Advanced Fuel Cell Membranes Based on Heteropolyacids

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Overview

Timeline
• Project start date: FY 2005
• Project end date: tbd
• Percent complete: tbd

Budget
• Total project funding
  – DOE share: $300k
• Funding received in FY05:
  – $150K (0.3 FTE)
• Funding for FY06:
  – $150K (0.3 FTE)

Targets
• Low humidity operation (25% RH).
• High conductivity ~0.1 S/cm
• Cost $40/m²

Barriers
• Barriers addressed
  – O. Stack materials and manufacturing costs
  – P. Durability

Partner/Subcontract
• Colorado School of Mines
  – Prof. Andrew M. Herring
  – Dr. Steven F. Dec
Objectives

• Develop the methodology for the fabrication of 3D cross-linked, hydrocarbon-based membranes using immobilized heteropolyacids (HPAs) as the proton conducting moiety.
  – Conductivity ~0.1 S/cm at 120°C and <1.5 kPa H₂O

• Develop immobilization technology based on covalent attachment of HPAs to oxide nano-particles.

• Acquire an improved understanding of HPAs and their salts made by custom synthesis.
  – HPAs make up a class of inorganic proton conductors that exhibit high proton conductivity at low humidity (below 25% RH) and at elevated temperatures (well above 100°C).

• Conduct relevant characterizations of the membranes to better understand their structural, chemical, and thermal properties/stability and proton conductivity.
HPAs: High H⁺ Conductivity, High Thermal Stability; Vast Structural Diversity; Known Redox Catalysts

Keggin
\[[\text{SiW}_{12}\text{O}_{40}]^{4-}\]

\[
\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 26\text{H}_2\text{O} \\
\text{(W12-STA)}
\]

Dawson
\[[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}\]

\[
\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62} \cdot x\text{H}_2\text{O}
\]

Lacunary (allows easy attachment points)
\[[\text{SiW}_{11}\text{O}_{39}]^{8-}\]

\[
\text{H}_8\text{SiW}_{11}\text{O}_{39} \cdot 26\text{H}_2\text{O} \\
\text{(W11-STA)}
\]
Strategies for Immobilizing HPAs

A. Binding Approaches:
   1. Covalent bonding to oxide nano-particles insitu, which can bond covalently to, or embed physically in, a polymeric matrix
   2. Direct embedding in a polymeric matrix
   3. Covalent bonding directly to a polymeric matrix (CSM/3M collaboration, poster #FCP-6)

B. Modification of Lacunary HPAs:
   1. By bonding with functional silanes that can then be cross-linked or polymerized

C. Fabrication Approaches:
   1. Sol gel method
   2. Immobilized via silylation onto supporting particles
   3. Simple blending

D. Polymeric Matrix:
   1. Organic
   2. Inorganic
   3. Organic-inorganic hybrid

Ref. 14: “Heteropoly and Isopoly Oxometalates,” by M. T. Pope, Springer-Verlag, New York, 1983, Chap. 7, Fig. 7.8, p. 126.
Key Concept and Components in Composite Membrane Fabrication

3-D Cross-linked Composite Matrix

1. Silane
   \[ \text{Si(OR)}_4 \xrightarrow{\Delta} \text{Si(OH)}_4 \xrightarrow{\text{H}_2\text{O}} \text{SiO}_2 \text{ nano-particles} \]
   \[ \text{General Rxn: } \text{M(OR)}_n \xrightarrow{\text{M(OH)}}_{\text{n}}, \text{W, etc.} \]

2. Functional Silane
   \[ = \frac{\text{Si(OH)}_3}{\text{Si(OH)}_3} \]

3. Molecular Cross-linker
   \[ \text{PMG: an ethylene-methylacrylate copolymer w/glycidyl functional groups} \]

4. Polymer
   \[ \text{P} \]

5. Heteropoly Acid (HPA)
   (a). Keggin [SiW\(_{12}O_{40}\)]\(^4-\)
   \[ \text{H}_3\text{SiW}_{12}\text{O}_{40} \xrightarrow{26\text{H}_2\text{O}} \text{W}_{12}\text{O}_{40}^{2-} \text{(W12-STA)} \]
   (b). Organic derivative with Silane
   \[ [\text{Si}(\text{SiW}_{11}\text{O}_{39})]^+ \text{ (ref. 1-4)} \]

Hydrolysis: \(\bigcirc\)
Condensation: \(\Delta\)
Cross-linking: \(\bigcirc\)
Procedure for Fabricating 3D Cross-Linked HPA/SiO₂/Functional Silane Sol Gel Composite & PEM Membrane with PMG

TEOS + Functional Silane + pH = 1.35 H₂O + HPA

aged (gelled) solution

diluted with THF or EtOH

Sol Gel Composite

Sol Solution

Liquid Mixture

Bonded STA%, IEC, & Other Analyses/Tests

solution cast

As-cast Film

thermal or UV X-linking

Cured PEM

Silanes: Methacrylate-type: Z-6030
         Epoxy-type: A-186, A-187

HPAs:   H₄SiW₁₂O₄₀ (W₁₂-STA)
        H₈SiW₁₁O₃₉ (W₁₁-STA)
        K₈SiW₁₀O₃₆ (KW₁₀-STA)

Host Polymer Dissolved in THF or EtOH

Curing Agent, X-linker

Polymer: PMG or BSPPO

(3D Network of SiO₂/silane/HPA/PMG)
Formation of SiO$_2$ Nano-Particles in Composite Matrix upon Thermal Treatments (TEM Analysis)

As grown with 10x diluted PEM-#9D solution

Annealed at 80°C for 20 min
Annealed at 140°C for 5 min
Annealed at 190°C for 2 min
Flexibility of PEM Membranes Fabricated with High HPA Loading

PEM-#9B,C,D Films: W12-STA/(PMG + Cross-Linker) = 174 Wt%
Immobilizing the HPA
Binding HPA with Z-6030 Silane in Sol Gel Composite ➔ W12-STA Retained

W12-STA/SiO\textsubscript{2}/Z-6030
(W12-STA washed off easily without Z-6030)
Chemical Stability Test of PEM Films in Fenton Reagent

**Fenton’s Reagent:**
4 ppm Fe$^{2+}$ + 3% H$_2$O$_2$

at 68°C

**Control (no W12-STA)**

**PEM-#5:** W12-STA at 165 wt%, cured at 145°C/2-ton/5-min

**PEM-#6:** W12-STA at 153 wt%, cured at 145°C/1-ton/5-min

Weight loss due to W12-STA extraction
PEM Mechanical Strength and Flexibility Reduced by Increasing HPA Loading

FTIR-ATR Spectra of Cured Control Blanks and PEM-#7

- **Low STA wt%**
- **Film Flexibility Reduced**
- **Control (no W12-STA & SiO₂)**
- **Control (no W12-STA)**
- **PEM-#7 (W12-STA at 174 wt%)**

(H₂O)
H⁺ Conductivity as a Function of Cell Temperature at 100% RH

Proton Conductivity of PEM-#9D, Film #1, Strip#3

Scan Rate (mV/s):
- 10
- 50
- 100

Temperature Conditions:
- 27°C/100%RH
- 40°C/100%RH
- 60°C/100%RH
- 70°C/100%RH
- 80°C/100%RH

Scan Range:
- -0.50V - +0.50V

Forward Scan (-0.50V - 0.0V)
Return Scan (0.0V - -0.50V)
Table 1. PEM Compositions vs Proton Conductivity Derived from I-V Curves of CV Scans

<table>
<thead>
<tr>
<th>PEM ID</th>
<th>HPA</th>
<th>Components</th>
<th>Weight Ratio</th>
<th>Best Proton Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Host Polymer</td>
<td>X-Linker</td>
<td>HPA/(PMG + X-Linker)</td>
</tr>
<tr>
<td>1</td>
<td>HSiW12Ox</td>
<td>BSPPO</td>
<td>No</td>
<td>0.56</td>
</tr>
<tr>
<td>2</td>
<td>HSiW12Ox</td>
<td>PMG</td>
<td>Yes</td>
<td>0.81</td>
</tr>
<tr>
<td>3</td>
<td>HSiW11Ox</td>
<td>PMG</td>
<td>Yes</td>
<td>1.09</td>
</tr>
<tr>
<td>4</td>
<td>KSiW10Ox</td>
<td>PMG</td>
<td>Yes</td>
<td>1.05</td>
</tr>
<tr>
<td>5</td>
<td>HSiW12Ox</td>
<td>PMG</td>
<td>Yes</td>
<td>1.50</td>
</tr>
<tr>
<td>6</td>
<td>HSiW12Ox</td>
<td>PMG</td>
<td>Yes</td>
<td>1.54</td>
</tr>
<tr>
<td>7</td>
<td>HSiW12Ox</td>
<td>PMG</td>
<td>Yes</td>
<td>1.74</td>
</tr>
<tr>
<td>8</td>
<td>HSiW12Ox</td>
<td>PMG</td>
<td>Yes</td>
<td>1.74</td>
</tr>
<tr>
<td>9B</td>
<td>HSiW12Ox</td>
<td>PMG</td>
<td>Yes</td>
<td>1.74</td>
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<tr>
<td>9C</td>
<td>HSiW12Ox</td>
<td>PMG</td>
<td>Yes</td>
<td>1.74</td>
</tr>
<tr>
<td>9D</td>
<td>HSiW12Ox</td>
<td>PMG</td>
<td>Yes</td>
<td>1.74</td>
</tr>
<tr>
<td>Nafion 112</td>
<td>SO3H</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>1</sup> Values of the proton conductivity at 120°C/23%RH are with large uncertainty because of rapidly lost linearity on I-V curves.
High H⁺ Diffusion Coefficients for Composite Membrane

Proton Diffusion Data from PFG-NMR Measurements

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>H⁺ Diffusion Coefficient (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.0 × 10⁻⁶</td>
</tr>
<tr>
<td>40</td>
<td>5.0 × 10⁻⁶</td>
</tr>
<tr>
<td>60</td>
<td>1.0 × 10⁻⁵</td>
</tr>
<tr>
<td>80</td>
<td>1.5 × 10⁻⁵</td>
</tr>
<tr>
<td>100</td>
<td>2.0 × 10⁻⁵</td>
</tr>
<tr>
<td>120</td>
<td>2.5 × 10⁻⁵</td>
</tr>
<tr>
<td>140</td>
<td>3.0 × 10⁻⁵</td>
</tr>
</tbody>
</table>

PEM-#5 (W12-STA at 150 wt%)
Nafion
(8.8 mS/cm at 80°C/100%RH)
DSC Thermograms of W12-STA, SiO₂, and Two Sol Gel Composites

Moisture Retaining Capability of W12-STA and Sol Gel Composites (DSC Analysis)

W12-STA/SiO₂/Z-6030
W12-STA/SiO₂/A-186

Moisture Retaining Capability of W12-STA and Sol Gel Composites

TGA and DSC Thermograms for PEM-20050823 Membrane

TGA and DSC of as-cast, 80°C-pressed, and 145°C-cured PEM

PEM-#6: W12-STA loading level at 153 wt%/ (PMG+ X-linker)
Summary of Accomplishments
PEM Fabrication and Performance

• We have shown the ability to retain HPAs into a polymer-composite matrix of our design.

• Properties of HPA-based composite PEMs:
  – high chemical stability (Fenton’s reagent test)
  – good thermal stability (with highly reactive W12-STA)
  – good mechanical flexibility
  – effective binding of silicotungstic acids (Wn-STA) with select functional silanes (n = 10, 11, 12)
  – high Wn-STA loading [HPA/(PMG + X-Linker) > 150 wt%]
  – moderate proton conductivity (25 mS/cm at 80°C/100%RH)

• Clear progress towards meeting the DOE targets
Achieving Fundamental Goals

Future Work

• To continue to improve/modify/optimize the current PEM composite formulation, fabrication, and processing conditions
  – to enhance PEM’s thermal stability in the 90-120°C range
  – to improve mechanical strength and flexibility
  – to reduce membrane thickness and improve film uniformity

• To continue to develop immobilization strategies for various HPAs, custom-synthesized at CSM, that show high proton diffusion coefficients and thermal stability.

• To understand the binding mechanism of HPA with functional silanes and SiO₂ nano-particles in the polymer matrix.

• To understand the proton conduction mechanism in the 3D cross-linked composite membranes in order to further improve proton conductivity at low humidity and elevated temperatures.
“One of the few new, alternative ideas for membranes in the whole DOE program”

• Issues:
  – …needs to present conductivity values for membranes with “fixed” HPAs…
    • Done
  - HPA approach is sound as a demonstration but water solubility must be addressed…
    • Excellent progress has been made in this regard
  – Nafion doped in HPAs has been shown to be feasible…the PI is in need of new insight.
    • Not part of our project, those figures were for introduction to HPAs only
    • Our project is focused on developing a composite hydrocarbon membrane using HPAs as the proton conducting moiety that will meet the DOE targets for operation at low RH and higher temperatures

• Future:
  – Need durability studies in actual operating fuel cell conditions and …thermal and RH cycling…gas crossover measurements
    • PEMs of 3D cross-linked PMG matrix were not available yet at the time
    • These subjects will be investigated for HPA-based PEMs this summer
Presentations and Publications


5. F. J. Pern, J. A. Turner, and A. M. Herring; “Hybrid Proton Exchange Membranes Based on Heteropoly-Acid and Sulfonic-Acid Proton Conductors,” ECS 2006, Abstract (accepted for oral presentation)


