

**Report Title:** Mechanism of Proton Transport in Proton Exchange Membranes: Insights from Computer Simulation

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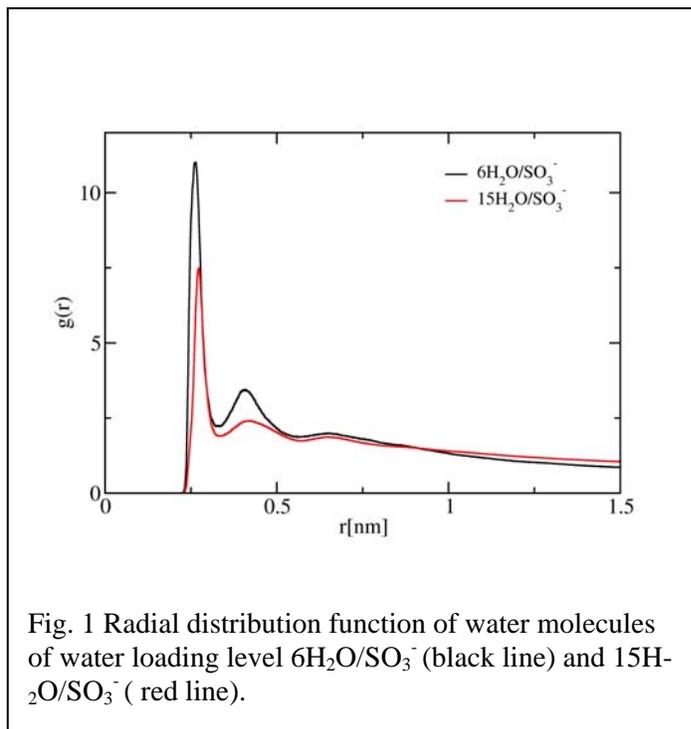
**Objectives:** This project involves the development and application of a unique multiscale computer simulation methodology for studying proton solvation and transport in proton exchange membranes (PEMs) for fuel cell applications. A key component of the project is an atomistic reactive molecular dynamics MD simulation approach that allows for the explicit and accurate treatment of proton shuttling in the MD simulation of complex systems having large system sizes and long MD simulation times. Another key objective is the bridging of the molecular scale proton transport information to mesoscopic models of PEMs that connect the proton transport with the features of the polymer morphology.

**Technical Barriers:** The computer simulation of the proton conductance behavior of proton exchange membranes must involve a description of the relevant physics over a wide range of length and time scales. These scales range from those involving the breaking and making of chemical bonds at the Angstrom and picosecond scales during the proton shuttling process through mediating water molecules, to the mesoscopic collective proton transport behavior of the polymer membrane behavior at the micrometer and microsecond scales. A systematic multiscale computational approach must therefore be developed and implemented, often within a high performance computing environment, to correctly describe proton exchange membranes.

**Abstract:** The solvation and transport of hydrated protons in proton exchange membranes (PEMs) such as Nafion<sup>TM</sup> will be described using a novel multi-state reactive molecular dynamics (MD) approach, combined with large scale MD simulation to help probe various PEM morphological models. The multi-state MD methodology allows for the treatment of explicit (Grotthuss) proton shuttling and charge defect delocalization which, in turn, can strongly influence the properties of the hydrated protons in various aqueous and complex environments. A significant extension of the methodology to treat highly acidic (low pH) environments such as the hydrophilic domains of a PEM will be presented. Recent results for proton solvation and transport in Nafion<sup>TM</sup> will be described which reveal the significant role of Grotthuss shuttling and charge defect delocalization on the excess proton solvation structures and transport properties. The role of PEM hydration level and morphology on these properties will also be described.

## Technical Report:

A. Simulations of Explicit Proton Transport in Nafion<sup>TM</sup> as a Function of Water Loading (Hydration). Novel atomistic reactive molecular dynamics(MD) simulations of 1100EW Nafion were performed for water loading of  $15\text{H}_2\text{O}/\text{SO}_3^-$ ,  $10\text{H}_2\text{O}/\text{SO}_3^-$ ,  $7\text{H}_2\text{O}/\text{SO}_3^-$  and  $6\text{H}_2\text{O}/\text{SO}_3^-$ . This work has extensively utilized the self-consistent iterative multi-state empirical valence bond (SCI-MS-EVB) method,<sup>1</sup> a generalization of the MS-EVB approach which allows for the treatment of solvation and the transport of *multiple* excess



protons under intermediate to high acid concentrations at an affordable computational cost. In addition to its exceptional computational efficiency relative to *ab initio* molecular dynamics, the SCI-MS-EVB method also scales linearly with the number of protons in the simulation box. The recently developed MS-EVB3<sup>2</sup> parameterization, which is also based on a more accurate underlying water model,<sup>3</sup> was also employed. These simulations have provided a better understanding of the physics of proton solvation and transport in the Nafion membrane as a function of water loading. The dynamical evolution of the excess protons, water distributions (cf. Fig. 1), and the cooperative motion of the sulfonate/hydronium ion pairs, as well as their associated solvation structures at different water loading levels, were the focus of this study.

The center of excess charge (CEC)<sup>4</sup> of the net positively charged hydrated proton electronic charge defect, which best characterizes the instantaneous location of the excess proton charge and most physically accurately describes the effects of Grotthuss proton shuttling, was used to characterize the structure and dynamics of the highly acidic Nafion environment. The water distributions were also characterized by radial distribution functions of the water molecules. As depicted in Figure 1, water clusters of water loading level  $6\text{H}_2\text{O}/\text{SO}_3^-$  are characterized by the high peak at  $\sim 0.26\text{nm}$ , while the relatively lower peak at the same position and the slightly larger amplitude at longer distance for water loading level  $15\text{H}_2\text{O}/\text{SO}_3^-$  indicate the existence of a water network that can facilitate the observed higher proton conductance.

The unusual proton transport behavior discovered previously in this project<sup>5</sup> was further studied at different water loading levels. The excess proton CEC displacement vectors were decomposed into a continuous displacement component due to “vehicular” (classical Einstein) diffusive motion and a component due to the discrete “hopping” displacement due to the identity change of the protonated water molecule via Grotthuss shuttling. The overall mean squared displacement (MSD) could then be written as the sum of the MSD of each component and an overlap term which describes the correlation of the two displacement vectors. Figure 2 displays the different components of the MSD for the two water loading levels,  $10\text{H}_2\text{O}/\text{SO}_3^-$  and  $6\text{H}_2\text{O}/\text{SO}_3^-$ . (The diffusion constant is proportional to the slope of the MSD at long times.) At all water loading levels studied, hopping (discrete) diffusion is somewhat faster than the vehicular motion. More interestingly, as the water loading level increases, the diffusion constant of

discrete motion increases faster than that for the continuous motion (e.g., at  $10\text{H}_2\text{O}/\text{SO}_3^-$ ), indicating the onset of water network formation which facilitates the Grotthuss hopping more than vehicular diffusion.

*B. Large Scale Molecular Dynamics of Nafion<sup>TM</sup> Morphological Models.* Atomistic molecular dynamics simulations of a very large scale were performed to study hydrated Nafion systems.<sup>6</sup> The simulations were large enough ( $\sim 2$  million atoms,  $\sim 30$  nm box length) to directly observe several hydrophilic domains at the molecular level. These systems consisted of six of the most significant and relevant morphological models of Nafion to-date: (1) the cluster-channel model, (2) the parallel cylinder model, (3) the local-order model, (4) the lamellar model, (5) the rod network model, and (6) a ‘random’ model

that does not directly assume any particular geometry, distribution, or morphology. Each system was initially built to closely approximate the proposed hydrophilic cluster structure in a given model. Molecular dynamics simulations were then used to observe resulting changes from and behavior of the assumed initial configurations. These simulations revealed fast intercluster ‘bridge’ formation and network percolation in all models. Sulfonate groups were found inside these bridges and played a significant role in percolation. Sulfonates also strongly aggregated around and inside clusters. Cluster surfaces were analyzed to study the hydrophilic-hydrophobic interface. Interfacial area and cluster volume significantly increased during the simulations, and radial distribution functions and structure factors were also calculated. All nonrandom models clearly exhibited the characteristic experimental scattering peak, underscoring the insensitivity of this measurement to hydrophilic domain structure and highlighting the need for future work to clearly distinguish morphological models of Nafion.

*C. Proton Transport in Non-Aqueous Electrolytes.* Anhydrous proton conduction media are important targets for applications in high temperature fuel cells given the difficulties with water as an electrolyte under such conditions. The MS-EVB methodology was therefore successfully extended to simulate excess proton transport in liquid imidazole,<sup>7</sup> which is a target non-aqueous electrolyte (or chemical derivatives of imidazole). As in aqueous systems, this approach allows proton transfer to simultaneously occur on both reaction sites (donor and acceptor) of the imidazole molecule. The underlying imidazole and imidazolium models were described by the generalized Amber force field (GAFF), while the imidazole MS-EVB model was parameterized to reproduce the *ab initio* proton shuttling potential energy surface (PES) of a protonated imidazole dimer in the gas phase. In bulk phase at 393K, the MS-EVB simulation yielded a proton diffusion coefficient of  $0.20 \text{ \AA}^2/\text{ps}$  and a Grotthuss hopping rate of  $1/36 \text{ ps}^{-1}$ , and both results are in good agreement with experiment. Despite the prevalence of a classical-like imidazolium structure with highly localized protonic charge defect, the charge delocalization was found to not be negligible process in the simulations. Rather, it was shown to enhance the rate of proton

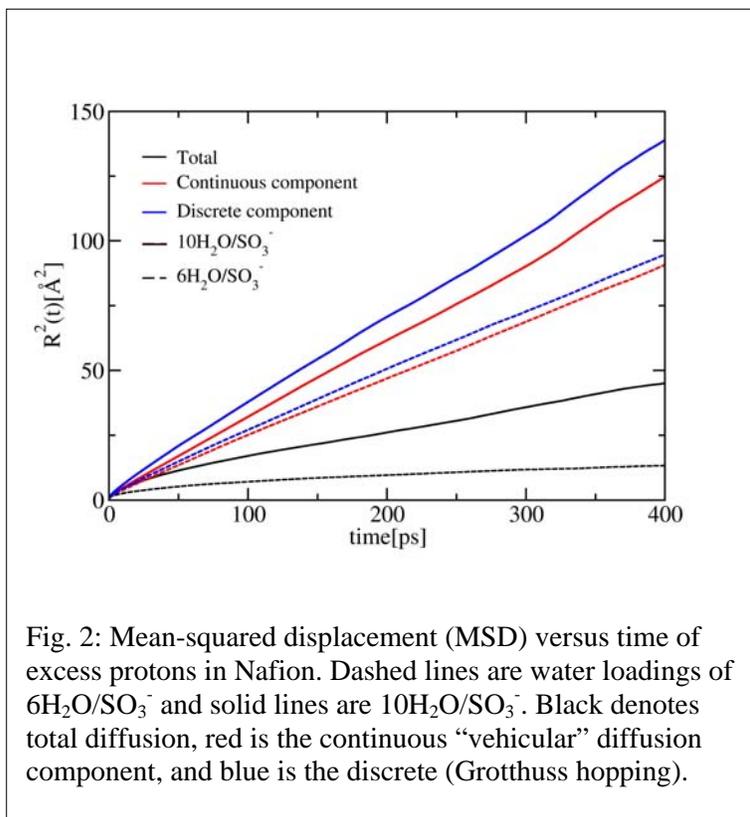


Fig. 2: Mean-squared displacement (MSD) versus time of excess protons in Nafion. Dashed lines are water loadings of  $6\text{H}_2\text{O}/\text{SO}_3^-$  and solid lines are  $10\text{H}_2\text{O}/\text{SO}_3^-$ . Black denotes total diffusion, red is the continuous ‘vehicular’ diffusion component, and blue is the discrete (Grotthuss hopping).

diffusion by approximately 40% through Grotthuss shuttling. Analysis of the MS-EVB states revealed that the imidazolium ion's first solvation shell by imidazole molecules is highly ordered, through the formation of hydrogen bonds, while the second solvation shell is highly disordered. Together with the importance of charge delocalization, this result demonstrated that reorientation of imidazole rings in the second solvation shell is the rate-limiting step for proton transfer.

**Future Directions:** Now that the atomistic-scale reactive MD (SCI-MS-EVB) simulations of proton transport in PEMs are well in hand, the role of polymer morphology in defining the mesoscopic proton conductance behavior can begin to be explored. This effort will involve increasingly larger SCI-MS-EVB simulations for select PEM morphological models, coupled to new mesoscopic simulation methods to describe both the polymer morphology and the proton transport on a unified, larger length and time scale, footing.

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## Publications acknowledging this DOE Grant:

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