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

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This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline

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

Budget

• Total project funding
  – DOE - $1,500K
  – Contractor - $375K
• Funding for FY07
  – $313K ($46K)
• Funding for FY08 to date
  – $125K ($45 K)

Barriers

– C Performance
– B Cost
– A Durability

Partners

• 3M - Industrial
• Project lead - CSM
Objectives

| Overall | • Fabricate a hybrid HPA polymer (polyPOM) from HPA functionalized monomers with:  
|         |   – $\sigma > 0.1$ S cm$^{-1}$ at 120°C and 25%RH |
| 2007    | • Synthesis and optimization of hybrid HPA polymers for conductivity from RT to 120°C |
| 2008    | • Synthesis and optimization of hybrid HPA polymers for conductivity from RT to 120°C with an understanding of chemistry/morphology conductivity relationships |
**Milestones 07/08**

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestone or Go/No-Go Decision</th>
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| Dec-07     | **Demonstrate conductivity of 70 mS cm\(^{-1}\) at 80% RH and room temperature –**  
30ºC 80% RH  50 mS cm\(^{-1}\)  
80ºC 100% RH >300 mS cm\(^{-1}\)  
*Comparable to PFSA membranes under FC operating conditions*  
120ºC 90%RH >70 mS cm\(^{-1}\)  
*Few measurements at this temperature to date* |
| June 08    | **Deliver membrane to topic 2 awardee –**  
Lower conductivity but more durable membrane selected for more consistent validation of results, delivered in April 08 |
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 1.1 – Phenyl link stability – complete
- Task 1.2 – Protonation approach – complete
- Task 2.1 – Development of HPA polymers – 50% complete
- Task 2.2 – Hybridization of polymer – 25% complete
Synthesis of Hybrid Monomer

\[
\begin{align*}
[\text{SiW}_{11}\text{O}_{39}]^{8-} + 2\text{RSi(OR')}_{3} + 4\text{H}^+ + \text{H}_2\text{O} & \quad \text{MeCN} \\
[\text{SiW}_{11}\text{O}_{39}(\text{SiR})_{2}\text{O}]^{4-} + 6\text{R'}\text{OH} & \quad \text{TBA}^+\text{Br}^- \\
\end{align*}
\]

\( R = \)

a. styryl \((-\text{C}_6\text{H}_5\text{CH}=\text{CH}_2)\)
b. Methacrylpropyl \((-\text{(CH}_2)_3\text{OCOCCH}_3=\text{CH}_2)\)
c. Vinyl \((-\text{CH}=\text{CH}_2)\)


Synthesis of PolyPOM

HSiW11(styryl)
2 monomer

R* → μν or heat

PolyPOM100s

Judeinstein, P. *Chem. Mater.* 1992, 4, 4-7
Design Space

- Only PolyPOM with >50wt% HPA have adequate proton conductivity
- Monomer components systematically varied with advice from 3M to emphasize film forming properties
- We can control chemistry
- Need to understand morphology

Vinyl methacrylate styrenyl ethylstyrenyl POM monomer, so far all based on HSiW11
Immobilization

100 MHz $^{13}$C CPMAS NMR

Aged membrane

- Residual organic vinyl protons slow to polymerize
- Leaching studies suggest small hydrocarbon oligomers leach out – not HPA polymer

As cast membrane
State of the art last year - PolyPOM50m

- Conductivity increases with POM content
- $\text{H}^+$ conductivity Comparable to PFSA ionomers at 100%RH and 80°C
- Conductivity depends on correct molecular engineering of film

- 25%RH
- 50% RH
- 75% RH
- 80% RH
- 100% RH
FSEC Results PolyPOM50v

4 Electrode Conductivity

- JLH-20-152a (4-9-08) 120C
- JLH-20-152a (4-8-08) 80C
- JLH-20-152a (4-8-08) 30C

Conductivity Calculated based on dry dimensions and no swelling.
Conductivity at 30°C for PolyPOM75v

30°C / 80% R.H.: 0.028-0.051 S/cm
80ºC PolyPOM75v – impressive conductivities >75%RH
Conductivity Calculated from Nernst-Einstein equation and NMR measurements at 100%RH
Challenge 1: Water uptake excessive
(similar to sulfonated hydrocarbon polymer)
SAXS indicates that monomer influences packing of HPA

<table>
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<th>Concentration/Level #</th>
<th>P</th>
<th>Rg [Å]</th>
<th>Eta [Å]</th>
<th>Packing Factor</th>
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<td>PolyPOM-24s L1</td>
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<td>3.4</td>
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<td>0.1</td>
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>50% HPA leads to significant clustering


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<td>4.6</td>
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Challenge 2: Morphology
(AFM shows cluster on the order of 100s of nm)

PolyPOM50v
Future Work

- Finish exploring design space for Si linked polyPOM – addition of dissociable proton functionalities should lead to high conductivity
- Develop more stable P linked polyPOM – move beyond model systems
- Fabricate polyPOM with significantly different polymer properties – 3M proprietary expertise
Summary

• Stable immobilized HPA (polyPOMs) are readily synthesized
• Si linked model compounds allow chemistry/morphology to be explored
• Proton conductivities comparable to PFSA ionomers were achieved before system optimization
• P linked and new polymer architectures readily available

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<th>April 2008</th>
<th>Project milestone</th>
<th>DOE 2010 target</th>
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<td>H⁺ conductivity</td>
<td>300 ms/cm 100%RH 80°C</td>
<td>70 ms/cm 80%RH, 30°C</td>
<td>100 ms/cm 25-40%RH at 120°C</td>
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