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Final Project Report

Project Title: Fluoroalkylphosphonic-acid-based proton conductors

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Recipient: Clemson University

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Working Partners: Mahesha Herath (grad student) and Li-Mei Jin (postdoc), Clemson. Qin Liu (grad student) and Brian W. Hopkins (postdoc), University of Utah.

Cost-Sharing Partners: Clemson University; University of Utah

Contact: Stephen Creager (Primary Contact), Clemson University. Phone, 864-656-4995; Fax, 864-656-6613; E-mail, screage@clemson.edu. Also, Darryl DesMarteau at Clemson University, and Gregory Voth, Grant Smith, and Oleg Borodin at University of Utah

DOE Managers: DOE HQ Technology Manager, Amy Manheim. DOE Field Project Officer; Gregory Kleen (formerly Reg Tyler).

Executive Summary

The overall objective of this research was to create new proton-conducting polymer electrolytes for use in energy conversion devices including hydrogen fuel cells that could operate at high temperatures (95 – 130 °C) and under low relative humidity (< 50% RH) conditions. The new polymers were based on the fluoroalkylphosphonic and phosphinic acid (FPA) groups (see illustration below) which offer prospects for rapid proton transport by a proton-hopping mechanism similar to that which operates in phosphoric acid, a well-known proton-transporting electrolyte that is used in a class of hydrogen fuel cells that work well under the conditions noted above and are already commercially successful. The two specific project objectives were as follows: (1) synthesize and characterize new proton-conducting electrolytes based on the fluoroalkylphosphonic and phosphinic acid (FPA) functional groups; and (2) create and apply new computer models to study protonic conduction in FPA-based electrolytes. The project was successful in creating the desired polymer electrolytes and also a series of molecular model compounds which were used to study proton transport in FPA electrolytes in general. Computer models were created to study both structure and proton-transport dynamics in the electrolytes, particularly the molecular model compounds. Rapid proton transport by a hopping mechanism was found in many of the model compounds and correlations with transport rates with molecular structure were identified. Several polymeric analogs of FPA model compounds were prepared and studied, however FPA-based polymeric materials having very high protonic conductivities under either wet or dry conditions were not obtained. Several possible reasons for the failure of polymeric materials to exhibit the expected high protonic conductivities were identified, including a failure of the polymers to adopt the phase-separated secondary structure / morphology necessary for high proton conductivity, and an unexpected polymer crosslinking effect of acidic groups having two P-OH groups. The project has lent insight into how FPA groups transport protons in both liquid and polymeric forms, which provides guidance to future efforts to design and prepare future generations of proton-conducting polymer electrolytes for hydrogen fuel cells and other types of electrochemical energy conversion and storage devices.

Summary of project activities.

Project work was pursued in two broad areas, the first relating to electrolyte synthesis and characterization and the second to computer modeling of proton conduction. Specific activities and accomplishments are documented in the project quarterly and annual reports. This final project report will summarize the activities and give context to the products developed / delivered during the project term.

Part 1. Electrolyte synthesis and characterization activities

Figures 1 and 2 present structures of small-molecule model compounds and polymer electrolytes that were synthesized and studied in the project. The model compound studies were pursued to provide guidance to studies on polymers and to allow for detailed study of proton conduction via the FPA acid groups. Proton transport in the model compounds was studied principally by electrochemical techniques (electrochemical impedance spectroscopy, EIS) and nuclear magnetic resonance techniques (pulsed field gradient nuclear magnetic resonance, or PFG-NMR, spectroscopy). Parallel studies of electrolyte viscosity were made to allow for study of an expected correlation between conductivity and viscosity. These studies are documented in two recent publications listed with the project deliverables. In brief, these papers report that anhydrous ionic conductivities of fluoroalkylphosphonic and phosphinic electrolytes are as good or better than that of trifluoromethyl sulfonic acid, also known as triflic acid, which is a model compound for the current industry-leading perfluorosulfonic acid (PFSA) ionomer electrolytes such as Nafion. High conductivities in the FPA model acids are due to a combination of low viscosity, high proton dissociation, and proton hopping as indicated by ion diffusivities measured by PFG-NMR spectroscopy that are 1.5 – 3 times higher for protons than for the F-containing conjugate bases. Comparisons of calculated conductivities obtained using the Nernst-Einstein equation to convert measured ion diffusivities into calculated conductivities, with measured conductivities obtained from electrochemical experiments, revealed the FPA acids to be highly dissociated, consistent with their amphiphilic character. Adding greater fluoroalkyl character to the model compound acids by lengthening their fluoroalkyl chains or using two chains instead of one was found to diminish conductivity, probably due to the fact that acid groups are diluted by fluoroalkyl groups which causes phase segregation to occur with hydrophilic, acid-rich regions being too small and too far separated from one another to allow for continuous proton transport across an entire bulk phase. Polymer electrolytes based on such materials would have to have large continuous acid-rich phases in order to exhibit high proton conductivity in the absence of water.

Additional studies were undertaken of the model acids with varying amounts of water added. In general, adding water increases conductivity by between one and two orders of magnitude at all temperatures. The largest effects were seen for the perfluorobutyl-phosphonic acid and bis-perfluorobutyl-phosphinic acid electrolytes which showed increases in conductivity of between 100X and 5000X when water was added. With approximately 20 water molecules added per molecule of acid, all the electrolytes

showed conductivities between 0.5 and 1.0 S / cm at 120 C, consistent with all of them being strong and fully dissociated acids in water. Details are given in the PhD dissertation of Dr. Mahesha Herath, a project working partner.

Figure 1. Structures of fluoroalkylphosphonic and phosphinic acid model compounds studied during the project term.

Figure 2. Structures of fluoroalkylphosphonic and phosphinic acid polymer electrolytes studied during the project term.

Polymer electrolytes containing FPA acid groups were prepared using variants on the methods developed over the past 15 years by DesMarteau and co-workers for other superacid-containing fluoropolymer electrolytes. Structures are given in Figure 2, and representative characterization data including conductivity data at 25 °C and 80 °C are given in Table 1. Only two samples (P18 and P21) showed conductivities comparable to that of Nafion 112 at 100% RH, and all samples showed a steeper drop-off in conductivity with decreasing RH (for example see Figure 3) than Nafion 112. TEM images of ionomers stained with lead ions (to improve TEM contrast) showed FPA ionomers having smaller ionic domains than in Nafion (see Figure 4), suggesting that on dehydration it may be easier for ionic domains in FPA ionomers to lose connection with each other than in Nafion. These results and others relating to ionomer synthesis and characterization are documented in the quarterly reports for the project.

Finally, one of the anions prepared for this project, the bis-trifluoromethyl-phosphinate anion, was used to prepare a room-temperature ionic liquid (RTIL) electrolyte with the butyl-methyl-imidazolium (BMIM) cation. This RTIL was found to have properties similar to that of well-known ionic liquid consisting of a TFSI anion and a BMIM cation, including a high ionic conductivity and a wide electrochemical potential window (along with the expected low volatility and flammability and excellent thermal stability). This work, which is described in a recent publication listed among the project deliverables, is only peripherally related to the overall project objective of producing proton-conducting electrolytes, however the target RTIL electrolyte could prove useful in other electrochemical devices such as advanced batteries and capacitors.

Table 1. Equivalent weight, water uptake and ionic conductivity at 100% RH for samples of various FPA-based ionomer membranes

membrane	P10	P12	P18	P21	P23	P24	P26	P27	Nafion 112
EW; g / equiv	750	1300	1100	1400	1450	740	580 ^a	1000 ^a	1100
H ₂ O uptake; 100 C	123%	13%	30%	-	-	-	-	-	-
Conductivity; 25 C, 100% RH	0.025	0.006	0.045	0.044	0.0005	0.006	0.028	0.012	0.060
Conductivity; 80 C, 100% RH	0.025	0.018	0.12	0.10	0.00023	0.017	0.034	0.010	0.12
a. Membranes after hydrolysis

Figure 3. Ionic conductivity for FPA ionomer sample P-18, compared with Nafion RE 212. Figure is taken from FY 2009 project annual report.

Figure 4. TEM images of three fluoroionomers following ion exchange with lead nitrate. Left, Nafion 1100 EW. Center, FPA sample prepared from ionomer P-26 in Figure 4 followed by extensive hydrolysis in boiling HCl to hydrolyze the protected acid group prior to lead exchange. Right, ionomer sample P-18. The domain structure in sample P-18 is less well developed than that in Nafion or the other FPA sample. Figure taken from FY 2009 project annual report.

Part 2. Computer simulation and modeling activities

Computational approaches were used to study structure and proton transport dynamics in FPA model compounds. A combination of quantum chemistry calculations, *ab-initio* and classical molecular dynamics simulations shown in Figure 5 was utilized to obtain improved understanding of FPA-based model compounds and, ultimately, to achieve predictive capabilities. Quantum chemistry studies of FPA/water complexes have demonstrated that at hydration levels of more than 3.5-4 waters per acid group a spontaneous acid deprotonation occurs. In contrast to these results only 3 waters are required for $\text{CF}_3\text{SO}_3\text{H}$ deprotonation indicating that $\text{CF}_3\text{PO}(\text{OH})_2$ is a weaker acid than $\text{CF}_3\text{SO}_3\text{H}$ as has been verified experimentally. DFT-based Born-Oppenheimer molecular dynamics simulations of 27 $\text{CF}_3\text{PO}(\text{OH})_2$ molecules under anhydrous conditions showed a significantly faster diffusion of proton compared to oxygen atoms (a factor of 2-3) indicative of the Grotthuss proton transport present in anhydrous $\text{CF}_3\text{PO}(\text{OH})_2$ as was subsequently confirmed by the pfg-NMR studies shown in Table 2. A high degree of $\text{CF}_3\text{PO}(\text{OH})_2$ self-dissociation (self-deprotonation) (>30%) in combination with a high excess proton hopping rate puts FPA among anhydrous materials with the highest observed Grotthuss contribution to proton conductivity.

Classical MD simulations were performed on a series of perfluoroalkyl phosphonic acid and phosphinic acid oligomers as a function of temperature without explicit proton transfer included in the model. Analysis of the hydrogen bonding networks obtained from these simulations allowed us to explain the experimentally observed trends for the $D(\text{H}_{\text{OH}})/D(\text{F}_{\text{CF}})$ shown in Table 2. Specifically, simulations showed that the structural arrangement needed for the Grotthuss proton transfer is present in fluoroalkyl-phosphonic acid-based materials (e.g. $\text{CF}_3\text{PO}_3\text{H}_2$ and $\text{C}_4\text{F}_9\text{PO}_3\text{H}_2$) and in bis(fluoroalkyl)phosphinic acid electrolytes having low fluoroalkyl content (e.g. $(\text{CF}_3)_2\text{POOH}$) but is largely absent in bis(fluoroalkyl)phosphinic acid electrolytes having high fluoroalkyl content (e.g. $(\text{C}_4\text{F}_9)_2\text{POOH}$).

Computational efforts also focused on implementing the Q-HOP algorithm (Lill & Helms, J. Chem. Phys., 2001, 115, 7993) for performing computationally expedient simulations of FPAs. As an example of these efforts, Table 2 presents a comparison of the absolute rates of fluorine self-diffusion, and the relative rates of proton and fluorine self-diffusion in $\text{CF}_3\text{PO}(\text{OH})_2$ as indicated by PFG-NMR (experiment) and MD simulation. Absolute F diffusivities agree to within about a factor of two which is excellent, and diffusivity ratios are also in excellent agreement.

The modeling work in this project was developed to a sufficiently sophisticated level that predictive work may now be possible with both liquid electrolytes and ionomers. In particular, combination of the modeling work from this project with multiscale models developed separately for bulk-scale materials including phase-separated polymer and ionomer materials, should provide entry into predictive capabilities for ionomers having a broad range of protogenic groups including phosphorous-based acids having proton hopping capabilities.

Figure 5. Computational approaches used for studies of model compounds.

Table 2. Computer simulation of proton hopping in $\text{CF}_3\text{PO}_3\text{H}_2$ FPA model compound.

Method	$D(\text{F}_{\text{CF}})$ 358 K (m^2/s)	$D(\text{H}_{\text{OH}})/D(\text{F}_{\text{CF}})$
NMR, 358 K	0.5	2.25
MD/Q-HOP, 358 K	0.98	2.1

Products developed under the award:

The following listing includes specific papers and presentations made on work performed with project support. There were no patent applications, web sites, or other products such as databases generated by the project, though, there certainly were several new chemical compounds and materials prepared and new data were acquired on these materials.

Publications

- Mahesha B. Herath, Stephen E. Creager, Alex Kitaygorodskiy, Darryl D. DesMarteau "Perfluoroalkyl Phosphonic and Phosphinic Acids as Proton Conductors for Anhydrous Proton-Exchange Membranes" *ChemPhysChem* 11, 2871-2878 (2010)
- Mahesha B. Herath, Stephen E. Creager, Alex Kitaygorodskiy, and Darryl D. DesMarteau "The Effect of Perfluoroalkyl Chain Length on Proton Conduction in Fluoroalkylated Phosphonic, Phosphinic and Sulfonic acids" *J. Phys. Chem. B*, 114, 14972-14976 (2010)
- Mahesha B. Herath, Tom Hickman, Stephen E. Creager, and Darryl D. DesMarteau "A New Fluorinated Anion for Room-Temperature Ionic Liquids", *J. Fluorine Chem.*, 132, 52-56 (2011).
- Jin LM, Creager S, DesMarteau DD "Bis(perfluoroalkyl)phosphinic acid-based polymers: A novel polymer for PEM fuel cell applications" *ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY* Volume: 236 Meeting Abstract: 106-FUEL Published: AUG 17 2008
- Liu Q, Borodin O, Smith GD "Quantum chemistry and molecular dynamics simulation studies of proton transport in the fluoroalkylphosphonic acid based electrolyte" *ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY* Volume: 237 Meeting Abstract: 379-POLY Published: MAR 22 2009

Presentations:

- 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.
- 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 Grotthuss*, Herndon, Virginia, June 2006.
- 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.
- 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.

- 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 Grotthuss, Herndon, Virginia, June 2006.
- Voth, G. "Molecular Dynamics Simulations of Proton Transport in Polymer Electrolyte Membranes," Gordon Conference on Fuel Cells, Bryant College, Rhode Island, July, 2006.
- 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.
- Voth, G. "Molecular Dynamics Simulation of Excess Proton Solvation and Transport in Polymer Electrolyte Membranes,"² Electrochemistry Gordon Conference, Ventura, CA, January, 2007.
- Borodin, O.; Lui, Q.; Smith, G. D. [Quantum Chemistry and MD Simulation Studies of Fluorinated Ionomers](#) 212th ECS October 7 - October 12, 2007, Washington, DC
- Mahesha B. Herath, Stephen Creager; Lie-Mi Jin, Arno Rettenbacher, Darryl DesMarteau, "Perfluoroalkyl Phosphonic Acid Based Proton Conductors for High Temperature Fuel Cells", 212th ECS October 7 - October 12, 2007, Washington, DC
- Borodin, O.; Lui, Q.; Smith, G. D. [Quantum Chemistry and MD Simulation Studies of Fluorinated Ionomers](#) 212th ECS October 7 - October 12, 2007, Washington, DC
- Mahesha B. Herath, Stephen Creager; Lie-Mi Jin, Arno Rettenbacher, Darryl DesMarteau, "Perfluoroalkyl Phosphonic Acid Based Proton Conductors for High Temperature Fuel Cells", 212th ECS October 7 - October 12, 2007, Washington, DC
- Jin LM, Creager S, DesMarteau DD "Bis(perfluoroalkyl)phosphinic acid-based polymers: A novel polymer for PEM fuel cell applications" American Chemical Society Meeting, Fall 2008, Philadelphia PA, August 2008 Symposium on Membranes for Energy and Fuel Applications
- 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
- 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
- G. A. Voth, ³Multiscale Simulation of Proton Exchange Membranes², Division of Polymeric Materials: Science and Engineering Symposium on ³Simulation of Hybrid Interfaces and Multi-Component Polymeric Materials², National American Chemical Society Meeting, Boston, MA, August, 2010.

- Stephen E. Creager*, Darryl D. DesMarteau, Mahesha Herath, Li-Mei Jin and Oleg Borodin, "Proton conduction in fluoroalkyl phosphonic and phosphinic acid electrolytes", Symposium in honor of Prof. Royce Murray, National American Chemical Society Meeting, Boston, MA, August, 2010.
- Oleg Borodin*, Jenel Vatamanu, Grant Smith "Structure and Ion Transport in Ionic Liquids and Liquid Electrolytes from Molecular Dynamics Simulations" 217th ECS Meeting, 2010, April 25-30, Vancouver, Canada
- G. A. Voth, ³Multiscale Simulation of Proton Exchange Membranes², Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2011, Asilomar, CA, February, 2011.