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# Charge Transfer, Transport, and Reactivity in Complex Molecular Environments: Theoretical Studies for the Hydrogen Fuel Initiative

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## Objectives

This theory program aims to apply modern theoretical and computational methods to enable a fundamental characterization and understanding of the selective transport of protons and molecular fuels through polymeric membranes, a process and a property central to the operation of polymer electrolyte membrane fuel cells (PEMFC). This molecular-level and mesoscale-level understanding is critical for the rational design of membrane materials with controlled transport, selectivity, and stability. The program supports one of the high priority research directions of the Hydrogen Fuel Initiative.

## Technical Barriers

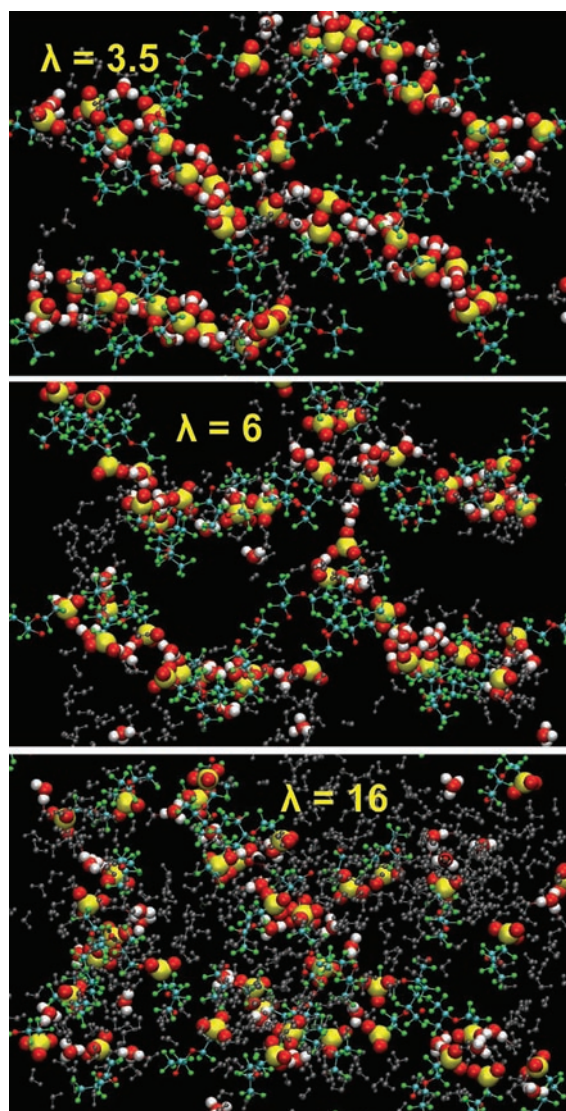
There is a pressing need to develop polymer electrolyte membranes (PEM) that conduct protons at low levels of hydration, do not degrade upon prolonged operation at elevated temperature, and offer selective ionic and molecular transport. A fundamental understanding of the factors affecting proton transport, mechanical properties, and chemical degradation will help optimize the chemistry of membranes for proton transport. This will enable rational design of the next generation of polymer membranes.

## Abstract, Progress Report and Future Directions

We have undertaken multi-scale simulations of proton transport and membrane dynamics that are informed by detailed *ab initio* quantum chemical

calculations. At the most fundamental level, the simulations must capture the quantum mechanical characteristics of proton transfer within a larger model that uses a classical representation of membrane pore dynamics. The simulations must accurately represent proton transfer, from/to acidic/basic sites, including water molecules, in the membrane, concerted proton transfers, collective proton transport through the membrane, and the transport of water and fuel molecules. The task is challenging, because the environment of the membrane is complex, the pore network morphology is dynamic, and the membrane dynamics takes place on much longer scales compared to proton transfer. We are carrying out fundamental investigations to characterize the chemical features that affect the performance of membranes including the chemical nature of protonation sites, local concentration of protons, and local level of hydration. Simulations at the meso-scale are in progress with the QHOP methodology of Lill and Helms<sup>1</sup>.

**Atomistic simulations of PEM under low hydration:** Molecular dynamics (MD) simulations of a model of a hydrated Nafion<sup>®</sup> (DuPont) membrane that included 40 sulfonate groups, 40 hydronium ions, and a varying number of water molecules corresponding to hydration levels  $\lambda = 3.5, 6, 11,$  and 16 water molecules per sulfonate groups, were performed using classical interaction potentials<sup>2-4</sup>. The effects of level of hydration and temperature on the nanostructure of the model membrane and on the vehicular transport of hydronium ions and water molecules were examined using classical molecular dynamics simulations. Through the determination and analysis of structural and dynamical parameters such as density, radial distribution functions, coordination numbers, means square deviations, and diffusion coefficients, we identified that hydronium ions themselves play a role in modifying the interfacial structure in the membrane at the sulfonate pendants. In the regime of low level of hydration, short hydrogen bonded linkages made of water molecules and also hydronium ions give a more constrained structure to the sulfonate pendants (see Figures 1-2). The diffusion coefficient for water was found to be in good accord with experimental data. The diffusion coefficient for hydronium ions was determined to be much smaller (6 to 10 times) than for water. Temperature was found to have a significant effect on the absolute value of the diffusion coefficients for both water and hydroniums. The diffusion coefficients of the hydronium ions are underestimated in comparison with experiment. This may be due in part to the neglect



**FIGURE 1.** Snapshots from MD simulations of model membranes at varying hydration levels  $\lambda = 3.5, 6,$  and  $16$ . They illustrate the existence of hydronium linkages between sulfonate groups at low hydration levels only (top figure). At high hydration level the hydronium ions are much less coordinated to the sulfonate groups (bottom figure).

in the present simulations of the Grotthuss mechanism of proton transfer and of concerted proton transfers which are known to make a significant contribution to the diffusion of protons in aqueous solution. We are currently incorporating these mechanisms through the mesoscale QHOP approach<sup>1</sup>. QHOP is a flexible protonation state simulation methodology designed to overcome the prohibitive expense of simulating proton hopping in macromolecular systems, such as PEMs. Q-HOP is based on the parameterization of proton hopping probabilities between donor and acceptor sites calculated from a combination of individual *ab initio*-derived proton hopping rates. For every site that may

be involved in proton hopping, all possible protonation states are included in the description of the system, and during the MD simulation proton hopping takes place dynamically through switching of the protonation states of donor and acceptor sites.

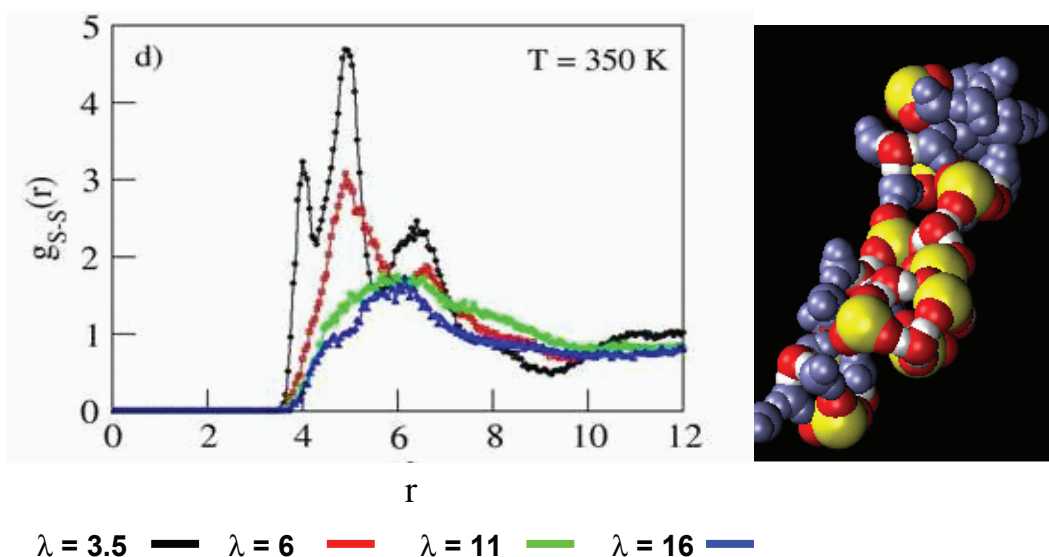
#### **Ab initio electronic structure and dynamics of acidic pendants in PEMs:**

In the regime of low hydration a membrane such as Nafion<sup>®</sup> may no longer be in its purely ionic form. Indeed Paddison<sup>6</sup> reported *ab initio* (DFT) calculations on the proton dissociation in molecules which mimic the hydrophilic components of hydrated Nafion<sup>®</sup> and found that it takes as few as 3 water molecules for the proton to transfer from the sulfonic group to the water solvent phase. The quantity of interest is the relative stability of neutral complexes [NC]  $\text{RSO}_3\text{H}\cdots(\text{H}_2\text{O})_n$  between the neutral acid and a cluster of  $n$  water molecules vs. ion pair complexes [IP]  $\text{RSO}_3^-\cdots\text{H}^+(\text{H}_2\text{O})_n$  between the base and a protonated



cluster. We carried out *ab initio* MP2 calculations to estimate the relative energies of the NC and IP complexes. The NCs were found to be more stable than the IPs for  $n = 1, 2$  by  $\sim 38$  kcal/mol and  $\sim 4$  kcal/mol respectively (the IPs are not stable structures on the potential energy surface (PES) for  $n=1,2$ ). The IP were found to be more stable than the NCs for  $n = 3, 4$  by  $\sim 5$  kcal/mol and  $\sim 7$  kcal/mol respectively (the NCs are not stable structures on the PES for  $n \geq 3$ ). In these calculations the non-stable complexes were determined through constrained optimizations. Thus these thermochemical data suggest that in low hydration conditions the sulfonate groups may be found in their ionic or neutral forms depending on the number of water molecules within the coordination sphere of the sulfonate group. The water coordination number to the sulfonate groups is a dynamic quantity that varies with during proton transport in the membrane. The relative stability of the NC and IP complexes will depend on the chemical nature of the acidic group R. Insight on the landscape of the PES for NC and IP complexes for various acidic groups can be obtained from *ab initio* molecular dynamics Car-Parrinello simulations and those are in progress. In excess proton conditions, protons can also bind to neutral acidic groups.

This work is supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (DOE). The computations were performed using the Molecular Sciences Computing Facility (MSCF) in the Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by the DOE's Office of Biological and Environmental Research (OBER) and located at PNNL.



**FIGURE 2.** S-S radial distribution function  $g(r)$  is indicative of a constrained structure of PFSA at low hydration level. The picture on the right, taken from a MD snapshot, shows hydronium ions linking pairs of sulfonate groups

This work benefited also from resources of the National Energy Research Scientific Computing Center (NERSC), which is supported by the Office of Science of the U.S. DOE.

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## Publications (including patents) acknowledging the grant or contract

1. Venkatnathan A., Devanathan R., and Dupuis M., "Proton Exchange Membrane under Low Hydration: Nanostructure and Hydronium Mobility from Atomistic Simulations", submitted to *J. Phys. Chem. C* (2007).

2. Devanathan R, Venkatnathan A, and Dupuis M, "Atomistic Simulation of Nafion Membrane: I. Effect of Hydration on Membrane Nanostructure", *J. Phys. Chem. B*, in preparation.
3. Glezakou V.A. and Dupuis M., "Thermochemistry of Perfluorosulfonic acid-water clusters at Low Hydration Level: Significance for Polymer Electrolyte Membranes", *Chem. Phys. Lett.*, in preparation.

## Invited and contributed presentations acknowledging the grant or contract

1. Dupuis M., "Proton Transfer and Transport in Complex Molecular Systems: Polymer Electrolyte Membranes", workshop on "Proton Solvation and Transport in Chemistry, Biology, and Materials Science: 200 Years After Grotthuss", G. Voth organizer, Washington D.C., June 2006.
2. Venkatnathan A., Devanathan R., and Dupuis M., "Atomistic Simulations of the Nanostructure and Proton Transport in Proton Exchange Membrane", poster, ACS National meeting, Chicago, March 2007.
3. Devanathan R., Venkatnathan A., and Dupuis M., "Atomistic and Mesoscale Simulations of Proton Exchange Membrane under Low Hydration", symposium on "Computational Electrochemistry for New Energies", ACS National meeting, Boston, August 2007.