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Mason K. Harrup  
Frederick F. Stewart  
Thomas A. Luther  
Tammy Trowbridge

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Mason K. Harrup, Frederick F. Stewart, Thomas A. Luther, Tammy Trowbridge

Idaho National Laboratory, P. O. Box 1625, Idaho Falls, ID 83415

### Introduction

Current proton exchange membrane (PEM) technologies are inadequate to address the projected needs for fuel cell performance above 80 °C. Continuing research into traditional ion carriers in novel membrane materials offers the promise of marginal improvement, representing only an evolutionary increase in performance. This conclusion is supported by the role of water in conduction. Thus, the key to better PEMs is **not** to eliminate water, but to change the role of water by developing ion carriers that will bind water more tightly than traditional sulfur or phosphorus based carriers resulting in materials that will conduct at higher temperatures. This change entails having a carrier structure that interacts more intimately with water and by increasing the ion carrier anionic charge to result in more tightly held inner shell protonated waters of hydration. Both of these factors synergistically act to maintain a critical water concentration at the carrier necessary for conduction. In this work, polyoxometalate (POM) clusters were selected to serve as these different proton carriers.

Nafion® is a sulfonated perfluoroethylene polymer that has been extensively studied for use as a fuel cell PEM. Considerable research has been conducted on its chemical and morphological structure, as summarized in three review articles.<sup>1-3</sup> The chemical structure of Nafion® entails three distinct portions: 1) a hydrophobic phase consisting of perfluoroethylene units; 2) sulfonated pendant groups, which form the hydrophilic phase; and 3) perfluoro-ether linkers between the hydrophilic and hydrophobic phases that form a mesophase. In practice, these phases tend to separate in the bulk material to form channels. Conduction is closely tied to the water content; suggesting that hydration about the sulfonate groups within the hydrophilic channels plays a dominant role. Thus, the real concern is not the anionic character of the ion carrier, but how tightly waters of hydration are held.

As POM syntheses are performed in water, the resulting clusters are hydrated. Reports of extensive hydration abound, for Keggin clusters up to 29 waters of hydration have been reported,<sup>5</sup> and some of these waters are known to be very tightly bound to the surface oxygens of the POMs.<sup>6</sup> These tightly bound waters are known to be able to form different protonated species with varying hydrogen bond strength<sup>7</sup>—indicating that proton mobility is facile in these bound waters. Further, TGA analyses have been recently performed that provide evidence that these tightly bound waters remain associated with the POM to temperatures as high as 350 °C.<sup>6</sup> These reports add significant credibility to our central hypothesis—novel proton carriers that retain their waters of hydration in a temperature regime above where “classical” carriers such as sulfonates and phosphates/phosphonates are completely dehydrated, destroying conductivity, are required to advance PEM fuel cell technology.

A few attempts to use POMs as proton carriers in PEM fuel cells have recently been reported. These attempts include doping true polymers like PBIs,<sup>8</sup> epoxy polymers,<sup>6</sup> and Nafion.<sup>9</sup> Several additional attempts were made to incorporate them into pseudo-polymeric composite systems by performing *in-situ* condensations with silica sols/methacrylates<sup>10</sup> and silica sols/glycols.<sup>11, 12</sup> Each of these approaches has reinforced the concept that POMs are a leading candidate to replace monoanionic proton carriers in the PEM membranes. In each of these studies, the bulk properties of the POM-doped membranes exhibited good conductivity when studies

are performed via AC impedance techniques. However, there have been few reports of these types of membranes being fabricated into membrane-electrode assemblies (MEAs) for actual fuel cell use. A more recent report supports this observed conductivity behavior, and has found that in actual MEAs, performance is not as good as expected due to high interfacial resistances.<sup>13</sup> Those investigators postulate that the dispersion of the carriers within the membrane lacks sufficient organization to function well. In order for these novel carriers to function effectively, organization of the POM within the polymer structure is the critical component. Our hypothesis in this work is that by controlling the nature of the counterions associated with the POM, the self-association of the POMs can be controlled, hence dictating the organization of the clusters within the host polymer matrix. To test this hypothesis, a suite of POMs that differed in the nature of the counterions were placed into polymer films and the organization of the POM determined by scanning electron microscopy (SEM).

### Experimental

**Polyoxometalate Synthesis.** The free acid forms of the polyoxometalates were prepared according to literature procedures. The  $H_3PW_{12}O_{40}$  was prepared according to the procedure of Wu,<sup>14</sup> the  $H_4SiW_{12}O_{40}$  was prepared according to North<sup>15</sup> and the  $H_6P_2W_{18}O_{62}$  was made according to Matcovik et al. using the batch method.<sup>16</sup> The polyoxometalate structures were verified with NMR and FTIR techniques. The various metathesized derivatives were made through the addition of the correct stoichiometric amounts of the alkali metal or quaternary ammonium salts as chloride salts. The speciation of the metathesized products was verified by base titration according to the methods of Finke et al.<sup>17</sup>

**Polymer Synthesis.** The sulfonated polyetheretherketone polymer (SPEEK) was prepared according to the method of Huang et al.<sup>18</sup> The degree of sulfonation of the final product was then determined by nuclear magnetic resonance (NMR) spectrometry.

The polyphosphazene polymers were prepared using the methods of Stewart et al.<sup>19</sup> The structures of the polyphosphazenes were verified using <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR analyses.

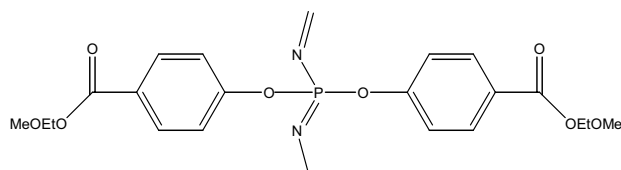
**Film Formation.** The POM loaded films were formed using solution casting techniques. All films that were produced used a ratio of 1.0:0.6 polymer:POM by weight. Films formed from the SPEEK polymer employed water as the casting solvent, while all films formed from the polyphosphazene employed DMSO as the solvent. Casting solutions were all approximately 10% polymer by weight. The films were cast on a substrate on a heated hot plate to induce film drying as quickly as possible without scorching the polymers.

### Results and Discussion

The first part of this work was to synthesize, purify, and characterize the free acid form of each of the three POMs:  $H_3PW_{12}O_{40}$ ,  $H_4SiW_{12}O_{40}$ , and  $H_6P_2W_{18}O_{62}$ . These were accomplished according to literature procedures and the structure of the POM validated against published reports. NMR and FTIR were primarily used to confirm the structure of each POM. These POMs were chosen as they represent two of the most common and synthetically accessible structural classes known.

Next, the polymer hosts had to be synthesized. Again following literature procedures, unfunctionalized polyetheretherketone was sulfonated by immersion in a sulfuric acid solution until the desired degree of sulfonation was achieved. The degree that was chosen was 2.47 meq/g. This was done because it would allow for the membrane formation solution to be aqueous-based. The polyphosphazene polymers were designed to mimic the SPEEK type polymers in that each possessed both a bulk hydrophobic region as well as a hydrophilic proton conductive region. The first of these polymers, the MEG ester, is shown in Figure 1. The other polyphosphazene

synthesized, the DEG ester, was the diethylene glycol analog of the structure shown in Figure 1.



**Figure 1.** Structure of the MEG ester polyphosphazene.

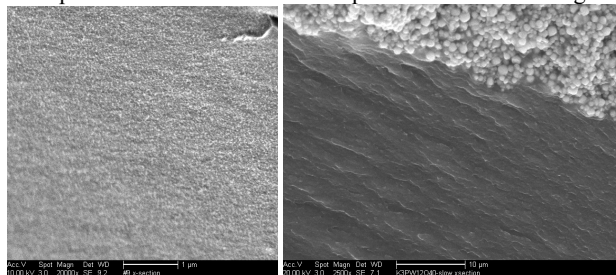
The next step in the process was to perform the metathesis reaction to generate the POM materials that were to be impregnated into the polymers hosts. The speciation of the counter cations was systematically varied from the free acid to the fully substituted forms using potassium for the SPEEK membranes. This was accomplished by adding a solution of the corresponding cation chloride to an aqueous solution of the free acid of the POM. The solution was then dried and the resulting solid collected. The counterion speciation was confirmed via titration with tetrabutylammonium hydroxide. A variety of membrane formation conditions for producing the POM/SPEEK composites also were investigated, chiefly polymer weight loading, POM addition methods, and membrane curing conditions. (heat, time, etc.) Both tetramethylammonium and tetrabutylammonium cations were then used for incorporation into the polyphosphazene composite membranes. These membranes were formed using the membrane formation techniques found to produce the best POM organization from the results of the POM/SPEEK studies. Table 1 gives a representative sampling of the various POM species that were synthesized.

**Table 1. Composition of Selected POM/Polymer Membranes**

POM	Counterions	Host matrix	POM	Counterions	Host matrix
PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	3H	SPEEK	SiW <sub>12</sub> O <sub>40</sub> <sup>4-</sup>	2H, 2 TBA	DEG ester
PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	3K	SPEEK	SiW <sub>12</sub> O <sub>40</sub> <sup>4-</sup>	4 TBA	DEG ester
SiW <sub>12</sub> O <sub>40</sub> <sup>4-</sup>	4H	SPEEK	P <sub>2</sub> W <sub>18</sub> O <sub>68</sub> <sup>6-</sup>	6K	DEG ester
SiW <sub>12</sub> O <sub>40</sub> <sup>4-</sup>	4K	SPEEK	PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	3H	MEG ester
SiW <sub>12</sub> O <sub>40</sub> <sup>4-</sup>	2K, 2H	SPEEK	PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	2H, 1 TMA	MEG ester
P <sub>2</sub> W <sub>18</sub> O <sub>68</sub> <sup>6-</sup>	6H	SPEEK	PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	1H, 2TMA	MEG ester
P <sub>2</sub> W <sub>18</sub> O <sub>68</sub> <sup>6-</sup>	6K	SPEEK	PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	3TMA	MEG ester
PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	3H	DEG ester	PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	2H, 1 TBA	MEG ester
PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	2H, 1 TMA	DEG ester	PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	1H, 2 TBA	MEG ester
PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	1H, 2TMA	DEG ester	PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	3TBA	MEG ester
PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	3TMA	DEG ester	SiW <sub>12</sub> O <sub>40</sub> <sup>4-</sup>	4H	MEG ester
PW <sub>12</sub> O <sub>40</sub> <sup>3-</sup>	2H, 1 TBA	DEG ester	SiW <sub>12</sub> O <sub>40</sub> <sup>4-</sup>	3H, 1 TMA	MEG ester

A wide variety of organizations of the POM in the host polymer matrix were observed by SEM. Some were found to be very inhomogeneous, where the POM self-associated into large aggregates, leaving the bulk of the host polymer containing no POM. Others however, exhibited extremely good organization where the POMs were found in small clusters of 5-10 discreet POMs and the distribution of these clusters was highly homogeneous throughout the host matrix. There were, of course, many instances between these extremes where the POM organization was somewhat homogeneous, but the clusters of POM were larger than found in some of the best

composite membranes. SEM micrographs of representative examples of the best and worst composites are shown in Figure 2.



**Figure 2.** Examples of good (left) and poor (right) organization of POM in the composite membranes.

### Conclusions

The obvious conclusion to be drawn here is that our initial hypothesis was correct. The nature of the speciation of the counter cations associated with the POM has a profound influence on the nature of the organization of the POM within the membrane matrix. Not surprisingly, a more hydrophobic suite of counter cations provides better organization in a more hydrophobic host polymer. Also, rapid membrane formation prevents “settling” of the high density POM as the membrane formation solvent evaporates. Finally, POMs with a lower ionic charge also appear to exhibit better organization, especially in the more hydrophobic host polymers. As there is clearly a wide variation in POM organization depending on counter cation speciation and membrane formation techniques, it is anticipated that further work in this area will afford the ability to control this organization and ultimately produce an improved fuel cell membrane. **Acknowledgement.** This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, Science, and Technology, and the INL Laboratory Directed Research & Development (LDRD) Program under DOE-NE Idaho Operations Office Contract DE-AC07-05ID14517.

### References

- Heitner-Wirguin, C.; *Journal of Membrane Science* 1996, 120, 1-33.
- Mauritz, K. A.; Moore, R. B.; *Chemical Reviews* 2004, 104, 4535-4585.
- Sondheimer, S. J.; Bunce, N. J.; Fyfe, C. A.; *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics* 1986, C26, 353-413.
- Kreuer, K. D.; *J. Membr. Sci.* 2001, 185, 29-39.
- Evans, H. T.; *J. Perspec. Struct. Chem.* 1971, 4, 1.
- Sweikart, M. A.; Herring, A. M.; Turner, J. A.; Dec, S. F.; Williamson, D. L.; McCloskey, B. D.; Boonrueng, S. R.; Sanchez, M.; *Journal of the Electrochemical Society* 2005, 152, A98.
- Proton Conductors: Solids, Membranes, and Gels - Materials and Devices*; Cambridge University Press: London, 1992.
- Gomez-Romero, P.; Asensio, J. A.; Borros, S.; *Electrochimica Acta* 2005, 50, 4715.
- Ramani, V.; Kunz, H. R.; Fenton, J. M.; *J. Membr. Sci.* 2004, 232, 31.
- Aparicio, M.; Castro, Y.; Duran, A.; *Solid State Ionics* 2005, 176, 333.
- Stangar, U. L.; Orel, N. G.; Schmitz, A.; Columban, P.; *Solid State Ionics* 2001, 145, 109.
- Honma, I.; Nakajima, H.; Nishikawa, O.; Sugimoto, T.; Nomura, S.; *Solid State Ionics* 2003, 162, 237.
- Vernon, D. R.; Meng, F.; Dec, S. F.; Williamson, D. L.; Turner, J. A.; Herring, A. M.; *Journal of Power Sources* 2005, 139, 141.
- Wu, H.; *J. Biol. Chem.* 43 (1920) 189.
- North, E. O.; *Inorg. Synth.* 1939, 1, 129.
- Matkovic, S. R.; Valle, G. M.; Gambaro, L. A.; Briand, L. E.; *Catalysis Today*, 2008, 133-135, 192.
- Weiner, H.; Aiken, J.D.; Finke, R.G.; *Inorg. Chem.* 1996, 35, 7905.
- Huang, R.Y.M.; Shao, P. H.; Burns, C. M.; Feng, X.; *J. App. Poly. Sci.*, 2001, 82, 2651.
- Stewart, F. F.; Lash, R. P.; Singler, R. E.; *Macromolecules* 1997, 30, 3229.