

## V.C.6 Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes

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### 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

Target Date met	80°C/100%RH April 2008	30°C/60%RH August 2008	120°C/<50%RH January 2009
H <sup>+</sup> conductivity	300 mS cm <sup>-1</sup>	126 ms cm <sup>-1</sup>	> 100 ms cm <sup>-1</sup>

RH – relative humidity

### FY 2011 Accomplishments

- Fabricated new HPA-based polymers based on two distinct polymer chemistries which are designed to allow the fabrication of films that will be highly proton conducting, durable, cost-effective and have the required mechanical properties of the proton exchange membrane (PEM) fuel cell membrane.
- Showed that the HPA linkages in one of these systems are robust and will survive 10 hours of boiling water.
- Demonstrated that the new polymers systems are able to show proton conductivities as high as the generation I model system films studied previously.



### Fiscal Year (FY) 2011 Objectives

- To develop a new class of proton exchange membranes 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 Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

### Introduction

Currently, fuel cells based on perfluorosulfonic acid (PFSA) PEMs are limited to operating conditions of  $\leq 80^{\circ}\text{C}$  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  $\leq 120^{\circ}\text{C}$  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 resources. Materials suitable for use in automotive PEM fuel cells are being developed that have high proton conductivities,  $>0.1\text{ S cm}^{-1}$  at 50% RH and operating temperatures of  $-30$  to  $120^{\circ}\text{C}$ , with low area specific resistance,  $<0.1\ \Omega\text{cm}^2$ . 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 HPAs 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 in rather low conductivities. The two key challenges that need to be addressed in practical membranes for fuel cell use, are utilization of all protons under elevated temperature, dry conditions, and immobilization of the water-soluble HPA.

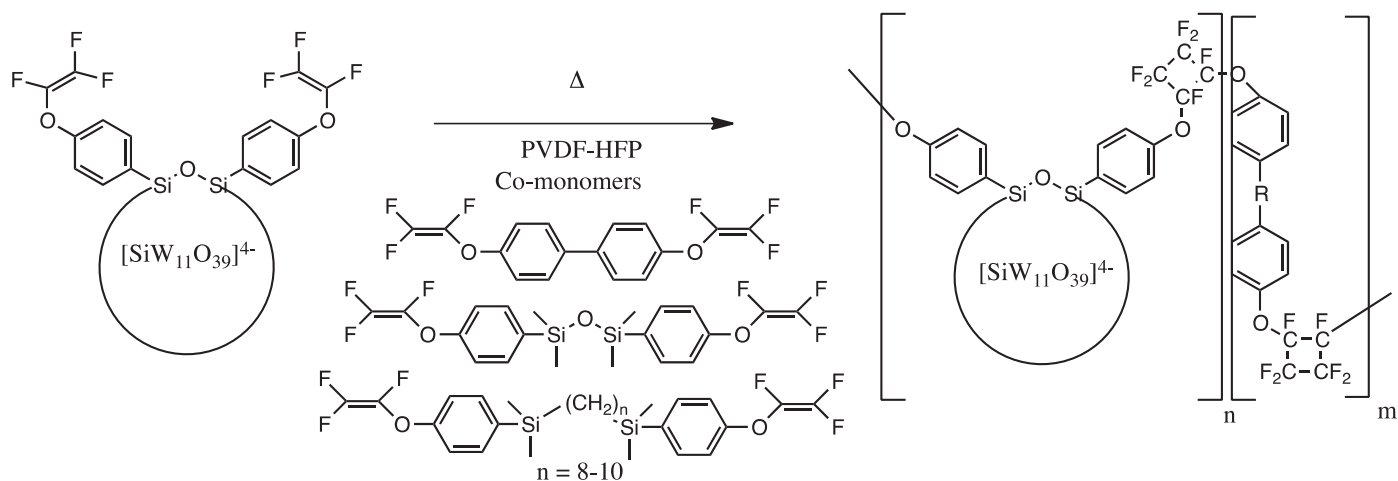
## Approach

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 initially chose to use acrylates as the co-monomers in this project because acrylates represent a polymer system in a kit leaving the synthetic effort to be devoted to making the HPA monomers. This polymer system allowed the chemistry to be easily varied so that the effect of morphology could be studied. In addition as these are free radical polymerizations the materials were obtained easily 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 previously been synthesized as gels [3], we are able to fully disclose our research using this model system. However, the system has certain inherent disadvantages. The acrylate ester linkage is unstable to hydrolysis and the polymers contain readily oxidizable methylene groups. In addition it has been clear the polymers with  $\geq 85$  wt% of the HPA are unstable to liquid water.

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 two new polymer chemistries so that we can address the additional criteria, such as cost, durability, and mechanical integrity that are need for a practical proton conducting polymer. We have also used nuclear magnetic resonance (NMR) to measure both the self-diffusion coefficient of water and to quantify the amount of water in the polymer. Comparing the NMR data with the proton conductivity data allows us to understand proton transport in these unique systems. We are correlating proton conductivity with morphology as observed by atomic force microscopy and small angle X-ray scattering (SAXS) to enable us to understand structure proton conductivity relationships.

## Results

In the final year of this project we down-selected to two practical polymer systems, both based on perfluorinated backbones. The first is based on trifluorovinyl ether (TFVE) monomers that can be thermally polymerized. In Figure 1 we show the general synthetic route to poly TFVE materials with HPA as the protogenic group. A lacunary HPA is functionalized with TFVE moieties via a silane linkage and is then copolymerized thermally with various bi-functional TFVE co-monomers. The polymerization results in a perfluorinated cyclobutane linkage between the co-monomers. As the materials are somewhat brittle we add 10-15 wt% of polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) so that thin films can be fabricated. The co-monomers consist of biphenyl or phenyl rings bridged by a silane or methylene chains.

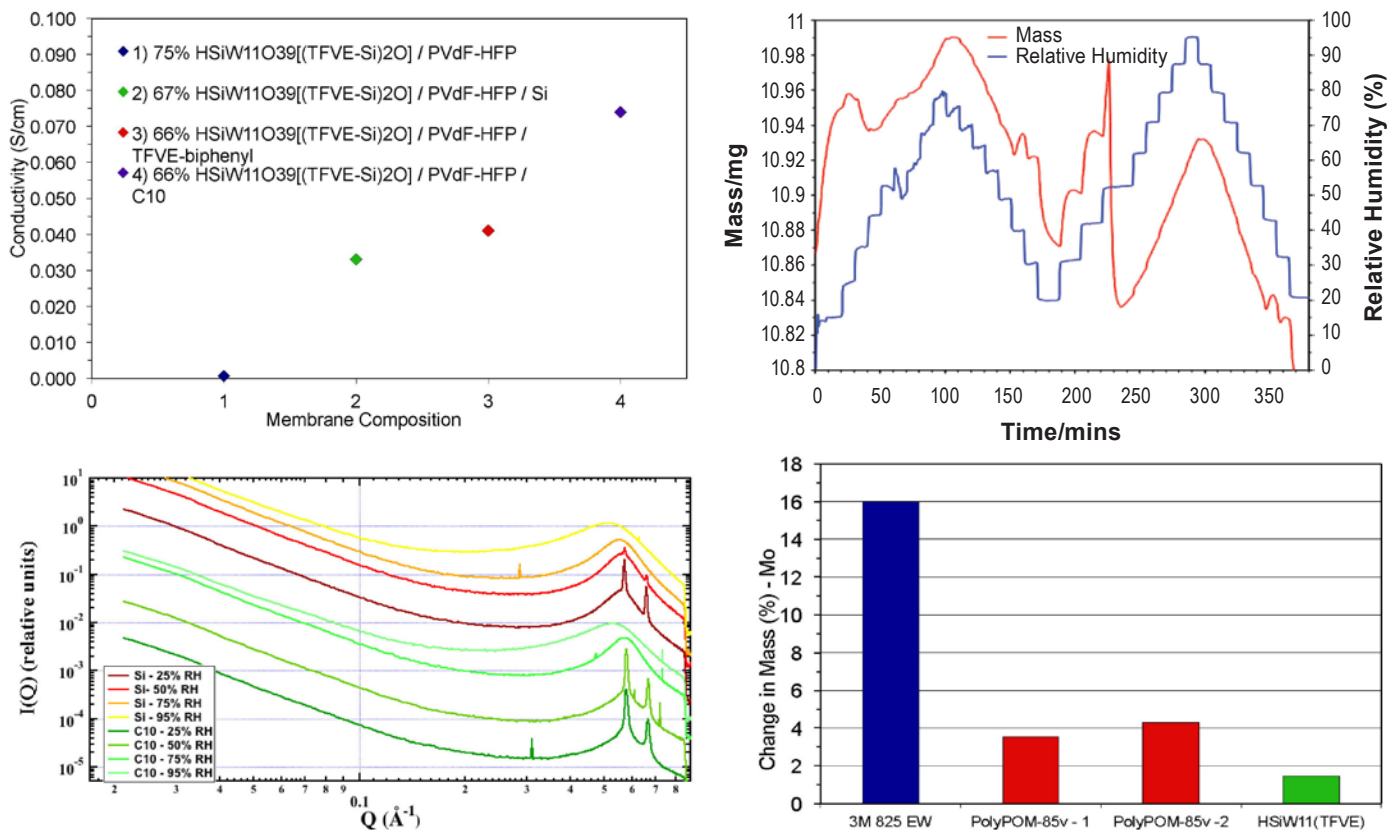


**FIGURE 1.** General Synthetic Route to Poly Trifluorovinyl Ether (TFVE) Materials with HPA

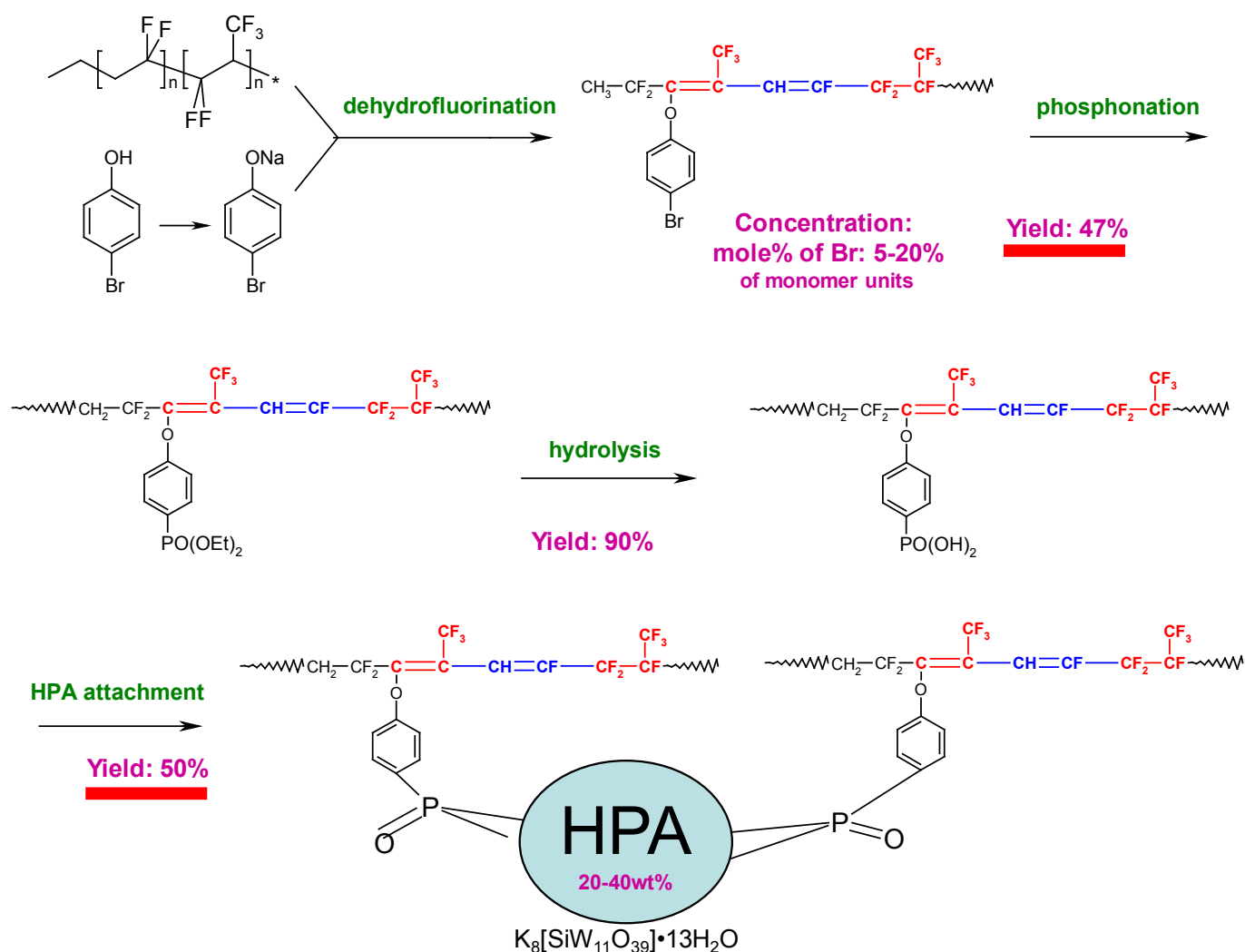
Pertinent data for these materials is shown in Figure 2. Obviously with four co-monomer and a range of wt% loadings of HPA monomer there is fairly large design space to probe. Our first observation, Figure 2, top left, was that the proton conductivity depended to a large extent on co-monomer chemistry. The homo-polymer, entry 1, even with a very large loading of HPA had negligible conductivity. Materials using the more ridged biphenyl co-monomer and the silicone bridged co-monomer had intermediate conductivity, entries 2 and 3, and the material with the largest conductivity had a long methylene chain incorporated into the polymer backbone. This initial screening pointed us towards further investigation of the co-monomers with methylene chain backbones. Results from this study show a non-linear dependence of proton conductivity with HPA loading, unlike the previously studied acrylate system. In the top right of Figure 2 we show the water uptake and loss during dynamic vapor sorption experiment for an HPA-TFVE polymer co-polymerized with the Si co-monomer. The material shows very little water uptake, but a phase change around 40 wt% water uptake and significant hysteresis on the second wet-up dry-down cycle. In another RH study involving the C10 methylene co-monomer the phase change is absent but significant water uptake is observed above 90% RH. The SAXS data for both

the C10 and the Si bridged co-monomers are shown in the bottom left of Figure 2. Here we see sharp Bragg peaks in the SAXS at low RH indicating that the phase present under drier conditions is crystalline, as the material becomes wetter the Bragg peaks disappear indicating an amorphous phase. It is this amorphous phase that we believe is strongly proton conducting. Finally in the bottom right of Figure 2 we show a comparison of the wt% water uptake between the 825 equivalent weight (EW) 3M ionomer our generation I polyPOM85v acrylate material and an HPA-TFVE material. It should be noted that the water uptake of the HPA proton conductors is much smaller than for the PFSA material and is 10 times lower for the HPA-TFVR polymer than for the PFSA material.

The second polymer investigated was a functionalized Dyneon™ polymer developed at 3M. In Figure 3 we show the general synthetic route to these polymers. First the polymer is dehydrofluorinated and functionalized with bromophenyl ether. The polymer is then phosphonated and hydrolyzed so that a lacunary HPA can be attached. Note that it takes two attachment points to attach one HPA moiety. We believe that HPA only attached to one are not immobilized, and thus, future work will be directed towards double attachment points for all HPA in the film. We discovered that for these materials the method of film



**FIGURE 2.** Top left, proton conductivity for TFVE polymers with differing co-monomers at 80°C and 80% RH. Top right, dynamic vapor sorption data for a TFVE polymer containing the Si co-monomer. Bottom left, SAXS data for a TFVE polymer with a C10 co-monomer and a Si co-monomer. Bottom right, comparison of wt% water uptake for the 3M 825 EW ionomer, the polyPOM85vinyl acrylate materials and a TFVE polymer with a Si co-monomer.



**FIGURE 3.** General Scheme Showing Functionalization of Dyneon™ Polymer with HPA Moieties

processing is extremely important. In Figure 4, left we show proton conductivity data comparing the HPA functionalized Dyneon™ polymer prepared with differing dissolution times on different liners with the 825EW 3M PFSA ionomer. Interestingly it was the material that was not fully dissolved when cast that gave the best proton conductivity. The material that was fully dissolved reorganized on casting to give dramatically poorer performance. We also compare the stress strain curves for the HPA functionalized Dyneon™ polymer, the 825 EW 3M PFSA ionomer, and our generation I polyPOM85v acrylate polymer. It can be seen that the Dyneon™-based film is much stronger than either the 3M ionomer or the generation I film.

### Conclusions and Future Directions

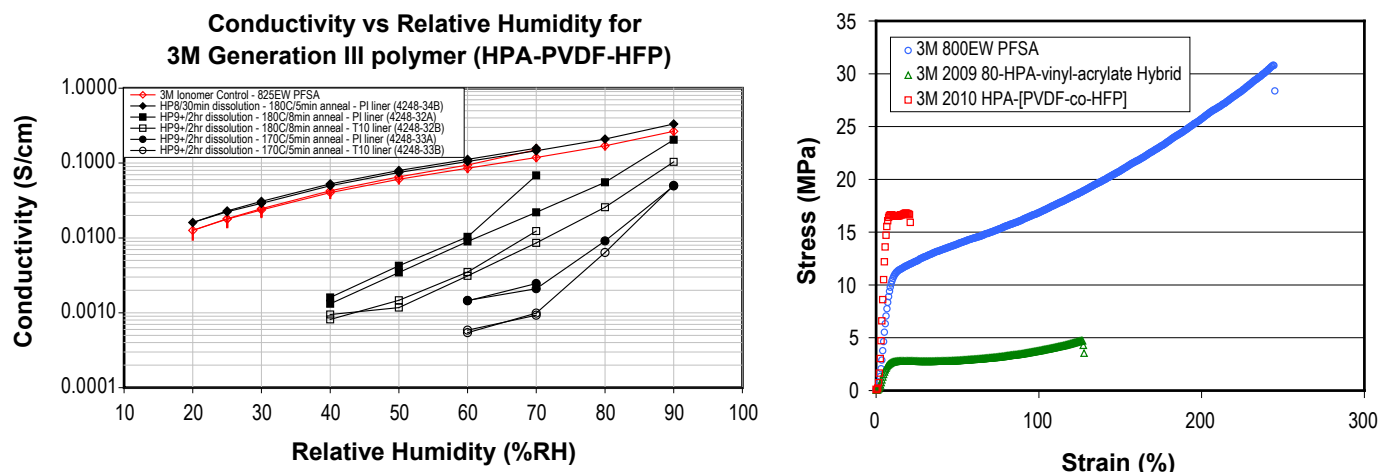
- We have functionalized two different perfluorinated polymer systems with HPA that will ultimately lead to

practical polymer systems for fuel cells run under hotter and drier conditions.

- The new polymers have very little water uptake and appear to be stronger than conventional ionomers.
- Although this project is ending, future work will focus on more robust HPA attachment and optimization of the films to meet all DOE targets for membranes.

### FY 2011 Publications/Presentations

- “High Temperature, Low Humidity Operation of Proton Exchange Membrane Fuel Cells” S.J. Hamrock and A.M. Herring, Encyclopedia of Sustainability Science and Technology, R.A. Myers, Ed., Springer, 2012, in press.
- “The use of polyoxometallates in fuel cell membranes.” S. Sachdeva, J.L. Horan, J.A. Turner, and A.M. Herring,\* submitted to “Fuel Cells”, A.B. Bocarsley, and D.M.P. Mingos, Eds, Structure and Bonding, Springer, 2011, 141, in press.



**FIGURE 4.** Left, conductivity data for the HPA functionalized Dyneon™ polymer and right, stress strain curves comparing the HPA Dyneon™ polymer, the 3M 825 EW PFSA ionomer and our generation I polyPOM85v acrylate polymer.

3. “Novel Hybrid Heteropoly Acid/Polymer Ionomers With Very High Proton Conductivity.” J.L. Horan, Mei-Chen Kuo, A.S. Perdue, F. Zhang, Z.C. Ziegler, J.D. Jessop and A.M. Herring, submitted to “Polymer Electrolyte Fuel Cells 10.” H. Gasteiger, H. Uchida, V. Ramani, A. Weber, T. Schmidt, T. Fuller, P. Strasser, P. Shirvanian, M. Inaba, M. Edmundson, F. Büchi, D. Jones, C. Lamy, R. Mantz, S. Narayan, R. Darling, T. Zawodzinski, Ed.s, *Electrochemical Society Transactions*, **2010**, 33, 839.

4. “Understanding the high proton conductivity observed in the polypoms in terms of morphology.” J.L. Horan, M.-C. Kuo, S. Sachdeva, H. Ren, A.S. Perdue, S.F. Dec, M.A. Yandrasits, S.J. Hamrock, M.H. Frey, and A.M. Herring. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.*, **2010**, 51, 728.

5. “The need for and the challenges of the perfect proton conducting polymer/composite.” A.M. Herring, *Polymer Preprints* **2010**, 51,686.

6. “Understanding the high proton conductivity observed in the polypoms in terms of morphology.” J.L. Horan, M.-C. Kuo, S. Sachdeva, H. Ren, A.S. Perdue, S.F. Dec, M.A. Yandrasits, S.J. Hamrock, M.H. Frey, and A.M. Herring, oral presentation, presented at the 239<sup>th</sup> ACS Meeting, San Francisco, CA, March 2010.

7. “The use of superacidic inorganic moieties for the promotion of proton conductivity.” A.M. Herring, G. Schlichting, M.-C. Kuo, J.L. Horan, M.H. Frey, H. Ren, S.J. Hamrock, oral presentation, presented 2010 Spring MRS meeting, San Francisco, CA, April 2010.

8. “Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes.” A.M. Herring, and M.N. Frey, oral presentation, to be presented at the at the DOE EERE Fuel Cell annual merit review, Washington, DC, June 2010.

9. “Introduction to Fuel Cells and Hydrogen Energy.” A.M. Herring, invited oral presentation, presented at NSF/ REMRSEC summer workshop for elementary and middle school students, Golden, CO, July 2010.

10. “The need for and the challenges of the perfect proton conducting polymer/composite.” A.M. Herring, invited oral presentation, to be presented at the 240<sup>th</sup> ACS Meeting, Boston, MA, August 2010.

11. “Hybrid inorganic/polymer ionomers for low RH fuel cell operation.” G.J. Schlichting, J.L. Horan, M.-C. Kuo, S.F. Dec, Z.Z., F. Zhang, J. Jessop, S. Nelson, and A.M. Herring, oral presentation, presented at the 240<sup>th</sup> ACS Meeting, Boston, MA, August 2010.

12. “Novel hybrid super acid/polymer ionomers with very high proton conductivity.” A.M. Herring, G.J. Schlichting, J.L. Horan, and M.C. Kuo, oral presentation, presented at ISPE-12, Padova, Italy, August 2010.

13. “Materials issues in polymer electrolyte fuel cells; research towards system compatible materials and more efficient, versatile electrocatalysts.” A.M. Herring, invited oral presentation, presented at the Rocky Mountain Section of the Materials Research Society, Boulder, CO, September 2010.

14. “Novel hybrid heteropoly acid/polymer ionomers with very high proton conductivity.” A.M. Herring, J.L. Horan, M.-C. Kuo, Z. Ziegler, and J. Jessop, oral presentation, presented at the 218<sup>th</sup> ECS Meeting, Las Vegas, NV, October 2010.

15. “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, November 2010.

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- Horan, James L.; Genupur, A.; Ren, H.; Sikora, Benjamin J.; Kuo, M.-C.; Meng, F.; Dec, Steven F.; Haugen, Gregory M.; Yandrasits, Michael A.; Hamrock, Steven J.; Frey, Matthew H.; Herring, Andrew M., *ChemSusChem* **2009**, 2, 226-229.