Final Report

Project Title: Computer Simulation of Proton Transport in Fuel Cell Membranes

Award Number: DE-SC0005418

PI Name: Gregory A. Voth

Recipient Name: The University of Chicago

Period of Performance: 09/01/2010 – 8/31/2018

Narrative

This DOE-supported research grant focused on understanding the nature of proton transport in complex systems such as proton exchange membranes (PEMs). The most unique aspect of the research was the development and implementation of a novel multiscale reactive molecular dynamics (MS-RMD) methodology. In this approach, covalent bonds can dynamically break and form, allowing one to accurately treat the proton hopping process essential to capturing the physics of proton transport. The Voth group applied this method to proton exchange membrane systems, providing insight into their proton transport mechanism. They found that protons can diffuse most rapidly in the water-rich regions, but that protons actually spend so little time in such regions that transport along the hydrophobic – hydrophilic interface controls the membrane performance. In addition, the group worked to increase understanding of acidic solutions, developing methods for simulating and interpreting experimental infrared vibrational spectroscopy for excess protons (acidic solutions). The group also implemented novel tools for developing proton transport reactive MD models using a relative entropy minimization scheme.

Below are the papers published in during the project with a brief explanation of the significance of each.

P1. M. K. Petersen, A. J. Hatt, and G. A. Voth, "Orientational Dynamics of Water in the Nafion Polymer Electrolyte Membrane and Its Relationship to Proton Transport", J. Phys. Chem. B **112***,* 7754–7761 (2008). This paper analyzed the dynamics of water in Nafion PEM using MS-RMD and found good agreement with the experimental data of Michael Fayer at Stanford.

P2. H. Chen, T. Yan, and G. A. Voth, "A Computer Simulation Model for Proton Transport in Liquid Imidazole", J. Phys. Chem. A **113**, 4507-4517 (2009). This was the first reactive MD paper for this important possible electrolyte.

P3. C. K. Knox and G. A. Voth, "Probing Selected Morphological Models of Hydrated Nafion Using Large Scale Molecular Dynamics Simulations", J. Phys. Chem. B. **114***,* 3205–3218 (2010). This was the first large scale atomistic MD paper to explore the various morphologies of Nafion PEM and their molecular scale properties.

P4. H. Chen, P. Liu, and G. A. Voth, "An Efficient Multi-State Reactive Molecular Dynamics Approach Based on Short-Ranged Effective Potentials", J. Chem. Theor. Comp. **6**, 3039–3047 (2010). This paper was a fundamental development of the MS-RMD approach that greatly improved its computational efficiency.

P5. S. Feng and G. A. Voth, "Proton Solvation and Transport in Hydrated Nafion", J. Phys. Chem. B **115**, 5903-5912 (2011); Addition and Correction, J. Phys. Chem. B **115**, 10570 (2011). This paper presented a comprehensive follow-up simulation of hydrated Nafion with excess protons in the system and with full Grotthuss hopping physics included via MS-RMD. The anti-correlation of hopping and vehicular proton transport that was discovered in our earlier work was also further analyzed.

P6. R. Jorn and G. A. Voth, "Mesoscale Simulation of Proton Transport in Proton Exchange Membranes", J. Phys. Chem. C ***116,*** 10476–10489 (2012). This paper presented a new mesoscopic model of PEMs in which proton transport over larger lengthscales can be explored for various PEM morphologies.

P7. R. Jorn, J. Savage, and G. A. Voth, "Proton Conduction in Exchange Membranes Across Multiple Length Scales", Acc. Chem. Res. ***45***, 2002–2010 (2012). This was a visible review article that summarized our work to that date on the simulation of proton transport in PEMs.

P8. S. Feng, J. Savage, and G. A. Voth, "Effect of Polymer Morphology on Proton Solvation and Transport in Proton Exchange Membranes", J. Phys. Chem C ***116***, 19104–19116 (2012). This paper used MS-RMD to discover the differences in proton transport behavior in different morphological models of PEM. Lamellar structures with thin water layers were found to be especially facile at proton transport.

P9. Y.-L. S. Tse, A. M. Herring, K. Kim, G. A. Voth, "Molecular Dynamics Simulations of Proton Transport in 3M and Nafion Perfluorosulfonic Acid Membranes", J. Phys. Chem. C **117**, 8079–8091 (2013). This simulation paper showed that the enhanced proton conductance of the 3M PEM is not likely to be attributed to proton transport behavior at the level of the individual water clusters in the PEM or due to the shorter sulfonate side chains of the 3M PEM. It must be modulated by larger scale mesoscopic structural differences and domain connectivity.

P10. J. Savage, Y.-L. S. Tse, and G. Voth, "The Proton Transport Mechanism of Perfluorosulfonic Acid Membranes", J. Phys. Chem. C **118**, 17436–17445 (2014). This is arguably the most important paper to come from the overall DOE project. In it, the underlying mechanism of proton transport in PEMs was revealed using MS-RMD. The hydrated protons are found to never exit from within two solvation shells of the PEM sulfonate side chains, but rather to hop between the water clusters that solvate the sulfonates. The excess protons thus essentially never escape into the "free water" pools that exist away from the sulfonates. Lower PEM water content (hydration) will change the nature and connectivity of the sulfonate hydrating water clusters, and hence the proton transport rates between them. The size of the free water pool is much less important.

P11. J. Savage and G. A. Voth, "Persistent Subdiffusive Proton Transport in Perfluorosulfonic Acid Membranes", J. Phys. Chem. Lett. **5**, 3037−3042 (2014). This MS-RMD simulation paper showed that the proton transport in hydrated regions of PEMs is subdiffusive for quite long times (many nanoseconds), something that must be carefully taken into account when extracting overall PEM proton transport behavior. These results also show that *ab initio* MD simulations of proton hopping and transport in PEMs are of limited use since they cannot generally be long enough in time to go beyond the subdiffusive regime.

P12. Y.-L. S. Tse, C. Knight, and G. A. Voth, "An Analysis of Hydrated Proton Diffusion in *Ab Initio* Molecular Dynamics", J. Chem. Phys. **142**, 014104(1-13) (2015). This is an extensive analysis of proton hopping and transport for AIMD simulations with a dispersion corrected BLYP functional. It was found that the results are highly dependent on initial conditions,

reflecting the underlying glassiness of the AIMD water (much too slow water self-diffusion, a very common issue in AIMD).

P13. S. Liu, J. Savage, and G. A. Voth, "Mesoscale Study of Proton Transport in Proton Exchange Membranes: Role of Morphology", J. Phys. Chem. C **119**, 1753–1762 (2015). In this paper, the reactive MD results are bridged with a mesoscopic model of the PEM, showing the importance of the side chain mediated proton transport at the mesoscopic level and, more importantly, that the PEM morphology likely changes with hydration level in order to explain the observed experimental trend in proton conductivity versus hydration.

P14. R. Biswas, Y.-L. S. Tse, A. Tokmakoff, and G. A. Voth, "Role of Pre-Solvation and Anharmonicity in Aqueous Phase Hydrated Proton Solvation and Transport", J. Phys. Chem. B **120**, 1793–1804 (2016). This paper defined the MS-EVB 3.2 model for the excess hydrated proton and also pointed to the critical role of four-fold water "pre-solvation" of the hydronium-like cation core for a successful Grotthuss proton hop to occur.

P15. J. Savage and G. A. Voth, "Proton Solvation and Transport in Realistic Proton Exchange Membrane Morphologies", J. Phys. Chem. C **120**, 3176–3186 (2016). This was a first of its kind study on the role of PEM morphology in defining proton transport behavior with explicit MS-RMD proton transport in the simulation, with the conclusion that the "rod-bundle" PEM model is most consistent with experiment.

P16. C. Arntsen, J. Savage, Y.-L. S. Tse, and G. A. Voth, "Simulation of Proton Transport in Proton Exchange Membranes with Reactive Molecular Dynamics", Fuel Cells. **16**, 695-703 (2016). This was a comprehensive invited review article of our extensive efforts in PEM simulations.

P17. R. Biswas, W. Carpenter, G. A. Voth, and A. Tokmakoff, "Molecular Modeling and Assignment of IR Spectra of the Hydrated Excess Proton in Isotopically Dilute Water", J. Chem. Phys. **145**, 154504(1-12) (2016). This was the first of two important papers in which our MS-RMD model was used to help interpret the cutting edge 2D-IR experiments in the Tokmakoff group on the hydrated excess proton.

P18. R. Biswas, W. Carpenter, J. A. Fournier, G. A. Voth, and A. Tokmakoff, "IR Spectral Assignments for the Hydrated Excess Proton in Liquid Water", J. Chem. Phys. **146**, 154507(1-11) (2017). (JCP Editor's Choice Paper, 2017) This is the second of two papers with the Tokmakoff group in which the key IR spectral features of the hydrated excess proton in HCl solution are explained with our modeling. This has been a high impact research effort.

P19. C. Arntsen, C. Chen, and Gregory A. Voth, "Reactive Molecular Dynamics Models from *Ab Initio* Molecular Dynamics Data Using Relative Entropy Minimization", Chem. Phys. Lett. **683**, 573-578 (2017). This was the first of two methodology papers showing how relative entropy minimization can be used to develop MS-RMD models from AIMD data (in this case the hydrated excess proton in water).

P20. R. Biswas and G. A. Voth, "Role of Solvation Structure in the Shuttling of the Hydrated Excess Proton", J. Chem. Sci. **129**, 1045–1051 (2017). This paper presents important additional information on the complex process of Grotthuss shuttling and the role of various transient solvation structures.

P21. C. Chen, C. Arntsen, and G. A. Voth, "Development of Reactive Force Fields Using *Ab Initio* Molecular Dynamics Simulation Minimally Biased to Experimental Data", J. Chem. Phys. **147,** 161719(1-7) (2017). This paper builds on P8 with additional relative entropy minimization methodology and, especially important, the use of experimentally biased AIMD simulation for the MS-RMD model fitting, to greatly improve the AIMD and hence resulting MS-RMD model accuracy (e.g., the underlying water structure and self-diffusion).