

V.D.7 Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes

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- (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 Interim 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 ⁺ conductivity	300 mS cm ⁻¹	126 ms cm ⁻¹	> 100 ms cm ⁻¹

RH – relative humidity

Accomplishments

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



Objectives

- To develop a new class of proton exchange membranes (PEMs) using polymers based on heteropolyacid (HPA) functionalized with organic monomers (poly-polyoxometalates, 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

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 relative humidities, 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 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 H₂ economy and enable a smooth transition from fossil fuels to H₂ 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°C , low area specific resistance, $<0.02 \Omega\text{cm}^{-2}$, and 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.

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 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 initially chose to use acrylates as the co-monomers in this project as their commercial availability and large variation made them a virtual 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 can be studied. In addition as these are free radical polymerizations the materials are 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 that could include that the acrylate ester linkage is unstable to hydrolysis and that polymers contain readily oxidizable methylene groups

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 new polymer chemistries so that we can address the additional criteria, such as cost, durability, and mechanical integrity that are needed 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. Comparing the NMR data with the proton conductivity data allows us to understand proton transport in these unique systems. In addition, we are correlating proton conductivity with morphology as observed by atomic force microscopy (AFM) and small angle X-ray scattering (SAXS) to enable us to understand structure proton conductivity relationships.

Results

We maximized the loading of HPA, the protogenic group in the acrylate model system. In Figure 1 we show data for an 85 wt% HPA substituted polymer. The proton conductivities at 95% RH are very impressive, 0.48 Scm^{-1} at 90°C . The E_a for this is 10 kJmol^{-1} similar to the 11 kJmol^{-1} reported for PFSA polymers [4]. At an RH of $\leq 80\%$ the E_a more than doubles to 23 kJmol^{-1} . At 50% RH the material achieves a proton conductivity of $>0.1 \text{ Scm}^{-1}$ at 80°C . These results are extremely encouraging, but unfortunately the material is somewhat brittle and seems to undergo morphological changes with RH and time from film forming. In Figure 2 we show some details of the morphology of these generation I films. The AFM image shows that the protogenic HPA part of the polymer forms a channelized network with channel diameter around 50-100 nm. These same channels that facilitate proton conduction are also speculated by us to be the micro-structural cause of the films inherent brittleness. We also show in this figure the stacked SAXS patterns for the material hydrated from a RH of 30% to 95%. A strong ionomer peak is

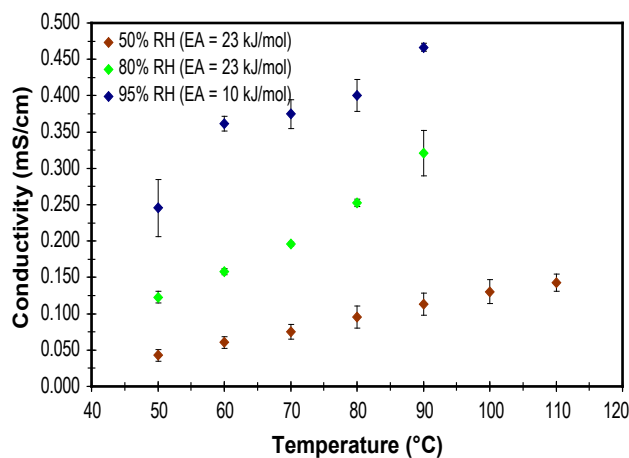


FIGURE 1. Proton conductivity data for a *co*-85 wt% $\text{H}_4[\text{SiW}_{11}\text{O}_{40}(\text{Si}(\text{CH}=\text{CH}_2)_2)_2]$ -*co*-butyl acrylate-*co*-hexanediol diacrylate polymer.

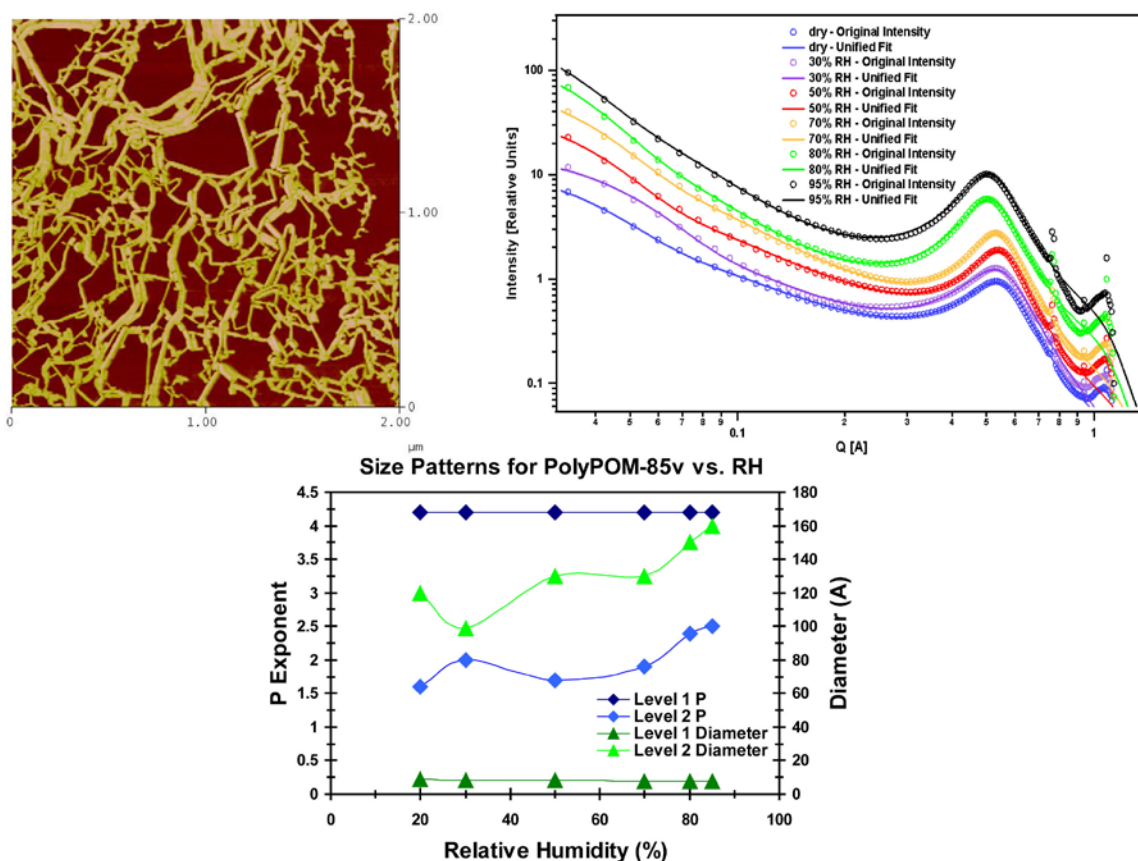


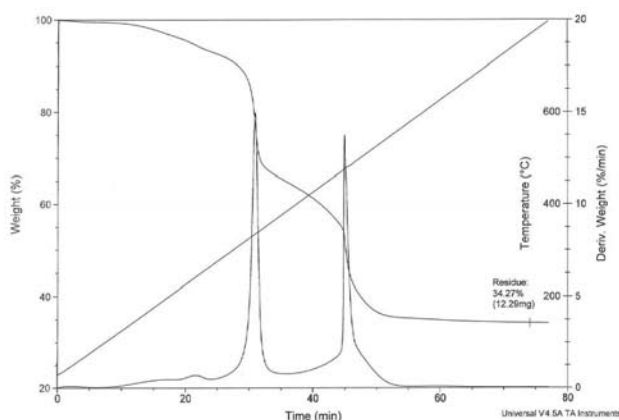
FIGURE 2. Morphological data for a *co*-85 wt% $H_4[SiW_{11}O_{40}(Si(CH=CH_2)_2)]$ -*co*-butyl acrylate-*co*-hexanediol diacrylate polymer, upper left AFM under ambient conditions, upper right, SAXS patterns, bottom, selected unified fit parameters from SAXS patterns.

observed at 5\AA^{-1} which shifts to the left with hydration. Using a unified Guinier and Porod fitting of the data gives a number of useful parameters, some of which are plotted at the bottom of the figure. The level 1 parameter are for the HPA moieties which maintain a diameter of 10\AA and spherical symmetry ($p=4$). The level 2 fit corresponds to the clustering of the HPA moieties, it can be seen that these clusters generally swell from 120 to 160\AA and become more symmetrical with more moisture (p increase from 3 to 4).

While the proton conductivities of these generation I acrylate films are impressive, they have a number of design flaws: 1) hydrolyzable ester linkages, and 2) a potentially oxidatively unstable methylene based backbone. To overcome these deficiencies and so that we can optimize the mechanical properties of the film we investigated two new generation II systems, designed to have no ester linkages. In system A the HPA was functionalized so that it could be co-polymerized into a perfluoro polymer. In system B a very simple polymerization scheme has been investigated. In a generation III approach, no ester linkages or methylene groups, being investigated at 3M, a perfluorinated polymer is functionalized such that the HPA can be

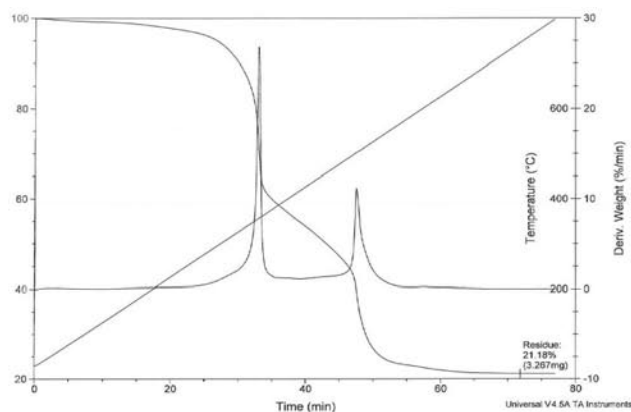
directly attached to the preformed polymer. Great difficulty was found in forming insoluble films from systems A and B, however we have recently found success blending these co-polymers with similar non-ionic polymers and have formed robust thin films.

The generation III films are the most advanced. Robust thin films have been obtained. These materials have been boiled in water for 10 h to investigate the robustness of the linkages to the HPA. Thermogravimetric analysis data for this test is shown in Figure 3. This figure shows that before leaching that polymer contained 34 wt% inorganic material and that after the leaching study the organic material was reduced to 21 wt%. Considering the severity of the test and that this system is still not optimized this result is remarkable and bodes well for future development of the system. In Figure 4 we show the proton conductivity data for the generation 3 film compared with the 3M 825 equivalent weight PFSA ionomer at 95°C . The conductivity is lower than the 3M ionomer, but consider that there is only 34 wt% of HPA in this material. The material does achieve 0.1 Scm^{-1} at 80% RH and 95°C . It should be obvious that the impressive conductivities obtained for



HPA-attached polymer

34% Inorganic Residue @ 800°C



HPA-attached polymer

(after leaching – 10hrs boiling water)
21% Inorganic Residue @ 800°C

FIGURE 3. TGA data for 3M generation III polymer before and after leaching in boiling water for 10 h.

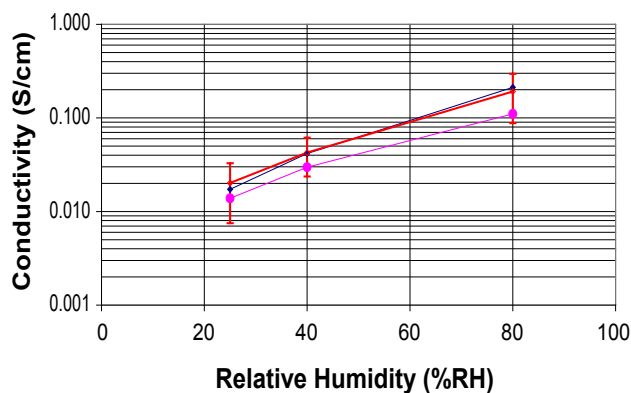


FIGURE 4. Proton conductivity data for 3M generation III polymer at 95°C, pink dots, compared with 3M 825 equivalent weight PFSA ionomer, red and blue upper traces.

the 85 wt% could be achieved in this system with much less HPA.

Conclusions and Future Directions

- Very high proton conductivities were obtained for generation I films with high loadings of HPA at 50% RH.
- Two new co-polymer systems were developed which have now been fabricated into films.
- A generation III film was developed in which significant amount of HPA were immobilized with respect to boiling water and adequate proton conductivity was observed.

We will continue to optimize generation II and III films for proton conductivity, oxidative stability and mechanical integrity. We will use SAXS, pulsed field gradient spin echo NMR and proton conductivity measurements to understand structure activity relationship in these films.

FY 2010 Publications/Presentations

1. “New PEM Fuel Cell Membranes for Higher Temperature, Drier Operating Conditions based on Heteropolyacids” A.M. Herring, N.V. Aieta, M.-C. Kuo, J.L. Horan, S.F. Dec, M.H. Frey, A. Genupur, S.J. Hamrock, M.A. Yandrasits, and G.M. Haugen, *Proceedings of the International Symposium on Materials Issues in a Hydrogen Economy*. P. Jena, A. Kandalam, Q. Sun, Ed.s, 2009, 273.
2. “Designing a New Ionomer From Scratch – Pushing Polypoms to the Limit,” J.L. Horan, Mei-Chen Kuo, H. Ren, A.S. Perdue, S.F. Dec, M.H. Frey, M.A. Yandrasits, S.J. Hamrock, and A.M. Herring, “Proton Exchange Membrane Fuel Cells IX.” T. Fuller, C. Hartnig, V. Ramani, H. Uchida, H. Gasteiger, S. Cleghorn, P. Strasser, T. Zawodzinski, D. Jones, P. Shirvanian, T. Jarvi, P. Zelenay, C. Lamy, P. Bele, Ed.s, *Electrochemical Society Transactions*, **2009**, 25, 1101.
3. “Probing The High Proton Conductivity Observed In The Polypoms.” A.M. Herring, M.H. Frey, Mei-Chen Kuo, J.L. Horan, H. Ren, S.F. Dec, and A. Perdue, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.*, **2009**, 54, 495.
4. “Towards a More Practical PolyPOM Ionomer.” A.M. Herring, M.H. Frey, M-C. Kuo, J.L. Horan, H. Ren, S.F. Dec, A. Perdue, *Fuel Cell Seminar Abstracts*, **2009**.
5. “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. Poly. Chem.*, **2010**, 51, 728.

6. “Materials Approaches to Improvements for Advanced Low and Intermediate Temperature Fuel Cells.” A.M. Herring, invited oral presentation, presented at the Summer School on Green Chemistry and Sustainable Energy, Golden, CO, July 2009.
7. “Designing A New Ionomer From Scratch – Pushing Polypoms to the Limit.” 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 42nd IUPAC Congress: Chemistry Solutions, Glasgow, UK, August 2009.
8. “Probing The High Proton Conductivity Observed In The Polypoms.” A.M. Herring, M.H. Frey, Mei-Chen Kuo, J.L. Horan, H. Ren, S.F. Dec, and A. Perdue, oral presentation, presented at the 238th ACS Meeting, Washington, D.C., August 2009.
9. “Designing a New Ionomer From Scratch – Pushing Polypoms to the Limit.” A.M. Herring, M.H. Frey, Mei-Chen Kuo, J.L. Horan, H. Ren, S.F. Dec, and A. Perdue, oral presentation, presented at the 216th ECS Meeting, Vienna, Austria, October 2009.
10. “Towards More Practical PolyPOM Ionomers.” A.M. Herring, M.H. Frey, Mei-Chen Kuo, J.L. Horan, H. Ren, S.F. Dec, and A.S. Perdue, poster presentation, presented at the Fuel Cell Seminar, Palm Springs, CA, November 2009.

11. “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 239th ACS Meeting, San Francisco, CA, March 2010.

12. “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.

References

1. Herring, A.M., *Polymer Reviews* **2006**, 46, 245 - 296.
2. Malers, J.L.; Sweikart, M.-A.; Horan, J.L.; Turner, J.A.; Herring, A.M., *Journal of Power Sources* **2007**, 172, 83.
3. 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.
4. M. Cappadonia, J.W. Erning, and U. Stimming, *Journal of Electroanalytical Chemistry*, **1994**, 376, 189.