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CONDUCTIVITY MEASUREMENTS OF SYNTHESIZED HETEROPOLY ACID MEMBRANES FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

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ABSTRACT

Fuel cell technology is receiving attention due to its potential to be a pollution free method of electricity production when using renewably produced hydrogen as fuel. In a Proton Exchange Membrane (PEM) fuel cell H_2 and O_2 react at separate electrodes, producing electricity, thermal energy, and water. A key component of the PEM fuel cell is the membrane that separates the electrodes. DuPont's Nafion[®] is the most commonly used membrane in PEM fuel cells; however, fuel cell dehydration at temperatures near 100°C, resulting in poor conductivity, is a major hindrance to fuel cell performance. Recent studies incorporating heteropoly acids (HPAs) into membranes have shown an increase in conductivity and thus improvement in performance. HPAs are inorganic materials with known high proton conductivities. The primary objective of this work is to measure the conductivity of Nafion, X-Ionomer membranes, and National Renewable Energy Laboratory (NREL) Developed Membranes that are doped with different HPAs at different concentrations. Four-point conductivity measurements using a third generation BekkTech[®] conductivity test cell are used to determine membrane conductivity. The effect of multiple temperature and humidification levels is also examined. While the classic commercial membrane, Nafion, has a conductivity of approximately 0.10 S/cm, measurements for membranes in this study range from 0.0030 – 0.58 S/cm, depending on membrane type, structure of the HPA, and the relative humidity. In general, the X-ionomer with $H_6P_2W_{21}O_{71}$ HPA gave the highest conductivity and the Nafion with the 12-phosphotungstic (PW_{12}) HPA gave the lowest. The NREL composite membranes had conductivities on the order of 0.0013 – 0.025 S/cm.

INTRODUCTION

As an energy conversion device, Proton Exchange Membrane Fuel Cells (PEMFCs) can potentially produce greater operating efficiency and no harmful emissions compared to conventional fossil fuel power sources. While PEMFCs have been shown to be an option for replacing petroleum based generators and engines, it will be necessary to overcome some economic and engineering problems in order for them to become commercially viable [1,2].

PEMFCs utilize a Poly (perfluorosulfonic acid) (PFSA) as the proton conducting electrolyte, most commonly DuPont's Nafion[®]. Literature has shown Nafion can produce high power densities at temperatures below 100°C. Nafion performs optimally at 80°C and at a high relative humidity, with a proton conductivity of 0.075 S/cm [3]. Full hydration is necessary for maximum proton conductivity, making Nafion not viable under high-temperature (>100°C) or low relative humidity conditions [4].

Membrane hydration presents a challenge to the PEMFC community, as operating temperatures of 120 and 200°C are optimal for automobile and stationary applications, respectively. In addition, reducing the need for external humidification would significantly reduce the complexity and cost of fuel cell systems [1]. PEMFC performance is governed by the conductivity of their PFSA membranes, which depends on the hydration state of the membrane. If the hydration is too low, the conductivity of the cell drops due to the decay of the electrolyte membrane, resulting in poor fuel cell performance. High levels of hydration, and the resulting excess water in the fuel cell, lead to cathode flooding, which also decreases a fuel cell's performance. Thus, the humidification of gases in the PEMFC is a crucial part of maintaining membrane conductivity and material stability [5,6].

Recent research on the improvement of PEM conductivity has focused on the use of hybrid membranes containing inorganic super acids [7,8]. Of these, heteropoly acids (HPAs) are a diverse group of materials known to have high proton conductivities at ambient temperatures. This, coupled with their ability to hold water at high temperatures, makes HPAs appealing candidates for high-temperature and/or low humidity PEMFC operation [9,10]. Vernon et al [11] have done work with heteropoly acids ($H_8SiW_{11}O_{39}$ and 11-SiWA) attached covalently to a polymer backbone in a PEM. Results suggest that, when fully hydrated, the hybrid membranes can achieve proton diffusion coefficients as high as those found in Nafion 117. The ex situ conductivity tests of these membranes showed that conductivity increases more rapidly with temperature, as compared to Nafion 117, suggesting that these hybrid membranes may be developed for higher operating temperature applications [11]. Additionally, results from Reed et al show that heteropoly silicotungstic acid (HSiW) and heteropoly arsenotungstic acid (HA_2W) doped Nafion 112 have a higher conductivity at elevated temperatures when compared to pure Nafion 112 [12]. Data from Ramani et al suggests that, like pure Nafion, the conductivity of hybrid membranes is also strongly humidity dependent [13]. Thus, there is a need to develop a better understanding of the factors related to the humidification needs of various HPA doped membranes.

This work investigates the effect of relative humidity on HPA doped membranes in an effort to meet the DOE specifications for high-temperature, low humidity PEMFC membranes (120°C, 25-50% relative humidity). Multiple types of synthesized HPA doped Nafion, X-Ionomer, and NREL Developed Membranes (NDMs) at various levels of relative humidity are examined. Information about the fabrication of X-Ionomer is proprietary.

MATERIALS AND METHODS

The Nafion and X-Ionomer hybrid membranes were prepared at Colorado School of Mines. The membranes were each doped with 3 different HPAs: 12-phosphotungstic (PW_{12}), Keggin boron ($\alpha-BW_{12}H$), and $H_6P_2W_{21}O_{71}$ at concentrations of either 1% or 5% by weight. Commercial samples of PW_{12} (Fisher Scientific A248-500) were employed; the other 2 HPAs were synthesized by chemists at Colorado School of Mines. Preparation of the Keggin boron and $H_6P_2W_{21}O_{71}$ followed the procedures of Rocchiccioli-Deltcheff et al [14] and Brauer [15] respectively. The HPAs were

physically blended with one of the ionomers. Each solution was then casted on a 280 X 175 mm glass plate and placed in an 80°C oven. A multiple clearance applicator was used to attain a membrane with a consistent thickness. The film remained in the oven for 20 minutes. Each membrane cooled to ambient temperature and was then placed back into the oven at 120°C for five minutes to execute the annealing process. After removal from the glass plate, each membrane of a specific HPA and ionomer combination were cut into squares of approximately 50 X 50 mm and placed into a small (~25 mL) vial.

In order to determine the hydration state of the membranes, we utilized isopiestic equilibration of the samples with water vapor above salt solutions, as described by Zawodzinski et al [16]. To completely dry the samples, the open vials were sealed in jars containing phosphorous pentoxide for several days. Weight measurements were taken periodically until a steady state was observed. The sample vials were placed in sealed saturated salt solution jars containing either NaBr, NaCl, MgCl, or KCl. These humidifying jars were then put in an 80°C hot water bath. Again, a constant sample weight was used to indicate equilibrium. Humidity values were determined using values established by Greenspan [17].

The NREL Developed Membranes (NDMs) were prepared by covalently bonding HPAs at a high weight percent (>100 weight percent HPA/polymer) to a host polymer, glycidyl methacrylate-type copolymer (PEMAGMA or PMG for short). While high HPA loadings in previous studies tended to result in mechanically fragile films, the current formulation used a dimethacrylate monomer molecular cross-linker, EGDMA, to improve the integrity of the membranes [18]. The fabrication process first included reacting saturated Keggin 12-HSiW or custom-synthesized Lacunary $H_8SiW_{11}O_{39}$ (11-HSiW) with a methacrylate-based binding silane. Next, a sol-gel approach was employed to produce nano-scaled SiO_2 with functional silanes to immobilize the HPA in a 3D network. EGDMA, a thermal curing agent, and the polymer host of PMG were introduced. PEM-type films were then made by casting the solution in PFA Petri dishes. The resulting films were next processed in an 80°C oven. After a one-hour drying period, the films were heated to approximately 145°C for 10 minutes under a 2-ton pressure to initiate the cross-linking reaction.

The ex situ membrane conductivity measurements of all membranes were determined via a third generation four-point BektTech® conductivity test cell. Membrane samples were cut into strips of approximately 24 mm in length and 3.6 mm in width and were held in the four-point probe apparatus with temperature and humidity controlled hydrogen gas. A back-pressure regulator (Globe Tech, Compu Cell GT) was used at the outlet of the anode and cathode. The temperature of the gas was controlled by a Scribner Associates, Inc. Series 890 and associated software, while the temperature of the conductivity cell was controlled by a separate bench-top controller (Omega CSC32). Gamry Instruments Potentiostat and Framework software was used to apply the external voltage to the cell. The conductivity of the hybrid membranes was calculated using the equation, $\sigma = L / (R \times W \times T)$, where L is the distance in the direction of ion flow between voltage probes, W is the measured width of the sample, T is the measured thickness of the sample, and R is the calculated resistance. The resistance

of the sample was calculated via the current and voltage drop measurements, based upon the distance between the 2 measurement electrodes. Sample thickness was obtained by using a Mitutoyo digital micrometer at 5 different locations along the length of the membrane. An average was then taken as representative of the membrane's thickness.

All conductivity tests were performed at a cell temperature of 80°C and with a hydrogen backpressure that varied from 14-20 psi. The humidification of the conductivity cell was determined using the Clausius-Clapeyron equation. The hydrogen gas in the experimental setup leaves the humidifiers at 100% relative humidity at a preset temperature and enters the cell, which was held at constant 80°C. By knowing the initial relative humidity and final temperature of the hydrogen gas, it is then possible to calculate the ΔT necessary to achieve the desired humidity level in the conductivity cell. The Nafion and X-Ionomer hybrid membranes were each tested at the same relative humidity to which they were equilibrated in the aforementioned humidification jars. The NDMs were each tested at 25%, 50%, and 100% relative humidity.

RESULTS

Table 1 shows conductivity values for Nafion and X-Ionomer control samples; both were tested in 79%, 74%, 51%, and 26% relative humidity environments. The conductivity values for the Nafion Control ranged from 0.0050 S/cm at 26% RH to 0.44 S/cm at 79% RH. The values for the X-Ionomer Control ranged from 0.023 S/cm at 26% RH to 0.27 S/cm at 79% RH.

| | Nafion Control Average Conductivity | X-Ionomer Control Average Conductivity |
|-----------------------|--|---|
| 79% Relative Humidity | 0.44 S/cm | 0.270 S/cm |
| 76% Relative Humidity | 0.28 S/cm | 0.255 S/cm |
| 51% Relative Humidity | 0.22 S/cm | 0.330 S/cm * |
| 26% Relative Humidity | 0.0050 S/cm | 0.023 S/cm |

* Represents anomalous data ranging from 0.190 S/cm to 0.530 S/cm

Table 1. Conductivity Results for Nafion and X-Ionomer Control Samples

Figures 1-4 show typical current-voltage results, and corresponding conductivity calculations, for Nafion hybrid membrane samples. Figure 1 shows results for membranes doped with α -BW₁₂H (1% by weight). Samples were tested at relative humidities of 79%, 51%, and 26% and demonstrated conductivities of 0.21, 0.15, and 0.21 S/cm respectively. Nafion membranes doped with H₆P₂W₂₁O₇₁ (5% by weight) tested at relative humidities of 79%, 74% and 51%, demonstrated conductivities of 0.58, 0.10, and 0.15 S/cm respectively (Figure 2). Nafion doped with PW₁₂ at 1% by weight, tested at relative humidities of 79%, 74% and 51%, demonstrated conductivities of 0.0061, 0.0081, and 0.53 S/cm respectively (Figure 3). Membrane samples containing PW₁₂ at 5% by weight, tested at two relative humidities — 51% and 26%, demonstrated conductivities of 0.27 and 0.0030 S/cm respectively.

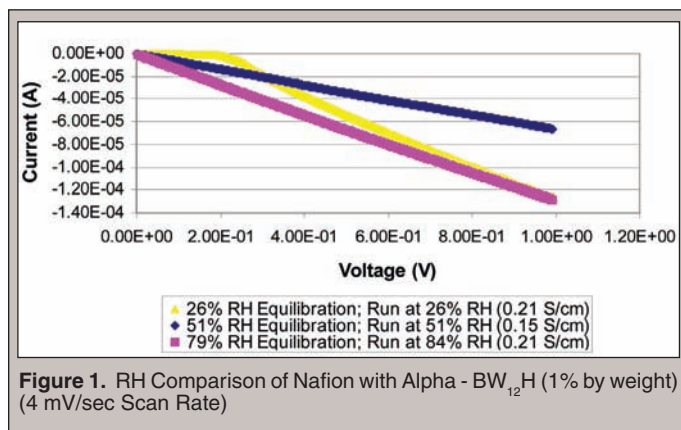


Figure 1. RH Comparison of Nafion with Alpha - BW₁₂H (1% by weight) (4 mV/sec Scan Rate)

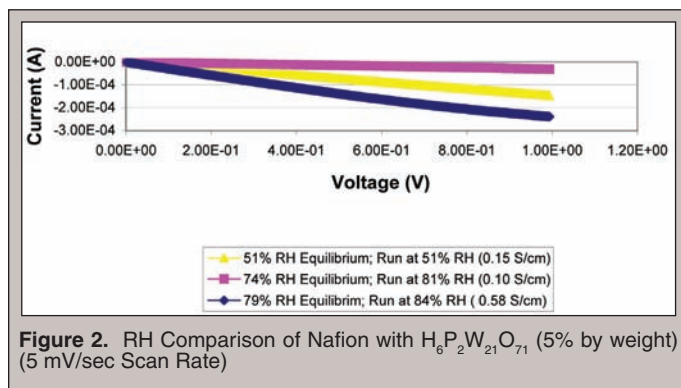


Figure 2. RH Comparison of Nafion with H₆P₂W₂₁O₇₁ (5% by weight) (5 mV/sec Scan Rate)

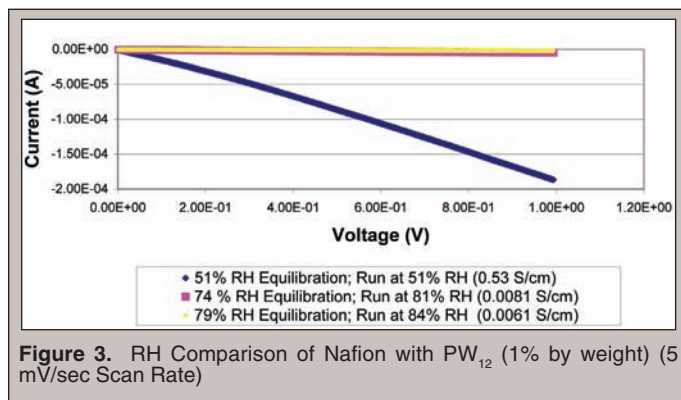


Figure 3. RH Comparison of Nafion with PW₁₂ (1% by weight) (5 mV/sec Scan Rate)

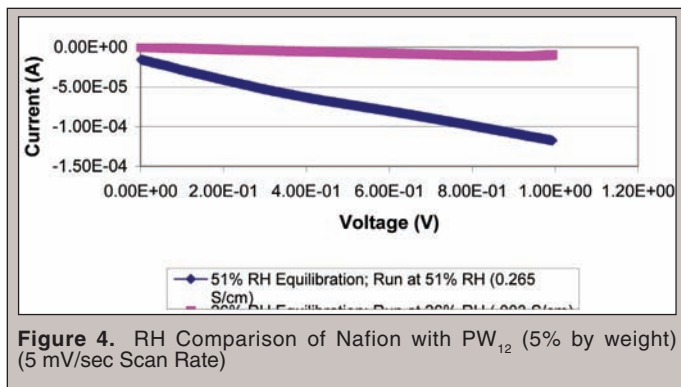


Figure 4. RH Comparison of Nafion with PW₁₂ (5% by weight) (5 mV/sec Scan Rate)

Figures 5 and 6 show the current-voltage results, and corresponding conductivity calculations, for X-Ionomer hybrid membrane samples. Figure 5 shows results for membranes doped with α -BW₁₂H at 5% by weight, tested at relative humidities of 79%, 74%, and 51%. They demonstrated conductivities of 0.42, 0.19, and 0.18 S/cm respectively. The results for X-Ionomer membranes doped with H₆P₂W₂₁O₇₁ (1% by weight), tested at four relative humidities — 79%, 74%, 51%, and 26%, show conductivities of 0.44, 0.16, 0.16, and 0.38 S/cm respectively (Figure 6).

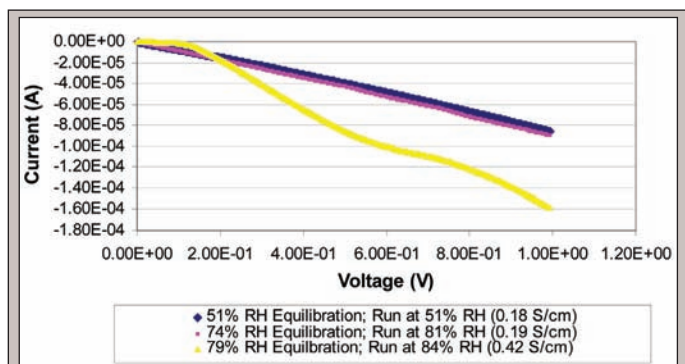


Figure 5. RH Comparison of X-Ionomer with Alpha - BW₁₂H (5% by weight) (5 mV/sec Scan Rate)

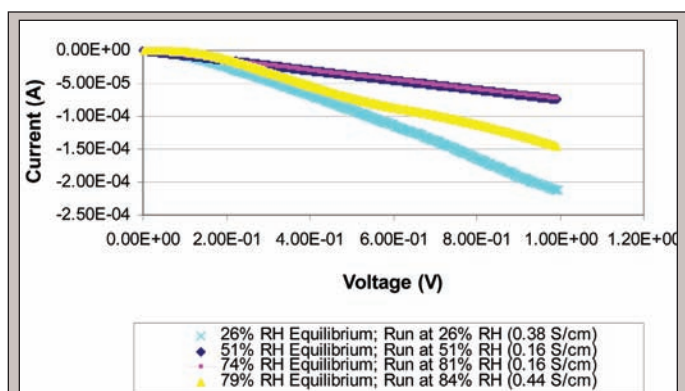


Figure 6. RH Comparison of X-Ionomer with H₆P₂W₂₁O₇₁ (1% weight) (5 mV/sec Scan Rate)

Conductivity results for the NDMs are shown in Table 2. Four membrane types were tested, two of which had two different casting dates. Data were collected for each membrane type and each casting date at a constant cell temperature of 80°C at 100%, 50%, and 25% relative humidity. The conductivity data from membrane 20050401B varied between the two casting dates with measurements at 25% RH of 0.0026 S/cm and 0.0000061 S/cm and measurements at 100% RH of 0.0065 and 0.0069 S/cm. Variation was also found between the two castings of membrane 20050404A. Here the data ranged from 0.0050 and 0.00013 S/cm at 25% RH to 0.0059 and 0.013 S/cm at 100% RH. The conductivities of membrane 20050426A ranged from 0.00093 S/cm at 25% RH to 0.0012 S/cm at 100% RH, while those of membrane 20050714B1#1 ranged from 0.0011 S/cm at 25% RH to 0.025 S/cm at 100% RH.

| | Conductivity at 100% RH | Conductivity at 50% RH | Conductivity at 25% RH |
|-------------------|-------------------------|------------------------|------------------------|
| Cast Date 4/12/05 | | | |
| 20050401B | 0.0065 S/cm | 0.0045 S/cm | 0.0026 S/cm |
| 20050404A | 0.0059 S/cm | 0.0025 S/cm | 0.0050 S/cm |
| Cast Date 5/11/05 | | | |
| 20050401B | 0.0069 S/cm | 0.0043 S/cm | 0.0000061 S/cm |
| 20050404A | 0.0130 S/cm | 0.009 S/cm | 0.000128 S/cm |
| 20050426A | 0.0012 S/cm | 0.00027 S/cm | 0.00093 S/cm |
| Cast Date 7/20/05 | | | |
| 20050714B1#1 | 0.025 S/cm | 0.025 S/cm | 0.0011 S/cm |

Table 2. Conductivity Results for NREL Developed Membranes.

DISCUSSION AND CONCLUSIONS

Conductivity results suggest that the doping of our Nafion and X-Ionomer hybrid membranes with the HPAs of this study increased the conductivity of the membranes. The conductivity values for the Nafion control ranged from 0.0050 S/cm at 26% RH to 0.44 S/cm at 79% RH. Comparatively, at 26% RH the Nafion membranes doped with α -BW₁₂H (1% by weight) and PW₁₂ (5% by weight) showed conductivities of 0.21 and 0.0030 S/cm respectively. For the α -BW₁₂H, this represents an increase over two orders of magnitude compared to the control. Though the PW₁₂ sample showed a conductivity slightly lower than that of the control, this same sample at 51% RH showed a conductivity of 0.27 S/cm, which is twice the conductivity reported in the literature for Nafion 117. The results shown for Nafion doped with α -BW₁₂H (1% by weight) in Figure 1 demonstrate a relatively constant conductivity (near 0.20 S/cm) as the RH is decreased from 79% to 26%. It is notable that at 26% RH this sample showed an increase in conductivity of almost two orders of magnitude compared to the control. Thus, it would be useful to study the effect doping this HPA at a higher weight percent (i.e. 5% by weight) into our Nafion membranes. Figure 2 for Nafion doped with H₆P₂W₂₁O₇₁ (5% by weight) shows conductivity at 79% RH of nearly six times that of Nafion 117. Even at a lower RH (51%), this membrane had a conductivity that was comparable the Nafion Control. The anomalous results shown in Figure 3 for Nafion doped with PW₁₂ (1% by weight) do not allow for a comparison of the effects of a higher weight percent for this HPA. As shown in the figure, the conductivity of the 1% by weight PW₁₂ varies from 0.0061 to 0.53 S/cm as the relative humidity is decreased from 79% to 51%. This is the opposite trend that would be expected and indicates possible systematic error or manufacturing defects during membrane preparation. Thus, further studies should be completed to better understand the relationship between conductivity and higher doping levels for PW₁₂.

The values for the X-Ionomer Control ranged from 0.023 S/cm at 26% RH to 0.27 S/cm at 79% RH. The data collected at 51% RH represent anomalous measurements for the membrane. Three scans were run at this RH — scan A yielded a conductivity of 0.19 S/cm, scan B yielded a conductivity of 0.53 S/cm, and scan C yielded a conductivity of 0.27 S/cm. This data trend suggests the possibility that excess water may have entered the conductivity cell

between scans A and B, resulting in an abnormally high conductivity measurement. The drop seen in the conductivity measurement of scan C indicates that the excess water could have begun to evaporate between the later two scans. Thus, this control membrane should be retested at 51% relative humidity to insure the accuracy of control comparisons.

Figure 5 shows that at 79% RH, doping the X-Ionomer with α -BW₁₂H (5% by weight) increased the conductivity by over 60%, while results at 74% and 51% are on the order of the conductivity of the control. All results presented indicate increased conductivity compared to Nafion 117. Similar results are shown in Figure 6 for the X-Ionomer doped with H₆P₂W₂₁O₇₁ (1% by weight). Here, again, at 79% RH, this membrane shows an increase in conductivity of over 60% compared to the control. Though the conductivity drops by a factor of three at 74% and 51% RH, the results at 26% RH (0.38 S/cm) are an order of magnitude higher than that of the control (0.023 S/cm). Thus, it would be useful to study H₆P₂W₂₁O₇₁ further, particularly the effect of doping this HPA at a higher weight percent (i.e. 5% by weight). In conclusion, results from this study show promising results for the doping of Nafion and X-Ionomer membranes with HPAs, in particular, α -BW₁₂H and H₆P₂W₂₁O₇₁. The results shown for Nafion doped with P \bar{W} ₁₂ suggest that this HPW should also be tested in the X-Ionomer membrane. Overall, in order to advance the technology of low-relative humidity fuel cell membranes, further research is recommended related to the dopant levels of these HPAs.

Though the conductivity results for the NDMs are all significantly lower than that of Nafion 117 (0.0012 – 0.013 at 100% RH), these data represent the first time mechanically flexible PEM films based on PMG with high HPA loading (>100% HPA/polymer) were fabricated. While more work is needed in modifying the formulation and improving the procedural details in solution preparation and film making, this represents a promising beginning for future work related to covalently bonding HPAs to their host polymer.

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