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: $150k

Barriers
• Barriers addressed
  – Thermal, Air and Water Management
  – Cost.
  – Durability

Partners
• 3M
• Colorado School of Mines.
Objectives and Approach

- To demonstrate dry inlet gas operation of HPA-based PEMs in FC at $T \geq 80^\circ C$.
- Synthesize and characterize selected “saturated” and lacunary heteropoly acids (HPA) that have high potential for the fabrication of FC membranes.
- Fabricate heteropoly acid-based proton exchange membrane (PEM)
  - Mechanically strong
  - Stable operation
  - Low-cost
  - Higher temperature/low humidity operation.
Example Structures of Three HPAs

1. Keggin (saturated)

\[ \text{[SiW}_{12}\text{O}_{40}]^{4-} \]
\[ \text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 22\text{H}_2\text{O} \]
(12-HSiW)

2. Lacunary (vacant sites)

\[ \text{[SiW}_{11}\text{O}_{39}]^{8-} \]
\[ \text{H}_8\text{SiW}_{11}\text{O}_{39} \cdot 26\text{H}_2\text{O} \]
(11-HSiW)

3. Dawson

\[ \text{[P}_2\text{W}_{18}\text{O}_{62}]^{6-} \]
\[ \text{H}_6\text{P2W}_{18}\text{O}_{62} \cdot x\text{H}_2\text{O} \]
(18-HP2W)
### TGA for Various HPAs
(after heating to 110 °C)

<table>
<thead>
<tr>
<th>HPA</th>
<th>Water of crystallization</th>
<th>Secondary structure water</th>
<th>Neutralization</th>
<th>Decomp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃PW₁₂O₄₀</td>
<td>1</td>
<td>50</td>
<td>6</td>
<td>164</td>
</tr>
<tr>
<td>H₈SiW₁₁O₃₉</td>
<td>2</td>
<td>60</td>
<td>7</td>
<td>152</td>
</tr>
<tr>
<td>H₆SiV₂W₁₀O₄₀</td>
<td>6</td>
<td>129</td>
<td>2</td>
<td>250</td>
</tr>
<tr>
<td>H₈SiV₃W₁₀O₄₀</td>
<td>7</td>
<td>183</td>
<td>2</td>
<td>477</td>
</tr>
<tr>
<td>H₆ZnW₁₂O₄₀</td>
<td>10</td>
<td>90</td>
<td>10</td>
<td>160</td>
</tr>
<tr>
<td>H₆P₂W₁₈O₆₂</td>
<td>4</td>
<td>114</td>
<td>3</td>
<td>290</td>
</tr>
<tr>
<td>NaₓHᵧP₂W₁₈O₆₂</td>
<td>7</td>
<td>60</td>
<td>5</td>
<td>114</td>
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<tr>
<td>H₆As₂W₂₁O₆₉</td>
<td>12</td>
<td>129</td>
<td>4</td>
<td>430</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>316</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₆P₂W₂₁O₇₁</td>
<td>4</td>
<td>170</td>
<td>3</td>
<td>350</td>
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<tr>
<td>H₂₁B₃W₃₉O₁₃₂</td>
<td>17</td>
<td>59</td>
<td>7</td>
<td>203</td>
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</tbody>
</table>
Proton Diffusion Coefficients of HPAs Determined by PF-NMR

<table>
<thead>
<tr>
<th>HPA</th>
<th>Max diffusion coefficient $x 10^{-6}$ cm$^2$s$^{-1}$</th>
<th>Temperature of maximum $D$, °C</th>
<th>$E_a$ before Max T, kJ mol$^{-1}$</th>
<th>IR H-bond strength</th>
<th>Secondary structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-HPW</td>
<td>25</td>
<td>117</td>
<td>13</td>
<td>20</td>
<td>H$^+$(H$_2$O)$_x$</td>
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<tr>
<td>12-HSiW</td>
<td>30</td>
<td>130</td>
<td>20</td>
<td>40</td>
<td>H$^+$(H$_2$O)$_x$</td>
</tr>
<tr>
<td>12-HZnW</td>
<td>2</td>
<td>108</td>
<td>27</td>
<td>30</td>
<td>H$_3$O$_2^+$, OH</td>
</tr>
<tr>
<td>12-HGeW</td>
<td>0.7</td>
<td>90</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11-SiW11</td>
<td>3</td>
<td>108</td>
<td>6</td>
<td>35</td>
<td>H$_3$O$_2^+$, OH</td>
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<tr>
<td>39-HB3W</td>
<td>7</td>
<td>128</td>
<td>8</td>
<td>18</td>
<td>H$^+$(H$_2$O)$_x$</td>
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<tr>
<td>18-HP2W</td>
<td>1.2</td>
<td>&gt;150</td>
<td>20</td>
<td>20</td>
<td>H$_3$O$^+$</td>
</tr>
<tr>
<td>21-HAs2W</td>
<td>3.7</td>
<td>&gt;150</td>
<td>18</td>
<td>18</td>
<td>H$_5$O$_2^+$</td>
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<tr>
<td>21-H$_2$Rb$_4$As2W</td>
<td>30</td>
<td>25</td>
<td>-</td>
<td></td>
<td>H$^+$(H$_2$O)$_x$</td>
</tr>
<tr>
<td>21-HP2W</td>
<td>2.3</td>
<td>110</td>
<td>24</td>
<td>27</td>
<td>H$_3$O$^+$</td>
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</tbody>
</table>
Polarization curves of PEM made of 12-HPW physically blended in PVDF-HFP

\[ \begin{align*}
\text{I (mA/cm}^2) \quad & \quad \text{E (V)} \\
0 & \quad 0.7 \\
200 & \quad 0.6 \\
400 & \quad 0.5 \\
600 & \quad 0.4 \\
800 & \quad 0.3 \\
1000 & \quad 0.2 \\
1200 & \quad 0.1 \\
1400 & \quad 0.0 \\
1600 & \quad 0.0 \\
1800 & \quad 0.0 \\
\end{align*} \]
Diffusion coefficient data for HPA doped Nafion® 112 protons
Polarization curves comparing Nafion® and HPA-doped Nafion®

120 °C Nafion® 112, 25% RH, No ionomer in electrode (ELAT) 0.5 mg/cm² 20% Pt on carbon.
Strategies for Immobilizing HPAs

A. Bonding Approaches:
   1. Covalent bonding directly to a polymeric matrix
   2. Covalent bonding to oxide nanoparticles, which can further bond covalently to, or embed physically in a polymeric matrix
   3. Direct embedding in a polymeric matrix

B. Modification of Lacunary HPAs:
   1. By bonding with functional silanes that can then cross-linked or be 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
Multiple Approaches for Making HPA-based Hybrid PEM

Sol gel composite having HPA covalently bonded to, or physically embedded, in SiO$_2$—silane matrix

Film forming property of polymer materials and methods for forming good polymeric membranes

HPAs synthesis and characterization

Sol gel synthesis method and conditions

mechanically strong, thermally stable, high performance, hybrid FCPEM membranes
Polymerization Methods for immobilizing H⁺ Carrier/Transmitter Composites

1. Post-Polymerization:  
\[ C=C\text{---Si-O-(H⁺)-O-Si-} \rightarrow C=C\text{---Si-O-(H⁺)-O-Si-} \]  
\[(H⁺): \text{ proton donor}\]

2. Pre-Polymerization  
\[ C-C\text{---Si}-(OR)₃ + \text{ (+ SiO₂) + (H⁺)} \rightarrow C-C\text{---Si-O-(H⁺)-O-Si-} \]

3. Co-Polymerization:  
\[ C=\text{C---Si}-(OR)₃ + (H⁺) \text{ (+ SiO₂) (+ Modifier)} \rightarrow C-C\text{---Si-O-(H⁺)-O-Si-} \]
Procedure for Fabricating Hybrid Composite PEM Membranes

TEOS + Functional Silane + pH=1.35 H₂O + HPA

Sol gel film or powders

aged (gelled) solution

diluted with EtOH or THF

Sol solution

Polymer dissolved in organic solvent (EtOH or THF)

Liquid Mixture

Curing Agent, X-linker

solution cast

As-cast film

thermal press/X-link or UV X-link

Cured PEM

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

HPAs: H₄SiW₁₂O₄₀ (12-HSiW)
H₈SiW₁₁O₃₉ (11-HSiW)
K₈SiW₁₀O₃₆ (10-HSiW)

Bonded STA%, IEC, & other analyses/tests
“Bonding HPA”: Sol Gel Composite (No Silane) ➞ 12-HSiW Washed Off

FJP-0108, SiO2-HSiWOx as-made; Tue Jan 21 10:58:29 2003
FJP-0108 (TEOS-HSiWOx) Powder Washed; Sat Jan 25 14:17:50 2003
HSiWOx powder in KBr Thu Nov 14 12:27:07 2002
TEOS-02 SiO2 Powder Washed; Sat Jan 25 15:05:02 2003

12-HSiW/SiO₂

As-made

H₂O-washed

12-HSiW

SiO₂ sol gel

Absorbance

Wavenumbers (cm⁻¹)
“Bonding HPA”: Sol Gel Composite (with
Z-6030 silane) \(\rightarrow\) 12-HSiW Retained

\[
\begin{align*}
12-\text{HSiW}/\text{SiO}_2/Z-6030
\end{align*}
\]
## HSiWxOy Bonded/Embedded to Silica/Silane Network and IEC of Sol Gel Composites

### Table 1. Molar Ratios vs. Weight% of Bonded HSiWOx and IEC of Composite Powders

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Composition</th>
<th>Molar Ratio Normaliz. to SiO2</th>
<th>Bonded/Total Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO2/Silane/HPA</td>
<td>COS/TEOS Silane HSiWOx Ratio (%)</td>
<td></td>
</tr>
<tr>
<td><strong>Cab-O-Sil Approach</strong></td>
<td></td>
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<tr>
<td>W12-STA</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>FJP-1004</td>
<td>COS/Z-6030/HSiWOx</td>
<td>1.00 0.62 0.016</td>
<td>39.06</td>
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<tr>
<td>FJP-1012</td>
<td>COS/HSiWOx</td>
<td>1.00 0.00 0.016</td>
<td>6.72</td>
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<tr>
<td>FJP-1126*</td>
<td>COS/Z-6030/HSiWOx</td>
<td>1.00 0.33 0.04</td>
<td>0.89</td>
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<tr>
<td><strong>Sol Gel Approach</strong></td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>FJP-0108</td>
<td>TEOS/HSiWOx</td>
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<td>15.26</td>
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<tr>
<td>TEOS-0111</td>
<td>TEOS/Z-6030/HSiWOx</td>
<td>1.00 0.63 0.04</td>
<td>36.80</td>
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<tr>
<td>TEOS-A186</td>
<td>TEOS/A-186/HSiWOx</td>
<td>1.00 0.90 0.03</td>
<td>88.24</td>
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<tr>
<td>TEOS-A187</td>
<td>TEOS/A-187/HSiWOx</td>
<td>1.00 1.01 0.03</td>
<td>79.20</td>
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<td>TEOS-0303A</td>
<td>TEOS/Z-6030/HSiWOx</td>
<td>1.00 1.88 0.06</td>
<td>95.17</td>
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<td>TEOS-0304</td>
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<td>W11-STA</td>
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<tr>
<td>TEOS-0403</td>
<td>TEOS/Z6030/HSiW11Ox</td>
<td>1.00 0.94 0.06</td>
<td>97.30</td>
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<tr>
<td>TEOS-0404</td>
<td>TEOS/A-186/HSiW11Ox</td>
<td>1.00 0.90 0.06</td>
<td>95.74</td>
</tr>
</tbody>
</table>

* Final solution pH~4.3; all others pH ≤ 1.0. **IEC are for H2O-washed powders.**
Water-retention capability of SiO$_2$, 12-HSiW, and two 12-HSiW/SiO$_2$/Silane sol gel composites (DSC Analysis)
12-HSiW/SiO₂/BSPPPO Hybrid PEM

TGA-FTIR Analysis:
PEM-0105 Oven-heated at 120°C for 1h

12-HSiW/BSPPPO = 44 wt%
SiO₂/BSPPPO = 13.5 wt%

BSPPPO: a specialty polypropylene oxide
TGA Analysis of a Hybrid Membrane and its Key Components

TGA Thermograms of PEM-0624A Membrane and its Key Components

Weight (%) vs. Temperature (°C)

12-HSiW
Nafion 117
TEOS-0304
Uncured PEM-0410A
Cured PEM

12-HSiW/SiO2/A-186/PEMAGMA

Universal V2.4F TA Instruments
Flexible, high-HSiW-loading hybrid PEMs are obtained for the first time

PEM-20050404A: 11-HSiW/TEOS/Z6030/PEMAGMA, STA/Polym=109 wt%
PEM-20050404B: 12-HSiW/TEOS/Z6030/PEMAGMA, STA/Polym=114 wt%

145C/10m Cured
Accomplishments/Progress - 1
– HPA and Doped Nafion®

- **HPAs**: A large number of HPAs based on the Keggin, Dawson, and more complex skeletons have been synthesized and their structural properties relevant to proton conduction elucidated by IR, NMR. Thermal stability of all proton conducting phases determined by TGA.
- Proton diffusion properties are characterized by pulse field gradient spin echo NMR. Many HPA have high diffusion coefficients and low activation energies for diffusion.
- **HPA/PVDF**: HPA high proton conduction under dry conditions was demonstrated in a PVDF matrix.
- **HPA Doped Nafion®**: Nafion® was doped with various HPA which interact strongly with the –SO₃H groups and in some cases dramatically improved proton diffusion.
- These doped Nafion® membranes were incorporated in MEAs and tested in a fuel cell, showing dramatic improvements at 120°C, but as the HPA in these systems are not immobilized this may be a result of improvements to the membrane/electrode interface.
Accomplishments/Progress – 2
-- PEM Fabrication and Performance

• **SiO$_2$ Sol Gel Composite-Polymer Hybrids:**
  – by simple mixing method
  – by “Two-Step” method
  – by direct copolymerization method
  – various host polymers
  – on-going work

• **Sol-gel synthetic methods:** Several are established for making HPA-containing sol gel composites with the functional silanes

• **HPA-containing hybrid PEM membranes:** Physical blending, two-step and direct copolymerization methods are developed.

• **Analytical procedures** are established for IEC, bleaching, structural, thermal stability analysis, electrical (conductivity), and fuel cell performance tests.
Summary

• A variety of HPAs have been successfully synthesized, characterized, and used for PEM fabrications.

• A variety of methods for immobilizing HPAs in different polymer matrices have been successfully demonstrated:
  – Physical blending/embedding
  – Sol gel composite-polymer hybrid
    – Flexible, cross-linked, high-STA-loading hybrid PEMs are obtained for the first time

• FC performance test results indicate the HPA-based PEMs are very promising for high-temp operations without the need of humidification.
Future Work

• Understand the synergistic interaction of HPA with ionomers in terms of improving proton conduction at low humidity/elevated temperatures

• Continue to develop immobilization strategies and optimize hybrid HPA for proton conduction
Hydrogen Safety

The most significant, potential hydrogen hazard associated with this project is fire and/or explosion due to either leak, ignition, or strong impact of the highly pressurized H₂ gas cylinders, resulting in personnel injuries and/or loss of equipment in the laboratory.
Hydrogen Safety

Our approach to deal with the potential hazard:

- A Standard Operating Procedure (SOP) has been implemented.
- All personnel involved in the use of compressed H$_2$ cylinders are required to take pertinent ES&H training at NREL and familiar with the SOP prior to being authorized for work.
- Personnel protective equipment (PPE) such as safety goggles or glasses are required when present in the lab. Wearing a face shield is required when changing the pressure regulator.
- The H$_2$ cylinders are well secured and properly capped when not in use. NFPA warning labels (e.g., High Pressure Gas, Flammable Compressed H$_2$) are attached to the cylinders. Valves are only opened to the necessary pressure.
- No hot work, open fire, and compressed O$_2$ cylinders are allowed nearby the H$_2$ cylinders or fuel cell test station.
- Regular check of leaking is conducted with soapy water solution.
- Fire extinguishers are available in the laboratory.
- Emergency response and exit are clearly stated in the SOP and also marked in the lab.