

BES033. Charge Transfer, Transport, and Reactivity in Complex Molecular Environments: Theoretical Studies for the Hydrogen Fuel Initiative

Michel Dupuis, Ram Devanathan,
Nagesh Idupulapati
Chemical and Materials Sciences Division
Pacific Northwest National Laboratory
902 Battelle Blvd.
Mail Stop K1-83
Richland, WA 99352
Phone: (509) 375-2617; Fax: (509) 375-4381
E-mail: michel.dupuis@pnl.gov

DOE Program Officer: William S. Millman
Phone: (301) 903-5805
E-mail: william.millman@science.doe.gov

Subcontractors: Pacific Northwest National
Laboratory

Abstract, Progress Report and Future Directions

We have performed multi-scale simulations of proton transport, water percolation and membrane dynamics in a number of promising fuel cell membranes. Our work takes into account the membrane morphological changes with hydration level, but is also informed by detailed *ab initio* quantum chemical calculations. At the most fundamental scale, our simulations capture the quantum mechanical characteristics of proton transfer as a function of hydration level for models of existing and proposed membranes. This provides us with fundamental understanding of the role of acidic pendants in proton dissociation. At the next higher level, our simulations determine the changes in proton hopping as a function of hydration level using quantum hopping molecular dynamics (Q-HOP MD) that is parameterized based on quantum chemical calculations. We are also using quantum mechanics/molecular mechanics (QM/MM) simulations starting from equilibrated configurations generated by classical MD to examine combined proton and water molecule transport. At higher scales, we use classical MD with reactive and conventional force fields to compare changes in membrane morphology and water network percolation in hydrated Nafion[®], Dow, Hyflon, SPEEK and Sulfonyl-Imide-based novel membranes. We are also exploring structure and dynamics in ionic liquids, such as triflic acid and diethylmethyl amine to understand anhydrous membranes. These simulations provided an integrated understanding of the influence of acidity and water network percolation on conductivity of PEMs.

Ab initio electronic structure and dynamics of acidic pendants in PEM's: We have examined proton dissociation in acidic units that are the building blocks for several promising polymeric electrolyte fuel cell membranes. Minimum energy structures for four acidic moieties with clusters of up to 6 water molecules were determined using density functional theory at the B3LYP/6-311G** level starting from chemically rational initial configurations. The perfluoro sulfonyl imide acid group (CF₃CF₂SO₂NHSO₂CF₃) was observed to be the strongest acid, due to the substantial electron withdrawing effect of both fluorocarbon groups. The hydrophilic functional group (CH₃OC₆H₃OCH₃C₆H₄SO₃H) of sulfonated polyetherether ketone (SPEEK) membrane was found to be the strongest base with the acidic proton dissociation requiring the addition of six water molecules and the hydrated proton being more tightly bound to the conjugate base. Even though both perfluoro sulfonyl

Objectives

This theory program aims to apply modern theoretical and computational methods to advance our fundamental understanding of proton transfer, charge transport and reactivity in complex molecular environments. The focus of the effort is in proton exchange membranes (PEMs) for fuel cells and the characterization of the relationship between membrane nanostructure, local chemistry around acidic sites, proton transfer, and proton and small molecule transport in PEMs. The overall goal is to develop fundamental new understanding of polymer materials and ionic liquids along a path to revolutionize energy technology.

Technical Barriers

It is desirable for PEM fuel cells to operate above 120 °C to achieve high catalytic efficiency, avoid poisoning of Pt-based catalysts by CO, enhance the kinetics of electrochemical reactions, recover waste heat and reduce the complexity of the fuel cell. However, existing PEMs do not perform well above 90 °C, because they require water to maintain good proton conductivity. In addition, polymer membranes undergo structural, chemical, and mechanical degradation upon prolonged operation at elevated temperatures and low humidity conditions. Even at lower temperatures (80 °C), existing membranes suffer from water management and fuel crossover problems. Fundamental understanding of the factors affecting proton transport, mechanical properties, and chemical degradation is needed to optimize membranes for proton transport.

imides and sulfonic acids (hydrophilic functional groups for sulfonyl imide and Nafion[®] ionomers respectively) required only three water molecules to exhibit spontaneous proton dissociation, the largest possible solvent-separated hydronium ion was attained only for the sulfonyl imide moiety. These results provide a scientific basis for understanding the improved conductivity of perfluorinated sulfonyl imide-based membranes relative to that of the widely-used Nafion[®] membrane.

Water network percolation and proton hopping in Nafion membrane: We have used percolation analysis following classical MD simulations of Nafion[®] for a large number of hydration levels ($\lambda = 1, 3, 5, 7, 9, 11, 13.5$ and 20 water molecules per sulfonate groups) to examine water clustering, connectivity of clusters and persistence of spanning clusters as a function of hydration level in Nafion[®] membrane. We have also used quantum hopping (Q-HOP) molecular dynamics method to compute the mean residence times (MRTs), rate constants and activation energies for proton transfer. At low hydration levels ($\lambda \leq 5$), clusters of water molecules and hydronium ions are isolated from each other and proton residence time on a water molecule is about 220 ps at 300 K. The average number of clusters decreases from more than 25 for $\lambda = 3$ to fewer than 4 for $\lambda = 7$. Multiple SO_3^- groups confine the H_3O^+ ion. Vehicular proton transport is hindered by steric hindrance and long-range structural transport is not possible due to the lack of connectivity of H_2O molecules.

Water network percolation occurs between $\lambda = 5$ and $\lambda = 6$ in agreement with estimates based on infrared spectroscopy experiments. This threshold was determined based on multiple criteria. In fact, we have proposed a new criterion for detecting percolation based on the relative probabilities of finding water molecules in the smallest and largest clusters. Near the percolation threshold, clusters are linked from time to time by

mobile H_2O molecules, so that transient spanning clusters form and disappear. At high hydration levels ($\lambda \geq 9$), a persistent spanning cluster permeates the membrane and creates water channels along which the proton can hop. At high λ , the proton residence time on a H_2O molecule drops by two orders of magnitude from the value at low λ . At higher hydration, proton transfer is faster due to ease of solvation of the proton, whereas at higher temperatures, protons are more mobile because thermal effects generate a larger number of favorable proton transfer geometries. At high λ , the rate constants approach that of proton transfer in bulk water. The proton diffusion coefficient for $\lambda = 15$ at 300 K is about $1.1 \times 10^{-5} \text{ cm}^2/\text{s}$ in good agreement with experiment. The understanding of water percolation and dynamics of proton transfer generated by this work could help in the design of future polymer membrane materials that have lower uptake of water and yet offer faster proton transfer and transport.

Nanophase structural dynamics of phenylated sulfonated poly ether ether ketone (Ph-SPEEKK membrane): We used classical MD to model solvated Ph-SPEEKK membranes in the presence of hydronium ions. We characterized the nanophase structure and dynamics as a function of water content for $\lambda = 3.5, 6, 11, 25,$ and 40; where λ is the number of water molecules per sulfonyl group. Pair correlation function analyses reveal that the nanophase segregation increases with solvation. The water and hydronium ion diffusion coefficients also increase with λ . While the average number of hydrogen bonds between hydronium ions and sulfonyl groups are dramatically affected by the hydration level, their average lifetime remains constant. The membrane is found to be relatively rigid and its overall flexibility shows little dependency as a function of water content. Compared to Nafion[®], water and ion diffusions are considerably smaller at lower hydration levels at room temperature. However, at $\lambda = 25$ and 40 these coefficients are comparable to that of Nafion[®] at

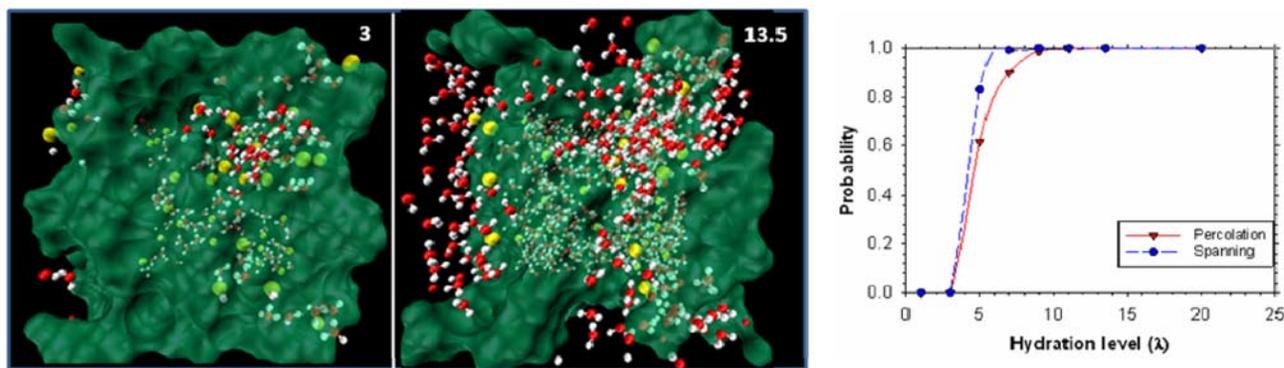


FIGURE 1. Perspective projection of H_2O molecules and H_3O^+ ions in Nafion for hydration levels of $\lambda = 3$ and 13.5. SO_3^- is shown as a large (yellow) bead. The backbone and pendant are shown as a transparent surface. Both percolation probability and spanning cluster formation probability reach almost 1.0 for $\lambda \geq 7$.

the same solvation levels. This study also indicates that solvent diffusion for Ph-SPEEK membranes at low hydration levels can be significantly improved at high temperatures.

Future directions include ab initio molecular dynamics of proton transport in model hydrated pendants and ionic liquid systems; extension of QM/MM simulations to novel membranes; and large scale massively parallel reactive force field simulations of the anode/electrolyte interface. The proposed work addresses several different length scales and represents the logical progression of effort from the work accomplished to date under this project.

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. 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.

Publications (including patents) acknowledging the grant or contract

1. Devanathan, R.; Venkatnathan, A.; Rousseau, R.J.; Dupuis, M.; Frigato, T.; Gu, W.; Helms, V. "Atomistic Simulation of Water Percolation and Proton Hopping in Nafion Fuel Cell Membrane", *Journal of Physical Chemistry B* (submitted).
2. Idupulapati, N.; Devanathan, R.; Dupuis, M. "Ab Initio Study of Hydration and Proton Dissociation For Various Acid-based Ionomer Membranes", *Journal of Physical Chemistry A* (submitted).
3. Devanathan, R. "Proton Exchange Membranes for Fuel Cells," *Encyclopedia of Inorganic Chemistry: Energy Production and Storage*, edited by Robert H. Crabtree, John Wiley & Sons, (to be published in 2010).
4. Devanathan, R. "Recent Developments in Proton Exchange Membranes for Fuel Cells," *Energy & Environmental Science* 1 (2008) 101-119.
5. Devanathan, R.; Venkatnathan, A.; Dupuis, M. "Atomistic Simulation of Nafion Membrane: I. Effect of Hydration on Membrane Nanostructure," *Journal of Physical Chemistry B* 111 (2007) 8069-8079.
6. Devanathan, R.; Venkatnathan, A.; Dupuis, M. "Atomistic Simulation of Nafion Membrane: II. Dynamics of Water Molecules and Hydronium Ions," *Journal of Physical Chemistry B* 111 (2007) 13006-13013.
7. Venkatnathan, A.; Devanathan, R.; Dupuis, M. "Atomistic Simulations of Hydrated Nafion and Temperature Effects on Hydronium Ion Mobility," *Journal of Physical Chemistry B* 111 (2007) 7234-7244.
8. Glezakou V.A.; Dupuis M.; Mundy, C.J. "Acid-Base Equilibria in Clusters and Their Role in Proton Exchange Membranes: Computational Insight", *Physical Chemistry Chemical Physics* 9 (2007) 5752-5760.

Invited and contributed presentations acknowledging the grant or contract

1. Devanathan, R (Invited Speaker) "Water Network Percolation and Proton Hopping in Nanopores of Nafion Membrane." Workshop on Molecular Simulation of Transport Phenomena in Chemistry and Biology 2009, Saarbrucken, Germany, October 2009.
2. Devanathan, R (Invited Speaker) "Proton transport in complex molecular environments" Workshop on Structure & Transport in Complex Systems, Saarbrucken, Germany, Oct 2009.
3. Dupuis, M. (Invited Speaker) Colloquium, Department of Physics, (Computational Solid State Theory and Materials Science group), MTU, Houghton, MI, Fall 2009.
4. Dupuis, M. (Invited Speaker) Colloquium, Department of Materials Science and Engineering, University of North Texas, Denton TX, Fall 2009.
5. Dupuis, M. (Invited Speaker) "Proton Exchange Membrane under Low Hydration Level: Insights from Atomistic Simulations and Electronic Structure Computations", Conference on Theory and Applications of Computational Chemistry (TACC), Shanghai, China, Sept. 2008.
6. Dupuis, M. (Invited Speaker) "Proton Exchange Membrane under Low Hydration Level: Insights from Atomistic Simulations and Electronic Structure Computations", Symposium on Materials for Energy Conversion, 2008 CSC meeting in Edmonton, Canada, May 2008
7. Dupuis, M. (Invited Speaker) "Charge Transfer, Transport, and Reactivity in Complex Molecular Environments", Hiroshima University, Hiroshima, Japan, Jan. 2008.
8. Dupuis, M. (Invited Speaker) "Charge Transfer, Transport, and Reactivity in Complex Molecular Environments: Theoretical Studies for the Hydrogen Fuel Initiative", National Institute of Advanced Industrial Science and Technology AIST, Tsukuba, Japan, Jan. 2008.
9. Dupuis, M. (Invited Speaker) "Proton Exchange Membrane under Low Hydration Level: Insights from Atomistic Simulations and Electronic Structure Computations", 58th Annual Meeting of the International Society of Electrochemistry, Banff, Canada, Sept. 2007.