Final Report

Project Title: Novel Approaches to Immobilized Heteropoly Acid Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes

Project Period: April 1, 2006 – September 30, 2011

Date of Report: January 2, 2012, Final Version May 20th 2012

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Award Number: DE-FG36-06GO16032

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Project Objective: To develop proton exchange membranes based on the polymerization of hybrid heteropoly acid (HPA) monomers that achieve a proton conductivity of $>0.1 \text{ S cm}^{-1}$ at 50% RH and 120°C. To utilize all of the protons in these systems at all applicable temperatures and humidities in fast proton transport. To fabricate practical membranes in which the HPA are immobilized.

Background: Currently, fuel cells based on perfluorosulfonic acid (PFSA) proton exchange membranes (PEMs) are limited to operating conditions of $\leq 80^\circ\text{C}$ and very high relative humidity operation, 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 $\leq 120^\circ\text{C}$ 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 H_2 economy and enable a smooth transition from fossil fuels to H_2 produced solely from renewable sources. Materials suitable for use in automotive PEM fuel cells will be developed that will have high proton conductivities, $>0.1 \text{ S cm}^{-1}$ at 50% RH and 120°C, low area specific resistance, $<0.02 \text{ } \Omega\text{cm}^{-2}$, suitable for incorporation in a fuel cell membranes electrode assembly with oxidative stabilities higher than observed for any PFSA ionomer to date.

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. We have now shown that a HPA based polymer can have very high proton conductivities at $>100^\circ\text{C}$ and RH of $<50\%$. The two key challenges that still need to be addressed, are utilization of all protons under elevated temperature, dry conditions and immobilization of the HPA in practical membranes for fuel cell use that are robust and have adequate mechanical properties.

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1. Executive Summary

Original research was carried out at the CSM and the 3M Company from March 2007 through September 2011. The research was aimed at developing new to the world proton electrolyte materials for use in hydrogen fuel cells, in particular with high proton conductivity under hot and dry conditions ($>100\text{mS/cm}$ at 120°C and $50\%\text{RH}$).

Broadly stated, the research at 3M and between 3M and CSM that led to new materials took place in two phases: In the first phase, hydrocarbon membranes that could be formed by photopolymerization of monomer mixtures were developed for the purpose of determining the technical feasibility of achieving the program's Go/No-Go decision conductivity target of $>100\text{mS/cm}$ at 120°C and $50\%\text{RH}$. In the second phase, attempts were made to extend the achieved conductivity level to fluorinated material systems with the expectation that durability and stability would be improved (over the hydrocarbon material). Highlights included:

- Multiple lots of an HPA-immobilized photocurable terpolymer derived from di-vinyl-silicotungstic acid (85%), n-butyl acrylate, and hexanediol diacrylate were prepared at 3M and characterized at 3M to exhibit an initial conductivity of 107mS/cm at 120°C and $47\%\text{RH}$ ("PolyPOM85v") using a Bekktech LLC sample fixture and TestEquity oven. Later independent testing by Bekktech LLC, using a different preheating protocol, on the same material, yielded a conductivity value of approximately 20mS/cm at 120°C and $50\%\text{RH}$. The difference in measured values is likely to have been the result of an instability of properties for the material or a difference in the measurement method.
- A dispersed catalyst fuel cell was fabricated and tested using a $150\mu\text{m}$ thick HPA-based photocurable membrane (above, "PolyPOM75v"), exhibiting a current density of greater than 300mA/cm^2 at 0.5V (H_2/Air 800/1800sccm $70^\circ\text{C}/75\%\text{RH}$ ambient outlet pressure).
- Multiple lots of a co-polymer based on poly-trifluorovinylether (TFVE) derived HPA were synthesized and fabricated into films, Generation II films. These materials showed proton conductivities as high as 1 S/cm under high RH conditions. However, the materials suffered from compromised properties due to impure monomers and low molecular weights.
- Multiple lots of an HPA-immobilized fluoropolymer derived from preformed PVDF-HFP (Generation III films) were synthesized and formed into membranes at 3M and characterized at 3M to exhibit conductivity reaching approximately 75mS/cm at $120^\circ\text{C}/40\%\text{RH}$ using a Bekktech sample fixture and TestEquity oven (optimized membrane, at close of program).
- Initial fuel cell fabrication and testing for this new class of membrane yielded negative results (no measureable proton conductivity); however, the specific early membrane that was used for the two 5cm^2 MEA's was later determined to have $<1\text{ mS/cm}$ at $80^\circ\text{C}/80\%\text{RH}$ using the Bekktech fixture, vs. ca. 200 mS/cm at $80^\circ\text{C}/80\%\text{RH}$ for samples of the later-optimized type described above. Future work in this area (beyond the presently reported contract) should include additional attempts to fabricate and test fuel cells based on the later-optimized Generation II and III polymer.
- A manufacturing study was performed which predicted no difficulties in any future scale up of the materials.

2. Technical Report of Activity and Findings

HPA's are a class of inorganic oxides that exhibit some of the highest solid state proton conductivity values known at room temperature. For example, 12-phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40-x}\text{H}_2\text{O}$) and 12-phosphomolybdic acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40-x}\text{H}_2\text{O}$) show proton conductivity values of 0.17S/cm and 0.18S/cm at 25°C, respectively.¹ They are also very easily functionalized. This project was concerned with fabricating novel polymeric materials where the protogenic group was a HPA either functionalized as a monomer or attached to a pre-formed polymer.

Task 1.1 Stability of phenyl-terminated Lacunary HPA

One of the preliminary areas of study was to examine the stability of the linkage between the lacunary heteropoly acid and the organic functional group under applicable conditions to those anticipated in fuel cell applications. The phenyl moiety was used as the surrogate organic moiety. In this study four compounds were tested representative of three types of linkage: Type 1 compounds contained linkages of two metallo atoms each double bonded to an individual oxygen atom, Type 2 compounds contained linkages of two metal atoms, and type 3 compounds.

In order to test the strength of the linkages present in these compounds they were boiled in solutions of 6M hydrochloric acid for 12 h. Only the type II compound survived this test. However, in our co-current polymer work it was shown that the Type I linkages with Si had significant stability in polymer systems and so work continued with type I Si linkages due to the ease of obtaining these molecules to act as model compounds.

Task 1.2 HPA immobilized on vinyl- or styryl-based polymer (ion-exchange)

We were initially concerned about ion-exchanging the HPA moieties, however, this never became an issue during the course of the project. In general the monomers were ion exchanged using cold conditions before incorporation into the polymers.

Task 1.3 Immobilized HPA clustering with hydrophobic monomer

A variety of monomers could be attached to the lacunary HPA and so a large scale study was set up. The co-monomer system of choice was based on acrylate chemistry. These functionalized monomers come in a very wide variety and some are also very inexpensive. The acrylate system represents somewhat of a polymer system in a kit and gave rise to the Generation I polymers.

These materials were fabricated primarily to enable the team to efficiently demonstrate that the materials had high proton conductivities at both the low temperature relatively wet milestone and at the high temperature relatively dry Go/No-Go criterion. Obviously they probably would not be sufficiently chemically stable to survive hot water hydrolysis and even with the oxidation protection from the HPA may also have been compromised by the relatively strongly oxidizing conditions of an operating fuel cell.

Methacrylsilane hybrid HPA

Both K-HPA-attached methacrylate (i.e. potassium salt of the hybrid monomer) and H-HPA-attached methacrylate (i.e. acid form of the hybrid monomer) were prepared successfully (please refer to reports of the HPA-attached vinyl hybrid material for the reaction procedure).ⁱⁱ Attempts were made to ter-polymerize HPA-attached methacrylate with n-butyl acrylate and isobornyl acrylate and initiator TPO-L by UV polymerization. The resulting membranes were not fully polymerized. After some time a film with the composition SiW11dimethacryl 98wt% and hexyl acrylate 2wt% gave a proton conductivity of 126 ms/cm at 31°C and 60% RH. Unfortunately this film did not survive temperature and humidity cycling above 50 °C. This result did, however, meet the initial milestone criteria of >70 ms/cm at 80 %RH and room temperature.

Styrylethylsilane hybrid HPA

Synthesis of K-HPA-attached Styrylethyl Hybrid Monomerⁱⁱⁱ

The monomer was synthesized as shown above. Three work-up procedures were attempted to isolate the desired product. From these studies it was shown that the double bond of the K-HPA-attached styrylethyl hybrid monomer was very sensitive to the ion-exchange conditions. If the K-HPA-attached styrylethyl hybrid monomer was ion exchanged at room temperature, the double bond polymerized. If K-HPA-attached styrylethyl hybrid monomer was ion exchanged at low temperature, 0 °C, the double bond was stable, but the ion exchange was not complete. This made the synthesis of H-HPA-attached styrylethyl hybrid membrane challenging. Ultimately, this challenge prompted a shift in effort toward preparation of different HPA-attached hybrid materials, specifically based on HPA-attached vinyl hybrid monomers (later in this report).²

XRF data showed that only 50% of potassium from K-HPA-attached hybrid monomer was exchanged by ion exchange in the monomer used for the polymerization studies. That is, after the ion exchange procedure, (K,H)HPA-attached hybrid monomer included a mixture of counter ions, K^+ and H^+ . It was named as (K,H)HPA-attached styrylethyl hybrid monomer. A hybrid membrane containing (K,H)HPA-attached styrylethyl hybrid monomer was prepared, and its conductivity was evaluated.

(K,H)HPA – styrylethyl hybrid monomer and 2-hydroxyethyl acrylate (HEA) were mixed together in equal weights and left to stir for overnight, resulting in a homogenous highly viscous liquid. This solution was cast between 2 silicone treated poly(ethyleneterephthalate) (PET) sheets and cured under UV for 3-4 hours. 2.5% Darocur 1173 was used as the initiator for the UV curing process. A membrane was obtained whose conductivity was measured as in Figure 1. The (K,H)HPA-attached styryl:HEA membrane had a relatively low conductivity value, which was not surprising considering that the material was not fully protonated.

Figure 1 Proton conductivity data of K,H-HPA attached with styrylethylsilane/HEA membrane.

Similarly frustrating results were obtained at CSM using styrylethyl HPA monomers. These proved to be extremely reactive during synthesis and their resultant yield very low. They were also very difficult to dissolve in anything and so polymerization attempts were unsatisfactory.

Vinylsilane hybrid HPA

Synthetic challenges associated with double bond preservation for the acid form of the HPA-attached styrylethyl and styrenyl hybrid monomers motivated a shift to another hybrid monomer, in particular an HPA-attached vinyl hybrid monomer. In the subsections that follow, synthesis, analysis, conversion to a membrane, and proton conductivity measurement results are reported for these materials.

Synthesis of K-HPA-attached Vinyl Hybrid Monomer

This monomer was synthesized by the above procedure which was scaled up eventually to the 100g scale. The chemical structure was confirmed by $^1\text{H-NMR}$. $^1\text{H-NMR}$ (DMSO): 5.9-6.1ppm (vinyl peaks), 3.7ppm (water peak).

The K-HPA-attached hybrid monomer was converted to acid form by ion-exchange. Amberlite IR-120 Plus (H^+) ion exchange resin was used to acidify K-HPA-attached hybrid material. The chemical structure was confirmed by $^1\text{H-NMR}$. $^1\text{H-NMR}$ (DMSO): 5.9-6.1ppm (vinyl peak), 4.6ppm (H_3O^+). Compared with K-HPA-attached vinyl hybrid monomer, the water peak shifted from 3.7ppm to 4.6ppm (moved to the down field), indicating that the HPA-attached vinyl hybrid monomer was in acid form.

Formation of Membranes Based on HPA-Attached Vinyl Hybrid Monomer

For membrane preparation, H-HPA-attached vinyl hybrid monomer was dissolved in n-butyl acrylate (BA) and 1,6-hexanediol diacrylate (HDDA) at different weight ratios. The loading of H-HPA-attached vinyl hybrid monomer was varied from 50% to 85%. Several hours of stirring was required to achieve maximum dissolution or dispersion of the H-HPA-attached hybrid monomer. Once H-HPA-attached vinyl hybrid monomer dissolved, 0.5-2.5 wt% of UV photo initiator, for example Darocur 1173 (2-hydroxy-2-methyl-1-phenyl-propan-1-one) or TPO-L, was added. The solution mixture was stirred for another 30min, then was sonicated for 10 min. The solution was settled on bench for 10 min to remove any bubbles before casting a membrane. A photograph of membrane solutions of H-HPA attached vinyl: n-BA: HDDA is shown in Figure 2. From the photograph, it can be seen that a relatively clear membrane solution was obtained when the loading of H-HPA-attached vinyl hybrid monomer was about 50% by weight. However, the membrane solution was turbid for a loading of H-HPA-attached vinyl

hybrid monomer of 75%. To form a membrane, the final solution was then cast between two layers of PET, cured by a UV lamp (Black Ray XX-15BLB-365nm BLB) for 24 hours to 48 hours. A dark blue flexible membrane (see Figure 3) was obtained initially, which turned to amber after exposure to air.

Figure 2 Mixtures of H-HPA-attached vinyl hybrid monomer: n-BA: HDDA. Top solution: H-HPA vinyl hybrid monomer: BA: HDDA= 3:0.9: 0.1 (75wt% hybrid monomer); Bottom solution: H-HPA vinyl hybrid monomer: BA: HDDA= 1:0.9: 0.1 (50wt% hybrid monomer).

Figure 3 As-cured H-HPA attached vinyl hybrid membrane: H-HPA vinyl: n-BA: HDDA=3:0.9:0.1 (75wt% hybrid monomer).

HPA Content and Stability of HPA-Attached Vinyl Hybrid Membrane in Water

Two aspects of the behavior of the vinyl hybrid membrane in contact with liquid water were studied. Two early lots of the material was studied for: i) the degree of immobilization of HPA, as determined by tendency to be leached in room temperature water, and ii) water uptake (mass) and swelling (dimensional) in room temperature water.

Procedures

To estimate the HPA content and the degree of immobilization of HPA for the two early lots of vinyl hybrid polymer membrane, thermogravimetric analysis (TGA) was carried out for as-formed film and for water-leached film. For leaching, a piece of hybrid membrane was soaked in water for 24 hours, and then dried for at least two days. For each sample, the weight fraction of material remaining after pyrolysis in the TGA instrument was taken to represent the content of HPA. For measurement, the TGA instrument was first stabilized at 30 °C, and then was heated to 800 °C at 10 °C/min.

To determine the water uptake (mass) and swelling parameters (dimensional), a membrane film was soaked in water for 30 min. The membrane initially swirled inwards as soon as it came in contact with water and slowly opened to become flat. Complete discoloration ("bleaching") of the membrane was observed. The final dried weight of the membrane was evaluated by drying the membrane at room temperature for 3 days.

Results

The inorganic contents of HPA-attached hybrid monomers, and the inorganic contents of HPA-attached hybrid polymer membrane before and after leaching, were obtained by TGA for the two early lots of material, as given in Table 1 and Figures 4 and 5. Table 1 also gives calculated (theoretical) inorganic content for the HPA, for the hybrid monomer in potassium form and in acid form, and for the polymer. For the potassium salt of the HPA ($\text{K}_8\text{SiW}_{11}\text{O}_{39} \cdot 13\text{H}_2\text{O}$), the potassium salt of the hybrid vinyl monomer ($\text{K}_4[(\text{CH}_2=\text{CH}-\text{Si})_2\text{O}]\text{SiW}_{11}\text{O}_{39} \cdot n\text{H}_2\text{O}$), and acid form of the hybrid vinyl monomer ($\text{H}_4[(\text{CH}_2=\text{CH}-\text{Si})_2\text{O}]\text{SiW}_{11}\text{O}_{39} \cdot n\text{H}_2\text{O}$), TGA results for both Batch I and Batch II were consistent with the theoretical predictions. However, TGA results showed that the inorganic content of the early lots of H-HPA attached vinyl:n-BA:HDDA 3:0.9:0.1 membrane was about 40-43% (see Figure 5), which was lower than the theoretical prediction, ca. 68%. The origin of this inconsistency between measured and theoretical inorganic content for the early lots of membrane polymer was never determined, but may have related to unintended material loss during TGA measurement under flowing gas. Notwithstanding this discrepancy, the above-described work to determine the water leaching behavior and the water uptake and swelling behavior was continued (below).

Table 1 Inorganic content of membrane precursors and membranes, as measured by TGA.

Material	Batch I	Batch II	Theoretical expected values based on 13H ₂ O molecules
	Inorganic content (weight %)		
K ₈ SiW ₁₁ O ₃₉ .13H ₂ O	93.2	92.58	92.74
K ₄ [(CH ₂ =CH-Si) ₂ O]SiW ₁₁ O ₃₉ .nH ₂ O	90.18	90.61	90.97
H ₄ [(CH ₂ =CH-Si) ₂ O]SiW ₁₁ O ₃₉ .nH ₂ O	91.28	Not done	90.38
H-HPA attached VINYL:N-BA:HDDA 3:0.9:0.1 membrane	40.22	42.73	67.78
H-HPA attached VINYL:N-BA:HDDA 3:0.9:0.1 membrane after leaching	55.22	56.20	-

Figure 4 Thermogravimetric analysis of HPA, K-HPA-attached vinyl hybrid monomer, H-HPA-attached vinyl hybrid monomer and H-HPA-attached vinyl hybrid copolymer membrane before leaching.

Figure 5 Thermogravimetric analysis of H-HPA-attached vinyl hybrid copolymer membrane after leaching.

Before continuing the report of findings for exposure to water, it is worthwhile to report quickly on the achievement and measurement of the intended weight percent loading of HPA in this class of material. In light of the discrepancy noted above for the total HPA content of the two early lots of H-HPA-vinyl: BA: HDDA (3:0.9:0.1) hybrid membrane, later, similarly formulated material was characterized by simple furnace burnout in loosely covered crucibles. For the later lot, three replicate film samples, H-HPA-attached vinyl: BA: HDDA (3:0.9:0.1) from batch 5, were evaluated. The measurement procedure was as follows:

- Step 1: weigh three clean crucibles; record the tare mass values
- Step 2: place a film sample into each crucible; record the mass of each crucible w/ film
- Step 3: place a loose cover on each crucible; load crucibles into a box furnace
- Step 4: heat crucibles at 10 °C/min to 800 °C, hold 10min, furnace cool
- Step 4: weigh each crucible; calculate inorganic residue (ash) left in each crucible
- Step 5: calculate the percentage of inorganic content from each piece of film

The data for this simple furnace burnout experiment are given in Table 2. The data indicate that the three replicate film samples gave consistent values of inorganic content. The average of inorganic content of H-HPA attached vinyl: BA: HDDA hybrid membrane was about 67%, which was the same as theoretically calculated value in Table 1.

Table 2 Inorganic content from simple furnace burnout experiment, batch 5 of (3: 0.9: 0.1) H-HPA-attached vinyl:BA:HDDA film (theoretical = 67.8%).

Sample	Tare mass (g)	Mass of crucible with film (g)	Mass of crucible with film after burnout (g)	Inorganic content (wt%)
No. 1	12.13830	12.16704	12.15745	66.6%
No. 2	12.93474	13.00246	12.98048	67.5%
No. 3	8.87459	8.94609	8.92307	67.8%
				average: 67.3%

Figure 6 Pictorial representation of leaching study on H-HPA attached vinyl: n-BA: HDDA 3:0.9:0.1 membrane.

Returning now to the water exposure experiments: The leaching solution was dried in an oven, and the resulting leachate was analyzed by TGA and NMR. The leached H-HPA-attached hybrid membrane was also dried and was evaluated by TGA. The TGA data for the sample after leaching experiment had similar weight loss behavior as the sample before leaching experiment, except that percentage of inorganic species left increased to 56%, higher than that inorganic content before the leaching experiment (see Figure 5).

To further describe the immobilization state of the HPA for the hybrid H-HPA-attached vinyl: n-BA: HDDA (3:0.9:0.1) membrane, a pictorial analysis is given in Figure 6. Comparing TGA data for the leached film and for the original film, the leached film had less organic (38% vs 53%), and thus higher inorganic content (56% vs 41%) (balance water). This indicates that some amount of organic components was lost or leached out during the leaching experiment. TGA analysis of the leachate showed that the leachant had 75% organic content and 19% inorganic content (balance water). The leachate was analyzed by $^1\text{H-NMR}$, which showed vinyl peaks around 5.8 ppm to 6.2 ppm. The presence of double bond in the leachate indicates that H-HPA-attached vinyl: BA: HDDA membrane was not fully polymerized, so some hybrid monomer or co-monomer leached out during leaching experiment, which caused the leached membrane to have less hydrocarbon component and more inorganic component. This might be overcome by extending the UV curing time. Considering the weight change for the samples during leaching, in combination with the TGA results for the leachant, it was determined that approximately 81% of H-HPA was immobilized onto the polymer.

Figure 6 also reports results for water uptake and dimensional changes upon exposure to liquid water for H-HPA-attached vinyl: n-BA: HDDA (3:0.9:0.1) membrane samples. Two sets of results are included in this regard. First, for exposure to water for 30 minutes, a membrane was measured to take on approximately 4% mass, to grow in the thickness dimension by approximately 27%, and to grow in the in-plane dimension by approximately 3%. Second, for exposure to water for 24 hours, followed by 3 days of drying in ambient conditions, a membrane was measured to have shrunk by approximately 18% in the thickness dimension and by approximately 21% in the in-plane dimension.

Conductivity of HPA-Attached Vinyl Hybrid Membranes

Membranes prepared as described above were characterized for their proton conductivity. More specifically, membranes comprising the H-HPA-attached vinyl hybrid monomer, n-butylacrylate (BA), and hexanedioldiacrylate (HDDA) were formulated with different levels of the HPA hybrid monomer. The membranes included a 10:1 proportion of BA:HDDA. The formulations are described below in terms of the weight percent content of the vinyl hybrid monomer. Alternatively, the formulations are described in terms of the mass ratios of H-HPA-vinyl hybrid monomer: BA:HDDA.

In the first measurements, conductivity of organic-inorganic hybrid polymer membranes was determined using a Bakktech sample fixture in a TestEquity environmental oven at 80°C, with relative humidity varying from 25% up to 100% and compared with a standard 800EW PFSA (perfluoro sulfonated acid) ionomer, “3M Ionomer.” Figure 7 reports the measured conductivity for membrane samples having 50wt% and 75wt% loadings of H-HPA-attached vinyl hybrid monomer. Further comparison with the conductivity of other PFSA membranes, including Nafion[®], can be done directly through reference to publications of past work.^{iv,v}

In the second measurements, conductivity of organic-inorganic hybrid polymer membranes was determined using a Bakktech sample fixture in a TestEquity environmental oven at 120°C and relative humidity 47%. Figure 8 reports the measured conductivity for membrane

samples having from 75wt% to 85wt% loadings of H-HPA-attached vinyl hybrid monomer. From lot to lot, the measured conductivity varied, with the highest measured conductivity reaching 107mS/cm. The results in Figures 22 and 23 reveal a strong dependence of conductivity on the H-HPA loading.

Figure 7 Measured proton conductivity at 80°C with varying relative humidity, for membranes incorporating the HPA-attached vinyl hybrid monomer (atmospheric pressure).

Figure 8 Measured proton conductivity at 120°C and approximately 47% relative humidity, for membranes incorporating the HPA-attached vinyl hybrid monomer (atmospheric pressure).

To further confirm the proton conductive properties of membranes incorporating H-HPA-attached vinyl hybrid, a film sample with 85wt% loading of the H-HPA-attached vinyl hybrid was prepared at 3M and sent to the third party, BekkTech LLC. The measurements carried out at BekkTech LLC indicated a proton conductivity of approximately 20 mS/cm at 120°C and 50% relative humidity (Figure 9). The difference in measured values for 3M and for BekkTech LLC is likely to have been the result of an instability of properties for the material or a difference in the measurement method.

Figure 9 Proton conductivity measurement results for 3M-prepared membrane incorporating 85wt% H-HPA-attached vinyl hybrid monomer (4139-62D), measured by BekkTech LLC.

Membrane Electrode Assembly (MEA) Testing for HPA-Attached Vinyl Hybrid Membranes

The proton conductivity results from 3M and BekkTech suggested the potential for preparation of a functioning fuel cell. The target for MEA testing was to generate a membrane that would be at least 50 cm² in area and 2 mils in thickness. Formation of such a thin, free-standing membrane proved challenging, due to adhesion between the membrane and the PET liner on which the membrane was cast. After several attempts, it was found that a membrane could be formed by using a new release liner, T10 (CPFilms Inc.), which is a type of PET film that is coated with release coating. As a proof of concept and to show that the H-HPA attached vinyl:BA:HDDA film does indeed conduct protons, a 50 cm² film was fabricated into a MEA using standard electrodes with Pt dispersed on carbon. The MEA was run as a H₂/air fuel cell at 70°C and 75% RH. On running successive polarization curves, the performance improved until 600 mAcm⁻² at 0.3 V with an area-specific resistance of 100 mΩcm⁻² was achieved (Figure 10). The fuel cell survived for 4 days. Considering that this MEA was not optimized in any way, the performance of the fuel cell under these relatively dry conditions suggested that this new ionomer class has significant potential for application in PEM for fuel cell. The high frequency resistance of the PEM in the MEA was equal to or less than that for Nafion[®] 112.

Figure 10 Polarization curve for the maximum performance of a 50cm² MEA constructed from a 150μm thick 75% H-HPA loading vinyl: BA hybrid membrane. H₂/air= 800: 1800sccm, 70 °C, 75% RH, ambient outlet pressure.

Mechanical Property Test for HPA-Attached Vinyl Hybrid Membranes

Figure 11 Tensile test result of 80wt% loading of H-HPA attached vinyl: BA: HDDA hybrid membrane; 25°C.

H-HPA-attached vinyl: BA hybrid membrane exhibited very promising proton conductivity, with values at 50% RH and 120 °C reaching the DOE target. However, the mechanical stability of this membrane was not adequate. For the MEA test, the fuel cell only survived for 4 days. A

tensile test result is shown in Figure 11. Compared with standard 3M PFSA ionomer, HPA-attached vinyl: BA hybrid membrane exhibited much lower strength. The membrane failed at a stress level of approximately 5 MPa, at 130% strain. The low strength of the membrane might have been due in part to this high loading of inorganic component in the hybrid membrane. It is also noteworthy that fuel cell operation resulted in flow of the membrane material under mechanical compression.

The best performing PolyPOM membranes to date, as measured by proton conductivity, include membranes synthesized with the Divinyl-11-silicotungstic acid hybrid monomer [HSiW11(vinyl)2] co-polymerized with butyl acrylate (BA) and 1,6-hexanediol diacrylate HDDA. A series of these membranes were synthesized by varying the concentration of the hybrid HSiW11(vinyl)2 monomer from 25 wt.% to 85 wt% (PolyPOM25-85v). The materials can no be fabricated easily in $>100\text{ cm}^2$ sheets of ca. $100\text{ }\mu\text{m}$. As shown in Figure 12 the materials are a transparent light brown.

Figure 12. Typical film that can now be produced for a polyPOM85v

Characterization Studies

Atomic force microscopy (AFM) was also used to characterize the morphology of PolyPOM membranes of varying hybrid monomer concentration. Figure shows the imaging of the inorganic and organic phases obtained through AFM. As the HPA monomer concentration increases in the membrane, a greater degree of phase separation through clustering and channeling of the inorganic phase is apparent which would explain the increase of proton mobility and conduction.

Figure 13. AFM phase image of PolyPOM-25v (a), PolyPOM-50v (b), PolyPOM-75v (c), and PolyPOM-85v (d) polymer films under ambient conditions.

Dynamic Studies

Dynamic studies performed on the membranes showed the structural and morphological response of the membranes under varying temperature and relative humidity conditions. These experiments included small angle scattering (SAXS) and dynamic vapor sorption (DVS). Proton mobility was also studied under dynamic conditions using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and pulsed field gradient spin echo (PFGSE) NMR. Finally, a fuel cell test was performed on a PolyPOM membrane electrode assembly (MEA) to demonstrate that a PEM membrane containing immobilized heteropoly acids as the sole proton conducting component could present a viable alternative to sulfonic acid based perfluorinated ionomers.

Dynamic SAXS experiments performed at the Advanced Photon Source (APS) at Argonne National Lab under varying temperature and relative humidity conditions show structural changes of membranes with different concentrations of HPA monomer. Figure 14 shows the morphological response of a PolyPOM-85v membrane at 80 °C as the humidity is ramped from 0% to 100% RH during two cycles. Two iso-scattering points at low q -regions of the SAXS patterns are apparent. This could be due to scattering from two transitioning phases. Another indication of transitioning phases is the disappearance of the crystalline peak that shows up in dry conditions in the first cycle but then disappears as the sample is humidified. This peak is essentially absent during the 2nd cycle.

Figure 14. Dynamic SAXS experiment for a PolyPOM-85v membrane during two humidification cycles (a then b).

The use of a unified fit model^{vi} indicates at least two levels of structural hierarchy (Figure 15). A strong scattering peak at q between 5 and 6 Å⁻¹ can be attributed to scattering from the HPA molecules imbedded in the polymer. The scattering model indicates a structural diameter of about 10 Å⁻¹ which is consistent with the HPA anion. This level one structure is constant with all membranes at all relative humidity as shown in Figure 16a. Larger, level two, structural features at lower q values are likely to result from HPA clustering. The size of the clusters increases with HPA monomer concentration irrespective of relative humidity conditions (Figure

16a). Figure 16b shows that the radius of gyration from level 1 is consistent with a Keggin anion, 1 nm, and that the cluster sizes increases with HPA loading.

Figure 15. Dynamic SAXS scattering experiments showing original intensity (symbols) and unified fit models (solid lines) for a PolyPOM85v membrane at various RH (a) and for membranes of different HPA monomer concentration at 80% RH (b).

Figure 16. Unified fit structural dimensions for PolyPOM membranes.

Dynamic vapor sorption (DVS) measures the water uptake of membranes equilibrated at selected relative humidity values. PolyPOM-85v membranes have similar water uptake characteristics as the 3M perfluorinated ionomer except at very high humidity where the PolyPOM-85v experiences up to 26 wt% water increase compared to 20 wt% water increase for the 3M membrane (Figure 17).

Figure 17. DVS measurements of water uptake in PolyPOM-85v and 3M membranes.

In-plane proton conductivity measurements determined by potentiostatic electrochemical impedance spectroscopy (PEIS) show that PolyPOM membranes with high concentration of the HPA monomer perform well compared to perfluorinated sulfonic acid membranes (Figure 18). As the HPA monomer concentration increases in the membrane, the activation energy approaches that of the perfluorinated sulfonic acid membrane. Area Specific Resistance (ASR) measurements for PolyPOM-80v and PolyPOM-85v membranes are very close to the DOE target. At 80 °C and 95% RH, the ASR for PolyPOM-85v is 0.032 Ohm-cm² and at 30 °C and 95% RH, the ASR is 0.087 Ohm-cm². The average thickness of these PolyPOM-85v membranes tested for conductivity is about 130 μm. PolyPOM-85v membranes with a reduced thickness of about 50 μm would meet the DOE ASR targets when tested under the same temperature and humidity conditions.

Figure 18. PEIS conductivity measurements for PolyPOM membranes at 80 °C (a) and 80% RH (b)

PFGSE NMR measurements show very high diffusion coefficients for the PolyPOM-85v membranes at 100% RH compared to the 3M ionomer (Figure 19). This is probably related to the increased water uptake of the PolyPOM-85v membrane compared to the 3M ionomer as confirmed by DVS measurements. At about 50% RH, both the PolyPOM-85v and the 3M ionomer have comparable water uptake measurements and diffusion coefficients.

Figure 19. PFGSE NMR diffusion coefficients of PolyPOM-85v and 3M ionomer

Task 2.1 Optimization of Task 1.3 membrane

Task 2.2 HPA w/ weak acid polymers

PolyTrifluorovinylether hybrid HPA (Generation II films)

The above described H-HPA-attached vinyl:BA:HDDA hybrid membrane material was developed to explore the potential for reaching useful levels of proton conductivity. However, this material does not possess adequate mechanical, thermal, and chemical properties for long-term fuel cell operation. The membrane degraded and failed during fuel cell performance testing. In order to improve this new type of membrane (polymer-immobilized HPA) for fuel cell applications, the material must not only have high proton conductivity, but also good thermal and chemical stability. For this reason we invested the time and effort in to developing partially and fully fluorinated polymers functionalized with HPA. In the first strategy reported here lacunary HPA were functionalized with trifluorovinylether functionalities. The synthetic scheme to make these is shown in the scheme below.

Unfortunately the formation of the brominated precursor is very hard to achieve in high purity and the resultant monomers were contaminated with up to 25% of the hydrogen substituted non-polymerizable molecule by NMR. This resulted in significant difficulties in forming high quality films.

We used a variety of co-monomers, which included several ridged biphenyl derivatives. However, in order to obtain materials with some flexibility we synthesized more rubbery monomer as shown below. We were not unduly concerned about the effect of oxidative stability of the resultant films by the presence of the methylene groups as we rationalized that they would be inaccessible to the hydrophilic channels containing any peroxide and that in a working fuel cell very little oxidative radical would be present due to the peroxide decomposing properties of the HPA.

Even use of these co-monomers produced somewhat brittle films. So a minimum amount of PVDF-HFP was added to the formulation to obtain flexible films suitable for testing. A general scheme for the polymerization is shown in the scheme below.

Some representative films are shown in Figure 20. It should be noted that while these films are opaque they are fairly light in color.

Figure 20. Representative polyHPA-TFVE/PVDF-HFP films.

The materials at this time are fairly heterogeneous and probably have low molecular weights. Dynamic vapor sorption experiments revealed phase changes between crystalline phases at low RHs, Figure 21. It can be seen from the sudden decrease in mass as the material rearranges that the amorphous phase occurs above 50%RH.

Figure 21. Typical DVS experiment for a polyHPA-TFVE/PVDF-HFP film.

The phase changes are also present in the SAXS data for many of these polymers. Bragg peaks are clearly visible in the patterns at low RH for the crystalline phase and are absent at high RH.

Figure 22. Representative SAXS data for two polyHPA-TFVE/PVDF-HFP films, Compound IV contains a biphenyl co-monomer and compound VII a decamethylene bridged co-monomer.

Despite the obvious materials issues still to be resolved a large amount of proton conductivity data was collected for these materials. Initially despite systematically fabricating films from all five co-monomers in our library as well as from the homopolymer, very few trends emerged. As is usual in the case of new materials a lot of the variability was due to an increasing competence in synthesis of the materials with time, as well as the profound effects of solvent and casting conditions on film properties. One common theme was that the homo-polymers had little proton conductivity while the highest proton conductivities were observed for films with the more flexible methylene chain linkages. This is very well illustrated in Figure 23.

Figure 23. Proton conductivity for a series of polyHPA-TFVE/PVDF-HFP films, Compound IV contains a biphenyl co-monomer related to the biphenyl derivative shown, and compound VII a decamethylene bridged co-monomer at 80 °C, RH 80%.

Recent data for a series of methylene chain linked materials reveals that there are clearly synergistic effect between components as no clear trend is observable other than C6 linkages are always less conducting and C8 always more so, as illustrated in Figure 24.

Figure 24. Proton conductivity for a series of polyHPA-TFVE/PVDF-HFP films with methylene linkages from C6 to C10, left at 95% RH, and right at 80% RH.

It should be noted that proton conductivity of the C10 film in Figure 24, would exceed the DOE RT milestone and survives all temperatures up to 90°C, showing a dramatic improvement on the Generation I film used to pass this milestone.

Unfortunately due to the lack of monomer purity and the poor film forming properties of these materials they proved unsuitable for fuel cell testing. Future work would be aimed at obtaining pure monomers and formulations that showed no phase change behavior.

PVDF-co-HFP hybrid HPA (Generation III film)

A second new HPA immobilization strategy was also proposed. The new strategy was based on immobilization of HPA onto a pre-formed fluoropolymer, poly (VDF-co-HFP), where VDF and HFP stand for vinylidene fluoride and hexafluoropropylene, respectively. As is well known in the fuel cell community, fluoropolymers generally exhibit greater thermal and chemical stability than hydrocarbon polymers.

However, poly(VDF-co-HFP) bears no native functional groups where HPA can be directly attached. A key task in the presently reported phase of the work was to functionalize the polymer with pendant groups that would react with heteropolyacid and yield a covalent bond between the two. Similar chemistry as was used for synthesizing hybrid monomers in earlier sections of this report was used for linkage of PVDF-co-HFP to lacunary HPA. Past studies have found that removal of an octahedral unit from a saturated heteropolyanion framework leads to increase and localization of the anionic charge, the resulting lacunary anion becomes highly nucleophilic and reacts easily with electrophilic groups such as -RPO^{2+} .^{vii} Accordingly, PVDF-co-HFP was first functionalized with pendant phosphonate groups.

Creation of pendant phosphonate groups on poly(VDF-co-HFP) became a substantial part of the presently reported phase of the program. The strategy that was pursued was a derivation of known dehydrofluorination chemistry for PVDF-co-HFP. More specifically, it is known that

PVDF-co-HFP can be substituted on its backbone by dehydrofluorination with phenols, which is the basis for bisphenol crosslinking of such fluoroelastomers.^{viii}

To build upon the known dehydrofluorination mechanisms, a new reaction scheme to immobilize HPAs to PVDF-co-HFP was pursued (See Figure 20). First, 4-bromo phenol is grafted to the polymer backbone, yielding a polymer containing bromophenyl functional group on the structure. Grafting the bromo functional group to the polymer was followed with conversion of that bromo functional group into a phosphonate ester group. From that point, the phosphonate ester group can be hydrolyzed into a phosphonic acid group, whereon the HPA can then be attached.

Due to their lengthy nature, the details regarding each step in the reaction scheme of Figure 25 to synthesize HPA-attached PVDF-co-HFP are not given in this report, including a significant quantity of analytical results. Yields are estimated.

Figure 25 Membrane synthesis and architecture (also referred to herein as “Generation III” membrane).

HPA Content and Stability of HPA-Attached Hybrid PVDF-co-HFP in Water

To determine the HPA loading and to confirm covalent attachment to the polymer, leaching and thermogravimetric studies were carried out on K-HPA-attached hybrid fluoromaterial (from rxn 4176-34A) and H-HPA-attached hybrid fluoromaterial (from rxn: 4176-52). For leaching, pieces of HPA-attached hybrid material (either K salt or acid form) were boiled in DI water for 5 hours, then was filtered. The resulting material was dried in a vacuum oven at 60-70°C for 6 hours. To determine the content of inorganic material present in the organic-inorganic hybrid material, thermogravimetric analysis (TGA) was performed on pieces of HPA-attached hybrid materials, without leaching and after leaching. The TGA showed that K-HPA-attached hybrid material included 25% inorganic material left after leaching, compared with 38% inorganic content before leaching. Note that the TGA data for the leached and then dried hybrid material indicate the presence of a significant amount of bound water (especially relative to the material that was not leached). Taking into account the change in apparent bound water, the proportion of original (before leaching) inorganic content (viz. HPA) that remained after leaching may be even higher than that suggested by the change in measured high-temperature residue from 38% to 25% upon leaching. These findings suggest that at least a portion of K-HPA was covalently attached to the phenylphosphonic acid functional group-containing polymer. To compare, the modified polymer, phenylphosphonic acid containing, dehydrofluorinated PVDF-co-HFP (before HPA attachment reaction) was also evaluated by TGA. TGA data show that no inorganic material was detected for the material before HPA attachment.

H-HPA-attached hybrid fluoropolymer after acidification by the soxhlet method was also studied by leaching. TGA results showed that the H-HPA-attached hybrid material (acid form) included 21% inorganic material left after leaching, compared with 34% inorganic content before leaching.

XRF study on H-HPA-attached hybrid fluoropolymer

The effectiveness of the ion exchange process for HPA attached hybrid material by the soxhlet method was evaluated by X-ray fluorescence (XRF). Samples of H-HPA-attached hybrid fluoropolymer, before and after leaching, were measured. XRF results (Figure 26) show that the potassium (K) concentration was nearly the same before and after leaching, and that the concentrations were very low. These findings suggest that ion exchange by soxhlet was an efficient method to acidify the HPA-attached PVDF-co-HFP hybrid material. Also, as expected, there was less silicon (Si) and less tungsten (W) present after leaching. These XRF results are consistent to the TGA findings listed above.

Figure 26 XRF data for the H-HPA-attached fluoropolymer, before and after leaching.

Membrane Preparation by Solution Casting

Solution casting is a traditional method to prepare a proton electrolyte membranes. Preferably, the membrane polymer would be easily dissolved in a convenient solvent and at arbitrary concentration. However, the H-HPA-attached hybrid “Generation III” fluoropolymer was not soluble or was only slightly soluble in the most organic solvents. N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) are the two solvents that were found to dissolve this hybrid material, but the solution had to be heated. Considering toxicity, DMSO was chosen as the preferred solvent for casting membranes.

H-HPA-attached hybrid fluoropolymer was added to DMSO at 3.5-4wt% concentration in a sample vial. The solution was stirred and was heated on a hot plate. The hot plate setting and the dissolution time were varied. The resulting hybrid polymer solution was then cast on polyimide (Kapton[®], DuPont) or silicone-treated PET (ClearSIL[®]T10, CPFilms) liner substrate, and then dried in an oven. In one example of a drying procedure, the wet membrane casting was heated from room temperature to 120°C first, kept at 120°C for 10min, then oven temperature was increased to 180°C for 5 minutes. A photograph of the H-HPA-attached hybrid membrane prepared by solution casting and the aforementioned drying and annealing procedure is shown in Figure 27.

Figure 27. H-HPA-attached hybrid PVDF-co-HFP fluoropolymer membrane prepared by solution casting.

Membrane Preparation by Hot Pressing

Figure 28. Sample E: H-HPA attached polymer “membrane,” pressed on Teflon® liner at 500 °F and 17,500 lb for 20 minutes. The material is more cohesive than in Samples C or D but remains hard and brittle.

Due to the challenges associated with polymer dissolution, attempts were made to fabricate membranes by hot pressing. This work attempted to duplicate and expand upon procedures set forth in previously published work on sulfonic acid functionalized PVDF-co-HFP.^{ix} In the referenced work, modified PVDF-co-HFP resins were pressed into films using a Carver press between two plates at a temperature of at least 100 °C. When the H-HPA-attached fluoropolymer was pressed, it usually formed a dark, charred, and brittle wafer. The resulting

materials from all pressing tests were ill-suited for further testing for use in fuel cell MEA's, Figure 28.

Conductivity of H-HPA-Attached Hybrid Fluoropolymer Membranes ("Generation III")

Solution-cast H-HPA-attached hybrid fluoromaterial membranes (acid form) were tested for proton conductivity at 80°C, 95°C, and 120°C and at different relative humidity levels. Measurements were made at 3M using a BekkTech LLC sample fixture (four-point probe, in-plane measurement) and a TestEquity environmental chamber.

To maximize proton conductivity, with the goal of meeting the DOE target, the synthetic work was aimed at maximizing the content of immobilized heteropolyacid in the materials. This began with efforts to maximize the mole percentage of phenylphosphonate ester functional group on the modified polymer. After a series of experiments that were carried out to optimize phosphonate reaction conditions, the conversion yield of phosphonation was increased from 22% to 46%. Secondly, the hydrolysis of the ethoxy groups was driven to 90% yield. Finally, for the materials reported in the present section on conductivity, approximately 50% of the hydrolyzed phosphonate groups were found to be attached to HPA in the final material (P-NMR). Such yields led to the contents of inorganic HPA reported above (TGA).

Especially for materials with maximum content of HPA, the Generation III hybrid polymer proved difficult to dissolve in a membrane casting solvent (as described above). Moreover, as a result of multiple attempts to prepare high-conductivity membranes from solvent-case membranes, it was discovered that the ultimate conductivity that could be measured was very sensitive to the conditions of dissolution in the membrane-casting solvent, as well as to the post-casting annealing step(s). Although the study reported below was somewhat empirical, in terms of temperature control during the dissolution step, its results point strongly to a clear dependence of properties on membrane preparation conditions.

Table 4 gives summary information regarding certain preparation conditions for a series of membrane samples that were cast from DMSO solution. All of the membranes were prepared by dissolving H-HPA-attached hybrid fluoropolymer in DMSO at 4% concentration. The resulting solutions were cast on either a polyimide liner (Kapton[®], DuPont) or a silicone-treated PET liner (T10, CPFilms). With respect to the aforementioned finding that the H-HPA-attached fluoropolymer hybrid material prepared from a high phosphonate conversion yield modified polymer required heating in DMSO for a long time and at high temperature to be dissolved, it is proposed that this is because the higher percentage of phosphonate group on the polymer backbone will lead to more crosslinking by attached HPA. The solutions used for casting the different membranes below, differed in terms of the hot plate setting and time over which the dissolving solution was heated (in glass vials).

Figures 29-31 give results for the conductivity measurements. A gentler dissolution condition for the H-HPA-attached hybrid fluoropolymer material in DMSO (0.5hr at hot plate setting of 8) resulted in higher measured proton conductivity for the resulting membranes. It is important to note that the more favorable (gentle) dissolution condition did not produce a homogeneous solution. Rather, the casting solution included some undissolved particulates. Another finding in Figures 29-31 relates to the effect of membrane annealing conditions. For

the more aggressive dissolution conditions (2hrs at hot plate setting of 9 or higher), a higher temperature final stage annealing condition (180°C for 8min) resulted in higher conductivity than was observed for a lower temperature final stage annealing condition (170°C for 5min). Finally, it was also found that the liner onto which the H-HPA-attached hybrid fluoropolymer membranes were cast affected the measured proton conductivity. The proton conductivity results (32A vs 32B, 33A vs 33B in Figures 43-44) show that the membranes cast on polyimide liners gave higher proton conductivity than the membranes cast on silicone-treated PET.

Table 4 H-HPA attached hybrid membranes prepared from phosphonate ester fluoropolymer containing 46% conversion yield of bromo to phosphonate ester.

Membrane Number	Liner onto which Membrane was Cast	DMSO Dissolution Conditions before Membrane Casting	Annealing Conditions for Membrane Casting
4248-32A	Polyimide	Hot Plate Setting 9 - ca. 2hrs	180°C/8min
4248-32B	Silicone treated polyester	Hot Plate Setting 9 - ca. 2hrs	180°C/8min
4248-33A	Polyimide	Hot Plate Setting 9 - ca. 2hrs	170°C/5min
4248-33B	Silicone treated polyester	Hot Plate Setting 9 - ca. 2hrs	170°C/5min
4248-34B	Polyimide	Hot Plate Setting 8 - ca. 0.5hr	180°C/5min

Figure 29. Proton conductivity data for H-HPA attached hybrid fluoropolymer (prepared from phosphonate ester polymer containing 46% conversion yield; 37wt% inorganic in final product, by TGA) at 80°C.

Figure 30. Proton conductivity data for H-HPA attached hybrid fluoropolymer (prepared from phosphonate ester polymer containing 46% conversion yield; 37wt% inorganic in final product, by TGA) at 95°C.

Figure 31. Proton conductivity data for H-HPA attached hybrid fluoropolymer (prepared from phosphonate ester polymer containing 46% conversion yield; 37wt% inorganic in final product, by TGA) at 120°C.

Two membranes were tested for fuel cell performance. Both membranes gave identical results. The findings for one of them are now described. Two 5cm² MEAs (membrane electrode assemblies) were tested. In both cases, the MEAs were evaluated under H₂/H₂ (hydrogen pump) and under N₂/N₂ flow conditions (as qualification, before H₂/air, typical fuel cell operation, would be done). In both cases, the resistances measured under H₂/H₂ and N₂/N₂ were the same.

No evidence of proton conductivity was observed, as the resistance measured corresponded to the very high typical electronic short resistance, in the range of $100\ \Omega\text{-cm}^2$. Pains were taken to minimize any possible wash-out of the proton conductor. In no case did the hydrogen pump resistance not equal the short resistance (N_2/N_2). Impedance measurements taken during all hydrogen pumps showed no frequency dependence. There was no evidence of ionic conductivity greater than that associated with the very high electronic short resistance. The membranes used for MEA testing were later determined to have $<1\ \text{mS/cm}$ at $80^\circ\text{C}/80\%\text{RH}$. Future work in this area (beyond the presently reported contract) should include additional attempts to fabricate and test fuel cells based on these later-optimized Generation III polymers.

Task 3.1 Defect-free Task 2 membrane processing w/ suitable mechanicals

Mechanical Study on H-HPA-Attached Hybrid Fluoropolymer Membrane

Figure 32. Stress-strain curve for PVDF-co-HFP hybrid HPA “Generation III” membrane (28wt% inorganic, by TGA); with comparison to HPA-attached vinyl hybrid copolymer (PolyPOM80v); 25°C .

A good proton exchange membrane need have not only good proton conductivity but also good stability and mechanical properties. Fluoropolymers are among the most chemically inert of all polymers, and they are known to remain stable in many chemical environments. A key motivator for shifting to a fluoropolymer form of the new ionomers based on covalently attached HPA (from Task 1 to Task 2) was the desire for improved chemical stability and mechanical properties. H-HPA-attached hybrid fluoropolymer did exhibit good stability during the ion exchange process. Also, the membranes retained their shape and form throughout all of the proton conductivity testing described above. H-HPA-attached hybrid fluoropolymer also exhibited an improvement with regard to mechanical properties, in terms of the tensile strength, as compared with Task 1 membrane. Tensile test data are reported below for a solution-case HPA-attached fluoropolymer hybrid material membrane. As shown in Figures 32 and 33, the HPA-attached fluoropolymer membrane exhibited a much higher modulus and greater strength than the Task 1 of HPA-attached vinyl hybrid membrane.

Figure 33. Instantaneous modulus for PVDF-co-HFP hybrid HPA “Generation III” membrane (28wt% inorganic, by TGA).

Task 3.2 Oxidative stability; Si and P; peroxide soak testing

None of the films were specifically tested for oxidative stability as none of the high loading generation I films, or the generation II, or generation III films were fully optimized for complete HPA stabilization. However, based on a large literature precedent, our own data on the dramatic improvement of oxidative stability of PFSA films by HPAs,^x and the more robust chemistry we feel confident in predicting that these materials have adequate oxidative stability for fuel cell applications.

3. Preliminary Manufacturability Outlook

At a USCAR Tech Team review in Detroit, Michigan on February 11, 2009 and at a Department of Energy review in Washington, D.C on February 24, 2009, 3M proposed to make a brief initial assessment of the manufacturability of any new materials developed during the remainder of the program (post-Go/No-Go). After passing the Go/No-Go gate, and as the program was concluding, the assessment meeting was indeed held at 3M (January 7, 2011).

The manufacturability assessment meeting was held in order to identify any key challenges that would be expected to arise if one attempted to scale up the materials developed in the latter stages of the program. In particular, the materials that were considered were the Generation III hybrid ionomers based on immobilization of lacunary silicotungstic acid on PVDF-co-HFP. The outlook that was generated as a result of the meeting is preliminary, which is to say that it should not be regarded as exhaustive and definitive. Rather, the outlook was

based on a high level review, and may have failed to uncover certain challenges that could prove ultimately to be significant, even limiting, to the technical or economic viability of the materials considered.

The January 7, 2011 assessment meeting (1.5hr) was attended by personnel from the 3M Corporate Research Materials Laboratory (CRML), the 3M Fuel Cell Components Program (FCCP), and the 3M Materials Resource Division (MRD). The 3M MRD is a unit of 3M Company that manufactures chemical feedstocks for other operating units within the company. The CRML attendees were the principal investigator for the present program (Frey) and the program's primary bench chemist (Ren). The FCCP attendees included three chemists, representing several years of experience in the development and commercialization of fuel cell membranes. The MRD attendees included a technical manager and three chemists, representing many years of technical expertise in fine chemical scale-up and manufacturing.

The agenda for the assessment meeting included a brief program introduction, followed by a presentation of details regarding the synthetic precursors, intermediates, conditions, yields, and separations (see Appendix). Finally, a discussion took place which was focused on collecting feedback from the non-program participants on the apparent manufacturing feasibility of the Generation III membrane ionomer (to the point of generating the material suitable for redissolution and casting; i.e., did not include a review of these latter two steps).

Notes, including quotations, from the meeting were as follows:

Selected high-level comments:

- "This is a complex fine chemical synthesis."... "Fine chemical processing is a lot like this."
- "Chemically, there are no showstoppers."... "No chemistry here that scares me."
- "I wouldn't be too discouraged."
- "There are no exotic conditions...normal glassware."

Selected detailed comments:

- "Process optimization is needed to improve volume utilization."
- "% solids of each of these process steps will have a big impact on your reactor volume efficiency."
- "A lot of dissolving and drying" ... "Can you avoid drying to a solid every time?"... "Can you do any steps neat?"
- "Can you do solvent exchanges?"... "keep it soluble?"
- "Can you use a different PVDF-HFP?...some may be easier than others...different molecular weight?"
- "To use less solvent, could you carry some impurities along, and then clean up just once, at the end?"

If one were to pursue this material commercially at 3M, next steps:

- Initiate "New Materials Introduction" program within MRD.
- Review for entry into MRD lab.
- Carry out focused work against detailed comments above.

The overall conclusions from the assessment meeting were as follows:

- The HPA-modified PVDF-HFP preparation appears likely to be feasible in manufacturing.
- Any additional development work on this type of material should include objectives related to solvent usage and process simplicity, as suggested above.

4. Conclusions

This report necessarily details the highlights of a 5 year program, literally hundreds of films were fabricated, many of which had poor proton conductivity or were unsuitable for testing. The Generation I films based on acrylate chemistry demonstrated that very high proton conductivities could be obtained, as shown in Table 5.

Table 5. Generation I film proton conductivities.

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

At the end of this five year project CSM has finished by continuing to optimize the trifluorovinylether, TFVE derived heteropoly acid (HPA) polymers, Generation II films, which can be co-polymerized with either C6, C8, C10 or biphenyl linking co-monomers. We have identified a significant problem in that many of our monomers are not pure; trace amounts of water in the synthesis have introduced hydrogen into the vinyl group making them inactive to polymerization. As the project has ended the resolution of this effort will have to be left until another day. The good news is that we have dramatically improved film forming by switching solvents from DMSO to DMAc. The films formed from DMAc are semi-transparent have greatly improved properties, and very high proton conductivities, unfortunately, they still require the addition of a small amount of PVDF-HFP for their formation.

The PVDF-HFP HPA functionalized materials, Generation III films produced at 3M also showed great promise but again time and resources prevented their full potential from being realized. Film forming procedures were optimized, but the HPA attachment was not.

A large number of publications and presentations resulted from this work. 3 more contributions to peer reviewed journals are planned in early 2012.

5. Publications and Presentations

1. “Novel Approaches to Immobilized Heteropoly Acid Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes”, A.M. Herring, oral and poster presentation, presented at the US DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program 2006 Annual Merit Review Meeting, Crystal City, VA, May 2006.
2. “Structure and dynamics of hybrid organic-inorganic membrane materials for fuel cell applications”, J.L. Horan, J.A. Turner, A.M. Herring, S.F. Dec, *Division of Fuel Chemistry Preprints- American Chemical Society*, **2006**, 51, 653.
3. “Structure and dynamics of hybrid organic-inorganic membrane materials for fuel cell applications”, J.L. Horan, J.A. Turner, A.M. Herring, S.F. Dec, oral presentation, presented at the 232nd American Chemical Society Meeting, San Francisco, CA, September 2006.
4. “Structure and Dynamics of Hybrid Organic-Inorganic Membrane Materials for Fuel Cell Applications.” James L. Horan, John Turner, Steven Dec, and Andrew M. Herring, poster presentation, presented at the 210th Meeting of The Electrochemical Society, Cancun, MX, October 2006.
5. “Using Inorganic Super Acids to functionalize PFSA ionomers or as stand alone proton conducting materials”, A.M. Herring, invited oral presentation, presented at Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2007, Asilomar, CA, February 2007.
6. “Heteropoly Acid Polymers for Automotive Fuel Cell Applications.” A.M. Herring, J.L. Horan, M.-C. Kuo, N.V. Aieta, and S.F. Dec, oral presentation, presented at the 211th ECS Meeting, Chicago, IL, May 2007.
7. “Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes” A.M. Herring, J.L. Horan, and M.-C. Kuo, oral presentation, presented at the US DOE Hydrogen, Fuel Cells & Infrastructure Technologies Program 2007 Annual Merit Review Meeting, Crystal City, VA, May 2007.
8. “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 58th Annual Meeting of the International Society of Electrochemistry, Banff, Canada, September 2007.
9. “Advances in Hybrid Organic-Inorganic Proton Exchange Polymer Membranes Incorporating Heteropoly Acids” J. L. Horan, S. F. Dec and A. M. Herring, oral presentation presented at the 212th ECS meeting, Washington, DC, October 2007.
10. “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.
11. “Advances in Hybrid Organic-Inorganic Proton Exchange Polymer Membranes Incorporating Heteropoly Acids” J. L. Horan, S. F. Dec and A. M. Herring, oral presentation presented at the 212th ECS meeting, Washington, DC, October 2007.

12. "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.
13. "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.
14. "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.
15. "PolyPOM membranes for hot and dry PEM fuel cell operation." A.M. Herring and M.H. Frey, oral presentation, presented to DOE Tech team, Detroit, MI, April 2008.
16. "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 213th ECS meeting, Phoenix, AZ, May 2008.
17. "Novel Approaches to Immobilized Heteropoly Acid (HPA) Systems for High Temperature, Low Relative Humidity Polymer-Type Membranes." A.M. Herring and M.H. Frey, oral presentation, presented at the DOE EERE H₂ review, Crystal City, VA, June 2008.
18. "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.
19. "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.
20. "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 214th ECS Meeting, Honolulu, HI, October 2008.
21. "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, to be submitted to "Proton Exchange Membrane Fuel Cells VIII." T. Fuller, K. Shinohara, V. Ramani, P. Shirvanian, H. Uchida, S. Cleghorn, M. Inaba, S. Mitsushima, P. Strasser, H. Nakagawa, H. A. Gasteiger, T. Zawodzinski, C. Lamy, Ed.s, *Electrochemical Society Transactions*, **2008**, 16, 699.
22. "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.
23. "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**.

24. "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.
25. "PolyPOM membranes for hot and dry PEM fuel cell operation." A.M. Herring and M.H. Frey, oral presentation, to be presented to the DOE Tech team, Detroit, MI, February 2009.
26. "Ionomer From Scratch – Pushing PolyPOMs to the Limit." A.M. Herring, invited oral presentation, to be presented at Advances in Polymer Electrolyte Membrane Fuel Cell Systems 2009, Asilomar, CA, February 2009.
27. "PolyPOM membranes for hot and dry PEM fuel cell operation." A.M. Herring and M.H. Frey, oral presentation, presented to the DOE, Washington, DC, February 2009.
28. "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 237th ACS Meeting, Salt Lake City, UT, March 2009.
29. "An Ionomer With Very High Proton Conductivity Derived From The Co-Polymerization of $H_4[SiW_{11}O_{40}(Si(CH=CH_2)_2)_2]$ 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.
30. "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.
31. "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.
32. "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.
33. "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, DC, August 2009.
34. "Fabrication and Characterization of Heteropolyacid Immobilized Membranes." S. Sachdeva, N. Sharma, M.M. Emery, S.J. Hamrock, and A.M. Herring, "Separators and Membranes for Batteries, Capacitors, Fuel Cells, and Other Electrochemical Systems." P. Arora, and V. Ramani, Ed.s, *Electrochemical Society Transactions*, **2009**, 19, 1058.
35. "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**.

36. "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.
37. "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.
38. "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.
39. "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.
40. "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.
41. "New approaches to composite PFSA membranes for enhanced fuel cell performance." A.M. Herring, S. Sachdeva, J. Rajeswari, G.M. Haugen, S.J. Hamrock, oral presentation, presented at the 217th ECS Meeting, Vancouver, Canada, April 2010.
42. "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 DOE EERE Fuel Cell annual merit review, Washington, DC, June 2010.
43. "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.
44. "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 240th ACS Meeting, Boston, MA, August 2010.
45. "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.
46. "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, to be presented at the 218th ECS Meeting, Las Vegas, NV, October 2010.

47. "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 218th ECS Meeting, Las Vegas, NV, October 2010.
48. "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.
49. "Novel hybrid super acid/polymer ionomers with very high proton conductivity." A.M. Herring, J.L. Horan, M.C. Kuo, G.J. Schlichting, Z. Ziegler, J. Jessop, oral presentation, presented at Pacifichem 2010, Honolulu, HI, December 2010.
50. "Hybrid inorganic/polymer composite membranes for very high proton conductivity." A.M. Herring, invited oral presentation, presented at Advances in Polymer Electrolyte Membrane Fuel Cell Systems 2011, Asilomar, CA, February 2011.
51. "Supporting platinum on nano-structured metal oxides for proton exchange membrane cathodes." A.M. Herring, M.-C. Kuo, R.J. Stanis, and N. Danforth, oral presentation, presented at the 241st ACS Meeting, Anaheim, CA, March 2011.
52. "Novel Hybrid Super Acid/Polymer Ionomers for Polymer Electrolyte Membrane Fuels Cells." A.M. Herring, invited oral presentation, presented at the University of Wyoming, Laramie, WY, April, 2011.
53. "New High Performance Proton Conducting Membranes for Hotter, Drier Operation of Polymer Electrolyte Fuel Cells." A.M. Herring, J.L. Horan, M.-C. Kuo, and G.J. Schlichting, *Proceedings of the European Fuel Cell Forum*. C. Hebling, Ed., **2011**.
54. "New High Performance Proton Conducting Membranes for Hotter, Drier Operation of Polymer Electrolyte Fuel Cells" A.M. Herring, J.L. Horan, M.-C. Kuo, and J.D. Jessop, M.H. Frey, and H. Ren, poster presentation, presented at the European Fuel Cell Forum 2011, Lucerne, Switzerland, June 2011.
55. "PolyPOM Hybrid Membranes from Practical Chemistries with Very High Proton Conductivities." A.M. Herring, J.L. Horan, M.-C. Kuo, J.D. Jessop, M.H. Frey, and H. Ren "Polymer Electrolyte Fuel Cells 11", H.A. Gasteiger, F.N. Büchi, V. Ramani, A. Weber, P. Shirvanian, T. Fuller, S.R. Narayanan, H. Nakagawa, M. Edmundson, D. Jones, H. Uchida, C. Lamy, P. Strasser, S. Mukerjee, R. Mantz, K. Swider-Lyons, and T. J. Schmidt, Ed.s, *Electrochemical Society Transactions*, **2011**, 41, 1595.
56. "Synthesis and Polymerization of Mono-Lacunary Keggin Polyoxometalate-based Trifluorovinyl ether (TFVE) with TFVE-Hydrosilation derivatives." M.-C. Kuo, A.M. Herring, and J.L. Horan, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel. Chem.*, **2011**, 56, 571.
57. "Microstructural Influence On Electrochemical Properties Of Polyoxometalate Ionomers." J.D. Jessop, J.L. Horan, M.-C. Kuo, A.M. Herring, *Prepr. Pap.-Am. Chem. Soc., Div. Fuel. Chem.*, **2011**, 56, 573.
58. "Novel Hybrid Heteropoly Acid or Zirconium Phosphonate/Polymer Ionomers With Very High Proton Conductivity." A.M. Herring, J.L. Horan, M.-C. Kuo, G.J. Schlichting, J.D. Jessop, M.H. Frey, and H. Ren, oral presentation, presented at Solid State Ionics – 18, Warsaw, Poland, July 2011.

59. "A perspective on research efforts towards new proton exchange membranes for hotter and drier fuel cell operation." A.M Herring, invited oral presentation, presented at Korean Institute of Science and Technology, Seoul, Korea, September, 2011.
60. "A perspective on research efforts towards new proton exchange membranes for hotter and drier fuel cell operation." A.M Herring, invited oral presentation, presented at Samsung Technical Center, Seoul, Korea, September, 2011.
61. "PolyPOM Hybrid Membranes from Practical Chemistries with Very High Proton Conductivities." A.M. Herring, J.L. Horan, M.-C. Kuo, J.D. Jessop, M.H. Frey, and H. Ren, presentation, presented at the 220th ECS Meeting, Boston, MA, October, 2011.

6. Task Schedule

Task Number	Project Milestones	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
	H ₂ Safety Plan	07/31/06			100%	Approved
	Project Management and Reporting	03/31/11			100%	Completed
1.1	Phenyl-link Stability	01/31/07	6/30/07	6/30/07	100%	Completed
1.2	Post- or Pre- ion exchange strategy Identified	06/30/07	6/30/07	6/30/07	100%	Completed
1.3	Demonstrate conductivity of 0.07 S cm ⁻¹ at 80% RH and room temperature	12/31/07	6/30/08	8/31/08	100%	Completed
	Deliver membrane to topic 2 awardee	6/30/08	4/30/08	4/30/08	100%	Completed
2.1	Synthesis and Optimization of hybrid HPA polymers for 120°C conductivity for Go/No Go Decision	3/31/09	2/13/09	2/13/09	100%	Go/No Go met at 3M and CSM, but not Bekktech/FSEC
2.2	Synthesis and selection of protonic additive for hybrid HPA polymers for 120°C conductivity for Go/No Go Decision	3/31/09	2/13/09	2/13/09	100%	Go/No Go met at 3M and CSM, but not Bekktech/FSEC
3.1	Down selection of material	03/31/10	9/30/10	9/30/10	100%	2 polymer mods-3M 3 Monomer systems -CSM
3.1	Optimization of material	03/31/11	9/30/11	9/30/11	100%	Completed
3.2	Achievement of acceptable oxidative stability	03/31/11	9/30/11	9/30/11	100%	Completed

7. Project Spending

Quarter	From	To	Estimated Federal Share of Outlays	Actual Federal Share of Outlays	Estimated Recipient Share of Outlays	Actual Recipient Share of Outlays	Cumulative
2Q06	4/1/06	6/30/06	31,914	31,969	3930	3930	35899
3Q06	7/31/06	9/30/06	58,160	90,764	12,134	12,134	102,208
4Q06	10/1/06	12/31/06	111,351	111,351	23,557	23,557	134,908
1Q07	1/1/07	3/31/07	157,542	157,542	36,253	36,253	193,795
2Q07	4/1/07	6/30/07	232,439	232,439	61,491	61,491	293,930
3Q07	7/31/07	9/30/07	404,008	404,008	92,817	92,817	496,825
4Q07	10/1/07	12/31/07	452,571	452,571	118,396	118,396	551,098
1Q08	1/1/08	3/31/08	529,753	529,753	131,430	131,430	661,183
2Q08	4/1/08	6/30/08	605,853	605,853	146,293	146,293	752,146
3Q08	7/1/08	9/30/08	646,912	646,912	160,272	160,272	807,184
4Q08	10/1/08	12/31/08	708,967	708,967	163,801	163,801	872,768
1Q09	1/1/09	3/31/09	804,866	763,807	189,913	189,913	976,234
2Q09	4/1/09	6/30/09	823,459	823,459	202,830	202,830	1,026,289
3Q09	7/1/09	9/30/09	857,693	857,693	209,379	202,830	1,067,074
4Q09	10/1/09	12/31/09	926,355	926,355	213,580	213,580	1,139,935
1Q10	1/31/10	3/31/10	985,638	985,638	301,873	301,873	1,287,511
2Q10	4/1/10	6/30/10	1,101,465	1,101,465	301,873	301,873	1,509,752
3Q10	7/1/10	9/30/10	1,229,768	1,229,798	351,733	351,733	1,581,531
4Q10	10/1/10	12/31/10	1,365,430	1,365,430	351,733	351,733	1,717,163
1Q11	1/1/11	3/31/11	1,460,000	1,460,000	375,000	375,000	1,835,000
2Q11	4/1/11	6/30/11	1,480,000	1,480,000	375,000	375,000	1,855,000
3Q11	7/1/11	9/30/11	1,500,000	1,500,000	375,000	375,000	1,875,000
Totals			1,500,000	1,500,000	375,000	375,000	1,875,000

8. References Cited

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