

Multiscale simulation of proton transport in PFSA membranes

John Savage, Gregory A. Voth

Department of Chemistry, James Frank Institute, Institute of Biophysical Dynamics, and the Computation Institute, University of Chicago, 5735 S. Ellis Ave., Chicago, Illinois 60637 USA

In order to improve conductivity in proton exchange membrane materials, it is essential to understand the mechanisms of proton transport through the current state of the art perfluorosulfonic acid (PFSA) membranes. Since the proton transport is determined by factors at different size scales, from ion pairing to movement between different hydrophilic regions, it is essential that we perform simulations that describe the proton dynamics at these various size scales correctly.

Proton transport in PFSA based membranes is very dependent on the structure of the water pores and the distribution of sulfonate groups within the pore, so atomistic scale simulations are required to investigate these effects. If one wants to correctly describe proton motion in water using molecular dynamics (MD), some description of the electronic degrees of freedom is necessary to enable the Grotthuss mechanism to occur. The reactive MD method developed in the Voth group has allowed this mechanism to be included in simulations at similar size and time scales as previous non-reactive simulations.^{1,2}

Recently we have used this method to determine the effect of polymer morphology on proton transport and solvation.³ Three of the most debated morphological models, the lamellar model, the cylinder model and the cluster-channel model were studied at different hydration levels and different pore dimensions. It was found that the proton mobility was improved by closer spacing of sulfonate groups on the hydrophilic pore surface and by closer spacing of different hydrophilic surfaces. We are currently using this method to compare PFSA polymers Hyflon and 3M to Nafion to determine the factors that that contribute to the improved proton conductivity in these membranes.

Because of the complicated structure of PFSA materials, it is important to perform simulations on larger scales than one or two hydrophilic pores. Unfortunately, these size scales are far larger than is feasible at atomistic levels of detail. Dissipative particle dynamics (DPD) simulations have shown promise in exploring structural properties at these size scales, but are unable to include proton transport. Continuum mechanics and non-equilibrium thermodynamics have been used to determine proton transport behavior at these length scales, however previous studies assume idealized shapes for the hydrophilic pores and have no connection to the atomistic level at which synthetic chemists would be interested in. Therefore, a smoothed particle hydrodynamics (SPH) method was developed in the group that can take structural information from DPD simulations as the

starting configuration and uses local dynamical information from reactive MD simulations to parameterize the equations for proton motion in the system.⁴ This method has already been validated for simple lamellar structures and static structures from DPD simulations and improvements to the method, including improvements to the equations of proton motion and inclusion of polymer fluctuations, are currently being developed.

Taken together, these multiscale simulations are providing a clearer picture of the factors affecting proton conductivity in these materials and will provide well-defined directions for experimentalists looking to improve PEM membranes through both synthetic and mechanical means.

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¹ Voth, G. A. *Accounts of Chemical Research*, **2006**, 39, 143

² Wang, F., Voth, G. A. *The Journal of Chemical Physics*, **2005**, 122, 144105

³ Feng, S., Savage, J., Voth, G. A. *The Journal of Physical Chemistry C*, **2012**, 116, 19104

⁴ Jörn, R., Voth, G. A. *The Journal of Physical Chemistry C*, **2012**, 116, 10476