BESH2018 Computer Simulation of Proton Transport in Fuel Cell Membranes

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Program Scope

Understanding the proton transport mechanism is essential for designing next generation proton exchange membranes (PEMs). Our research focuses on the development and application of computational models that can accurately treat proton transport. Grotthuss shuttling, i.e., proton transfer involving the rearrangement of covalent and hydrogen bonds, is a primary mechanism for proton transport in aqueous systems. We have therefore developed a highly accurate reactive molecular dynamics (RMD) approach, which explicitly treats bond breaking and formation, to study proton transport in water and PEM systems. With such a tool, we are able to investigate the influence of morphology, hydration level, and temperature on proton transport in PEMs.
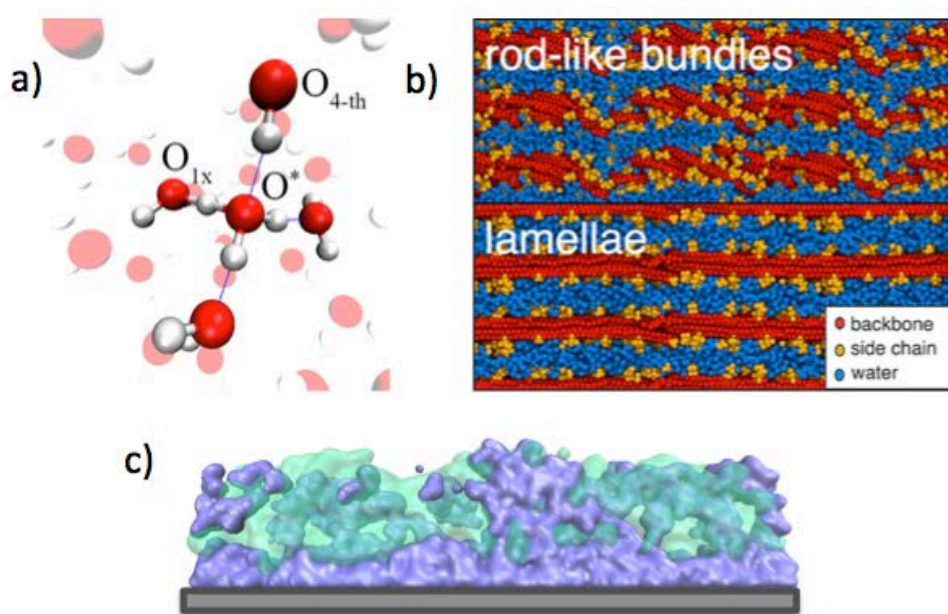
FY 2016 Highlights

In order to capture the proton transfer mechanism most accurately, we have updated our model used to simulate the process. [1] The new model is fit to MP2 and additive-increase/multiplicative decrease data, and shows an improved (higher) proton diffusion constant. The primary difference with the updated model is the inclusion of a presolvation water in the hydronium solvation structure, which allows the hydronium to be transiently 4-fold coordinated (see Figure 1a). Because water is typically 4-fold coordinated, when the hydronium molecule undergoes transfer and forms water, the solvation structure is more stable, thus allowing for more efficient proton hopping and enhancing the overall proton diffusion constant.

We have also continued our study of proton transport in perfluorosulfonic acid (PFSA) membranes, in particular investigating the effect of morphology. [2] Several experimental groups have proposed ordered straight-chain morphologies for PFSA membranes: lamellar structures with alternating slabs of hydrophobic and hydrophilic domains; and bundles, in which the polymer chains form nanorods surrounded by hydrophilic regions. To better understand the role of morphology in proton transport, we built structures according to two experimental proposals and calculated diffusion properties as a function of hydration level (see Figure 1b). Simulating morphologies with straight chain polymers of equivalent weights and length scales relevant to experiment required that we increase the size of our simulations by a factor of three over previous work, which demanded a major programming effort to improve the parallelization algorithm for our RMD work.

Our simulations yielded several interesting results. First, we found that proton transport is fastest in systems with lamellar morphologies. This speed is the result of several key features. Water diffusion is also fastest in the lamellar morphology (which effects proton transport) and is in fact faster than experimental water diffusion. The lamellar morphology also has the smallest surface area at the hydrophobic-hydrophilic interface, and because all of the charged sulfonate groups reside at this

interface, a smaller surface area forces these groups to be closer together. Our previous work on PFSA materials of varying side chain length has shown that the primary mechanism of proton transport in PEM systems involves the excess hydrated proton getting "passed" between adjacent sulfonate groups. Our current work also shows that this mechanism can be enhanced through morphology by minimizing the surface area of the interface.

We also propose that the bundle morphology is most representative of experiment. While the proton diffusion constant is understated for the system, the water diffusion very

Figure 1. (a) Solvated hydronium molecule with transient presolvation water shown. (b) Snapshots of bundle and lamellar morphologies showing phase separation between hydrophobic backbone and water regions, with sulfonated side chains extended into aqueous region. (c) Thin film morphology with the aqueous layer rendered blue, the polymer layer rendered green, and the catalyst shown in black.

closely reflects experimental values. We use the Simple Point Charge/flexible water model in our RMD simulations, which has been shown to give a very accurate diffusion constant. As stated above, the water diffusion constant is too high in the lamellar morphology, and given the accuracy for the bundle morphology with respect to experiment (and the accuracy of bulk water with respect to experiment), we suggest the bundle morphology is the more realistic of the straight-chain morphologies.

We have also started simulations of PFSA thin film membranes, which involve a three-phase interface with air and a catalyst layer (see Figure 1c). Thin film membranes have been shown to have very different transport properties from bulk membranes, so we set out to determine the morphological, hydration, and temperature effects on proton transport in such systems. Consistent with experiment, we find that the proton diffusion constant of thin films is greatly reduced in comparison to bulk membranes. In addition, we have modulated the hydrophobicity of the catalyst layer, and found a substantial effect on the morphology. As hydrophilicity of the catalyst surface increases, water, hydronium, and sulfonate side chains aggregate at the catalyst layer, and push the polymer backbone to the air interface.

References

1. R. Biswas, Y.-L. S. Tse, A. Tokmakoff, and G. A. Voth, "Role of Presolvation and Anharmonicity in Aqueous Phase Hydrated Proton Solvation and Transport", J. Phys. Chem. B **120**, 1793-1804 (2016).
2. J. Savage and G. A. Voth, "Proton Solvation and Transport in Realistic Proton Exchange Membrane Morphologies", J. Phys. Chem. C **120**, 3176-3186 (2016).