Fluoroalkyl-phosphonic-acid-based proton conductors

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and
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University of Utah
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This presentation does not contain any proprietary or confidential information
Overview

Timeline

• Start: April 2006
• Finish: March 2011
• Forty percent complete

Barriers

• Barriers
  – A,B,C; Durability / Cost / Performance.
• Targets
  – Membrane conductivity > 0.07 S/cm at 20 °C and water partial pressure of 1.5 kPa
  – Membrane conductivity > 0.10 S/cm at operating temp (120 °C) and water partial pressure of 1.5 kPa

Budget

• Total project funding
  – DOE $1,500,000
  – Contractor $381,000
• Funding for FY 06 and 07
  – $450,000 rec’d from DOE for work performed between April 2006 and Sept 2007
• Funding for FY08
  – None to date

Partners

• Dr. Alex Kitaygorodskiy, Clemson
• Dr. Ashok Krishnaswami, JEOL
• Professor Klaus D. Kreuer, Max Planck Institute, Stuttgart, GE
  (all these will help with NMR studies of proton transport rates)
### Objectives / Tasks / Milestones

| Specific project objectives | (1) **Synthesize and characterize new proton-conducting electrolytes** based on the fluoroalkylphosphonic acid functional group; and  
(2) **Perform simulation study** of structure and proton conduction in fluoroalkylphosphonic acid-based electrolytes. |
|----------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Year 2 Tasks and Milestones (April 2007 – March 2008) | • Synthesize and/or purify at least 5 g each of one or more trifluorovinyl-ether (TFVE) fluoroalkylphosphonic acid monomers.  
• Complete development and validation of classical force fields for fluoroalkylphosphonic and fluoroalkyl-bis-phosphinic acids and perform MD simulations of these acids as a function of fluoroalkyl chain length  
• Perform DFT-based Born Oppenheimer Molecular Dynamics (BOMD) simulations of CF$_3$PO$_3$H$_2$ and (CF$_3$)$_2$POOH acids.  
• Complete synthesis of TFVE monomer and development and validation of models and begin MD, CGIS and MPM simulations  
• **Milestone: Year 2 (24 months from start):** Test the membrane for electrolyte conductivity of at least 0.07 S/cm at 80% RH at ambient temperature and deliver a sample membrane to the Topic 2 contractor for evaluation. |
# Approach

<table>
<thead>
<tr>
<th><strong>Task 1.0</strong> Synthesize new fluoroalkylphosphonic-acid-based electrolytes.</th>
<th><strong>Task 5.0</strong> Perform computer simulations of fluoroalkylphosphonic-acid electrolytes.</th>
</tr>
</thead>
<tbody>
<tr>
<td>– Small-molecule acid model compounds</td>
<td>– Perform classical and DFT-based Born Oppenheimer Molecular Dynamics (BOMD) of various of fluoroalkylphosphonic-acids</td>
</tr>
<tr>
<td>– Trifluorovinylether (TFVE) monomers</td>
<td></td>
</tr>
<tr>
<td>– Copolymers of TFVE monomers with tetrafluoroethylene (TFE) to give ionomer membranes</td>
<td></td>
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</tbody>
</table>

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<thead>
<tr>
<th><strong>Task 2.0</strong> Characterize new fluoroalkylphosphonic-acid-based electrolytes.</th>
<th><strong>Task 6.0</strong> Perform computer simulations of fluoroalkylphosphonic acid electrolyte / heterocycle/water mixtures.</th>
</tr>
</thead>
<tbody>
<tr>
<td>– Structure, purity, ion (proton) transport rates (diffusivity, conductivity)</td>
<td>– As in Task 5.</td>
</tr>
</tbody>
</table>

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<thead>
<tr>
<th><strong>Task 3.0</strong> Demonstrate conductivity of at least 0.07 S/cm at 80% RH at ambient temperature.</th>
<th><strong>Task 7.0</strong> Project Management and Reporting.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>– Deliver membrane(s) to Topic 2 awardee; periodic reports; annual reviews</td>
</tr>
</tbody>
</table>

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<thead>
<tr>
<th><strong>Task 4.0</strong> Demonstrate conductivity of at least 0.10 S/cm at 50% RH at 120 °C.</th>
<th></th>
</tr>
</thead>
</table>
Electrolyte Structures

I. \[ \overset{O}{\underset{\parallel}{\text{F}\text{--}(\text{CF}_2)_n\text{--}\text{P}(\text{X})(\text{OH})}} \quad \text{X = OH, R}_f \]

II. \[ \overset{O}{\underset{\parallel}{\text{CF}_2\text{--CFO}}} \quad (\text{CF}_2\text{CFO})_n\text{--}(\text{CF}_2)_m\text{--}\text{P}(\text{X})(\text{OH})} \quad \text{n=1, m=2} \]

III. \[ \overset{O}{\underset{\parallel}{\text{--}(\text{CF}_2\text{--CF})_a\text{--}(\text{CF}_2\text{CF}_2)_b\text{--}}} \quad \text{CF}_3 \]

<table>
<thead>
<tr>
<th>I.</th>
<th>Small molecule model compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>II.</td>
<td>Trifluorovinylether monomers</td>
</tr>
<tr>
<td>III.</td>
<td>Fluoroalkylphosphonic acid ionomers</td>
</tr>
</tbody>
</table>
Technical Accomplishments

FPA electrolytes

1. Synthesis and Characterization
Model Compound Structures

\[
\begin{align*}
\text{CF}_3 & \quad \text{P} \quad \text{O} \quad \text{OH} \\
\text{OH} & \\
\text{C}_4\text{F}_9 & \quad \text{P} \quad \text{O} \quad \text{OH} \\
\text{OH} & \\
\text{CF}_3 & \quad \text{P} \quad \text{O} \quad \text{CF}_3 \\
\text{OH} & \\
\text{C}_4\text{F}_9 & \quad \text{P} \quad \text{C}_4\text{F}_9 \\
\text{OH} & \\
\text{CF}_3 & \quad \text{S} \quad \text{O} \quad \text{OH} \\
\text{SO} & \\
\end{align*}
\]
## Table 1. Physical Constants for Perfluoroalkylphosphonic and Sulfonic Acids

<table>
<thead>
<tr>
<th></th>
<th>Solid/Liquid at RT</th>
<th>mp, °C</th>
<th>bp, °C (p, mm Hg)</th>
<th>H₂O solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃PO₃H₂</td>
<td>solid</td>
<td>81-82</td>
<td>High</td>
<td>soluble</td>
</tr>
<tr>
<td>(CF₃)₂PO₂H</td>
<td>liquid</td>
<td>-</td>
<td>182 (760) b)</td>
<td>soluble</td>
</tr>
<tr>
<td>CF₃SO₃H</td>
<td>liquid</td>
<td>-</td>
<td>160-162 (760) c)</td>
<td>soluble, but solid at 1:1 molar mixture</td>
</tr>
<tr>
<td>C₄F₉PO₃H₂</td>
<td>liquid</td>
<td>-</td>
<td>170-175 (0.5 )d)</td>
<td>soluble</td>
</tr>
<tr>
<td>(C₄F₉)₂PO₂H</td>
<td>liquid</td>
<td>-</td>
<td>High</td>
<td>insoluble</td>
</tr>
</tbody>
</table>


Conductivity of CF$_3$PO$_3$H$_2$ and H$_3$PO$_4$

(CF$_3$)$_2$POOH

Conductivity $\sigma$ (S/cm)

$0.07$ S/cm

$\text{CF}_3$ – P – $\text{CF}_3$

$\text{HO}$
Ref 2: *Giner Electrochemical systems LLC. DOE Hydrogen review 2007 pg 8*
C₄F₉PO₃H₂

Conductivity \( \sigma \) (S/cm)

- C₄F₉PO₃H₂ : H₂O = 1 : 20
- C₄F₉PO₃H₂ : H₂O = 1 : 3
- C₄F₉PO₃H₂ : H₂O = 1 : 0

Conductivity: 0.07 S/cm
$\text{CF}_3\text{PO}_3\text{H}_2 + \text{CF}_3\text{SO}_3\text{H}$ mixture

$1000/T (\text{K})$

Conductivity $\sigma$ (S/cm)

- CF$_3$PO$_3$H$_2$ : H$_2$O = 1 : 0 (by # moles)
- CF$_3$SO$_3$H : H$_2$O = 1 : 0 (by # moles)
- 80% CF$_3$PO$_3$H$_2$ : 20% CF$_3$SO$_3$H (by weight)
Summary of FPA model compound studies

- Bis(trifluoromethyl)phosphinic acid \(\text{((CF}_3\text{)}_2\text{P(O)(OH))}\) has the highest anhydrous conductivity of all the FPAs tested. It is above that of anhydrous triflic acid and just below that of anhydrous phosphoric acid.

- Addition of small amounts of water causes dramatic increases in conductivity for all acids tested.

- Replacing \(\text{CF}_3\) with \(\text{C}_4\text{F}_9\) in FPAs decreases conductivity especially under very dry conditions.

- Mixtures of superacids (e.g. triflic acid) with FPAs so far do not produce electrolytes having enhanced conductivity. More work is planned in this area, as models for polyfunctional (e.g. terpolymer) ionomers.
Bis-fluoroalkyl-phosphinic acid ionomers

- Should be quite strong acids, proton dissociation is favored
- Should be better surfactant in Na⁺ form than the mono-fluoroalkylyphosphonic acids, therefore more likely to produce good ionomers by emulsion co-polymerization with TFE in water
- Should / could promote proton transport by a hopping mechanism (testing is in progress with model compounds)

Monomer 7, \( R_f = C_4F_9 \)

Monomer 11, \( R_f = CF_3 \)

Bis(fluoroalkyl)-phosphinic acid
Trifluorovinyl ether monomer

\[
\begin{array}{c}
F_2C\equivCF \\
\text{OCF}_2\text{CF} \equiv \text{OCF}_2\text{CF}_2\text{P} \equiv \text{OH} \\
\text{CF}_3
\end{array}
\]

\( R_f: C_4F_9; CF_3 \).
Synthesis of Monomer 11

Monomer 11 was obtained in good yield in multi-gram amounts.
Aqueous emulsion co-polymerization of TFVE monomers with TFE

**Monomer feed from syringe pump**

**Stirred, temperature-controlled autoclave**

**TFE tank behind explosion-proof wall**
### Typical conditions for copolymerization of trifluorovinyl ether monomers (7 and 11) with TFE

<table>
<thead>
<tr>
<th>Conditions</th>
<th>P10</th>
<th>P12</th>
<th>P14</th>
<th>P15</th>
<th>P18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor</td>
<td>450 mL</td>
<td>450 mL</td>
<td>450 mL</td>
<td>450 mL</td>
<td>450 mL</td>
</tr>
<tr>
<td>Monomer</td>
<td>7 (R_f = \text{C}_4\text{F}_9)</td>
<td>7</td>
<td>7</td>
<td>7</td>
<td>11 (R_f = \text{CF}_3)</td>
</tr>
<tr>
<td>Monomer in the autoclave (g)</td>
<td>4</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Surfactant (\text{C}<em>7\text{F}</em>{15}\text{COONH}_4) (g)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>(\text{NaH}_2\text{PO}_4) (g)</td>
<td>0.77</td>
<td>0.77</td>
<td>0.77</td>
<td>0.77</td>
<td>0.77</td>
</tr>
<tr>
<td>(\text{Na}_2\text{HPO}_4) (g)</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
<td>1.35</td>
</tr>
<tr>
<td>(\text{K}_2\text{S}_2\text{O}_8) (mg)</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>30</td>
</tr>
<tr>
<td>Pressure of TFE (psi)</td>
<td>110-105</td>
<td>185-180</td>
<td>110-105</td>
<td>80-75</td>
<td>85-80</td>
</tr>
<tr>
<td>Total TFE drop (psi)</td>
<td>24</td>
<td>40</td>
<td>23</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>Stirring speed (rpm)</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>65</td>
<td>65</td>
<td>65</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>(\text{H}_2\text{O}) (ml)</td>
<td>260</td>
<td>260</td>
<td>260</td>
<td>260</td>
<td>220</td>
</tr>
<tr>
<td>Head space (ml)</td>
<td>190</td>
<td>190</td>
<td>190</td>
<td>190</td>
<td>230</td>
</tr>
<tr>
<td>Polymer weight (g)</td>
<td>3.8</td>
<td>3.95</td>
<td>2.5</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Equiv weight (g / equiv)</td>
<td>750</td>
<td>1300</td>
<td>1000</td>
<td>910</td>
<td>1000</td>
</tr>
<tr>
<td>Water uptake, meth 1, 100C</td>
<td>123%</td>
<td>16%</td>
<td>74%</td>
<td>80%</td>
<td>30%</td>
</tr>
<tr>
<td>Water content, meth 2, 25C</td>
<td>47%</td>
<td>7%</td>
<td>37%</td>
<td>39%</td>
<td>-</td>
</tr>
</tbody>
</table>
Because of the good solubility of these polymers, membranes were readily formed from casting solutions. As examples, membranes from ionomers P10 and P18 are shown below.

**P10**
- **Copolymer from copolymerization of** $R_F P(O)(ONa)C_4F_9$ **with TFE**
- Membrane from P10
- Thickness: 64um
- Flexible and tough
- Colorless after boiling in HNO₃

**P10-mem**

**P18**
- **Copolymer from copolymerization of** $R_F P(O)(ONa)CF_3$ **with TFE**
- Membrane from P18
- Flexible and tough
- Colorless
- Smooth and even

**P18-mem**
Proton conductivity data were acquired for ionomer samples at 100% RH at ambient, 80°C and 120°C. The membranes were hydrated by soaking in hot deionized water for 12h prior to study.
Summary of FPA ionomer studies

• Bis(fluoroalkyl)-phosphinic acid ionomers from monomer 11 (R_f = CF_3) are readily prepared and have much improved properties over earlier generation ionomers from monomer 7 (R_f = C_4F_9).

• Further improvements will be sought via low-EW ionomers from monomer 11, and via terpolymers with mixed FPA and FPA / sulfonimide monomers
Technical Accomplishments

FPA Electrolytes.

(2) Computer modeling
Simulations Approach

Quantum Chemistry Calculations on Representative Gas-Phase Clusters

Classical MD simulations (no explicit proton hopping) (100s of molecules)

DFT-based Born Oppenheimer Molecular Dynamics (BOMD) simulations using BLYP.
27 molecules - CF$_3$PO$_3$H$_2$
24 molecules - (CF$_3$)$_2$POOH

Classical MD simulations with explicit proton hopping (MS-EVB, Q-HOP) (100s of molecules)
Quantum Chemistry: How Many Waters are Needed to Deprotonate Acid Groups?

- It takes 4 waters to deprotonate one phosphonic acid group, however, it takes only 7 waters to deprotonate 2 phosphonic acid groups

\[ CF_3PO_3H_2 + 4H_2O \quad \quad 2CF_3PO_3H_2 + 7H_2O \]

*Calculations have been performed at mPW1PW91/6-31G(d,p)*
Quantum Chemistry: Water-Mediated Internal Proton Transfer

The distance between an acid oxygen and water oxygen (donor-acceptor) is fixed to values (2.4 Å – 2.7 Å) and the barrier for the proton transfer between the donor and acceptor is studied using quantum chemistry calculations.

Despite that in the FPA-(H₂O)₃ cluster both acid protons are localized at the acid for the most energetically stable configuration. We find that there is a low barrier for the water mediated proton transport from one FPA oxygen to another.

As proton “1” shifts towards a water molecule, proton “2” shifts to the neighboring water, while proton “3” shifts towards the acid group resulting in an intermolecular water mediated proton transfer.

Results are shown for the mPW1PW91/6-31G* level.
Quantum Chemistry: Barriers for Proton Transfer

- The barrier for proton transfer from CF$_3$PO$_3$H$_3^+$ to CF$_3$PO$_3$H$_2$ is much lower than from CF$_3$PO$_3$H$_2$ to CF$_3$PO$_3$H$^-$
- Barriers as a function of distance are used in MD simulations to incorporate explicit proton hopping

Calculations have been performed at mPW1PW91/6-31+G(d,p) level
Born-Oppenheimer Molecular Dynamics:

- Trifluoromethyl phosphonic acid (FPA) (CF$_3$PO$_3$H$_2$) system contains 27 molecules.
- *Bis*(trifluoromethyl) phosphinic acid (bFPA) (CF$_3$)$_2$POOH system contains 24 molecules.
- Equilibrated at 393K using classical force.
- Born-Oppenheimer MD performed using BLYP DFT.
- 10ps of AIMD equilibration using temperature scaling.
- 40ps of NVE simulation time. (15ps complete for bFPA)
- AIMD and classical RDFs agree well, especially at short ranges.
Proton Transport in CF₃PO₃H₂

- Proton diffusion is significantly faster than diffusion of the oxygen atoms to which the protons are nominally bonded.
- On average, autoionization exceeds 20% at 393K.
- A significant Grotthuss component of PT is indicated.

Proton transport in (CF₃)₂POOH from BOMD simulations is currently under investigation
If conductivity is estimated from classical MD simulations assuming complete acid self-dissociation and no ion correlations and no Grotthuss mechanism for proton transfer, one observes:

- **Orthophosphoric acid**: experimental value is much larger than estimate from classical MD indicating that the Grotthuss mechanism is dominating proton transfer;
- **Fluorophosphonic acid and bis-fluorophosphinic acids**: experimental data are closer to MD estimates indicating that Grotthuss proton transfer is less efficient in these acids than in PO₄H₃.
Aggregation of acid groups

$\text{C}_8\text{F}_{19}\text{PO}_3\text{H}_2$ exhibits good acid group aggregation giving rise to possible proton conducting pathways, while $(\text{C}_4\text{F}_9)_2\text{POOH}$ does not exhibit acid group aggregation.

Hydrogen and oxygen have been increased in size to highlight acid group aggregation.
Future work

• Conductivity studies on small-molecule FPA model compounds will focus on low water contents and on mixtures of FPAs with superacids (e.g. sulfonomide acids) as models for terpolymer ionomers

• PFG NMR studies on FPAs will measure atom self-diffusion coefficients to evaluate Grotthuss conduction.

• Water uptake studies on FPAs will be pursued at variable RH

• Ionomer studies will focus on lower EW ionomers, terpolymers, and on strategies for stabilizing H-bonded proton transport pathways.

• MD simulations (MS-EVB or Q-hop) will focus on acid-water mixtures with explicit proton hopping included