

V.M.16 Fluoroalkylphosphonic Acid-Based Proton Conductors

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Objectives

- Synthesize and characterize new proton-conducting electrolytes based on the fluoroalkylphosphonic acid functional group.
- Create and apply new computer models to study protonic conduction in 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 (MYPP):

- (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 MYPP, as revised April 27, 2007, are relevant to this project:

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

Accomplishments

- Synthesized gram to multigram quantities of three small-molecule fluoroalkyl and difluoroalkyl phosphonic acids (FPAs) and two trifluorovinyl ether (TFVE) fluoroalkyl phosphonic acid monomers, as indicated in Figure 1.
- Measured ionic conductivity of small-molecule FPAs at variable temperature and water content.
- Synthesized ionomers via co-polymerization of the two TVFE monomers with tetrafluoroethylene (TFE).

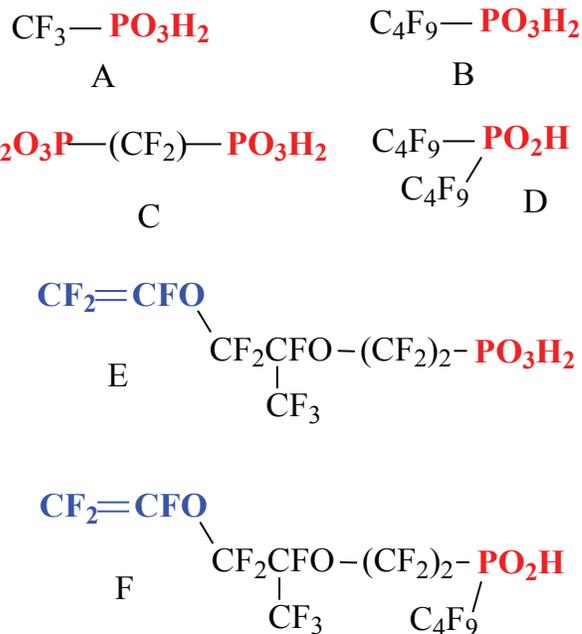


FIGURE 1. Structures of Selected FPA Model Compounds and TFVE Monomers

- Quantum chemistry studies of fluoroalkylphosphonic acid/water complexes have been completed with a focus on acid deprotonation as a function of acid hydration number.
- Classical force fields for simulations of fluoroalkylphosphonic acids have been developed.
- Advances have been made in the Multi-State Empirical Valence Bond (MS-EVB) method of simulating proton transport processes. These advances make possible high-efficiency simulations of proton transport in polymer electrolyte membranes (PEMs) under the target relative humidity and temperature conditions.



Introduction

This research is focused on synthesis, characterization, and computer simulations of proton conduction in a family of fluoroalkylphosphonic acid-based comb-branch ionomers and related small molecules which comprise liquid-phase electrolytes. The target materials are excellent candidates for use in high-temperature (120°C) low-humidity (25-50% relative humidity [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 startup and shutdown 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.

Molecular modeling part of the project is expected to provide insight into material structure and proton transport and ultimately guide synthesis of novel FPA-based ionomers. Development of accurate quantum chemistry-based force fields and novel simulation methodologies for handling proton transport are

needed in order to achieve this goal. The existing MS-EVB methods are computationally very expensive to efficiently simulate proton transport in relatively dry materials with very high proton concentrations expected to occur at (RH=20% at 120°C). Recently developed “Self Consistent Iterative” approach to MS-EVB (denoted as SCI-MS-EVB) can efficiently handle explicit proton transport in simulations with more than one proton but breaks down at high proton concentrations. During the first year of this project we have developed and implemented a novel methodology for multiproton MS-EVB simulations. In this methodology the well separated protons are treated through the SCI approach, however, as two or more protons get too close together, they are dynamically combined into a multiproton supercomplex described by a single EVB matrix. This dynamic approach to defining EVB complexes makes realistic MS-EVB simulations of very high proton density environments computationally feasible. In addition to methodological advances, quantum chemistry studies of model FPA/water clusters have been performed

Results

Part 1. Synthesis and characterization of new proton-conducting electrolytes based on the fluoroalkylphosphonic acid functional group.

Figure 1 presents structures of three FPA model compounds and two TFVE FPA monomers that were synthesized over the past year. Compounds A, B, C and E are monofluoroalkylphosphonic acids, as was originally planned for the project. Compounds D and F are difluoroalkylphosphonic acids. These were studied because in preliminary studies seeking to co-polymerize TFVE monomers with TFE, monomer E did not polymerize well but monomer F did. We therefore decided to deviate from the original project plan to investigate the dialkylphosphonic acids.

Conductivity data were acquired for liquid FPA model compounds and monomers at variable temperature with variable amounts of water added. Figure 2 presents some representative results. Trifluoromethylphosphonic acid (compound A) is highly conductive both without water and with a small amount (3 equivalents) and a large amount (20 equivalents) of water added. Compound C is less conductive, which may reflect its higher viscosity. Compound E is still less conductive which could reflect high viscosity and also low acid weight percent. Conductivities always increased with increasing temperature, and also with increasing water content.

Part 2. Quantum chemistry and simulation study of model compounds of fluoroalkylphosphonic acid-based electrolytes. Quantum chemistry calculations have been performed on trifluoromethylphosphonic acid (TFMPA) interacting with up to 6 water molecules in order to understand the structure of the hydrogen

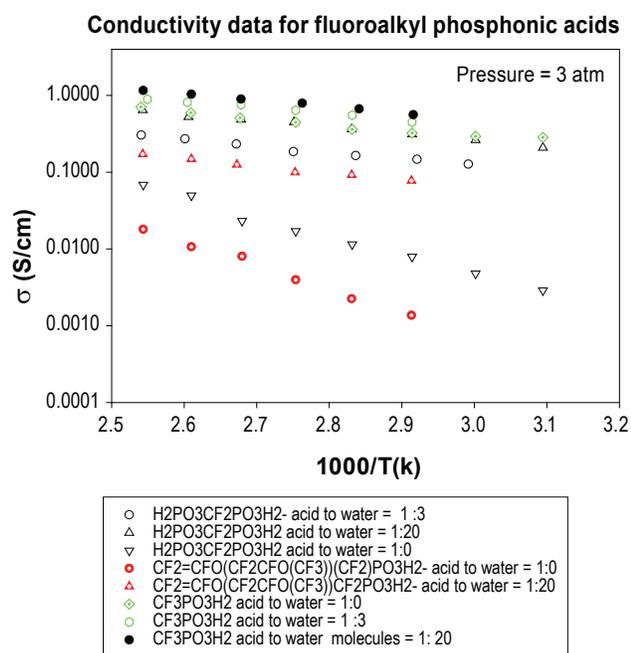
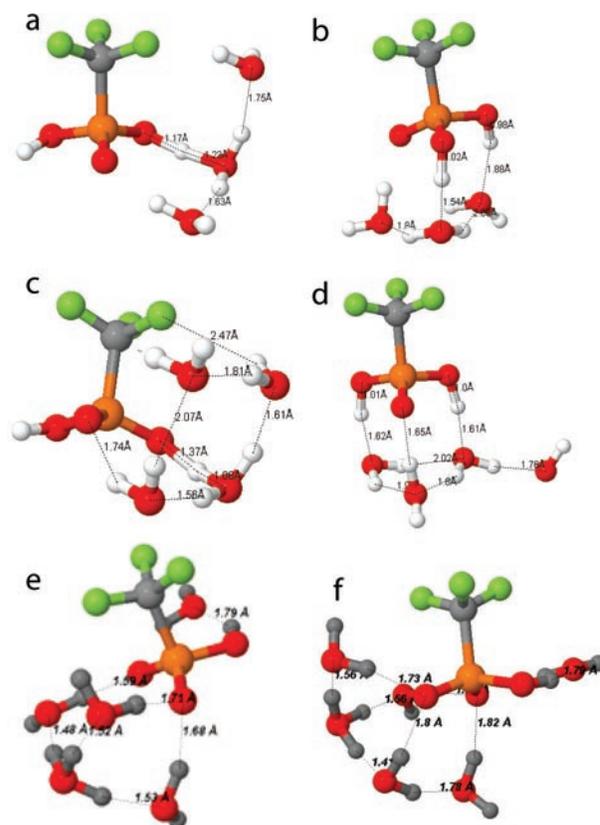


FIGURE 2. Selected Conductivity Data for FPAs with Variable Amounts of Water Added to the FPA Samples in Liquid Phase

bonding network formed around TFMPA. Figure 3 illustrates some of the results of these calculations. No proton dissociation is observed if TFMPA is complexed with one or two water molecules. Addition of the third water to TFMPA results in a proton being shared between TFMPA oxygen and oxygen of water as shown in Figure 3 complex a. Addition of the fourth water leads to TFMPA deprotonation as shown in Figure 3 complex c. Further addition of water leads to the excess proton being located in the second solvation shell of TFMPA as shown in Figure 3 complexes e, f. Figure 3 also demonstrates that formation of a good hydrogen bonding network is essential to TFMPA deprotonation. For example, hydrogen bonding in complexes b and d in Figure 3 significantly deviates from the favorable hydrogen bonding arrangement with the $O_w \dots H_w - O_w$ angle being close to 180 degrees resulting in both protons being localized at the TFMPA for complexes b and d compared to complexes a and c that have a shared proton and a deprotonated acid due to formation of a more favorable hydrogen bonding network. A minimal number of waters needed to deprotonate TFMPA is four, which is one water molecule higher than the number of waters needed to deprotonate triflic acid previously found by Paddison. The table next to Figure 3 shows water binding energies to TFMPA. Incremental binding energies were found in a range of 9.3 to 13 kcal/mol and are only weakly dependent on the hydration number.



Complex	ΔE^a (kcal/mol)	$r(\text{POH} \dots O_w - H_w)^b$ (Å)	$r(\text{POH} \dots O_w - H_w)^b$ (Å)
FPA		0.96	
FPA + H ₂ O	-11.0	1.0	1.67
FPA + 2 H ₂ O	-20.8	1.04	1.5
a FPA + 3 H ₂ O	-31.8	1.17	1.23
b FPA + 3 H ₂ O	-33.8	1.02	1.54
c FPA + 4 H ₂ O	-41.4	1.01	1.62
d FPA + 4 H ₂ O	-43.2	1.37	1.08
e FPA + 5 H ₂ O	-52.6	2 nd solv. shell	
f FPA + 6 H ₂ O	-64.7	2 nd solv. shell	

^a Binding energy ($\Delta E = E^{\text{complex}} - E^{\text{acid}} - nE^{\text{water}}$) calculated using mPW1PW91 density functional and aug-cc-pvDz basis set.

^b O_w and H_w denote oxygen and hydrogen atoms of water, respectively.

FIGURE 3. Selected Results from Quantum Chemistry Studies of Trifluoromethylphosphonic Acid/Water Clusters

Quantum chemistry investigation of two TFMPA molecules hydrated with up to eight water molecules are currently underway. A barrier to anhydrous (excess) proton transport in a TFMPA dimer has also been studied using ab initio quantum chemistry calculations. Classical force fields for simulations of model FPA/water mixtures have been developed.

Conclusions and Future Directions

Work in progress in the synthesis and characterization area will focus on synthesis of new FPAs and larger amounts of the FPAs in Figure 1, and on optimization of polymerization reactions involving TFVE monomers in Figure 1, including a focus on the bis(fluoroalkyl)phosphonic acids which have been little studied before now. Ionomers that form membranes will be evaluated with respect to conductivity under the DOE target conditions. In addition, studies by pulsed-field-gradient nuclear magnetic resonance (NMR) and by quasielastic neutron scattering (QENS) are planned to evaluate proton transport rates in liquid electrolytes. These data will be useful for interpreting conductivity data, and also for validating computer models.

With the necessary methodological work complete, SCI-MS-EVB/MS-EVB hybrid simulations of proton transport in FPA-based PEM materials can be carried out. Indeed, such simulations are now under way. As described above, these simulations hold promise for informing the design of more efficient PEM materials. These simulations are expected to begin bearing useful data in the very near term.

FY 2007 Publications/Presentations

1. Borodin, O.; Smith, G. D. "Quantum Chemistry Studies of Fluorophosphonic Acid-Water Clusters and Initial MD Simulations of Proton Transport" Fuel Cells 2007, February 18-21, 2007, Asilomar, California.
2. Creager, S. "Proton transport in fluorosulfonimide and fluoroalkylphosphonic acid ionomer electrolytes" Department of Energy Sponsored Workshop: Proton Solvation and Transport in Chemistry, Biology, and Materials Science: 200 Years After Grothuss, Herndon, Virginia, June 2006.
3. DesMarteau, D. "Some approaches towards higher-temperature PEMs Using fluorosulfonimide and fluoroalkylphosphonic acid ionomers" Fuel Chemistry Division Symposium on Fuel Cell Chemistry and Operation, National American Chemical Society Meeting, San Francisco, California, September, 2006.
4. Voth, G. "Molecular Dynamics Simulation of Excess Proton Solvation and Transport in Polymer Electrolyte Membranes," Symposium of Computer Modeling in Electrochemistry, National Meeting of the Electrochemical Society, Denver, Colorado, May, 2006.
5. Voth, G. "Solvation and Transport of Excess Protons in Aqueous, Biomolecular, and Materials Systems," Department of Energy Sponsored Workshop: Proton Solvation and Transport in Chemistry, Biology, and Materials Science: 200 Years After Grothuss, Herndon, Virginia, June 2006.
6. Voth, G. "Molecular Dynamics Simulations of Proton Transport in Polymer Electrolyte Membranes," Gordon Conference on Fuel Cells, Bryant College, Rhode Island, July 2006.
7. Voth, G. "Molecular Dynamics Simulation of Excess Proton Solvation And Transport in Polymer Electrolyte Membranes," Fuel Chemistry Division Symposium on Fuel Cell Chemistry and Operation, National American Chemical Society Meeting, San Francisco, California, September 2006.
8. Voth, G. "Molecular Dynamics Simulation of Excess Proton Solvation and Transport in Polymer Electrolyte Membranes, Electrochemistry Gordon Conference, Ventura, California, January 2007.