

# V.G.8 Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes

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Contract Number: DE-FG36-06GO16032

Subcontractor:  
3M Corporate Research Materials Laboratory, St. Paul, MN

Project Start Date: April 1, 2007  
Project End Date: March 31, 2011

## Objectives

- To develop a new class of proton exchange membranes (PEMs) using polymers based on heteropoly acid (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 temperature 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:

- Durability
- Cost
- 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. One membrane electrode assembly (MEA) was built and tested for four days before failure at 70°C and 75% RH with an area specific resistance of 0.1  $\Omega\text{cm}^2$ .

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

Characteristic	Units	2010	CSM 2008 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	0.05 <sup>b</sup>
-20°C	Siemens/cm	0.01	TBD
Operating Temperature	°C	≤120	120 <sup>c</sup>

<sup>a</sup> At 70% RH and 80°C

<sup>b</sup> 70% RH and 30°C

<sup>c</sup> Temperature of maximum performance: 0.2 Siemens/cm has been achieved at 120°C and 80% RH  
TBD - to be determined

## Accomplishments

- Achieved a proton conductivity of >0.1 Siemens/cm from 30-120°C and 100% RH comparable to a current state-of-the-art membrane.
- Achieved a proton conductivity of >0.1 Siemens/cm from 70-120°C and 80% RH comparable to a current state-of-the-art membrane.
- Showed that the need for water for high proton conduction decreases with HPA loading.



## Introduction

Currently, fuel cells based on perfluorosulfonic acid (PFSA) PEMs are limited to operating conditions of ≤80°C and very high RHs, 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 ≤120°C and low RH 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 H<sub>2</sub> economy and enable a smooth transition from fossil fuels to H<sub>2</sub> produced solely from renewable sources. Materials suitable for use in automotive PEM fuel cells are being developed that have high proton conductivities, >0.1 S cm<sup>-1</sup> at 80% RH operating temperatures of 30-120°C, low area specific resistance, <0.1 Ωcm<sup>-2</sup>, suitable for incorporation in a fuel cell membranes electrode assembly. We anticipate that the use of HPAs will generate membranes 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°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. In this years work, we have concentrated on making films with very high HPA loadings. We have also use nuclear magnetic resonance (NMR) to measure both the self diffusion coefficient of water and to quantify the amount of water. Comparing the NMR data with the proton conductivity data allows us to understand proton transport in these unique systems.

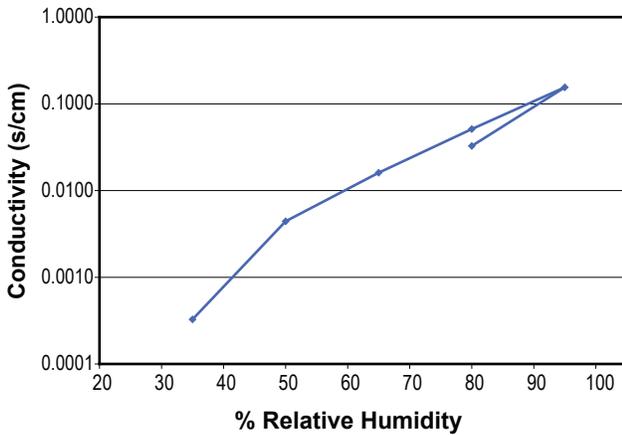
## Results

In the previous years' work, films were fabricated from polymers that were composed of 50 wt% HPA monomers. The best results were obtained with HPA monomers that were functionalized with methylmethacrylate as the functional group. While

these films gave proton conductivities >0.1 Scm<sup>-1</sup> at 80°C and 100% RH (the current operating condition of a PEM fuel cell) they had inadequate proton conductivity at lower temperatures and RHs. Additionally the methylmethacrylate linkage was unstable to hydrolysis.

In order to make more robust films, we moved to other HPA functionalized monomers. Ethyl styrenyl, styrene and vinyl were all investigated. We eventually settled on vinyl HPA monomers as these were easily fabricated, the synthesis of styrene monomers was difficult and ethyl styrenyl monomers were not available in a pure form. In order to increase the conductivity of the films we increased the loading of HPA monomer to 75 wt%. The HPAs used in this work were all the lacunary H<sub>8</sub>SiW<sub>11</sub>O<sub>39</sub>. In general the comonomer was butyl acrylate with a small amount of cross-linking additive. The polymerizations were carried out by ultra violet (UV) irradiation of the monomers pressed between two UV transparent sheets in the presence of a free radical initiator for several days. This resulted in initially flexible yellow/brown transparent films that slowly became brittle on standing. This film will be referred to here as polyPOM75v. The films smelled strongly of acrylate and solid state NMR showed the vinyl groups of the acrylate group volatilized over time. Leaching studies indicated that in general it was the butylacrylate and small organic oligomers that were preferentially leaching from the film.

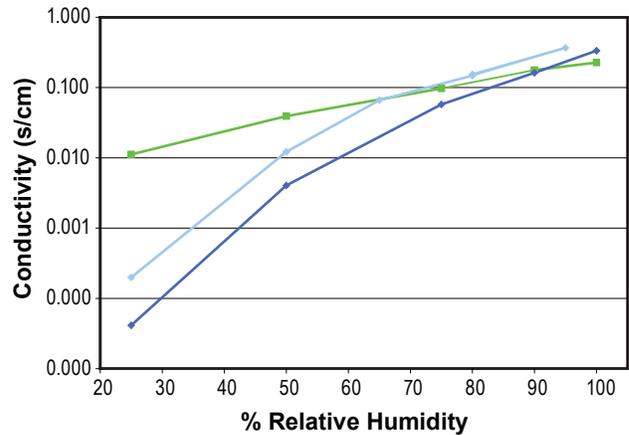
Because of the unstable nature of the 75 wt% HPA films a 50 wt% HPA vinyl polymer film was submitted for third party testing. This material not surprisingly had inadequate conductivity when tested at RH <100%. The 50 wt% film only achieved a conductivity ≥0.1 S cm<sup>-1</sup> at >80°C and 100% RH. The 75 wt% HPA films show much more promise and it only remains for a method to complete the polymerization for a stable film with high proton conductivity to be achieved. In Figure 1 we show the log plot of proton conductivity versus RH for a polyPOM75v at 30°C. It can be seen that the proton conductivity falls off steeply below 50% RH but is >0.1 Scm<sup>-1</sup> at 100% RH. In Figure 2 we show proton conductivity data for two different films of the same composition at 80°C. As with all materials of this nature the variation on performance between the two films is not unexpected as subtle changes in the processing conditions can dramatically change the proton conductivity of the film. This phenomenon will be investigated in the future. It is clear that both films out perform the low EW 3M ionomer at >90% RH and that one film has a proton conductivity >0.1 Scm<sup>-1</sup> at >70% RH. Unfortunately the proton conductivity rapidly falls off at <60% RH. This is similar to other hydrocarbon-based ionomer films. A single 50 cm<sup>2</sup> unoptimized MEA was constructed from the polyPOM75v and tested at 70°C and 75% RH until failing after four days. The MEA achieved a current density of 600 mAcm<sup>-2</sup> at 0.3 V and an area specific resistance of 100 mΩcm<sup>-2</sup>.



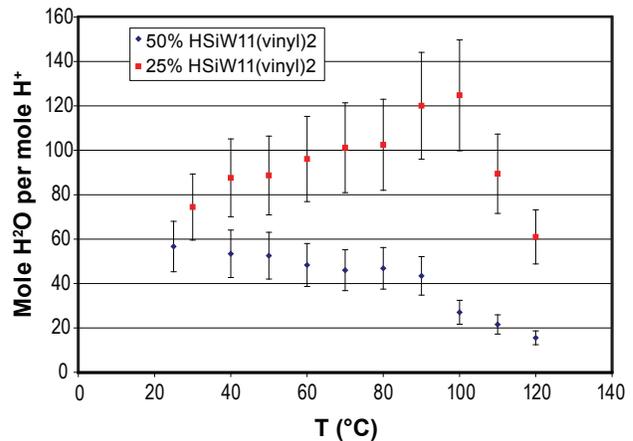
**FIGURE 1.** Proton Conductivity Versus Temperature at 30°C for a polyPOM75v

Extensive use is made of NMR to understand the nature of proton conduction in these materials. Self-diffusion coefficients of water are measured by pulse field gradient spin echo NMR and the number of protons in the sample by well calibrated spin counting experiments. A knowledge of the diffusion coefficient and the number of protons allows the proton conductivity to be calculated assuming a vehicular mechanism from the Nernst-Einstein equation. The agreement between the measured in-plane conductivity and the calculated conductivity is sufficiently good to infer that vehicular transport dominates in these systems over Grotthuss or proton hopping transport. In Figure 3 we show the results of the spin counting experiment for films with 25 and 50 wt% HPA content, polyPOM25v and polyPOM50v. These films contain large amounts of water per proton and the water content decreases with HPA loading. Initial measurements on the polyPOM75v film suggest that even less water is required in these materials for proton transport.

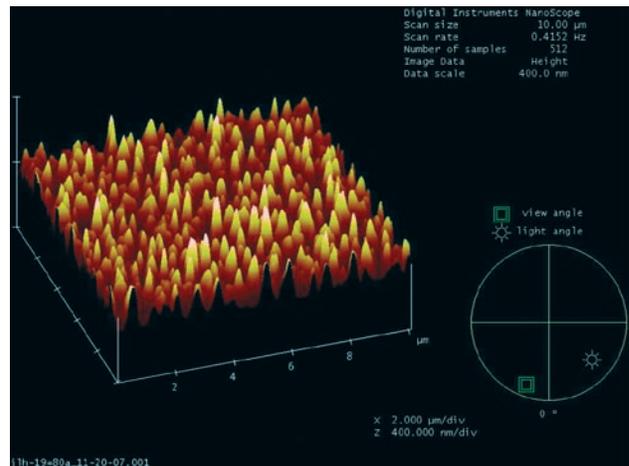
As we wish to relate proton conduction to morphology, the films are studied by both atomic force microscopy (AFM) and small angle X-ray scattering (SAXS). In general, the AFM images are featureless at HPA contents <50 wt%. Above 50 wt% HPA as shown in Figure 4 for a polyPOM50v the films are obviously phase-segregated into hydrophobic and hydrophilic regions. The cluster size appears to be on the order of 100s of nms. The SAXS patterns can be modeled to show the presence of spheres of radius 0.4 nm as expected for a HPA anion. Below 50 wt% HPA content, no aggregation can be modeled and the spheres are generally 100s of nm apart. At 50 wt% HPA content the SAXS patterns can only be modeled as aggregates of HPA anions. This evidence appears to strongly suggest that polyPOM films must have at least a 50 wt% HPA to phase separate and allow HPA proton conducting aggregation.



**FIGURE 2.** Proton conductivity versus temperature at 80°C for two different preparations of polyPOM75v (blue and light blue) compared to a 800EW 3M ionomer film (green).



**FIGURE 3.** Moles of Water per Proton ( $\lambda$ ) at 100% RH for a polyPOM25v (red squares) and a polyPOM50v (blue diamonds)



**FIGURE 4.** AFM Image of a polyPOM50v Film

## Conclusions and Future Directions

- High proton conductivities of  $>0.1$  Siemens/cm can be achieved by fabricating films with  $>50$  wt% HPA.
- As the HPA content is increased, the water content of the films decreases and the proton conductivity increases.
- At  $>50$  wt% HPA content, the films phase separate and the HPA aggregates, facilitating proton transport.
- Future work will focus on films with  $>75$  wt% HPA using co-monomers with more diverse chemistry and developing a more in-depth understanding of the effect of chemistry and morphology on proton conduction in these materials.

3. “Understanding Proton Conduction in a Series of Novel PolyPOM Ionomers.” J.L. Horan, M.-C. Kuo, and A.M. Herring, oral presentation, presented at the 58<sup>th</sup> Annual Meeting of the International Society of Electrochemistry, Banff, Canada, September 2007.
4. “Novel materials for proton conduction based on the polyoxometallates” A.M. Herring, invited oral presentation, presented at the International symposium on materials issues in a hydrogen economy, Richmond, VA, November 2007.
5. “Understanding Proton Conduction in a Unique Series of PolyPOM Polymers.” A.M. Herring, J.L. Horan, M.-C. Kuo, S.F. Dec, M.H. Frey, L. Ren, A. Genupur, M.A. Yandrasits, and S.J. Hamrock, oral presentation, presented at the 213<sup>th</sup> ECS meeting, Phoenix, AZ, May 2008.

## FY 2008 Publications/Presentations

1. “Advances in Hybrid Organic-Inorganic Proton Exchange Polymer Membranes Incorporating Heteropoly Acids.” J.L. Horan, N.V. Aieta, J.E. Leisch, M.-C. Kuo, S.F. Dec and A.M Herring, “Proton Exchange Membrane Fuel Cells VII.”, T. Fuller, H.A. Gasteiger, S.J Cleghorn, V. Ramani, T. Zhao, T.V. Nguyen, A.T. Haug, C. Bock, C. Lamy, and K. Ota, Eds Electrochemical Society Transactions, 2007, 11, 97.
2. “Advances in Hybrid Organic-Inorganic Proton Exchange Polymer Membranes Incorporating Heteropoly Acids.” J.L. Horan, N.V. Aieta, J.E. Leisch, M.-C. Kuo, S.F. Dec and A.M Herring, presented at the the 212<sup>th</sup> ECS meeting, Washington, D.C., October 2008.