Computer Simulation of Proton Transport in Fuel Cell Membranes

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Objectives

We seek to understand the multiscale coupling of proton transport and polymer morphology in proton exchange membrane (PEM) materials using a combination of detailed reactive molecular dynamics (MD) and mesoscale coarse-grained (CG) simulations, which will help guide future membrane development efforts.

Technical Barriers

The main technical barrier this year is to increase the scalability of the coarse-grained smoothed particle hydrodynamics (CG-SPH) method in order to simulate extremely large-scale systems. We foresee a positive outcome with input from specialists in Argonne National Lab through the INCITE program.

Abstract

Our major advancements this year using reactive MD have been in exploring the effects of morphology and side chain length on proton transport.

Using cylindrical, lamellar, and cluster model morphologies with our multistate empirical valence bond (MS-EVB) reactive MD method, we revealed two different proton translocation mechanisms. The prevalence of these mechanisms depended on the morphology used and the interfacial spacing for a given morphology.

Our investigation into the promising new short side chain 3M membrane using reactive MD also implicitly highlighted the effect of morphology, since there was essentially no difference in the local transport properties between 3M and Nafion, even though 3M conducts much better in experiment.

We have also taken steps to examine these morphological effects at previously inaccessible length and time scales using our novel smoothed particle hydrodynamics (SPH) method. This method was validated using simple lamellar-like structures and also random morphologies derived from dissipative particle dynamics (DPD) simulations.

Progress Report

A. Proton Conductivity at the Mesoscale: Pushing the Limits of Simulation with Multiscale Modeling of Proton Exchange Membranes

We have completed the validation of our CG-SPH simulation method which has been parameterized using our reactive MD simulations and will provide closer connection to experimental results.[1,2] The method combines a CG model for the polyelectrolyte membrane[3] with a smoothed particle hydrodynamics (SPH)[4] description of the proton concentration diffusion in order to study proton conduction through heterogeneous materials. The SPH proton transport is parameterized using our previous Multistate Empirical Valence Bond (MS-EVB) reactive MD simulations[5,6] to capture the impact of local water environments on proton transport coefficients. The combined CG-SPH method gives a foundation for exploring the mesoscale regime for proton conduction that lies beyond atomistic approaches, while providing a higher resolution than traditional engineering calculations of transport properties. The goal is to achieve a higher degree of predictive capability at length scales that can capture the heterogeneity inherent to the phase-segregated morphology of hydrated Nafion.

The CG-SPH method has recently been applied to the example of the Nafion membrane at a variety of hydration levels. The CG model, in conjunction with dissipative particle dynamics, reveals phase-segregated structures with water channels that expand upon further hydration and are nanometers in width. Configurations from these simulations are used in the SPH algorithm to simulate proton transport under an applied concentration gradient. The SPH equations are integrated until a steady state is achieved and volume averaging can be used to extract an effective conductivity. Examination of the steady state concentration profiles shows the presence of significant variations in the proton distribution throughout the water channels of the membrane, in agreement with recent experiments, and demonstrates the important role of including local nanoscale effects to understand the mesoscale transport of protons. In comparing these results with experiments, nearly quantitative agreement was found at higher hydration levels where the CG model is expected to perform well.

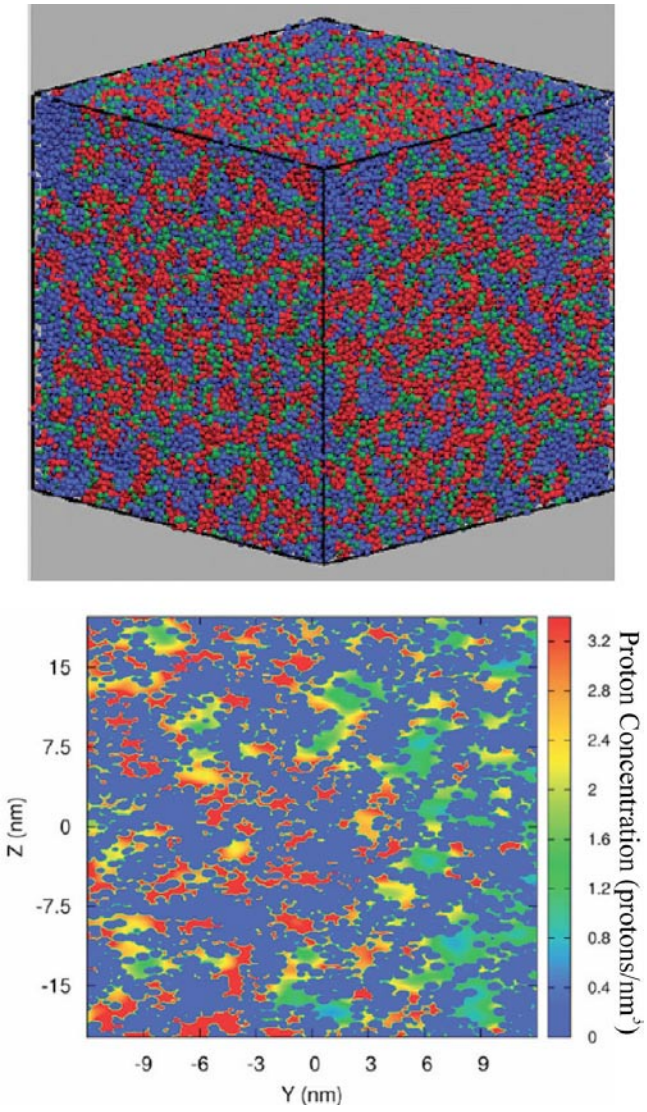

FIGURE 1. (Top) Equilibrated DPD morphology used for SPH simulations. Water beads are blue, polymer backbone red, and side chain green. (Bottom) Results from SPH simulation showing proton concentration in the above morphology.

B. Morphological Effect on Proton Solvation and Transport in Hydrated Nafion

Simulations for three of the main morphological models of Nafion currently proposed in the literature were performed using the self consistent iterative MS-EVB (SCI-MS-EVB) method.[7] The three morphological models included the lamellar structure, the cylinder model, and the cluster-channel model. Each structure was studied at a series of hydration levels and the spacing between the interfaces of the hydrophilic and the hydrophobic regions was varied to extract the geometric factors affecting proton solvation and transport. It was found that for a given hydration level in the lamellar and cylindrical models, increasing the interfacial spacing resulted in greater concentrations of protons near

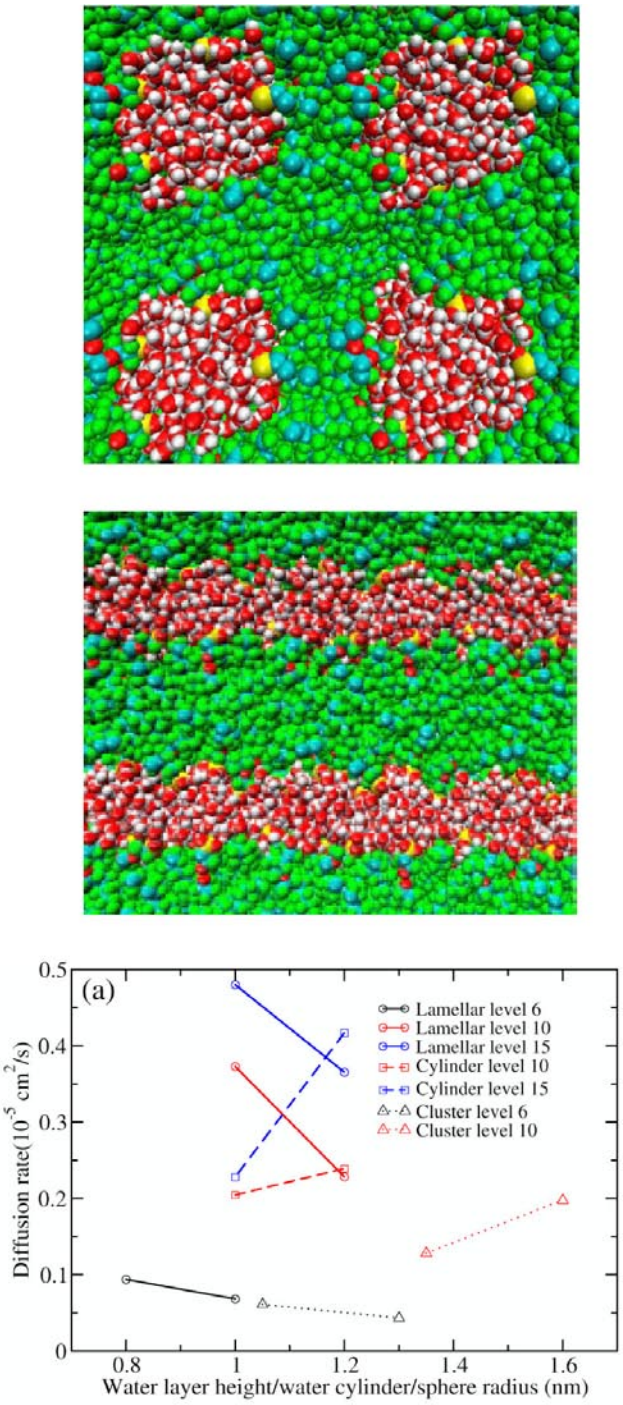

FIGURE 2. (Top) Snapshot of the cylinder-type model. (Middle) Snapshot of the lamellar-type model. (Bottom) Proton diffusion coefficients calculated for lamellar, cylinder, and cluster-channel models at hydration level 6, 10, and 15.

the sulfonate groups. It was also found by examination of the amplitudes of the EVB states that the excess protons near the sulfonate groups tended to be in Zundel-like ($H_5O_2^+$) structures. Interestingly, in contrast to the lamellar and cylindrical models, the cluster-network model showed a decrease in interfacial protons as the interfacial spacing was

increased. These results can be justified by the observation that while increasing the hydrophilic regions size results in a greater amount of non-interfacial water occupying the hydrophilic region, the sulfonate groups also become more closely spaced. This results in an entropic force pushing the protons towards the bulk-like water, and an enthalpic force attracting the protons to the interface. In the lamellar and cylindrical models the attractive enthalpic force dominates. However, because of the larger relative increase in the bulk like water in the cluster network model the entropic force is comparatively larger.

Analysis of the proton transport showed a large dependence on geometry and hydration level, which varied depending on which morphological model was being employed.[8] These results suggested different transport mechanisms were occurring as the size of the water domains changed in the different models and so a detailed analysis of the diffusion pathways was carried out. In the lamellar and cylindrical models, the protons preferred to travel along the interface of the hydrophilic regions, especially at higher interfacial spacings, which agrees well with the structural results. The closer packing of sulfonate groups in the lamellar model resulted in higher diffusion rates, as the proton was more easily able to hop from sulfonate to sulfonate between the sheets. The cluster-network model showed markedly lower diffusion rates as the protons had some probability of being trapped in the connecting channel; however, diffusion within the water clusters showed similar mechanistic behavior to the other models.

C. Comparison of Local Proton Transport in 3M and Nafion Membrane

The 3M membrane is a promising alternative proton exchange membrane to Nafion. Even though their chemical structures are similar, the 3M membrane, whose side chain is shorter, conducts better than Nafion. Previously, it was conjectured that a PEM membrane with a shorter side chain may promote the Grotthuss mechanism and that may be why the 3M conductivity is better than Nafion. By including both vehicular and Grotthuss mechanisms in the SCI-MS-EVB simulations[7], the conjecture can be directly tested.

In our study,[9] different equilibrium and dynamical properties of 3M and Nafion were compared at three different hydration levels (5, 9, and 14) with two different temperatures (300 K and 353 K). The morphology of these membranes was chosen to be random. To isolate the differences coming from only the side chains, the backbones for both membranes were kept the same and the same equilibration process was performed. The most important result is that the biggest difference in the self-diffusion constant of the hydrated proton center of excess charge (CEC) was only 56% at hydration level 14 at 300 K, while the differences at other conditions were much smaller. We found no evidence that the local proton transport in the two membranes can cause

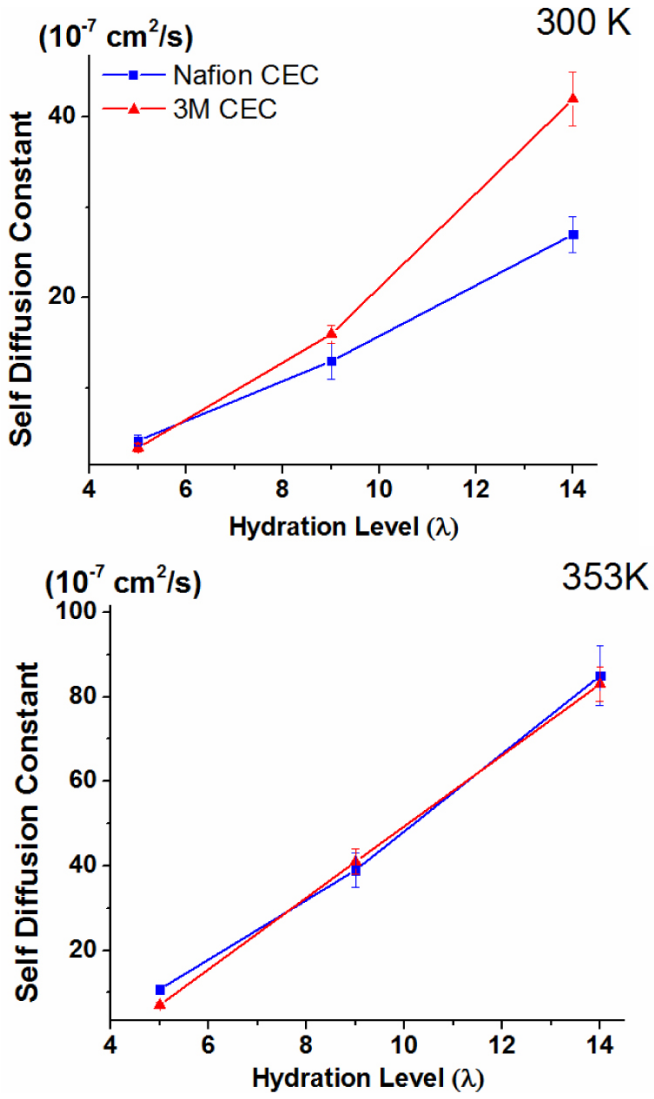

FIGURE 3. Calculated hydrated proton CEC in 3M and Nafion as a function of hydration level at 300K and 353K.

a difference in their conductivity. Gaining insight from the work by Feng and Voth,[8] differences in the morphology globally can lead to very different diffusion constants of excess protons. The random morphology chosen for the systems is probably not an accurate description of the true structure(s). This reinforces the idea that a more complete picture of the actual morphology of these membranes is likely required to obtain a better understanding of proton transport in these membranes as well as to obtain better overall agreement between the calculated diffusion constants and the experimental measurements.

Future Directions

The current development of the CG-SPH model is focused on introducing water and polymer movement to match physical systems more closely. This movement will

be incorporated using methods similar to DPD to introduce thermal noise into the equations of motion. With this method validated, we can begin to explore the effect of morphology on the large-scale proton transport through the membrane. Using a methodology similar to previous efforts in the group, we will choose several candidate morphologies and explore the differences in long-range transport across these morphologies, hopefully providing a clearer connection to conductivity experiments.

Recent algorithmic developments to our MS-EVB code have made longer length and time scales available. We plan to take this opportunity to investigate further the causes for the difference in conductivities between the various perfluorosulfonic acid membranes such as Nafion, Hyflon, and 3M, and to bridge those results into the CG-SPH model in a multiscale fashion.

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Publication list acknowledging the DOE grant in the past year

1. Jorn, R.; Voth, G. A., Mesoscale Simulation of Proton Transport in Proton Exchange Membranes. *J. Phys. Chem. C*. **2012,** *116*, 10476-10489.

2. Jorn, R.; Savage, J.; Voth, G.A., Proton Conduction in Exchange Membranes across Multiple Length Scales. *Acc. Chem. Res.* **2012,** *45*, 2002-2010.

3. Feng, S.; Savage, J.; Voth, G.A., Effects of Polymer Morphology on Proton Solvation and Transport in Proton-Exchange Membranes. *J. Phys. Chem. C*. **2012,** *116*, 19104-19116.

4. Tse, Y.-L.S.; Herring, A.M.; Kim, K.; Voth, G.A., Molecular Dynamics Simulations of Proton Transport in 3M and Nafion Perfluorosulfonic Acid Membranes. *J. Phys. Chem. C*. **2013**. [Online early access] DOI: 10.1021/jp400693g