Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes

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Project ID
FC039

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Overview

Timeline
• April 1\textsuperscript{st} 2006
• March 31\textsuperscript{st} 2011
• 80\% Complete

Budget
• Total project funding
  – DOE - $1,500K
  – Contractor - $375K
• Funding for FY09
  – $300K ($45K)
• Funding for FY10 to date
  – $300K ($45 K)

Barriers
– C Performance
– B Cost
– A Durability

Partners
• 3M - Industrial
• Project lead - CSM
### Objectives/Relevance

<table>
<thead>
<tr>
<th>Year</th>
<th>Details</th>
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| **Overall** | • Fabricate a hybrid HPA polymer (polyPOM) from HPA functionalized monomers with:  
  – $\sigma > 0.1 \text{ S cm}^{-1}$ at 120°C and <50% RH  
  (Barrier C) |
| **2010** | • Optimize hybrid polymers in practical systems for proton conductivity and mechanical properties  
  (Barrier C and A) |
| **2011** | • Optimize hybrid polymers for proton conductivity, mechanical properties, and oxidative stability/durability  
  (Barrier A, B, and C) |
Unique Approach

- **Materials Synthesis** based on HPA Monomers, Novel “High and Dry” proton conduction pathways mediated by organized HPA moieties – A NEW Ionomer System

- **Task 3.1** – Optimization of proton conductivity and mechanical properties, through chemistry tuned for practical applications (eventual down selection) – 50% complete

- **Task 3.2** – Optimization of proton conductivity, mechanical properties, and oxidative stability through chemistry tuned for practical applications and peroxide decomposition functionality of HPA – 10% complete
Approach - use Functional Inorganic Super Acids: Heteropoly acids

+ High proton conduction, e.g. 0.2 S cm$^{-1}$ at RT for 12-HPW
+ Thermally stable at the temperatures of interest, <200 °C
+ Synthetically Versatile - even simple salts are interesting

+/-
  - Water soluble – but easily immobilized by functionalization in polymers
  - Reduced form – electrically conductive, but fuel cell membrane environment generally oxidizing, however can be used to advantage on anode
  - Proton conductivity dependency on water content/interaction with polar/protonic components
  - Varied chemistry with peroxides
Approach - Generational Development

• Generation I films – Acrylate co-monomers, polymer system in a kit, but, ester linkages, methylene groups

• Generation II films – methylene groups
  – Could be good for cost reasons as HPA imparts strong oxidative stability

• Generation III films – no methylene groups
## Technical Accomplishments

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go Decision</th>
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<tbody>
<tr>
<td>Jan 09</td>
<td><strong>Demonstrate conductivity of 100 mS cm(^{-1}) at 50% RH and 120ºC –</strong></td>
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<tr>
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<td>30ºC 60% RH 120 mS cm(^{-1})</td>
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<tr>
<td></td>
<td>120ºC 46% RH &gt;100 mS cm(^{-1})</td>
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<td></td>
<td><em>Current automotive operating conditions</em></td>
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<tr>
<td></td>
<td>&gt;90ºC 50%RH &gt;100 mS cm(^{-1})</td>
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<tr>
<td></td>
<td><em>Target automotive operating conditions</em></td>
</tr>
<tr>
<td>Jan 10</td>
<td><strong>Deliver membrane to topic 2 awardee</strong></td>
</tr>
<tr>
<td></td>
<td>Generation I film sent for MEA Development</td>
</tr>
<tr>
<td>March 10</td>
<td><strong>Material Optimization</strong></td>
</tr>
<tr>
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<td>3 new material platforms under development, generation II and III films.</td>
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</table>
Synthesis of the Hybrid Monomer

\[
\text{HSiW11} + 2 \text{triethoxystyrylsilane} + 4H^+ + H_2O \rightarrow \text{HSiW11(styryl)2 monomer} + 6 \text{ethanol}
\]

Judeinstein, P. Chem. Mater. 1992, 4, 4-7
Generation I Film: PolyPOM-85v - HSiW11(vinyl)2/BA/HDDA Co-polymer

- 85 wt% $\text{H}_4\text{SiW}_{11}\text{O}_{39}(\text{C}_2\text{H}_3\text{Si})_2\text{O}$ Proton Conducting Co-monomer [HSiW11(vinyl)2]
- 12.5 wt% Butyl Acrylate (BA)
- 2.5 wt% 1,6-Hexanediol diacrylate (HDDA)

\[
\text{HSiW11(vinyl)2} + \text{Butyl Acrylate (BA)} + \text{1,6-Hexanediol diacrylate (HDDA)} \rightarrow \text{PolyPOM85v/BA}
\]

- $\rho = 2.58 \text{ g cm}^{-3}$
- <100 $\mu$m
Technical Accomplishment I: Generation I

PolyPOM-85v high conductivity

- 50% RH (EA = 23 kJ/mol)
- 80% RH (EA = 23 kJ/mol)
- 95% RH (EA = 10 kJ/mol)
- DOE Milestone
Morphological studies PolyPOM 85v, 80°C

Size Patterns for PolyPOM-85v vs. RH

- P Exponent
- Diameter (Å)

- Level 1 P
- Level 2 P
- Level 1 Diameter
- Level 2 Diameter

Relative Humidity (%)

Packing for PolyPOM-85v vs. RH

- ETA (Å)
- Packing Level

- Level 1 ETA
- Level 1 Packing

Relative Humidity (%)

Intensity [Relative Units] vs. Q [Å]

- dry - Original Intensity
- dry - Unified Fit
- 30% RH - Original Intensity
- 30% RH - Unified Fit
- 50% RH - Original Intensity
- 50% RH - Unified Fit
- 70% RH - Original Intensity
- 70% RH - Unified Fit
- 80% RH - Original Intensity
- 80% RH - Unified Fit
- 95% RH - Original Intensity
- 95% RH - Unified Fit
PolyPOM-85v – Morphologically unstable

- Generation I films developed to demonstrate High Conductivity
- Become brittle with time.
- New Film Chemistries developed to solve mechanical problems
Membrane IIa Characteristics – simple approach; inexpensive co-monomers if oxidative stability proven

• ~0.1 to 0.2 mm thick
• Clear yellow color or dark opaque brown color
• Flexible, easy to manipulate
• High HPA Loading
• **Soluble in water**
  • Work is ongoing to solve this problem by investigating how to increase cross-linking and molecular weight.

Membrane IIb Characteristics – more sophisticated robust chemistry
Insoluble in water, thin flexible films when supported (expanded PTFE, hydrocarbons) new co-monomers in development
Conductivity Measurements at for first Il a Co-polymers
Encouragingly high

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<tr>
<th>Sample #</th>
<th>Conductivity (mS/cm)</th>
<th>Standard Deviation</th>
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<tbody>
<tr>
<td>1</td>
<td>56</td>
<td>0.291</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>0.283</td>
</tr>
</tbody>
</table>

95 °C and 50% RH

80 °C

Conductivity (s/cm) vs. Relative Humidity (%) graph
Technical Accomplishment III: Generation III films achieved via attachment to robust polymers

Details are withheld as proprietary (not on this slide)

New to 3M (took 2 tries)
Core 3M chemistry
Extension of 3M chemistry
Core CSM chemistry
Extension of CSM chemistry

2nd Generation HPA Hybrid Electrolyte

Changes w.r.t. Phase I (ended Feb09)
- Different backbone
- New linkage
- Different film-forming process

Features
- More durable (chem & mech)
- Expected to be easier to mfr.
- Crosslinkable
- Expecting better reproducibility
3M Immobilization generation III, HPA immobilized

Thermogravimetric Analysis:
Indicator of heteropolyacid incorporation and immobilization

Z-functionalized Polymer

0% Inorganic Residue @ 800°C

Z-functionalized polymer

Thermogravimetric Analysis:
Indicator of heteropolyacid incorporation and immobilization

2nd Generation HPA Hybrid Electrolyte

Acid Form

HPA attached polymer

0% Inorganic Residue @ 800°C

34% Inorganic Residue @ 800°C

HPA attached polymer

21% Inorganic Residue @ 800°C

All samples vacuum-dried 60-70°C/5hrs before TGA
3M Immobilization Generation III: Un-optimized conductivity high

- First result high conductivities for only 20wt% HPA
- Optimization for high conductivity ongoing
Collaborations

• Prime: Colorado School of Mines – University
• Sub: 3M Corporate Material Research Laboratory
• Other Collaborators: the following have agreed to manufacture MEAs from promising films.
  – 3M Fuel Cell Components Group
  – FSEC
  – GM (has offered to test promising materials)
Proposed Future Work

Technical Advancement of 3M Generation III

Processing effects on conductivity
- Annealing conditions
- Solvent selection
- Membrane morphology

HPA incorporation
- Yield of z-functionalization
- Yield of HPA attachment
- Goal is to maximize both

Fuel cell demonstration
- Polarization curve
- Area-specific resistance
- Initial stability assessment vs. 1st generation (vinyl-HPA/co-acrylate)

Technical Advancement of CSM Generation II

Demonstrate Insolubility
- Optimal co-monomer to HPA ratio

Improve Film Properties
- Optimize HPA content – conductivity and oxidative stability
- Optimize Morphology
- Optimize mechanicals

Fuel cell demonstration
- Send samples to FSEC, 3M, GM

Chemical processing
- Large scale raw materials sourcing
- Equipment needs
- Handling issues

3M Manufacturing study

Membrane formation
- Suitability of existing film-forming equipment
- Chemical/materials handling issues
- Failure modes

MEA fabrication
- Status of program materials vs. mechanical requirements
- Compatibility with other materials in construction
- Storage and handling
Summary Slide

- Consistently High Proton Conductivity in Robust films
- 3 New Film Chemistries developed
  - High Oxidative stability
  - Excellent Mechanical properties

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<tr>
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<th>DOE target 2010</th>
<th>FY09</th>
<th>FY10</th>
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<tr>
<td><strong>H⁺ conductivity</strong></td>
<td></td>
<td></td>
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<tr>
<td>At 20°C</td>
<td>70 mS/cm</td>
<td>126 mS/cm</td>
<td>50 mS/cm</td>
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<tr>
<td>60%RH, 31°C</td>
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<td>50%RH, 50°C</td>
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</tr>
<tr>
<td><strong>H⁺ conductivity</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>at 120°C</td>
<td>100 mS/cm</td>
<td>100 mS/cm</td>
<td>&gt;100 mS/cm</td>
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<tr>
<td>47%RH</td>
<td></td>
<td></td>
<td>&lt;50%RH</td>
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