V.G.11 Fluoroalkylphosphonic-Acid-Based Proton Conductors

Stephen Creager (Primary Contact),
Darryl DesMarteau
Clemson University (CU)
Hunter Lab
Department of Chemistry
Clemson, SC 29634
Phone: (864) 656-4995; Fax: (864) 656-6613
E-mail: screage@clemson.edu

DOE Technology Development Manager:
Terry Payne
Phone: (202) 586-9585; Fax: (202) 586-9811
E-mail: Terry.Payne@hq.doe.gov

DOE Project Officer: Reg Tyler
Phone: (303) 275-4929; Fax: (303) 275-4753
E-mail: Reginald.Tyler@go.doe.gov

Technical Advisor: John Kopasz
Phone: (630) 252-7531; Fax: (630) 972-4405
E-mail: kopasz@anl.gov

Contract Number: DE-FG36-06GO16031

Subcontractor:
University of Utah, Salt Lake City, UT

Start Date: April 2006
Projected End Date: March 2011

Objectives

- Synthesize and characterize new proton-conducting electrolytes based on the fluoroalkylphosphonic acid functional group; and
- Perform quantum chemistry and molecular dynamics simulation studies of fluoroalkylphosphonic acid-based electrolytes.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(C) Performance

(E) System thermal and water management

Technical Targets

The following technical targets from Table 3.4.11, Membranes for Transportation Applications, from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, as revised April 27, 2007, are relevant to this project:

- Membrane ionic conductivity >0.10 S/cm at <120°C and water partial pressure of 1.5 kPa for transportation applications (2010 target)
- Area specific resistance <0.02 ohm cm^2 under similar conditions

Accomplishments

- Continued with synthesis and characterization of fluoroalkyl phosphonic and difluoroalkyl phosphinic acid (FPA) model compounds. Bis-trifluoromethylphosphinic acid ($(CF_3)_2PO(OH)$) was found to have higher anhydrous ionic conductivity than trifluoromethane sulfonic (triflic) acid.
- Synthesized two new trifluorovinylether (TFVE) monomers having bis(fluoroalkyl)phosphinic acid group, and prepared ionomer membranes from these monomers by co-polymerization with tetrafluoroethylene (TFE).
- Measured ionic conductivity of select membrane samples at select temperatures and variable relative humidity.
- Density functional theory (DFT)-based Born-Oppenheimer molecular dynamics (BOMD) simulations have been performed on fluoroalkyl phosphonic model compounds. BOMD simulations of difluoroalkyl phosphinic acid model compounds are underway.
- Quantum chemistry studies of multiple fluoroalkylphosphonic acid complexes with water have been completed.
- Classical molecular dynamics simulations have been performed on phosphoric acid, fluoroalkyl phosphonic and difluoroalkyl phosphinic acid model compounds as a function of temperature.

✧ ✧ ✧ ✧ ✧

Introduction

This research is focused on synthesis, characterization, and computer simulations and quantum chemistry studies of proton conduction in a family of fluoroalkylphosphonic-acid-based combbranch ionomers and related small molecules which comprise liquid-phase electrolytes. The target materials are excellent candidates for use in high-temperature (120°C) low relative humidity (25-50% RH) polymer electrolyte fuel cell (PEFC) power sources for transportation applications. The target ionomers will contain no water-soluble components therefore they will be able to withstand repeated contact with liquid water, as is inevitable in a transportation PEFC that will inevitably experience frequent start-up and shut-down cycling.

Approach

We are following a dual approach involving synthesis and characterization of FPA electrolytes focusing on ion conduction under a wide range of conditions of temperature and water content (humidity), coupled with computer modeling work that will help explain whether and how proton transport can be facilitated by a Grotthuss-like hopping mechanism, and how the membrane morphology/cluster structure is important in proton transport. The synthesis part focuses on small-molecule FPAs, TFVE FPA monomers, and FPA ionomer membranes prepared by co-polymerization of TFVE monomer with TFE. Characterization focuses on molecular structure and ionic conductivity at variable temperature and water content.

The modeling portion of the project is expected to provide insight into material structure and proton transport and ultimately guide synthesis of novel FPA-based ionomers. Quantum chemistry calculations of FPA/water clusters will provide water structure, the number of waters needed to deprotonated FPA acid and binding energies. DFT-based BOMD simulations focus on proton transport occurring in small simulated systems (tens of small FPA oligomers) during ~10 ps simulations. Classical molecular dynamics simulations without explicit proton hopping provide transport properties and structural information such as hydrogen bonded network occurring larger simulation cells and routinely access tens of nanosecond simulation times. Molecular dynamics (MD) simulations utilizing explicit proton hopping (multi-state empirical valence bond and Q-HOP) will focus on FPA conductivity and proton transport.

Results

Part 1. Synthesis and Characterization of New Proton-Conducting Electrolytes based on the Fluoroalkylphosphonic Acid Functional Group. Figure 1 presents conductivity data at variable temperatures and water content for two FPA model compounds having one and two trifluoromethyl groups bonded to phosphorous respectively. In all cases conductivities are quite high (well above 100 mS/cm) when as little as three waters per acid group are present. Of special note are the data for the $(CF_3)_2PO(OH)$ model compound (Figure 1, right), for which conductivity in the absence of any added water was higher than that of triflic acid (data not shown, but available from Giner, Inc. in previous DOE Hydrogen Program reports). Data from the Fiscal Year 2007 report for the present project showed that conductivity is also affected by the size of the fluoroalkyl groups, albeit in complex ways. These data indicate that FPAs in general are suitable for use as protogenic groups in ionomers.

Several new FPA-based ionomers were prepared this year. Sample P-18, for which the structure is shown at top right of Figure 2, is of special interest given the positive results on model compound $(CF_3)_2PO(OH)$. Details on the preparation and characterization of this and several related ionomers are provided in our presentation from the 2008 Hydrogen Annual Merit Review. In our hands at Clemson, conductivities for the P-18 FPA ionomer are comparable to, and in some cases slightly better than, that of Nafion®, at 100% RH. Data from Bekktech for sample P-18 are presented in Figure 2, and they tell a different story, with conductivity at 30°C and 80% RH being substantially less than that for Nafion®. We believe this finding reflects several things, including some effects possible detrimental effects of pre-treatment that may have resulted in Al^{3+} incorporation into the polymer and some possible loss of acid group. These problems are thought to not have affected samples studied at CU (because slightly different preparation protocols were followed) and they were not detected until after the samples were sent for analysis. Ongoing work is expected to result in improved performance.

Part 2. Quantum Chemistry and Simulation Studies of FPA Model Compounds. A combination of quantum chemistry calculations and a number of simulation approaches has been utilized to obtain improved understanding of FPA-based model compounds. Analysis of the mean square displacements of protons and oxygen atoms from DFT-based BOMD simulations of 27 $CF_3PO(OH)_2$ have clearly shown a significantly faster diffusion of proton compared to oxygens (Figure 3). This finding is characteristic of Grotthuss proton transport present in anhydrous $CF_3PO(OH)_2$. Ongoing studies are focused on other acids, longer times, samples containing some water, and eventually, structures more closely related to phase-separated ionomers.

Classical MD simulations have been performed on a serious of perfluoroalkane phosphonic acid and phophinic acid oligomers as a function of temperature without explicit proton transfer included in the model. MD simulations predicted that the self-diffusion coefficients of $CF_3PO(OH)_2$ and $(CF_3)_2POOH$ are faster than the self-diffusion coefficient of orthophosphoric

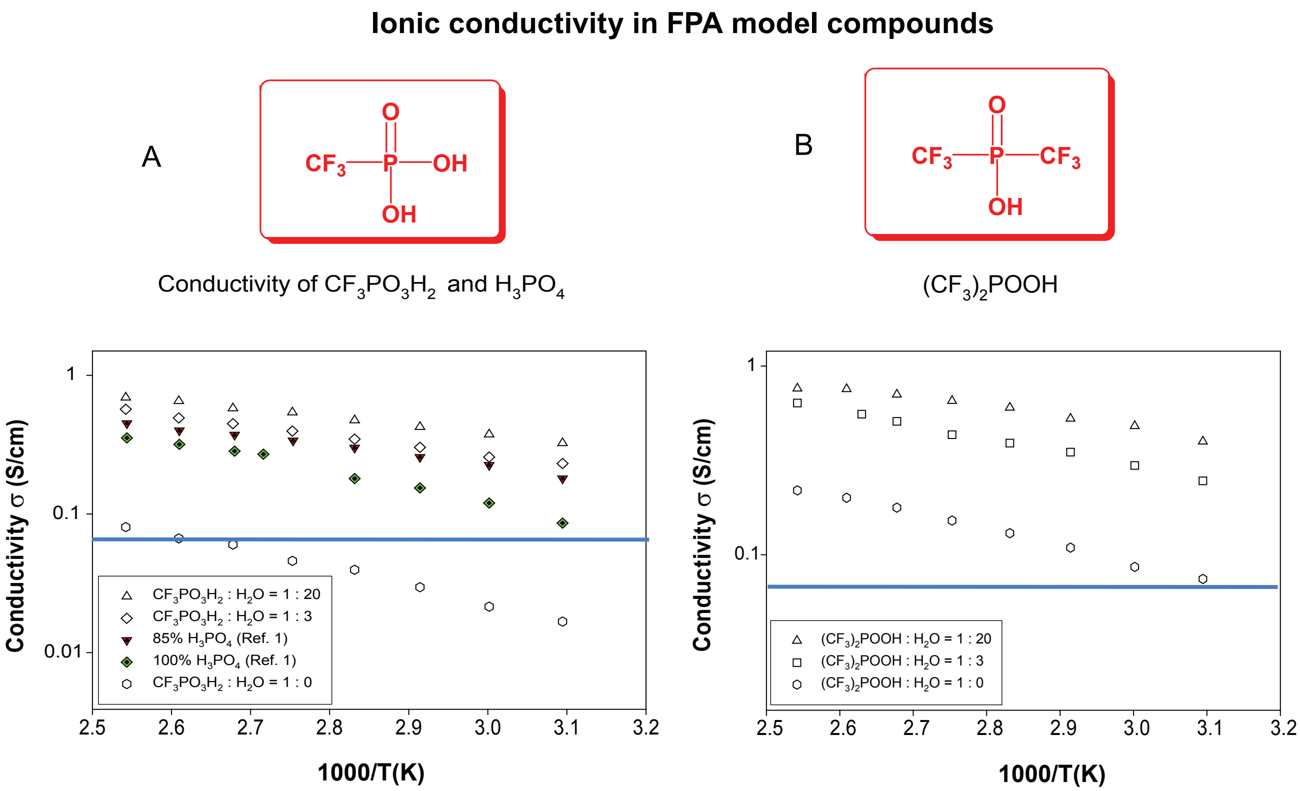

FIGURE 1. Ionic conductivity of (A) trifluoromethylphosphonic acid; and (B) bis(trifluoromethyl)-phosphinic acid at variable temperature and with variable amounts of water added to the sample. Blue lines show DOE conductivity milestone (0.07 S cm-1) for year 2 for ionomers. (Chin and Chang, J Appl Echem 19, 95 (1989)).

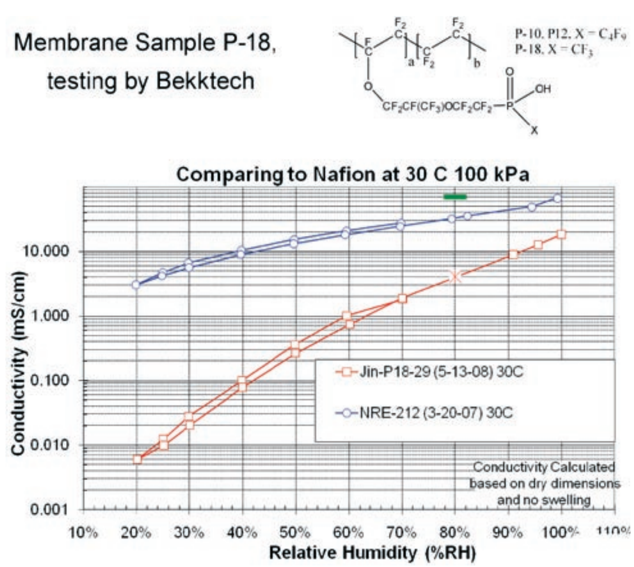

FIGURE 2. Ionic conductivity data for ionomer P-18, from Bekktech, and 30°C at variable RH. Data for Nafion® NRE-212 are shown for comparison.

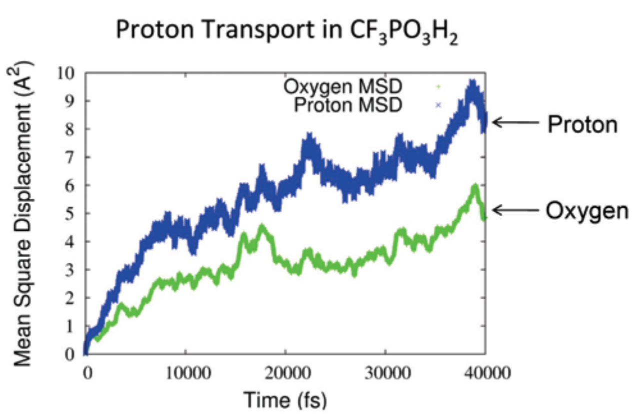

FIGURE 3. Results of a DFT-based BOMD simulation focusing on proton and oxygen transport rates in the trifluoromethyl phosphonic acid $(CF_3)_2PO(OH)_2)$ model compound. Blue - proton mean square displacement (MSD), green - oxygen MSD. Greater proton MSD suggests action of Grotthuss-style proton hopping. Greater proton MSD suggests action of Grotthuss-style proton hopping. Autoionization exceeds 20 percent which is also consistent with Grotthuss-style proton hopping.

acid. Interestingly, we observe good agreement between simulation predictions and experimental data for the orthophosphoric acid published by Kreuer group (1993). Increasing the size of the perfluoroalkyl tail decreases acid self-diffusion coefficient but it still remains within a factor of 2-3 of PO_4H_3 self-diffusion coefficient.

In addition to analysis of transport properties, we performed a detailed analysis of the topology of the hydrogen bonded network and distribution of acid groups. Figure 4 presents an example of acid distribution for two acids $C_8F_{19}PO(OH)_2$ and $(C_4F_9)_2POOH$ illustrating that for the same equivalent molecular weight acids groups segregate and form a percolating hydrogen bonded network in $C_8F_{19}PO(OH)_2$, while no long range percolating hydrogen bonded network has been formed for $(C_4F_9)_2POOH$. This finding indicates the structural arrangement needed for the Grotthuss proton transfer is present in $C_8F_{19}PO(OH)_2$ and is largely absent in $(C_4F_9)_2POOH$. These simulations are consistent with experimental observations reported last year of relatively low conductivity in bis(perfluorobutyl)phosphinic acid FPA samples.

Conclusions and Future Directions

Conductivity studies on small-molecule FPA model compounds will focus on lower water contents and on mixtures of FPAs with superacids (e.g. sulfonimide acids) as models for terpolymer ionomers. A collaboration with Giner, Inc. was initiated to measure water uptake by FPA liquids and ionomers from various RH environments using a microbalance method/instrument of their development. These data will help to correlate studies at variable water content, to studies at variable RH. Pulse field gradient nuclear magnetic resonance studies on FPAs will be pursued to measure atom self-diffusion coefficients to evaluate Grotthuss conduction and validate results of MD and BOMD simulations. Ongoing and future BOMD and MD simulations will focus on model acid samples containing various fraction of water as well as variation of the equivalent molecular weight of FPA model compounds.

Work will continue aimed at refining monomer and ionomer synthesis to give better materials, meaning materials having higher molecular weight, greater homogeneity (less "blockiness"), and higher ion-exchange capacities while still retaining mechanical properties. This work will be tightly coupled with ionic conductivity measurements to be performed both

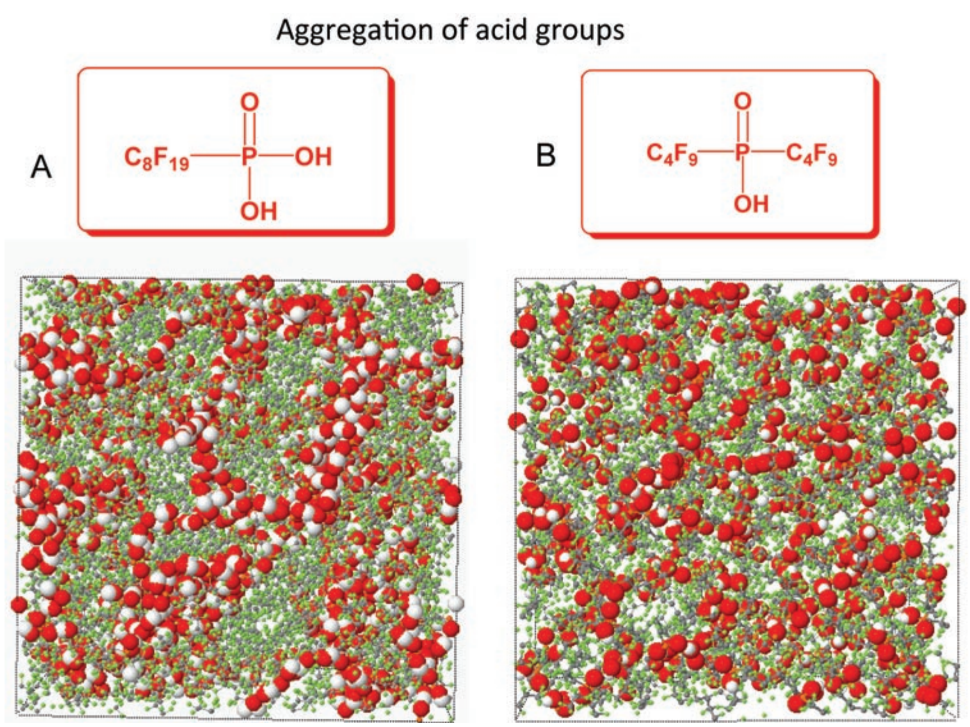

FIGURE 4. Results of classical MD simulations which reveals the development of domain structures in samples of liquid $C_8F_{19}PO(OH)_2$ (A) but not in $(C_4F_9)_2POOH$ acid (B). Oxygen and hydrogen atoms are highlighted in red and white, and enlarged.

in-house under variable temperature/RH conditions, and also by Bekktech. These data will be useful for interpreting conductivity data, and also for validating computer models.

FY 2008 Publications/Presentations

1. Creager, S., "New electrolytes for electrochemical power sources", Potter's Lodge meeting on electrochemistry, August 2007.

2. Creager, S., "Fluorinated electrolytes for batteries and fuel cells" Southeast Regional ACS meeting, Greenville SC, October 2007.

3. DesMarteau, D., "Proton Exchange Membranes for Fuel Cells" Sharif, I.; Rettenbacher, A.; DesMarteau, D.D. Abstracts, 59th Sotheast Regional Meeting of the ACS, Greenville, SC, 2007.

4. DesMarteau, D., "High Temperature Proton-Conducting Fluoropolymer Electrolytes for PEM Fuel Cells" Rettenbacher, A.; Creager, S.; DesMarteau, D.D.; Sharif, I.; Smith, D. W. Abstracts, 59th Southeast Regional Meeting of the ACS, Greenville, SC, 2007.

5. DesMarteau, D., "Synthesis and Characterization of a BisperfluoroalkylPhosphonic Acid-Based Polymer and Membrane" Jin, L.-M.; Zhuang, D.-Q.; Hickman, T., Creager, S.; DesMarteau, D.D. Abstracts, 59th Southeast Regional Meeting of the ACS, Greenville, SC, 2007.

6. Herath H, Proton Transport in Fluoroalkylphosphonic Acid Electrolytes" Herath, M.; Rettenbacher, A.; Creager, S.; DesMarteau, D.D. Poster presentation, 59th Southeast Regional Meeting of the ACS, Greenville, SC, 2007.

7. Borodin, O.; Lui, Q.; Smith, G. D. "Quantum Chemistry and MD Simulation Studies of Fluorinated Ionomers" 212th ECS Meeting, October 7 - October 12, 2007, Washington, D.C.

8. Lui, Q.; Borodin, O.; Smith, G.D. "The Hydration And Proton Dissociation In The Interaction Between Fluorocarbon-Based Phosphonic Acid And Water Clusters" The 2007 Annual AIChE Meeting, Salt Lake City, UT (11/03-11/09).

9. Voth, G. "Molecular Dynamics Simulation of Excess Proton Solvation and Transport in Polymer Electrolyte Membranes", Physical Chemistry Division Symposium on Computational Electrochemistry for New Energy, American Chemical Society Meeting, Boston, Massachusetts, August, 2007.

10. Voth, G. "Proton Solvation and Transport in Aqueous and Biomolecular Systems: Insights and Surprises Revealed by Computer Simulation", Physical Chemistry Division Seminar, Iowa State University, Ames, Iowa, November, 2007.

11. Voth, G.; "Proton Solvation and Transport in Aqueous and Biomolecular Systems: Insights and Surprises Revealed by Computer Simulation", International Meeting on Diffusion, Solvation and Transport of Protons in Complex and Biological Systems, Eilat Bay, Israel, January, 2008.

12. Voth, G. "Proton Solvation and Transport in Aqueous Systems: Insights and Surprises from Molecular Simulation", UCSB Theory Lecture, University of California Santa Barbara, Santa Barbara, California, March, 2008.