

# V.M.13 Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes

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## Objectives

- To identify fuel cell stable linkages between HPA and organic moieties.
- To develop a new class of proton exchange membranes using polymers based on HPA functionalized with organic monomers (polyPOMs).
- To understand the mechanism of proton conduction in the polyPOMs and optimize it for proton conduction under low humidity higher temperatures fuel cell operating conditions.

## 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:

- (A) Durability
- (B) Cost
- (C) Performance

## Technical Targets

The materials have so far only been evaluated in terms of proton conductivity at various temperatures and relative humidity (RH), Table 1. No measurements have been made at this time in regard to durability.

**TABLE 1.** Progress Towards Meeting Technical Targets for Membranes for Transportation Applications

Characteristic	Units	2010	CSM 2007 status
Inlet water vapor partial pressure	kPa	<1.5	Variable
Membrane conductivity at inlet water vapor partial pressure and:			
Operating temperature	Siemens/cm	0.1	0.1 <sup>a</sup>
20°C	Siemens/cm	0.07	0.1 <sup>b</sup>
-20°C	Siemens/cm	0.01	TBD
Operating Temperature	°C	≤120	80 <sup>c</sup>

<sup>a</sup> At 80% RH

<sup>b</sup> for a water soluble system, 0.01 Siemens/cm at 70% RH has been achieved for an immobilized system

<sup>c</sup> temperature of maximum performance 0.01 Siemens/cm has been achieved at 120°C.

## Accomplishments

- Demonstrated that fuel cell capable stable HPA-monomer linkages can be fabricated. PhP-HPA model complexes survived boiling in both 6 M HCl and 3 wt% H<sub>2</sub>O<sub>2</sub>.
- Demonstrated that the water soluble HPA can be immobilized as polyPOMs. The salt form of the polyPOM could actually be ion-exchanged to the acid form by boiling in aqueous acid with little loss of HPA.
- Achieved a proton conductivity of 0.1 Siemens/cm at 80°C and 100% RH comparable to a current state-of-the-art membrane.



## Introduction

Currently, fuel cells based on perfluorosulfonic acid (PFSA) proton exchange membranes (PEMs) are limited to operating conditions of ≤80°C and very high relative humidities, because proton conduction in these materials

depends on the presence of water. For automotive applications it is desirable to operate the fuel cell at a temperature of  $\leq 120^\circ\text{C}$  and low relative humidity to enable the use of existing radiator technology and to eliminate the parasitic loads and system complications associated with externally humidifying the gas streams. Displacement of internal combustion engines by PEM fuel cells would dramatically facilitate the adoption of the  $\text{H}_2$  economy and enable a smooth transition from fossil fuels to  $\text{H}_2$  produced solely from renewable sources. Materials suitable for use in automotive PEM fuel cells will be developed that will have high proton conductivities,  $>0.1 \text{ S cm}^{-1}$  at 50% RH and  $120^\circ\text{C}$ , low area specific resistance,  $<0.02 \Omega\text{cm}^2$ , suitable for incorporation in a fuel cell membranes electrode assembly with oxidative stabilities higher than observed for any PFSA ionomer to date.

## Approach

Of all the inorganic proton conductors that have been exploited for fuel cell applications the HPA may have the greatest potential as they not only have high proton conductivities but they have significant synthetic versatility [1]. In previous work (DE-FC02-0CH11088) we have shown that the HPAs have very high proton conductivities at room temperature and can be operated at ambient conditions in a fuel cell using dry gases. Importantly, we demonstrated that some of the protons in HPA have very impressive rates of proton diffusion at elevated temperatures,  $>100^\circ\text{C}$  under dry conditions. The residual protons in these systems are immobile at elevated temperatures resulting, however, in rather low conductivities. The two key challenges that need to be addressed, therefore, are utilization of all protons under elevated temperature, dry conditions, and immobilization of the water soluble HPA in practical membranes for fuel cell use.

The team assembled includes inorganic and polymer chemists and chemical and materials engineers from both CSM and 3M. CSM and 3M fabricate the HPA monomers and the extensive knowledge of polymers at 3M is heavily exploited. The polymer system in this project is not restricted, but the mode of proton conduction is mediated by the HPA.

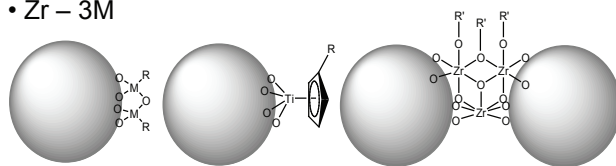
## Results

The HPA while promising proton conductors for fuel cell applications are in general water soluble. It is, therefore, critical to the success of any PEM-based on HPA that they be immobilized in such a way that they retain and preferably have enhanced proton conducting properties. The HPA are a large group of transition-metal oxides that are based on W or Mo and nucleated around a heteroatom that may be almost any cation chosen from the periodic table. The most

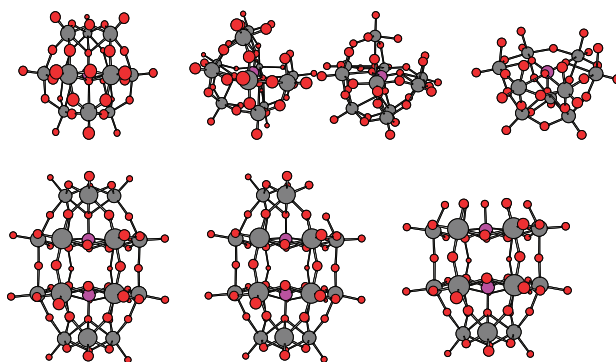
common structures are the Keggin anion, based on one heteroatom and 12 metal-O octahedra and the Wells-Dawson anion based on 2 heteroatoms and 18 metal-O octahedra, Figure 1. Because of the synthetic versatility of the HPA there are a number of linkage chemistries available to bond polymerizable groups to the HPA. To functionalize HPA we take advantage of the fact that they may be degraded in base selectively by 1, 2, or 3 metal-O octahedral to produce lacunary HPA. We may then condense the lacunary HPA with another organo-metallic compound under acidic conditions to produce a functionalized hybrid HPA. We have so far screened all the linkages in Figure 1 for stability under acidic or oxidizing conditions. Phenyl derivatives of the HPA using the available linkages were boiled in either 6 M HCl or 3 wt%  $\text{H}_2\text{O}_2$ . While the cpTi derivatized HPA showed some stability in peroxide only the PhP-HPA survived both the acid and the oxidizer. Although these conditions may be somewhat harsh a fuel cell is expected to survive up to 40,000 h and in automotive applications many load cycles and so we believe that the R-P-HPA bond is robust enough for fuel cell use.

One synthetic subtlety that we are working on is the need to make the resultant polyPOM materials as a free acid so that it can conduct protons. Much of the available HPA/POM chemistry exploits the solubility of HPA in non-aqueous solvents by use of large organic cations. The concern is that these cations may be hard to remove by ion-exchange with acid once the polyPOM

- $\text{M} = \text{P}, \text{Si}, \text{Ge}, \text{Sn}$
- $\text{R}, \text{R}' = \text{Phenyl}$
- $\text{Zr} - 3\text{M}$



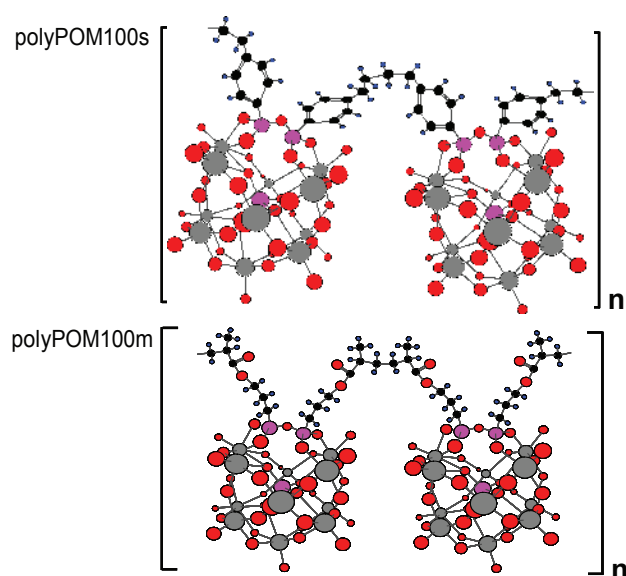
### • Lacunary HPA



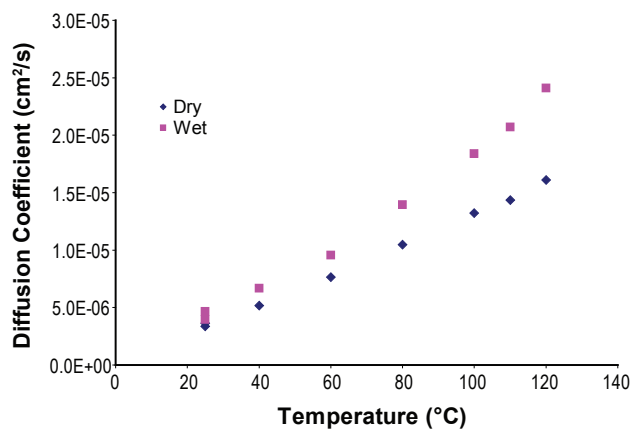
**FIGURE 1.** Schematic of HPA Linkage Chemistry and Lacunary HPA Based on Keggin and Wells-Dawson Structures

has been polymerized. We have now shown that free acid proton conducting polyPOMs may be produced either from pre-ion exchange of the monomer or post ion-exchange of the polymer.

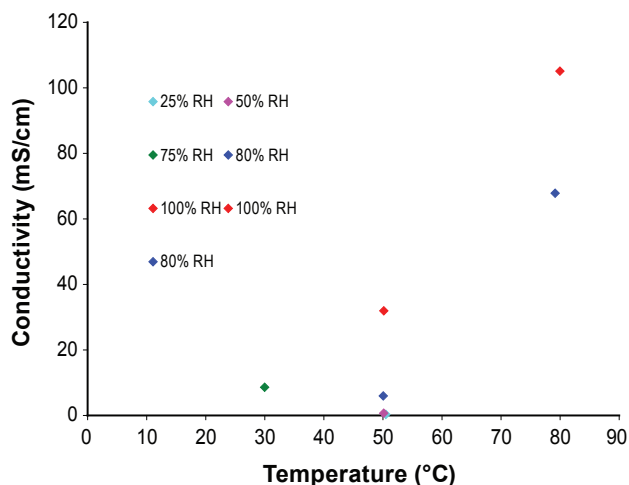
The two model systems that we have initially worked on are styrenyl and methylmethacrylate. Neither is expected to be oxidatively stable in a working fuel cell, but both offer advantages in synthetic versatility so that we can design systems for optimum proton conductivity. The structures of the homopolymers are represented in Figure 2. Encouragingly, self diffusion proton diffusion coefficients as measured by pulse field gradient spin echo (PFGSE) nuclear magnetic resonance (NMR) increases with increasing temperatures, Figure 3. Encouraging the



**FIGURE 2.** Structures of the StyrenylHPA Homopolymer, PolyPOM100s, and the Methylmethacrylate Homopolymer, PolyPOM100m



**FIGURE 3.** Self Proton Diffusion Coefficients as Measured by PFGSE NMR for a PolyPOM50s



**FIGURE 4.** Proton Conductivities for a PolyPOM50m

data for the dry systems is only slightly lower than for the material measured under saturated conditions.

Unfortunately, with these preliminary systems we are unable to achieve high proton conductivities under hot and dry conditions. Proton conductivities for a polyPOM50m are shown in Figure 4. While the conductivity of this materials is not high enough under many conditions a proton conductivity of  $>0.1$  Siemens/cm is achieved at 80°C and 100% RH. The conductivity of the same material in water was comparable and only fell slightly on stirring indicating that the vast majority of the HPA is truly immobilized. This is a very significant result in that we have achieved the same conductivity as a state-of-the-art PEM using a completely new and novel proton conducting functionality.

## Conclusions and Future Directions

In FY 2007 we have demonstrated a number of important results concerning new PEMs based on HPAs. Firstly we showed conclusively that we can fabricate immobilized HPA systems that are still proton conductors. Secondly, and very significantly, we have achieved the same conductivity as state-of-the-art PEMs at 80°C and 100% RH. Future work will be directed at:

- Improving our understanding of proton conduction in the polyPOMs with regard to hot and dry fuel cell operation.
- Developing polyPOMs with improved stability and chemical versatility based on P-based linkages.

## FY 2007 Publications/Presentations

1. "Structure and dynamics of hybrid organic-inorganic membrane materials for fuel cell applications", J.L. Horan, J.A. Turner, A.M. Herring, S.F. Dec, Division of Fuel

Chemistry Preprints- American Chemical Society, 2006, 51, 653.

2. "Exploiting the Advantages of Heteropoly Acids for PEM Fuel Cell Membranes." A.M. Herring, invited oral presentation, presented at Argonne National Laboratory, IL, October 2006.
3. "Structure and Dynamics of Hybrid Organic-Inorganic Membrane Materials for Fuel Cell Applications." James L. Horan, John Turner, Steven Dec, and Andrew M. Herring, poster presentation, presented at the 210<sup>th</sup> Meeting of The Electrochemical Society, Cancun, Mexico, October 2006.
4. "Using Inorganic Super Acids to functionalize PFSA ionomers or as stand alone proton conducting materials", A.M. Herring, invited oral presentation, presented at Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2007, Asilomar, CA, February 2007.
5. "Heteropoly Acid Polymers for Automotive Fuel Cell Applications." A.M. Herring, J.L. Horan, M.-C. Kuo, N.V. Aieta, and S.F. Dec, oral presentation, presented at the 211<sup>th</sup> ECS Meeting, Chicago, IL, May 2007.
6. "Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes" A.M. Herring, J.L.Horan, and M.-C. Kuo, oral presentation, presented at the US DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program 2007 Annual Merit Review Meeting, Crystal City, VA, May 2007.
7. "Understanding Proton Conduction in a Series of Novel PolyPOM Ionomers." J.L. Horan, M.-C. Kuo, and A. M. Herring, oral presentation, to be presented at the 58<sup>th</sup> Annual Meeting of the International Society of Electrochemistry, Banff, Canada, September 2007.

## References

1. "Inorganic – Polymer Composite Membranes for Proton Exchange Membrane Fuel Cells." A.M. Herring\* *Polymer Reviews*, **2006**, 46, 245.