performed by Devanathan et al.[21] Comparison of the formation of water pores in Nafion with that in the SSC membrane showed that the greatest differences occurred at low water contents where the SSC provided greater water domain connectivity and that increasing the equivalent weight in both polymer membranes diminished water clustering and connectivity.[22] Recent reports have begun to raise concerns about the use of relatively small simulation box sizes to probe the morphology, with some dependence of the water clustering on the box size chosen.[23] Regardless of the impact of the box size itself, larger simulation sizes will clearly be needed to incorporate the true heterogeneity of the PFSA membrane structure, given the anticipated size of individual pores.

Further evidence of the importance of incorporating large-scale MD simulations of PFSA membranes into the study of hydrated domains has recently been published by our group for a series of different Nafion morphologies.[24] A Monte Carlo type growing algorithm was implemented to reproduce cylinders, connected spheres, slabs, and randomly connected pores of water in MD simulation boxes that were 30 nm on each side, in total around 2 million atoms, in order to compare the behavior of the different water network models at the mesoscale. Since the trajectories used were only on the order of tens of nanoseconds, the point of this exercise was not to obtain the truly equilibrated structure for Nafion, since the size of the polymer chains generated preclude appreciable relaxation of the intertwined backbones on such short time scales. Rather, the focus in this work was on the behavior of the side chains, waters, and hydronium ions in the structure that readily reorganized during the atomistic trajectory.

Large MD simulations revealed several important effects in the water network that had not previously been seen with

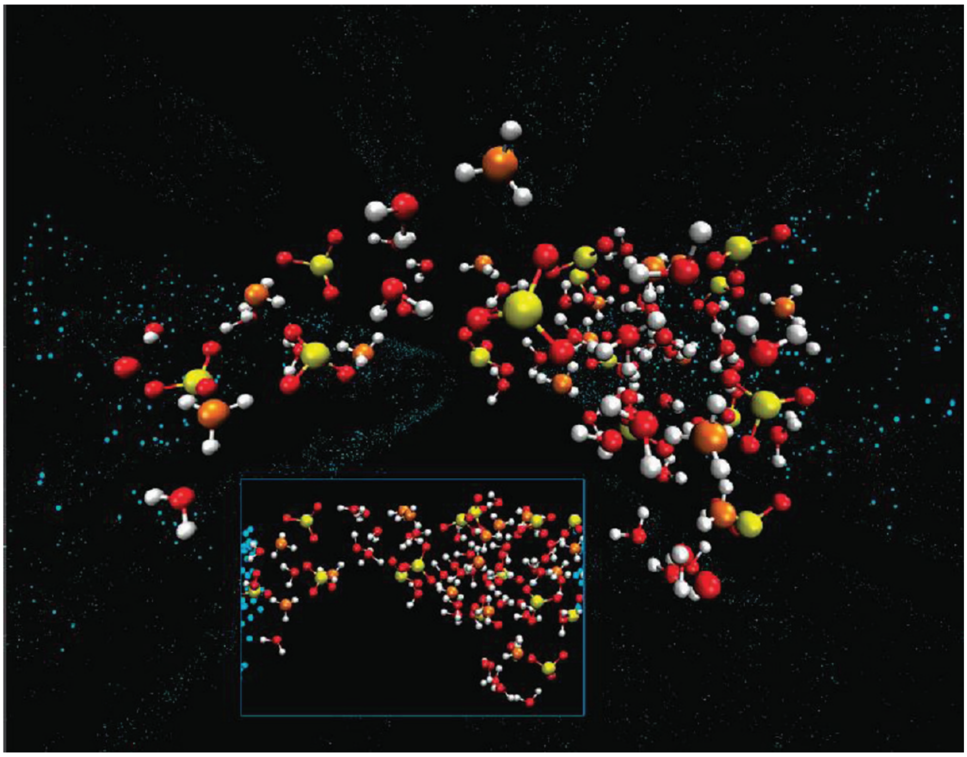

FIGURE 2. Snapshot of Nafion modeled as a group of parallel cylinders of water (shown in teal) and the formation of small water wires connecting these domains during the simulation. Reprinted with permission from ref 24. Copyright 2010 American Chemical Society.

smaller box sizes. One effect concerned the formation of water channels between individual water clusters after the initial structures were annealed and equilibrated (see Figure 2). Even for models without pre-existing network connections, such as the parallel cylinder model, small water wires were formed between the hydrophilic domains. The presence of both sulfonate side chains and hydroniums in these water wires argues for the importance of the side chain mobility in assisting these intercluster connections. A second quantity estimated from these large-scale MD studies was the solvent-accessible surface area of the pores themselves, which served to reinforce the complexity of the networks formed in the hydrated membrane by yielding surface areas comparable to those found in zeolites, which are widely known to possess high surface areas for the purpose of catalysis. Another advantage to performing MD on large-scale systems was to allow for distributions in pore sizes and connectivity in each model, which are often lacking in calculations with nanometer box sizes. This dispersion in cluster characteristics plays a vital role in determining structure factors and the behavior of the scattering spectrum for the membrane. It was observed that the power-law dependence used in previous work to defend the parallel cylinder model could be replicated by using randomly placed spheres of water with a distribution in sizes.

Despite the advent of powerful supercomputers capable of executing large MD simulations with millions of atoms for tens or even hundreds of nanoseconds, it is inevitable that some time scales and system sizes will not be computationally practical. If one desires to truly probe the equilibrated structure of Nafion with polymer chains comparable to experiment and simulations sizes that accurately sample the structure of PFSAs, for example, a reduced description of the system is necessary that compromises on the level of detail included to obtain meaningful information. The well-known practice of coarse graining seeks to replace the atomistic representation of molecules with collective degrees of freedom consistent with the underlying atomistic properties. One of the most aggressive coarse-grained models used to date for Nafion was proposed by Wescott et al.[25] and replaces eight tetrafluoroethylene units in the backbone with a single interaction bead. Using the same bead size, the side chain is also represented by a single particle, and the Nafion polymer is reduced to a repeat unit consisting of three beads. This model was used in conjunction with self-consistent mean field theory to study the size of water domains in hydrated Nafion and their behavior with increasing λ, which agreed qualitatively with previous reports and showed an interesting dependence on initial conditions at low hydration. Dissipative particle dynamics (DPD) is another mesoscale method that retains the description of the evolution of the system in a manner consistent with classical hydrodynamics and has a structure similar to that of MD.[26] The particles in DPD evolve via a modified Brownian dynamics that conserves momentum and has been applied to model diblock copolymer structures.[27] The method was first applied to hydrated Nafion by Yamamoto and Hyodo with a simulation box side length of 28.4 nm,[28] demonstrating the ability of the method to address the mesoscale morphology of PFSA membranes. This work was later extended by Wu et al. to compare water networks in Nafion with the 3M PFSA membrane and the SSC membrane.[29] They discovered a similar trend in the dispersity of water for the 3M PFSA as a result of increasing equivalent weight as observed from atomistic simulations with SSC. Moreover, they found that the 3M membrane could produce significantly larger pore sizes as a function of hydration, a result that has important implications for membrane design.

IV. Proton Conduction in Nafion at the Mesoscale

Substantial progress has been made in developing accurate methods to simulate proton transport within individual water clusters in PFSA membranes and the simulation of the water network and pore connectivity at the tens of nanometers length scale. To our knowledge, however, investigation of proton transport and polymer morphology together at the mesoscale in a consistent simulation has not been extensively addressed. The closest efforts include variations of percolation theory with some connections to atomistic parameters[4] and studies focusing on diffusion of neutral species in the Nafion membrane using DPD.[30,31] Regarding the former contribution, proton transport has been decomposed into the effects of local acidity in the membrane (i.e., proton concentration) and the water channel properties of confinement and connectivity. While the method used to connect these components relies on substantial approximations and neglects the details of variation in local environments within the membrane (i.e., using effective material parameters in fits to experiment), the authors obtained reasonable agreement with measured conductivities as a function of water content. In addition, this work was connected with a multiscale effort to study diffusion with a combined MD-confined random walk algorithm that required as inputs the confining water cluster size and a probability for intercluster transitions. Additional DPD simulations have combined static structures for the membrane with kinetic Monte Carlo to study water transport and gas permeability in Nafion resulting from hydrogen and oxygen crossover.[30,31] These methods have not been extended to study proton transport, however, and have the disadvantage of requiring a mapping between the DPD structure and the kinetic Monte Carlo grid, which implies a static membrane structure.

In contrast to grid-based methods for proton transport and methods dependent on effective material parameters to describe the water network, we have recently developed an approach to model proton diffusion in arbitrary water networks using a grid-free representation. Our approach relies on the combination of a coarse-grained model for the membrane structure and a mesoscale method to incorporate transport at length scales beyond our previous MS-EVB studies. Smoothed particle hydrodynamics (SPH) provides a particle-based representation for integrating the conservation equations for mass, momentum, and energy. SPH previously has been applied to a number of fluid-flow problems and the study of galaxy formation.[32] SPH has also been implemented to study macroscale materials properties such as diffusivity in porous materials and heat conduction. At its core, SPH involves the description of a field variable as an integral over a set of interpolation points connected by smoothing functions. Mathematically, SPH can be described by two approximations:

$$A(\mathbf{r}) = \int A(\mathbf{r}')\delta(\mathbf{r} - \mathbf{r}')\mathrm{d}\mathbf{r}' \tag{1}$$

$$\approx \int A(\mathbf{r}')W(|\mathbf{r} - \mathbf{r}'|, h)\mathrm{d}\mathbf{r}' \Big/ \int W(|\mathbf{r} - \mathbf{r}'|, h)\mathrm{d}\mathbf{r}' \tag{2}$$

$$\approx \sum_i \frac{m_i}{\rho_i} A(\mathbf{r}_i)W(|\mathbf{r} - \mathbf{r}_i|, h) \Big/ \sum_i \frac{m_i}{\rho_i} W(|\mathbf{r} - \mathbf{r}_i|, h) \tag{3}$$

where the field variable $A(\mathbf{r})$ has been written as an integral over a delta function distribution in eq 1 and approximated in subsequent steps. In the first approximation, the delta function is replaced by a weighting, or smoothing, function of finite support h, which acts like a delta function in the limit of h approaching zero. In eq 3, this approximate integral is discretized onto a finite number of interpolation points, represented by i, which are given the characteristics of a physical particle with a

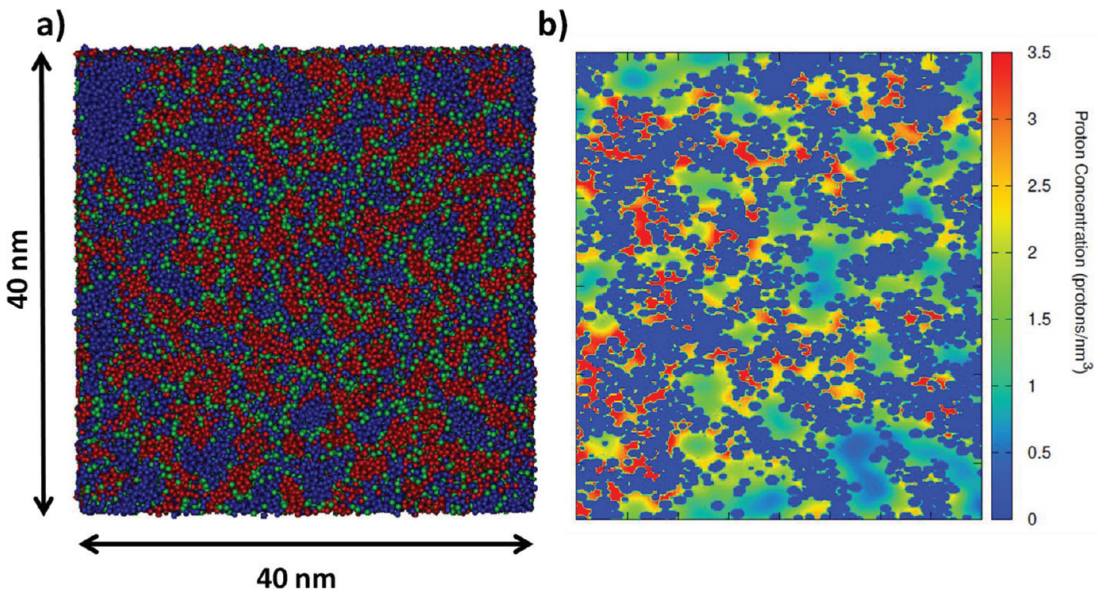

FIGURE 3. (a) DPD snapshot of the equilibrated Nafion structure with a $\lambda = 15$ water content along with (b) the SPH steady state proton concentration for a section of the membrane. In (a) the red corresponds to a polymer backbone bead, blue corresponds to a water bead, and green corresponds to a side chain bead. In (b) the proton concentration is shown by the sidebar.

volume described as the ratio of the quasi-particle mass to density, m_i and ρ_i, respectively. The value of $A(\mathbf{r})$ is expressed as a weighted summation over the quasi-particles in a manner analogous to pairwise interactions between atoms in classical MD. By applying the general scheme in eqs 1−3 to the conservation equations, analogous expressions can be obtained to describe the evolution of the field via the evolution of the quasi-particle quantities. For the case at hand, our interests lie in proton diffusion through a complex water network, and thus, attention is restricted to local concentrations and fluxes of protons moving through the system. Each SPH particle is attributed with a given proton concentration that evolves in time according to the following equation:[33]

$$\frac{\mathrm{d}C^{\mathrm{i}}_{+}}{\mathrm{d}t} = \sum_j \frac{m_j}{RT\rho_j}\left(C^{j}_{+}D^{j}_{+} + C^{i}_{+}D^{i}_{+}\right)\left(\mu^{i}_{+} - \mu^{j}_{+}\right)F_{Ij} \Big/ \sum_j \frac{m_j}{\rho_j}F_{Ij} \tag{4}$$

where F_{ij} is a function related to the weighting function introduced in eqs 1−3, $C_+{}^{i}$ is the proton concentration of particle *i*, $D_+{}^{\mathrm{i}}$ is the local diffusion coefficient at *i* that can be obtained from MS-EVB calculations, and $\mu_+{}^{i}$ is the proton chemical potential at SPH particle *i*. The factor of m_i/ρ_i has the same meaning as in eqs 1−3, *R* is the ideal gas constant, and *T* is the temperature. The expression for the chemical potential was also extended to include the local electrostatics, which were found to be important for determining the behavior of conductivity with respect to water content.[33]

By applying eq 4 to coarse-grained water particles in a simulation of the membrane morphology, a mapping is created between the SPH particles and the coarse-grained model and is used to propagate the excess proton diffusion dynamics within a qualitatively correct membrane structure. Equation 4 implies an unconventional strategy for coarse graining in which the beads themselves carry composition information that can be exchanged with their neighbors in a manner similar to momentum exchange during collisions in an MD simulation. The method does not restrict the SPH particles to be distributed on a lattice of points and can accurately incorporate the random distribution of water beads within a cluster from coarse-grained structures. Hence, the method can also be interfaced with a fluctuating polymer, evolving subject to coarse-grained forces concomitant with protons diffusing through the structure.

In this work,[33] we adopted a DPD approach to determine the coarse-grained membrane structure based on the Nafion model of Wescott et al.[25] This model aggressively coarse-grains each Nafion monomer into three beads that are used to create polymer chains containing 15 evenly spaced sulfonate groups and introduces water beads that contain on average 10.5 water molecules. The interaction parameters for each bead were adapted from the Flory parameters reported by Wescott et al., and the hydration level in the structure was varied from $\lambda = 5$ to 15. A snapshot for the resulting DPD structure is shown in Figure 3a for the highest hydration level considered, and one can see the clear nanophase segregation and the formation of large water clusters that connect to span the simulation box. In order to account for the modulation of transport properties by the sulfonate groups, as evidenced in the MS-EVB studies where the vehicular and hopping transport mechanisms are tuned with proximity to the side chains,[16] a coordinate-dependent diffusion coefficient was included in eq 4. A proton gradient was applied across the structure by using SPH boundary particles, and eq 4 was propagated to steady state including the presence of charged sulfonate groups and accounting for local modification of D.[33] Figure 3b shows the resulting concentration profile across the structure, and an anisotropic distribution of proton concentration within the pores of the membrane is evident. Rough comparisons can be made between the ratio of proton concentrations at the pore walls and the pore centers to recent spectroscopic estimates of proton concentrations in Nafion. While regions in Figure 3b can be identified in which the ratio of protons in a single domain appears to vary by about a factor of 1.5−2, experiments suggest this number should be closer to 2 or 3 at high hydration levels.[34] Interestingly, the conductivities calculated for the steady state represented in Figure 3b give reasonable agreement with experiment within a factor of 2. Taken together with the agreement with experimental estimates of the local changes in concentration within the water channels, these results suggest that our simple model is capturing the basic physics required to describe proton transport in complex PFSA membrane environments.

V. Summary and Future Directions

We have discussed recent modeling of PFSA proton exchange membranes, with special attention paid to the proper treatment of the proton transport mechanism at the angstrom level, modeling the morphology of the hydrated membrane at the mesoscale, and emerging multiscale methods to connect these efforts and bridge information from atomistic simulations into macroscopically relevant properties. The SCI-MS-EVB approach provides an accurate and efficient MD framework for the inclusion of both vehicular and Grotthuss transport of protons at the length scale of individual pores in hydrated systems, while large-scale MD and coarse graining can be used to investigate structure at the mesoscale. The recently developed multiscale DPD-SPH approach to study proton conduction in more random morphologies, which also accounts for local electrostatics and variations in proton mobility, was found to compare favorably with experimental measurements at high hydration levels. With these techniques, the foundation has been laid to perform truly multiscale modeling of PFSA membranes with some confidence in its predictive capability for membrane design efforts.

Ongoing work in our group includes the exploration of new membrane systems and continued improvement of our existing computational methods from MS-EVB to mesoscale transport. With regard to the former effort, we are actively pursuing the application of the techniques discussed here to the SSC membrane as well as to hydroxide exchange systems for alkaline fuel cells. Efforts are also under way to expand the parallel scaling performance of SCI-MS-EVB simulations to achieve much larger simulation sizes and to develop coarse-grained models with more rigorous connection to large-scale atomistic MD simulations. In addition, more accurate quantification of the change in proton transport characteristics as a function of distance from the sulfonate counterions will be important in the further development of our overall multiscale simulation framework.

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BIOGRAPHICAL INFORMATION

Ryan Jorn received his B.A. in 2003 from Ripon College, with a major in physics and chemistry. During his graduate research with Tamar Seideman at Northwestern University, he studied electron scattering from molecules, vibrational energy flow in molecular wires, and the construction of nonadiabatically driven molecular machines. He was awarded a Ph.D. from Northwestern University in 2009. His current research at Argonne National Laboratory is focused on electron and ion transport in condensed phases relevant to energy storage and dynamics at the interfaces within electrochemical systems.

John Savage received his B.Sc. in chemistry in 2007 from National University of Ireland, Galway. He is currently a graduate student at the University of Chicago in the Voth research group, where his research and interests include the multiscale simulation of proton transport in fuel cell membranes and charge transport in condensed phases.

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FOOTNOTES

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