

## VII.B.10 Advanced Fuel Cell Membranes Based on Heteropolyacids

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### Objectives

- Acquire an improved understanding of heteropolyacids (HPAs) and their salts. HPAs make up a class of inorganic proton conductors that exhibit high proton conductivity at low humidity (below 25% relative humidity [RH]) and at elevated temperatures (well above 100°C).
- Apply that understanding to fuel cell membrane technology by developing mechanically strong, low-cost, durable, high-performance HPA-based proton exchange membranes (PEMs) that can operate in a fuel cell at a low level of humidification of  $\leq 25\%$  RH.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- B. Cost
- D. Thermal, Air and Water Management

### Technical Targets

This project addresses the technical targets from Table 3.4.12 of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan. Table 3.4.12 shows the DOE technical targets for membranes for transportation applications, and our specific targets being addressed are membrane conductivity and cost. Also included is operation at low relative humidity.

### Approach

The work is broken down into five steps:

- Synthesize and characterize selected “saturated” and lacunary HPAs that have high potential for the fabrication of fuel cell (FC) membranes.
- Synthesize and characterize HPA/organic polymer mixtures and fabricate low-cost, mechanically strong, HPA-based PEMs.
- Synthesize and characterize HPA/inorganic polymer mixtures where the HPA is immobilized.
- Measure proton diffusion at low humidity ( $<25\%$  RH) and in the temperature range of 0°–120°C.

- Demonstrate HPA in a membrane electrode assembly (MEA) in a fuel cell at less than 25% RH for the input gases.

## Accomplishments

During the relatively short performance period of ~4 months under the current funding, we have made significant progress on the basis of previous studies.

- Demonstrated the synthesis and characterization of various saturated and lacunary HPAs.
  - We have synthesized a large number of HPAs based on the Keggin, Dawson, and more complex structures and elucidated their structural properties relevant to proton conduction using infrared (IR) and nuclear magnetic resonance (NMR). We used thermogravimetric analysis (TGA) to determine the thermal stability of all the phases.
  - Pulse field gradient–NMR (PFG-NMR) was used to characterize proton diffusion properties. Many HPAs were found to have high diffusion coefficients and low activation energies for diffusion, as shown in Table 1.

**Table 1.** Proton Diffusion Coefficients of Various HPAs Determined by PFG-NMR

HPA	Max diffusion coefficient $\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$	Temperature of maximum D, $^{\circ}\text{C}$	$E_a$ before Max T, $\text{kJ mol}^{-1}$	IR H-bond strength, $\text{kJ mol}^{-1}$	Secondary structure	
12-HPW	25	117	13	20	$\text{H}^+(\text{H}_2\text{O})_x$	cubic
12-HSiW	30	130	20	40	$\text{H}^+(\text{H}_2\text{O})_x$	cubic
12-HZnW	2	108	27	30	$\text{H}_5\text{O}_2^+$ , OH	cubic
12-HGeW	0.7	90	35			cubic
11-SiW11	3	108	6	35	$\text{H}_5\text{O}_2^+$ , OH	cubic
39-HB3W	7	128	8	18	$\text{H}^+(\text{H}_2\text{O})_x$	sheets
18-HP2W	1.2	>150	20	20	$\text{H}_3\text{O}^+$	triclinic
21-HAs2W	3.7	>150	18	18	$\text{H}_5\text{O}_2^+$	
21-H <sub>2</sub> Rb <sub>4</sub> As2W	30	25	–		$\text{H}^+(\text{H}_2\text{O})_x$	channels
21-HP2W	2.3	110	24	27	$\text{H}_3\text{O}^+$	

- Demonstrated that various HPAs that are physically embedded in fluoropolymers can operate in the absence of gas humidification.
  - HPA in PVDF: HPA high proton conduction under dry conditions was demonstrated in a PVDF matrix.
  - HPA-doped Nafion<sup>®</sup>: Various HPAs interact strongly with the sulfonic acid groups in the Nafion and, in some cases, dramatically improved proton diffusion. These HPA-doped Nafion membranes were incorporated in MEAs and tested in a fuel cell, showing dramatic improvements at 120°C. However, because the HPAs in these systems are not immobilized, these observations may result from improvements in the membrane/electrode interface.
- Demonstrated the feasibility of either physically embedding or chemically covalently bonding the saturated and lacunary HPAs via sol-gel synthetic methods with functional silanes for making composite

nano-scaled silica/HPA/polymer hybrid membranes. Figure 1 schematically illustrates the multiple approaches that follow:

- Simple mixing method
- “Two-step” method
- Direct copolymerization method
- Flexibility with various host polymers
- Demonstrated for the first time the fabrication of mechanically flexible, covalent-bonded, and ~100% cross-linked hybrid composite films with high silicotungstic acid (STA)/polymer ratio (>100 wt%).
  - In preliminary conductivity measurements, one such membrane, made using a simple solution cast method, exhibited ~0.013 S/cm at 80°C and 100% RH.
- Analytical procedures are established for bleaching, structural, thermal stability analysis, electrical (conductivity), and fuel cell performance tests.

### Future Directions

Our plans for advancing the task activities follow:

- Understand the synergistic interaction of HPA with ionomers in terms of improving proton conduction at low humidity and elevated temperatures.
- Continue to develop immobilization strategies and optimize hybrid HPA for proton conduction.
- Continue to improve the PEM membrane fabrication methods with greater control of film thickness and compositional uniformity.
- Continue to determine and improve the conductivity of various HPA-containing PEMs to achieve the targeted 0.1 S/cm at low humidity (25% RH) and elevated temperatures (80°–120°C).
- Conduct fuel cell tests for performance and durability of HPA-containing PEMs.

### Introduction

The primary objective of this work is to develop low-cost, high-performance, HPA-based PEMs to replace the conventional sulfonic acid (SFA)-based PEMs, which require a relatively high level of moisture for proton conduction at temperatures typically below 80°C. HPAs are known to have high proton conductivity and high thermal stability at temperatures >250°C. Their abilities to conduct protons in the absence of moisture have been demonstrated by our group. In this work, we have collaborated closely with the fuel cell group at the Colorado School of Mines and 3M, focusing on the development of novel HPA-based composite membranes and MEAs for fuel cell applications.

## Multiple Approaches for Making HPA-based Hybrid PEM

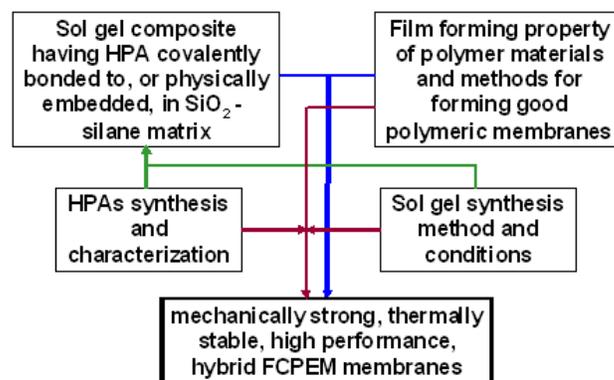
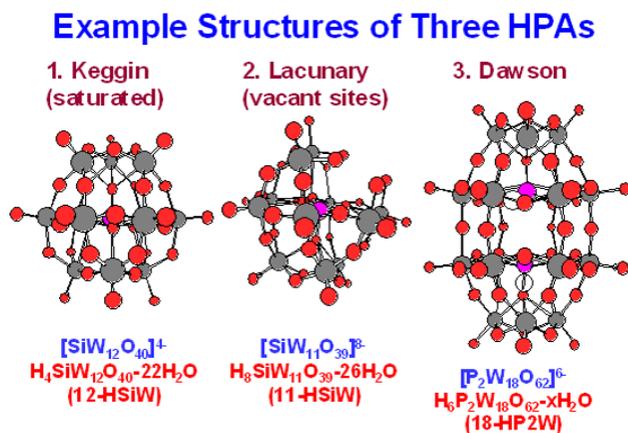


Figure 1. Synthesis Pathways for Composite HPA Membranes

### Approach

To fabricate HPA-based hybrid PEMs for fuel cell applications, two main issues need to be resolved. The first is that the HPAs that are most suitable for the PEM applications must be identified and characterized. To determine this, we synthesized a number of potential candidates and characterized them thoroughly with Fourier transform infrared (FTIR; for molecular structure), TGA (for thermal stability), and PFG-NMR (pulsed field gradient nuclear magnetic resonance) spectrometry. The HPAs that are more likely to be viable for PEM applications are those with higher proton diffusion coefficients as determined by PFG-NMR, shown in Table 1. There are three major types of HPAs



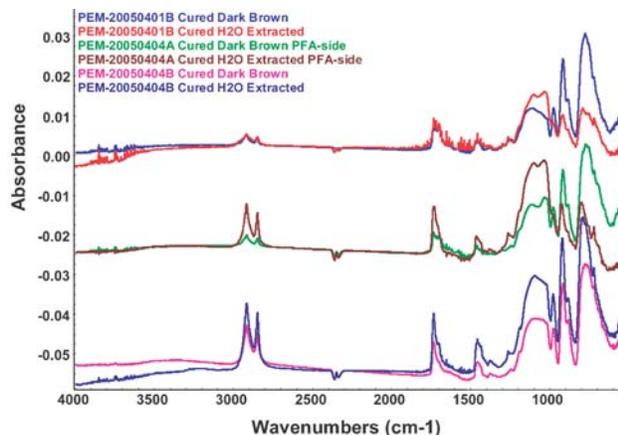
**Figure 2.** HPA Structures: Saturated Keggin, Lacunary with Vacant Sites, and Dawson

(illustrated in Figure 2) as categorized by their structures: saturated Keggin, lacunary with vacant sites, and Dawson.

The second issue is how the HPA is incorporated and fabricated into suitable PEM films. In this regard, we have been investigating a number of methods and “host” polymers, as exemplified in Figure 1. The simplest method is to physically blend or embed HPA in a host polymer and cast it into a membrane. A potential problem of this approach is the leaching of HPA by water during operation because the HPA molecules may not be strongly held by the host polymer. A better method is to covalently bond HPA to the host polymer. To facilitate this, we employ a sol-gel approach to produce nano-scaled silicon dioxide ( $\text{SiO}_2$ ) with functional silanes to immobilize the HPA in a 3-D network. The functional silanes can be further covalently polymerized and cross-linked with the host polymer matrix. Furthermore, the lacunary HPA, such as 11-HSiW (see Figure 2), has a vacant site that can form covalent bonds with the siloxy group of silane. Therefore, in principle, a silane with a functional group such as methacrylate or epoxide ring can be used to form the bridge (i.e., covalent bonding) between the HPA and the host polymer. This approach is one area of our research.

## Results

We have synthesized a large number of HPAs in our work and characterized their structural, thermal, and proton diffusion properties. In the making of



**Figure 3.** FTIR-ATR spectra, from top to bottom, grouped for the three cured hybrid films *before* and *after* water extraction: PEM-20050401B (12-HSiW, blue versus red), PEM-20050404A (11-HSiW, green versus light blue), and PEM-20050404B (12-HSiW, purple versus black)

PEMs, in addition to the physical blending method, we have successfully demonstrated for the first time the feasibility of covalently bonding HPA at a high weight percent level (>100 wt% HPA/polymer) to a host polymer as discussed in the Approach section. For example, custom-synthesized lacunary  $\text{H}_8\text{SiW}_{11}\text{O}_{39}$  (11-HSiW) was reacted first with a methacrylate-based binding silane. Then, nano-scaled  $\text{SiO}_2$  was introduced via sol-gel conversion, along with a molecular cross-linker, a thermal curing agent, and a polymer host of glycidyl methacrylate-type copolymer (PMG). After casting into films from the solutions, the air-dried membranes were pressed and cured at  $\sim 145^\circ\text{C}$ , during which the methacrylate functional groups were polymerized and nearly 100% cross-linked covalently to the PMG polymer host. PEM films prepared by this method have shown that a high level of HPAs could be retained in the 3-D matrix even after soaking in an  $85^\circ\text{C}$  water bath for almost 1 day. Figure 3 shows the FTIR-ATR (attenuated total reflection) spectra confirming the presence and retention of 10-, 11-, and 12-HSiW in the silica/PMG matrix before and after soaking in an  $85^\circ\text{C}$  water bath for nearly 1 day. We have also immobilized saturated Keggin and lacunary STAs (10-, 11-, and 12-HSiW) in the matrix of silica/Nafion.

Preliminary conductivity measurements of the 11-HSiW-PMG film using a 4-probe cell

demonstrated a proton conductivity of ~13 mS/cm at 80°C and 100% RH. This shows about three orders of magnitude improvement over previous films.

### **Conclusions**

- We have successfully synthesized, characterized, and used a variety of HPAs for PEM fabrications.
- We also successfully demonstrated two methods for immobilizing HPAs in different polymer matrices:
  - Physical blending/embedding
  - Sol-gel composite-polymer hybrid
- Flexible, cross-linked, high-HSiW-loading hybrid PEMs have been obtained for the first time.
- Fuel cell performance test results indicate the HPA-based PEMs are very promising for high-temperature operations without the need for humidification.

### **FY 2005 Publications/Presentations**

1. Advanced Fuel Cell Membranes Based on Heteropolyacids. Poster presentation at the 2005 DOE Hydrogen Program Review Meeting, Washington, DC, May 24, 2005.

2. Pern, F. J., Turner, J. A., Meng, F., and Herring, A. M. Sol-Gel SiO<sub>2</sub>-Polymer Hybrid Heteropoly Acid-Based Proton-Exchange Membranes. Abstract submitted to the Materials Research Society 2005 Fall Meeting, Energy and The Environment Symposium, Session A: The Hydrogen Cycle—Generation, Storage, and Fuel Cells.
3. Herring, A. M., Turner, J. A., Dec, S. F., Meng, F., Stanis, R. J., Aieta, N., Kuo, M.-C., and Horan, J. The Use of Heteropolyacids in Proton Exchange Membrane Fuel Cells. Presented to 3<sup>rd</sup> European Fuel Cell Forum, submitted to Fuel Cells.
4. Meng, F., Dec, S. F., Turner, J. A., and Herring, A. M. Immobilization of Heteropolyacids in Silica Matrix. Manuscript in preparation.
5. J. Turner gave an invited talk at the University of Nevada, Las Vegas entitled “Fuel Cell Technology and the Sustainable Hydrogen Economy.”
6. J. Turner gave a presentation (at NREL) on “Hydrogen Fuel Cells” as part of a course on energy given to the Federal Energy Management Agency.
7. J. Turner gave an invited talk at Augsburg College entitled “Fuel Cell Technology and the Sustainable Hydrogen Economy” in Minneapolis, MN.