

V.D.7 Fluoroalkylphosphonic-Acid-Based Proton Conductors

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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 $<120^{\circ}\text{C}$ 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

- Completed synthesis and characterization of fluoroalkyl phosphonic and difluoroalkyl phosphinic acid (FPA) model compounds.
- Measured proton conductivity of FPA and other (fluoroalkyl-sulfonic and -carboxylic) acid model compounds under dry (anhydrous) and wet (variable number of waters per acid) conditions. FPAs show highest anhydrous conductivity of all model acids tested.
- Measured $^1\text{H}^+$ and ^{19}F self-diffusion coefficients for neat acids by pulsed-field gradient-nuclear magnetic resonance (PFG-NMR). Higher diffusivity for $^1\text{H}^+$ indicates that proton hopping occurs in FPAs but not for other acids.
- Correlations of conductivity and diffusivity with viscosity support this conclusion.
- ^{31}P NMR spectra reveal absence of pyrophosphates in neat FPA samples, suggesting that FPA dehydration does not occur to any appreciable extent.
- Born-Oppenheimer Molecular Dynamics (BOMD) and Q-HOP MD (a molecular dynamics simulation that includes quantum chemistry calculations) simulations support the conclusion that proton hopping occurs in neat FPA samples but not in other model acids.
- Simulations also show domain/proton transport network formation in some FPA samples but not others. Domains are small and incomplete in samples with a low mass fraction of acid and a high mass fraction of fluoroalkyl groups.
- Continued synthesis of FPA ionomers having a range of structures including some with protecting groups to enable processing as membranes prior to deprotection to make acids.

- Imaged ionomer domain structure by transmission electron microscopy (TEM) with Pb^{2+} staining; difluoroalkyl phosphonic acid ionomers shown to have smaller protonic domains than fluoroalkyl phosphonic acid ionomers.
- Conductivity values for FPA membranes were measured and are below milestones but are steadily improving.



Introduction

This research is focused on synthesis, characterization, and computer simulation and quantum chemistry studies 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) 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 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, trifluorovinyl ether (TFVE) FPA monomers, and FPA ionomer membranes prepared by co-polymerization of TFVE monomer with tetrafluoroethylene. 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 deprotonate FPA acid and binding energies. Density functional theory-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 bonding networks occurring in larger simulation cells and routinely access tens of nanosecond simulation times. Molecular dynamics (MD) simulations utilizing explicit proton hopping (MS-EVB and Q-HOP) will focus on FPA conductivity and proton transport.

Results

Figure 1 presents anhydrous conductivity data for FPA and other fluoroalkyl model acid compounds over a range of temperatures from 50 to 120°C . Conductivities are high for all acids except the carboxylic acid, however they are highest for the two FPA compounds. Viscosity measurements on the model compounds (data not shown) reveal that the FPA compounds have the highest viscosity, but also the highest conductivity. This is a counterintuitive result which strongly suggest a role for structure diffusion (i.e. proton hopping) in the FPA model compounds, but not in any of the other model compounds. Measurements were also acquired on samples having various amounts of water intentionally added (data not shown). In general, and as expected from prior work, adding water to acid samples always increased conductivity, by a combination of promotion of proton dissociation, proton hopping in the water phase, and lowering of viscosity.

Structure diffusion/proton hopping in neat acids can be quantified by independently measuring the self-diffusion coefficients for the acidic proton and the conjugate base. Such a measurement can be made by PFG-NMR spectroscopy of ^1H and ^{19}F self-diffusion coefficients for fluoroalkyl-substituted model acid compounds. Table 1 presents data acquired in this manner for all the model compounds studies in this work. The highlighted areas show the ratio of proton to fluorine self-diffusion coefficients; a ratio above 1

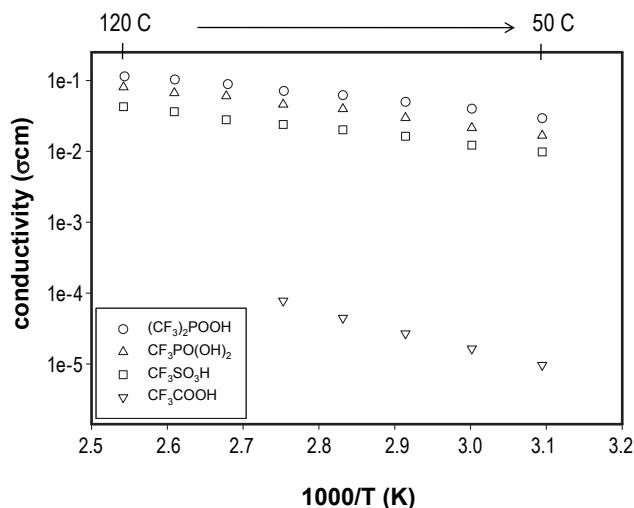


FIGURE 1. Anhydrous conductivity data for FPA and other fluoroalkyl model acid compounds over a range of temperatures from 50 to 120°C .

TABLE 1. Proton and fluorine self-diffusion coefficients for neat samples of fluoroalkyl-substituted acid model compounds obtained from PFG- NMR experiments (left portion of table) and from Q-HOP computer simulations (right portion of table).

Compound	Experiments; at 85°C			Simulation; 85°C	
	$10^{10}D(H_{OH})$	$10^{10}D(F_{Rf})$	$D(H_{OH})/$ $D(F_{Rf})$	$10^{10}D(H_{CF_3})$	$D(H_{OH})/$ $D(F_{Rf})$
$CF_3PO(OH)_2$	1.12	0.50	2.25	0.98	2.1
$(CF_3)_2POOH$	9.47	5.99	1.58	--	--
CF_3SO_3H	10.8	10.7	1.00	--	--
CF_3COOH	33.0	33.0	1.00	--	--
$C_4F_9PO(OH)_2$	0.26	0.14	1.94	--	--
$C_4F_9SO_3H$	4.87	4.87	1.00	--	--
$(C_4F_9)_2PO(OH)$	0.14	0.12	1.17	--	--

indicates a contribution from proton hopping/structure diffusion to proton transport. Ratios above 1 were obtained only for the FPA acids; fluoroalkyl-sulfonic and -carboxylic acids showed no evidence of proton hopping. These results suggest that ionomers containing high concentrations of FPA groups could have high conductivity under conditions of low water availability.

Table 1 also includes a column showing a calculated ratio of proton to fluorine self-diffusion coefficient for one model acid, $CF_3P(O)(OH)_2$. The magnitude of the fluorine self-diffusion coefficient from the Q-HOP simulation agrees with experiment to within a factor of

two, and the ratio of proton to fluorine self-diffusion coefficient is in excellent agreement with experiment. This finding validates the model and suggests that it could be used with other structures to predict proton hopping rates for new structures not yet synthesized.

Figure 2 presents structures for several FPA-containing ionomers that were synthesized and studied in the reporting period. The compounds in red squares were studied in particular depth, including measurements of conductivity for membrane samples at variable temperatures and relative humidities. Of particular note are compounds P-26, P-27 and P-29, which have a hydrolyzable protecting group on one of the FPA acid groups. Ionomers with this protecting group in place are processible into membranes which is an advance over FPA ionomers without protection which up to now have been difficult to process.

Conductivity data have been acquired for samples of nearly all the compounds shown in Figure 2. A full discussion of these data is beyond the scope of this report; however, the data can be summarized by noting that samples have not yet been prepared which show conductivities that meet or exceed the technical targets for this project. The reasons for this finding are still not fully clear, given the promising results from the model compounds. Possible contributing factors could include the following: low acid content in ionomers (lower than in the model compounds); poor water uptake in ionomers; and too much/too little crosslinking ionomers which could inhibit formation of domains suitable for

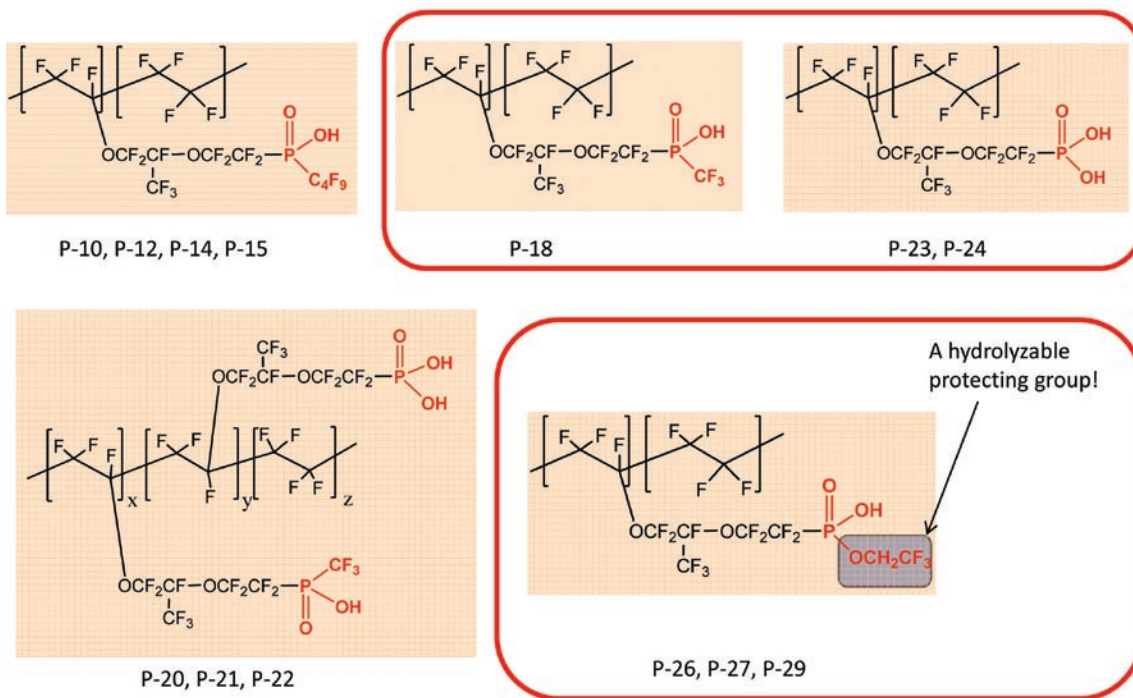


FIGURE 2. Structures of FPA-containing ionomer materials prepared in the reporting period.

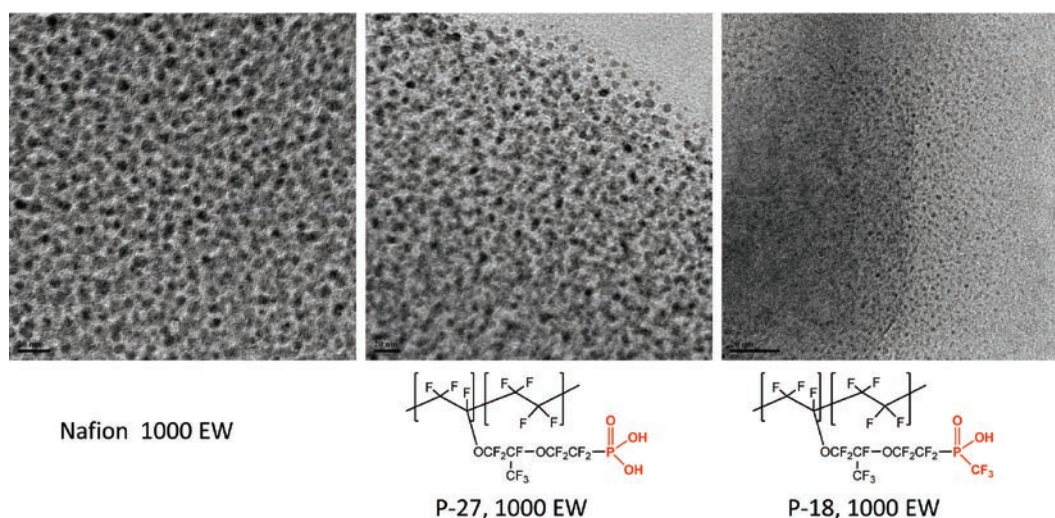


FIGURE 3. TEM images of two FPA ionomers and a Nafion® (1,100 equivalent weight) sample. Ionomers were stained by substituting protons for lead ions prior to imaging to provide better TEM image contrast.

rapid proton conduction. Another consideration is the polymer structure itself, particularly the molecular weight and the variation in equivalent weight with reaction progress during the course of ionomer synthesis. It seems likely that, were the project to continue, consistent improvements would be made in the synthesis methods used to make ionomers, which would produce materials having higher molecular weight, improved homogeneity in molecular weight and equivalent weight, and reduced “blockiness” in copolymers resulting in less brittle and more processible materials that would produce membranes having more well-formed ionic domains, and therefore higher conductivity.

Figure 3 shows TEM results which illustrate the domain structures which form for two of the ionomers from Figure 2. A sample of 1,100 equivalent weight Nafion® is also shown for comparison. The images reveal that the fluoroalkylphosphonic acid ionomer (P-27) has a domain structure similar to that of Nafion®, whereas the fluoroalkylphosphonic acid ionomer (P-18) has much smaller and less well formed domains. This is a curious finding since the larger domains should correlate with higher protonic conductivity, however the P-18 sample had a high conductivity. There is much yet to learn about structure and proton transport in these ionomer materials.

Conclusions and Future Directions

Model compound studies indicate that FPA protogenic groups show excellent promise for achieving high proton conduction rates in ionomers under conditions of low water availability. Proton hopping is demonstrated in the FPA acids but not in any other model acids. Ionomers prepared to date have not shown high conductivity, though conductivities have

steadily improved throughout the project term. Further refinement of synthesis procedures would undoubtedly bring about further improvements in conductivity, as would a focus on lower equivalent weight materials. Were the project to continue, these would be the directions it would follow. In addition, studies would be pursued on terpolymers having FPA groups combined with other acids, e.g. fluoroalkyl-sulfonic and -sulfonimide acids. These combinations might offer a possibility of proton hopping via protonated FPA groups, and also controlled crosslinking of low-equivalent weight ionomers via small amounts of FPA groups. The later approach could enable stabilization of low-equivalent-weight ionomers that would otherwise be water soluble, but which could have very high ionic conductivity.

FY 2009 Publications/Presentations

1. Q. Liu, O. Borodin, G.D. Smith “Quantum chemistry and molecular dynamics simulation studies of proton transport in the fluoroalkylphosphonic acid based electrolyte” Spring National ACS Meeting, Salt Lake City, UT, March 22–26, 2009.
2. O. Borodin, Q. Liu, B. Hopkins, G. Voth, M. Herath, D. DesMarteau, S. Creager, L. Jin, A. Kitaygorodskiy “Molecular Dynamics Simulations and Experimental Studies of Fluoroalkylphosphonic Acids” Advances in Polymer Electrolyte Membrane Fuel Cell Systems 2009, Feb. 15–18, 2009 Asilomar Conference Grounds, Pacific Grove, CA.
3. Stephen E. Creager, Darryl D. DesMarteau, Oleg Borodin, “Fluoroalkylphosphonic Acid Proton Conductors”, Presentation to Tech Team, Detroit, MI, January 2009.

4. Stephen E. Creager, Darryl D. DesMarteau, Oleg Borodin, "Fluoroalkylphosphonic Acid Proton Conductors", Presentation to DOE staff, Washington, D.C., February 2009.
5. Stephen E. Creager, Darryl D. DesMarteau, Mahesha Herath, Limei Jin, Arno Rettenbacher, Iqbal Sharif, Bing Liu "Proton-conducting fluoroalkylphosphonic and phosphinic acid electrolyte membranes for electrochemical energy conversion", Fluoropolymers 2008 conference, Charleston, SC, October 2008.
6. Stephen E. Creager, Darryl D. DesMarteau, Mahesha Herath, Limei Jin, Arno Rettenbacher, Iqbal Sharif, Bing Liu, "Proton-conducting electrolyte membranes for electrochemical energy conversion," Membranes Gordon Research Conference, New London, NH, August 2008.
7. Mahesha B. Herath, Alex Kitaygorodskiy, Stephen E. Creager, Darryl D. DesMarteau, "Proton Conductivity and PFG NMR Diffusion Studies in Perfluorinated Phosphonic Acid Based Systems" Poster presentation at Pittsburgh Conference, March 2009.