

# V.D.11 Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes

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## 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:

- (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, Table 1.

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

Condition	80°C/100% RH	30°C/<80% RH	120°C/<50% RH
Target H <sup>+</sup> conductivity	100 mS cm <sup>-1</sup>	> 70 mS	100 mS cm <sup>-1</sup>
Date Met	April 2008	August 2008	January 2009
H <sup>+</sup> conductivity achieved	300 mS cm <sup>-1</sup>	126 ms cm <sup>-1</sup>	>100 ms cm <sup>-1</sup>

RH – relative humidity

## Accomplishments

- Fabricated ionomer films based on HPAs with high loadings that have proton conductivities >0.1 S cm<sup>-1</sup> at >80°C and <50% RH. The results were verified independently by 3M and Scribner and Associates.
- Showed that proton conductivity was strongly correlated with chemistry, best performance was from films containing only HPA as the protogenic group.
- Also showed that process conditions strongly influenced morphology that affected all film properties. Ultraviolet (UV)-cured films were brittle, but had proton conductivities that made all targets shown above, whereas thermally cured films were much stronger but had poor proton conductivity.



## Introduction

Currently, fuel cells based on perfluorosulfonic acid (PFSA) PEMs are limited to operating conditions of ≤80°C and very high inlet RHs, because proton conduction in these materials depends strongly 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 hydrogen economy and enable a smooth transition from fossil fuels to hydrogen produced solely from renewable sources. Materials suitable for use in automotive PEM fuel cells are being developed that have high proton conductivities,  $>0.1 \text{ S cm}^{-1}$  at 80% RH operating temperatures of  $-30$  to  $120^\circ\text{C}$ , low area specific resistance,  $<0.1 \text{ } \Omega\text{cm}^{-2}$ , suitable for incorporation in a fuel cell membrane electrode assembly. We anticipate that the use of HPAs will generate membranes with oxidative stabilities higher than observed for any PFSA ionomer to date.

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 [2]. 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.

## Approach

Our approach is to functionalize HPA with monomers so that they can be fabricated into polymeric materials with the use of a suitable co-monomer. We chose to use acrylates as the co-monomers in this project because this represents a polymer system in a kit leaving the synthetic effort to be devoted to making the HPA monomers. This polymer system allows the chemistry to be easily varied so that the effect of morphology can be studied. In addition as these are free radical polymerizations the materials are easily obtained as films from the polymerization of the cast solutions of co-monomers. We are the first research group to fabricate proton-conducting free-standing films of these materials, but as they have been previously synthesized as gels [3], we are able to fully disclose our research using this model system. However, the system has certain inherent disadvantages that include an acrylate

ester linkage that is unstable to hydrolysis, and polymers that contain readily oxidizable methylene groups and an oxidizing super acid moiety.

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 year's work we have concentrated on making films with even higher HPA loadings, pushing the system to the limit. We have also used nuclear magnetic resonance (NMR) to measure 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. In addition we are now correlating proton conductivity with morphology as observed by atomic force microscopy (AFM) and small angle X-ray scattering.

## Results

Figure 1 shows the design space that was probed in this system and the eventual practical limit with the polyPOM acrylate approach that gives proton conductivities that exceed the DOE goals. The initial intent was to co-polymerize the HPA monomers with acrylates substituted with proton containing groups with various degrees of proton dissociation. HPA-co-hydroxyethyl acrylate polymers all had lower proton conductivities than HPA-co-butyl acrylate polymers, presumably as the HPA could not dramatically increase the dissociation of protons in the hydroxyl groups. We, therefore, concentrated on the butyl acrylate system as the other alternatives such as carboxylic acid, sulfonic acid and phosphonic acid substituted acrylates provided additional problems in increased solubility of the system

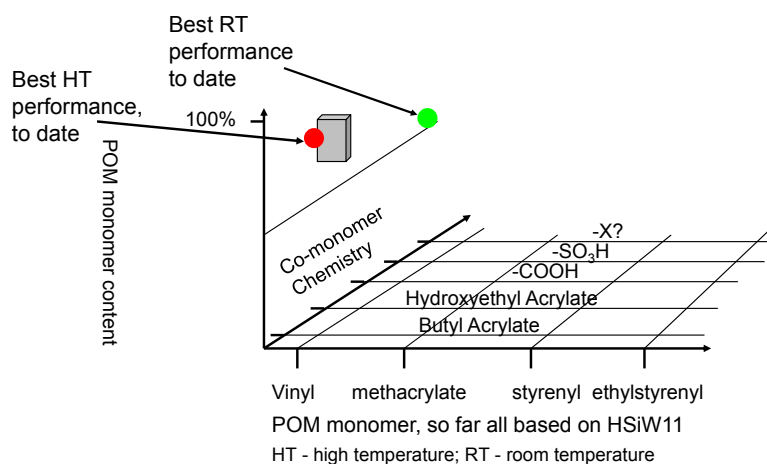
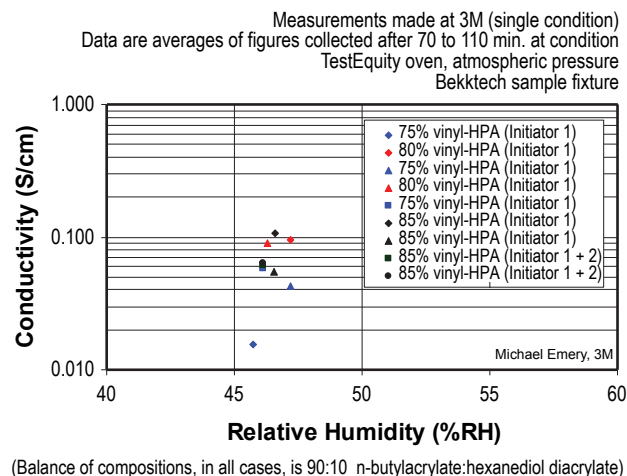


FIGURE 1. Design Space for PolyPOMs based on Acrylate Chemistry

and in the case of carboxylic acid decreased stability of the eventual PEM. The linkage was chosen to be Si as functionalized silanes are readily available commercially, again minimizing resource intensive synthetic efforts. We had a choice of free radical polymerizable groups with which to functionalize the HPA which included vinyl, methacrylate, styrenyl and ethylstyrenyl. The styrenyl monomers had solubility issues precluding their use in a solvent free system and the ethylstyrenyl silane was only available as a mixture of isomers which did not allow for complete characterization of the material. The methacrylate monomer produced films with interesting proton conducting properties but these materials had severe structural deficiencies at moderate temperatures. Only vinyl substituted monomers easily gave films with desirable properties.

It was found that the material needed to be  $\geq 50$  wt% HPA to achieve phase separation and high conductivity. A 75 wt% HPA material was found to have proton conductivity *ca.* 10% higher than for a standard sample of Nafion<sup>®</sup> 212 at 100% RH from 30 to 120°C [4,5]. However, the proton conductivity of the material below 70% RH rapidly dropped off, as is also typical for a number of hydrocarbon-based PEMs. As this was not a solution that would result in a PEM that could operate in a fuel cell without inlet humidification it was decided to increase the loading of the HPA monomer. A loading of 85 wt% of HPA monomer has so far proven to be the limit achievable in these films as considerable amounts of solvent are required at high HPA loadings resulting in films with poorer properties. Whereas the polymers with 75 wt% of HPA were well behaved and easily characterized, the materials with 80 and 85 wt% proved to have considerable variability in their properties. In Figure 2 we show the in-plane proton conductivities of a series of polyPOMs with HPA loadings varying



**FIGURE 2.** Variation of proton conductivity for a series of P(SiW<sub>11</sub>XV-co-butyl acrylate-co-1,6-hexanedioldiacrylate) films where X is <75 wt%.

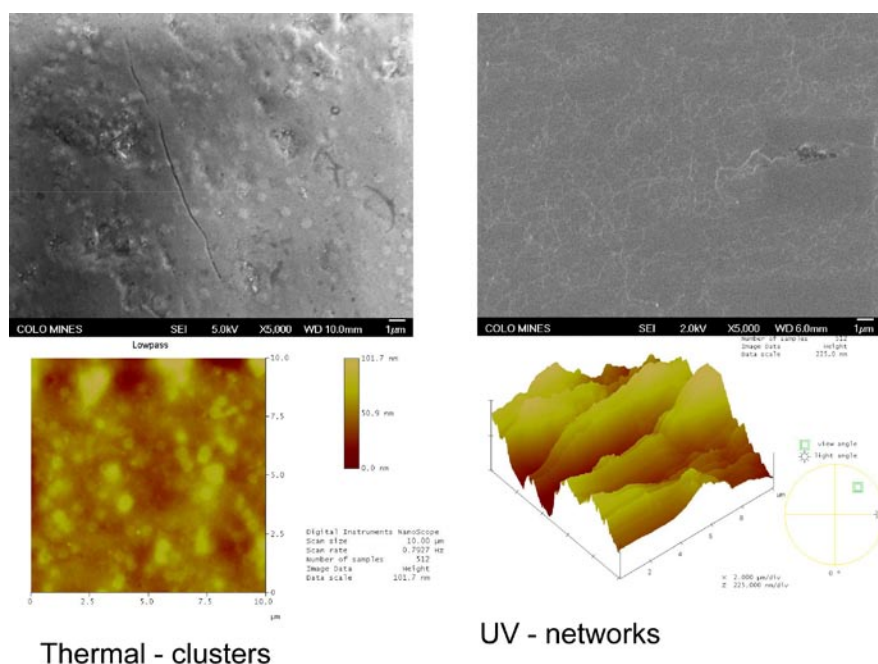
from 75 to 85 wt%, at 120°C and <50 % RH. The proton conductivities vary from 15 to 110 mS cm<sup>-1</sup>. Both an 80 wt% and an 85 wt% sample had proton conductivities of *ca.* 100 mS cm<sup>-1</sup> at these conditions, this is significant because this represents a practical proton conductivity at an RH where inlet humidification would not be required in the fuel cell system. This result is very exciting, but we were frustrated by the fact that this result was hard to reproduce.

From observations that the film properties seemed to change with time when the films were left exposed to ambient conditions and that film properties could be enhanced by storing the films in a humid environment we decided to probe the effect of film morphology. Two extremes of curing conditions were chosen, UV curing with minimal solvent and thermal curing using solvent in an oven at 120°C for the same formulation of poly(SiW<sub>11</sub>80wt%Vinyl-co-17.5wt%butyl acrylate-co-2.5wt%1,6-hexanedioldiacrylate). This resulted in two films of radically different properties. The thermally cured film appeared ductile and strong; whereas the UV-cured film was somewhat brittle. The micro structure of these two films is contrasted in Figure 3. It can be seen that the thermally cured film has a clustered morphology in both the environmental scanning electron microscope (ESEM) and AFM. The clusters are large *ca.* 500 nm. For the UV-cured film a network morphology is observed and AFM shows a striated morphology consistent with what would be imagined to be a brittle material.

Generally we observe high proton conductivities for the UV-cured films as opposed to the thermally-cured films, *e.g.* >80 mS cm<sup>-1</sup> and <20 mS cm<sup>-1</sup>, respectively at 120°C and 50% RH. When we examine the self diffusion coefficients of these materials by pulsed field gradient spin (PFGSE) NMR, Table 2 shows some typical data, we see that diffusion of protons is restricted in both materials as it differs dramatically between short length scales D(0) and its limit, D(∞) at long length scales. The self diffusion of protons in the thermally cured film seems to be much more severe on a qualitative basis than the UV-cured film as D(0) is six times larger than D(∞) in the thermally cured films and only three times larger in the UV-cured film. However the diffusion coefficients are an order of magnitude lower for the thermally cured film at 120°C and 50% RH. When we combine the diffusion coefficients, D, with the concentration of protons, c, as measured from carefully calibrated spin counting experiments in the Nernst Einstein equation (Equation 1)

$$\sigma = \frac{cDz^2F^2}{RT} \quad [1]$$

We see that the predicted proton conductivities are close to the measured values. Only the UV-cured film would have practical proton conductivity under the conditions of no inlet humidification at 120°C.



**FIGURE 3.** Variation in morphology caused by thermal curing (left) and UV-curing (right) for a poly(SiW<sub>11</sub>,80V-co-butyl acrylate-co-1,6-hexanedioldiacrylate) film as shown by ESEM (top) and AFM (bottom).

**TABLE 2.** Self diffusion data from PFGSE NMR at 120°C and 56% RH, and proton conductivities calculated from the Nernst–Einstein equation ( $\lambda = 1$ ) at both limiting ( $\infty$ ) and perfect (0) diffusion lengths of a 80 wt% HPA polymer.

Polymerization Method	$D(0) \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	$D(\infty) \times 10^5$ (cm <sup>2</sup> s <sup>-1</sup> )	$\sigma(0)$ (mS cm <sup>-1</sup> )	$\sigma(\infty)$ (mS cm <sup>-1</sup> )
Thermal	0.84	0.13	65	10
UV	2.48	0.95	191	73

## Conclusions and Future Directions

- High proton conductivities of  $>0.1$  S cm<sup>-1</sup> at 120°C and  $<50\%$  RH can be achieved by fabricating films with  $>85$  wt% HPA.
- The correct morphology is key to achieving high proton conductivities and can be controlled by process conditions.
- Future work will focus in transferring this technology to new more practical polymer systems that will be optimized not only for proton conductivity, but also oxidative stability and mechanical strength.

## FY 2009 Publications/Presentations

1. “Pushing polypolyoxometalates to their limits of proton conductivity.” J.L. Horan, S.F. Dec, M.C. Kuo and A.M. Herring, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.*, **2008**, 53, 756.

2. “Using Heteropoly Acids to Enable PEM Fuel Cell Technology.” A.M. Herring, invited oral presentation, presented at Illinois Institute of Technology, Chicago, IL, October 2008.

3. “Pushing polypolyoxometalates to the limits of their proton conductivity.” J.L. Horan, A.M. Herring, S.F. Dec, M.C. Kuo, oral presentation, presented at the 214<sup>th</sup> ECS Meeting, Honolulu, HI, October 2008.

4. “Pushing Proton Conductivity to the Limit in a Series of POM Polymers.” A.M. Herring, J.L. Horan, M.-C. Kuo, S.F. Dec, M.H. Frey, A. Genupur, L. Ren, M.A. Yandrasits, and S.J. Hamrock, “Proton Exchange Membrane Fuel Cells VIII.” T. Fuller, K. Shinohara, V. Ramani, P. Shirvanian, H. Uchida, S. Cleghorn, M. Inaba, S. Mitsuhashi, P. Strasser, H. Nakagawa, H.A. Gasteiger, T. Zawodzinski, C. Lamy, Ed.s, *Electrochemical Society Transactions*, **2008**, 16, 699.

5. “A New Ionomer Based on Novel PolyPOM Materials.” A.M. Herring, J.L. Horan, M.-C. Kuo, S.F. Dec, M.H. Frey, A. Genupur, L. Ren, M.A. Yandrasits, and S.J. Hamrock., *Fuel Cell Seminar Abstracts*, **2008**.

6. “A New Ionomer Based on Novel PolyPOM Materials.” A.M. Herring, J.L. Horan, M.-C. Kuo, S.F. Dec, M.H. Frey, A. Genupur, L. Ren, M.A. Yandrasits, and S.J. Hamrock, Oral presentation, presented at the Fuel Cell Seminar, Phoenix, AZ, October 2008.

7. “An Ionomer With Very High Proton Conductivity Derived From The Co-Polymerization of H<sub>2</sub>[SiW<sub>11</sub>O<sub>40</sub>(Si(CH=CH<sub>2</sub>))<sub>2</sub>] with Butyl Acrylate and Hexanediol Diacrylate.” J.L. Horan, A. Genupur, L. Ren,



B.J. Sikora, M.-C. Kuo, F. Meng, S.F. Dec, M.H. Frey, G.M. Haugen, M.A. Yandrasits, S.J. Hamrock, and A.M. Herring,\* *Chem. Sus. Chem.*, **2009**, 2, 226.

8. “New composite proton exchange membranes for fuel cell applications based on polyPolyoxometalates.” A.M. Herring, J.L. Horan, M.-C. Kuo, S.F. Dec, M.H. Frey, A. Genupur, L. Ren, M.A. Yandrasits, and S.J. Hamrock, invited keynote oral presentation, presented at the 2008 Fall MRS meeting, Boston, MA, December 2008.

9. “PolyPOM membranes for hot and dry PEM fuel cell operation.” A.M. Herring and M.H. Frey, oral presentation, presented to the DOE Tech team, Detroit, MI, February 2009.

10. “Designing an Ionomer From Scratch – Pushing PolyPOMs to the Limit.” A.M. Herring, invited oral presentation, presented at Advances in Polymer Electrolyte Membrane Fuel Cell Systems 2009, Asilomar, CA, February 2009.

11. “Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes.” A.M. Herring, M.H. Frey, S.F. Dec, S.J. Hamrock, G. Haugen, M.A. Yandrasits, H. Ren, A. Genupur, M. Emery, M.-C. Kuo, J.L. Horan, S. Sachdeva, A. Perdue, B. Sikora, oral presentation, presented at the 237<sup>th</sup> ACS Meeting, Salt Lake City, UT, March 2009.

12. “Further Understanding of Polyoxometallate Modified Titania Electrodes for Photoelectrochemical Water Splitting.” A.M. Herring, P. Vallett, M.-C. Kuo, T. Furtak, J.A. Turner and M.T. Lusk, presented at the 215<sup>th</sup> ECS Meeting, San Francisco, CA, May 2009.

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