

Short communication

Membranes based on basic polymers and perfluorinated acids for hotter and drier fuel cell operating conditions

J.M. Larson^{a,*}, S.J. Hamrock^a, G.M. Haugen^a, P. Pham^a,
W.M. Lamanna^a, A. Butenhoff Moss^b

^a 3M Company, 3M Center, St. Paul, MN 55144, United States

^b Pace Analytical, Minneapolis, MN, United States

Received 21 November 2006; received in revised form 29 March 2007; accepted 4 April 2007

Available online 11 April 2007

Abstract

Proton exchange membranes for fuel cells that operate under hotter and drier conditions are of interest for improved heat rejection and to reduce poisoning by carbon monoxide in reformed hydrocarbon fuels. Polybenzimidazole/phosphoric acid membranes have good conductivity under hot, dry conditions but require use of very high amounts of platinum catalyst to overcome high over-potentials due to strong poisoning by phosphoric acid. Polybenzimidazole membranes made using bis-fluorinated acids were found to provide significantly better fuel cell performance at 100–110 °C under ambient pressure with 80 °C inlet dew point compared to membranes with phosphoric acid. Addition of simple metal oxides provided optimal conductivity.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Proton conductivity; High temperature; Low humidity; Bis-sulfonyl imide; Membrane; Fuel cell

1. Introduction

Operation of proton exchange membrane (PEM) fuel cells based on the use of perfluorinated sulfonic acid membranes (PFSA) is limited typically to operation at ≤ 80 °C due to loss of conductivity at higher temperatures caused by reduced water content in the membrane. There are several potential benefits which can be realized by using membranes with improved conductivity at higher temperatures and/or under drier conditions:

- (1) reduced poisoning of Pt catalysts by CO in reformed hydrocarbon fuels;
- (2) simpler and less expensive humidification systems;
- (3) lower parasitic power losses since compressors would not be needed;
- (4) improved heat rejection due to the greater temperature difference between cell temperature and the environment, which would allow reduction in radiator size and more efficient use of waste heat.

For fuel cells for automotive applications, there is a need is for membranes that allow temperature excursions up to 120 °C. For stationary power, there are needs for reduced catalyst poisoning from carbon monoxide present in reformed fuels, and for systems which can utilize the waste heat generated. Both of these can be achieved through higher temperature operation.

For membranes that require retention of water for conductivity, the mole fraction of water in the fuel stream needed to maintain conductivity becomes increasingly greater as the temperature increases. The use of pressure to retain water becomes obligatory at ≥ 100 °C. To achieve these benefits, membranes that are less dependent on water for conductivity are needed.

There have been several approaches for development of membranes that are less dependent on water [1–3]. For polybenzimidazole-phosphoric acid membranes, operation at temperatures up to 200 °C has been reported [4–6]. This type of membrane has been commercialized by PEMEAS. Poisoning of cathode Pt catalysts by phosphoric acid, however, has required the use of very high amounts of platinum [6]. Loss of phosphoric acid has also been a problem. To avoid leaching of phosphoric acid, complex procedures for start-up and shutdown are required. In addition, start-up is complicated by low perfor-

* Corresponding author. Tel.: +1 651 736 7338; fax: +1 651 733 0648.

E-mail address: jmlarson@mmm.com (J.M. Larson).

mance at $\leq 120^\circ\text{C}$. Use of cross-linkable phosphonates has been proposed to improve retention of the electrolyte [7].

In this report, we describe the preparation of membranes using basic polymers such as polybenzimidazoles, perfluorinated sulfonic and imide acids, and inorganic additives such as simple metal oxides. Fluorinated acids have long been the subject of evaluation as electrolytes. Fundamental electrochemical studies were reported in 1985 [8]. Fluorinated acids were added to phosphoric acid fuel cells to decrease poisoning of the Pt catalyst [9]. Perfluorinated monomeric to polymeric sulfonimides were evaluated as additives for phosphoric acid fuel cells [10]. Thus, while studies on fluorinated acids themselves, as additives to other electrolytes, and as pendant groups in ionomers such as NafionTM have been reported, there have been no previous reports on fluorinated acids in membranes formed using basic polymers. Membranes formed by filling the pores of porous membranes prepared using solvent induced phase separation processes have been reported [11].

2. Experimental

2.1. Membrane preparation

Two types of polymers were used for membrane formation with bis-fluorinated acids: poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole] (PBI from Celanese) and PBIO (trade name for a phenylene oxide benzimidazole) from Fumatech. The polymers were vacuum dried and then dissolved in either dry dimethylacetamide (DMAc) for PBI or *N*-methylpyrrolidinone (NMP) for PBIO, using a pressure vessel. The structure given in Fig. 1 was consistent with elemental analysis, proton magnetic resonance, and infrared spectroscopy of PBIO.

The following fluorinated acids were prepared by the 3M Company. For the C4-bis-imide, the C₄F₉-group were linear.

- Disulfonate (DS): HO₃S(CF₂)₄SO₃H;
- C1-bis-imide (C1BI):
CF₃SO₂NHSO₂(CF₂)₄SO₂NHSO₂CF₃;
- C4-bis-imide (C4BI):
C₄F₉SO₂NHSO₂(CF₂)₄SO₂NHSO₂C₄F₉.

The DS and C1BI were tetrahydrates. The fluorinated acids were dissolved in either just dry NMP or DMAc. A solution of the polymer was then added to a solution of acid to provide the desired ratio of equivalents of acid(s) to base, coated onto a glass plate, heated at 140°C in a circulating air oven for 4 h to remove solvent, and cooled in ambient air to form the

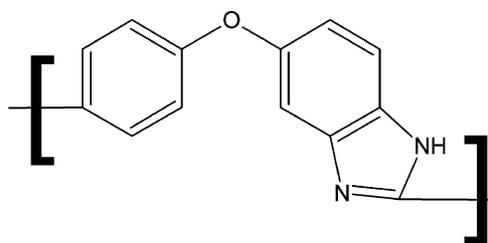


Fig. 1. Structure of PBIO.

membrane. No further mass loss was observed after heating for longer than 4 h at 140°C . For membranes having metal oxides, the metal oxide was dispersed in a solution of the polymer by adding the dry inorganic oxide, about 14 ceramic milling cylinders (type BRUNHP050 from U.S. Stoneware Corporation, East Palestine, OH), and 25–30 g of ~ 10 wt.% polymer solution to a 120 ml screw-cap glass bottle. The sealed bottle was rolled on a bottle roller at ≤ 100 rpm for 12–24 h typically. The dispersion of inorganic oxide and polymer was then added to a solution of acid(s). Except for this preliminary dispersion step, the remainder of the preparation was the same as for the procedure given above. The silica used was an amorphous fumed silica having $100\text{ m}^2\text{ g}^{-1}$ surface area that was purchased from Alfa Aesar. All steps prior to coating were done under rigorously dry conditions. Coating was done under ambient conditions. For comparison, PBI/phosphoric acid membranes were prepared by dissolving the PBI in trifluoroacetic acid followed by addition of 85% phosphoric acid [12].

2.2. Conductivity

Conductivity was determined by ac impedance using a Bekk-Tech conductivity cell by conditioning at 120°C for 180 min and then scanning from 120°C to 80°C in 10° increments with 90 min hold time at each temperature followed by returning to 120°C in a similar fashion. Inlet humidification was kept constant at an 80°C dew point for all temperatures.

2.3. Fuel cell evaluation

Fuel cell electrodes having 0.4 mg cm^{-2} of Pt were prepared by coating a catalyst ink onto a carbon paper gas diffusion layer. Membrane electrode assemblies (MEAs) were tested in a Fuel Cell Technologies single serpentine 5-cm^2 cell. Gas flow rates for H₂ and air were fixed at 100 and 500 sccm, respectively. Inlet humidification was kept constant at an 80°C dew point at all temperatures.

2.4. Retention of acid

Relative resistance to washing out of the acids was determined by adding 5-cm^2 pieces to a 50 ml beaker containing 25 ml water while stirring with a micro magnetic stir bar and observing pH change versus time using multi range pH paper.

2.5. Morphological characterizations

Differential scanning calorimetry was done using a TA Instruments Q1000 (#130, Cell RC-296) Modulated Differential Scanning Calorimeter in standard DSC mode using standard Q1000 TA aluminum pan at a scan rate of $20^\circ\text{C min}^{-1}$. For initial experiments, evaluation with retention of water was of interest, so sealed pans were used and the upper temperature was limited to 150°C . Heating above 150°C was found to rupture the cells and contaminate the measurement cell with acid, so subsequent evaluations were done with punctured lids, the upper temperature limited to 150°C for the first scan to remove water

without splattering, and only then going to higher temperatures for the second scan.

Elastic moduli were evaluated from 25 °C to 200 °C in tension (dynamic mechanical analysis) using a Rheometric's Solid Analyzer (RSA II) at 1 Hz (6.28 rad s⁻¹) with heating at 3 °C min⁻¹ and cooling to 25 °C under dry nitrogen. A 6.5 mm × 23.4 mm × 0.030 mm strip was mounted in the clamps and tightened. Pre-determined amplitude and frequency were applied and the stress response was measured.

X-ray diffraction was done using a Phillips vertical diffractometer, Cu K α radiation, and proportional detector registry of the scattered radiation. The unit was fitted with variable incident slits, fixed receiving slits, and graphite monochromator. Scans were conducted from 3° to 45° (2 θ) using a 0.05° step size and 6 or 32 s dwell time. X-ray generator settings of 45 kV and 35 mA were employed. Scans were conducted under ambient conditions on materials that had been conditioned under ambient humidity and also under flowing dry nitrogen.

Thermal gravimetric analysis was done using a TA Instruments 2950 HI-Resolution Thermogravimetric Analyzer. An initial heating rate of 50 °C min⁻¹ was applied with a resolution setting of 4.0. Under these conditions, the instrument heated until weight loss was detected, the temperature stabilized until weight loss diminished, and then heating recommenced.

3. Results and discussion

3.1. Membrane formation

Addition of solutions of PBIO in NMP to solutions of either imide or sulfonate acids or mixtures thereof provided homogeneous solutions after simple mixing without precipitation. Addition of solutions of PBI in DMAc to solutions of imide acids in DMAc also gave homogeneous solutions, but addition of even very dilute PBI in DMAc solutions to solutions of the DS acid resulted in immediate precipitation. For this latter case, addition of solutions of DS to solutions of PBI also resulted in precipitation even for very dilute solutions. Blending salts of the acids with the polymers followed by re-acidification after membrane formation, as typically done for blending acidic and basic polymers, was not possible since that procedure would have washed the acids out of the membrane.

The ratio of acid to basic polymer used for membrane formation was designated in terms of equivalents of acid to equivalents of base. Note that PBI has two basic nitrogens per repeat unit, whereas PBIO has only one. Thus, a membrane composition resulting from addition of one equivalent of PBIO to two equivalents of DS and two equivalents of C1BI was designated as DS:C1BI:PBIO = 2:2:1. For reasonable strength, the total equivalents of acid per equivalent of basic polymer were about $\leq 4:1$, though self supporting membranes having up to a total of 8.5 equiv. of acid were prepared.

3.2. Membrane characterization by DSC

Addition of either C1BI or C4BI to PBI or PBIO resulted in significant plasticization of the polymer. DSC results for

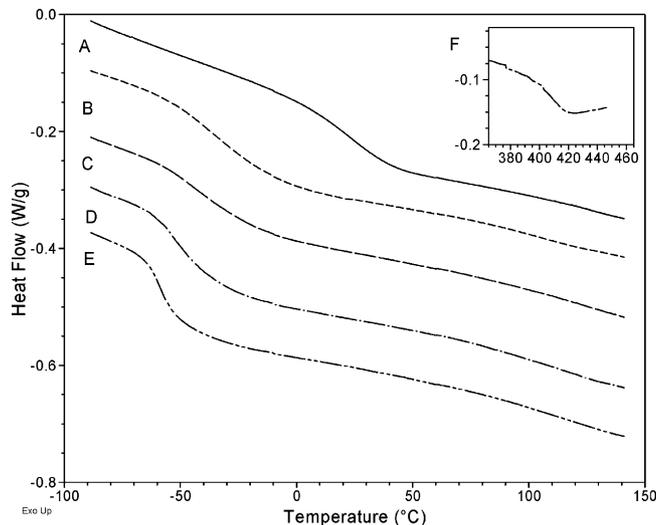


Fig. 2. DSC results after six scans at ≤ 150 °C in sealed pans. A: C1BI:PBI = 1:1; B: C1BI:PBI = 2:1; C: C1BI:PBI = 2:1 + silica; D: C1BI:PBI = 3:1; E: C1BI:PBI = 4:1; F: PBI (insert frame).

hydrated C1BI:PBI membranes are given in Fig. 2. For clarity, the curves were spread apart on the heat flow axis. The relative intensities are correct but the absolute position on the heat flow axis has no meaning. These results showed a large decrease in T_g for addition of even one equivalent of C1BI and additional decreases for each additional equivalent. For C1BI:PBI = 4:1, the T_g was -56 °C. Addition of silica for C1BI:PBI = 2:1 further decreased the T_g . The T_g for dry PBI membrane was 420 °C and 355 °C for PBI membrane that was hydrated (about 16 wt.% water). The C1BI:PBI membranes were hydrated merely by exposing to ambient air (~ 22 °C and 30–40% RH). The initial DSC evaluations were done using sealed pans to look for changes between first and second heats that were not related to loss of water. Results showed no change in T_g for six heat and cool cycles for scans up to 150 °C. As mentioned in Section 2.5, exceeding 150 °C resulted in rupture of the lids and contamination of the instrument cell with acid, so subsequent experiments were done using punctured lids and limited upper temperature for the first scan to 150 °C to ensure removal of water before scanning to a higher temperature on the second scan.

For PBIO itself, a broad endotherm was seen in the first heat but was absent in the second heat, which was consistent with removal of water (see Fig. 3). The T_g for dry PBIO was 238 °C and 81 °C for humidified PBIO. As for PBI membranes above, conditioning and DSC analyses were similar to the second procedure used for PBI:C1BI membranes. Addition of one equivalent of C1BI to PBIO introduced some crystalline order as indicated by an endotherm at 65 °C in the first heat. This endotherm was absent in the second heat and a T_g at 76 °C was observed. For addition of 4 equiv. of C1BI to PBIO, there was only a T_g at -61 °C for the first heat. For the second heat, the T_g moved to -48 °C, there were two broad endotherms between 50 °C and 200 °C with maximum for one at 90 °C and the other at 163 °C, and there was an exotherm at 19 °C. For addition of one equivalent of DS, for the first heat there was a T_g at 69 °C and a broad

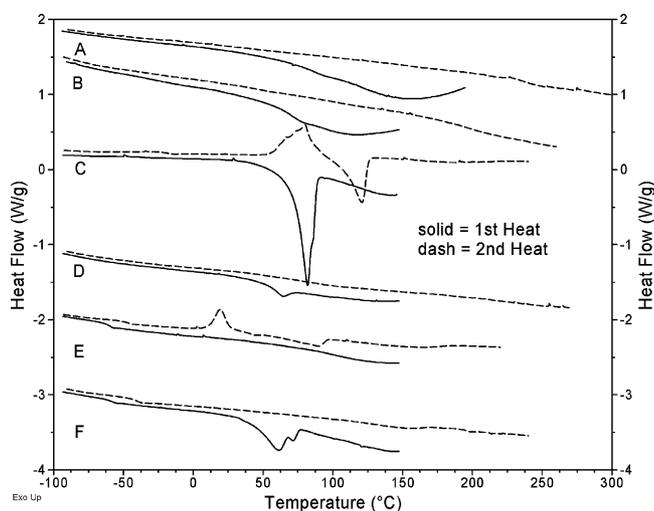


Fig. 3. DSC results for first heat and second heat for PBIO and PBIO with fluorinated acids. A: PBIO; B: DS:PBIO = 1:1; C: DS:PBIO = 4:1; D: C1BI:PBIO = 1:1; E: C1BI:PBIO = 4:1; F: DS:C1BI:PBIO = 2:2:1.

endotherm with maximum at 113 °C. For the second heat, however, there was no endotherm and the T_g moved up to 197 °C. Thus, the main effect for addition of one equivalent of DS to PBIO was just to depress the T_g . For addition of 4 equiv. of DS, however, there was no T_g in the first heat, a strong endotherm at 82 °C and a broad endotherm at about 120 °C. For the second heat, a T_g at -20 °C, an exotherm at 80 °C, and endotherm at 121 °C were observed. These results showed that morphology changed as a function of the equivalents of DS added.

DSC results in Fig. 3 for a DS:C1BI:PBIO membrane were different from those for either the DS:PBIO or C1BI:PBIO membranes. For the first heat, there was a T_g at -59 °C and endotherms at 61 °C and 72 °C. For the second heat, the T_g moved to -42 °C and there was only a broad endotherm at 149 °C.

For PBIO-acid membranes, the DSC results showed that both the C1BI and DS acids introduced ordering and to a much higher degree for the DS. The occurrence of exotherms followed by endotherms (recrystallization followed by melting) in the second heats for C1BI:PBIO = 4:1 and DS:PBIO = 4:1 membranes showed that reordering processes in these membranes after heating/cooling were slow or the absorption of water was needed for the reordering to occur. Similarly for the DS:C1BI:PBIO = 2:2:1 membrane, movement of sharp endotherms in the first heat to a broader endotherm in the second heat at a higher temperature indicated that reordering to the original morphology was slow or that water was needed for the reordering to occur. For PBIO, addition of either DS or C1BI acids introduced order that was not present for the amorphous polymer itself.

DSC results for scrupulously dry acids showed that they themselves were crystalline solids. Melting points were: DS at 174 °C, C1BI at 189 °C, and C4BI at 175 °C. After exposure to humid atmosphere, however, the DSC results were much more complex with multiple melting points, T_g transitions in some cases, and recrystallization followed by melting transitions.

3.3. Membrane characterization by XRD

XRD results for PBIO showed that it was perfectly amorphous. For PBIO-acid membranes, XRD patterns were found to be different as a function of the type of acid(s), the ratio of acid to polymer, the presence of inorganic oxides such as silica, and whether hydrated or dry. For both DS:PBIO = 4:1 and DS:C1BI:PBIO = 2:2:1 membranes, crystallite size was too large to estimate by XRD other than to say that the size was >1500 Å. Crystallite size was about 600 Å for DS:PBIO = 4:1 with 19 wt.% silica and for DS:C1BI:PBIO = 2:2:1 with 16 wt.% silica. For DS:PBIO = 4:1, the crystallinity index was about 0.5 with or without added silica. For DS:C1BI:PBIO = 2:2:1, the crystallinity index was about 0.3 without added silica and about 0.2 for membrane having about 20 wt.% silica.

3.4. Membrane characterization by TGA

Results for TGA analysis are given in Table 1. The results provided were for the first major mass loss not related to loosely bound water. While many more TGA results were obtained and could be the subject of much more extensive discussion, the results in Table 1 suffice to determine the limiting thermal stability of these materials relative to their intended use temperature.

While PBIO was somewhat less stable than PBI as indicated by a mass loss of 12% at 288–292 °C as compared to 4% at 418–491 °C, the thermal stability for PBIO as indicated by TGA was still very good. Thermal stability for the three acids was also good with clean loss of most of their mass at 300–320 °C. Thermal stability of polymer-acid membranes, however, was of more interest. For the most part, there was only minor loss of mass at temperatures similar to those for which the acids themselves disappeared. For these cases, the stability of the polymer-acid membrane was actually better than for the acid itself and not that much poorer than for PBIO or PBI. While a mixed comparison, mass losses for DS:PBIO = 4:1 and for DS:C1BI:PBIO = 2:2:1 was significantly higher than for C1BI:PBI = 4:1. Also curious was that the 10% mass loss for DS:PBIO = 1:1 began at a lower temperature than for the other polymer-acid membranes. In any case, these strong fluorinated acids did not appear to significantly degrade the thermal stability of the polymer.

Table 1

TGA results for first mass loss not associated with loss of loosely bound water for polymers and polymer-acid membranes

Material	Range (°C)	% Mass loss
PBI	418–491	4
PBIO	288–392	12
DS	305–307	89
C1BI	299–306	89
C4BI	313–322	93
C1BI:PBI = 1:1	266–313	10
C1BI:PBI = 4:1	274–306	12
DS:PBIO = 1:1	196–278	10
DS:PBIO = 4:1	302–316	57
DS:C1BI:PBIO = 2:2:1	257–274	67

Table 2
Maxima observed in DMA tan delta curves

Membrane	DMA tan delta maxima	
	First heat (°C)	Second heat (°C)
PBIO	~110 (weak)	100 (strong)
DS:PBIO = 1:1	100 (w), 185 (s)	125
DS:PBIO = 3:1	60 (w), 110 (w), 175 (s)	110 (w), 185 (s)
DS:PBIO = 4:1	30, 65, 100, 125, 180 (s)	185
DS:C1BI:PBIO = 2:2:1	155	~130

3.5. Membrane characterization by DMA

Results for DMA tan delta maxima for PBIO and PBIO with added acids are given in Table 2. The relative magnitude of the tan delta maxima were indicated qualitatively as either strong (s) or weak (w) in Table 2. The elastic modulus (E') for PBIO and for PBIO with added acids was about 2×10^{10} dyne cm^{-2} . For PBIO, there was a shallow minimum for E' at about 110 °C in the first heat, but E' remained about 10×10^{10} dyne cm^{-2} for the first heat. For the second heat, however, there was a rapid decrease in E' to a minimum of 10×10^7 dyne cm^{-2} at about 100 °C followed by an increase to 10×10^9 dyne cm^{-2} at 160 °C. During three additional heats, the E' curves moved somewhat closer to that for the first heat. Similar trends were observed for the loss modulus (E''). There were similar differences between first and second heats for PBIO with added acids. For addition of DS to PBIO, the number of tan delta maxima seen in the first heat increased for each added equivalent of acid. For the second heat, there was only one tan delta maximum except for the DS:PBIO = 3:1 case. Differences between first and second heats were most likely due to removal of water during the first heat, which showed that absorbed water had significant effects on E' and E'' . For the DS:C1BI:PBIO = 2:2:1 membrane, however, there was only one T_g for the first heat and for the second heat, which indicated that its mechanical properties were less affected by the loss of water than for the other membrane types. While a minimum was still observed for E' and E'' in the first heat at 155 °C, the results for the second heat were uncomplicated and were similar to what would be seen for a normal viscoelastic polymer.

DSC results also showed significant differences between first heats and subsequent heats if water were allowed to escape. The differences were ascribed in part to the loss of water, slowness of reordering and/or the need for absorbed water for reordering. The same could be said for the DMA results.

3.6. Resistance of acids to wash out

Results of qualitative experiments to compare the resistance to wash out of perfluorinated acids from PBIO membranes as compared to phosphoric acid from PBI are shown in Fig. 4. The results showed that the rate of wash out increased as equivalents of DS to PBIO increased. For DS:PBIO = 4:1, the rate of pH change was similar to PBI with 3 equiv. of phosphoric acid (600 mol% as described by Savinell and Litt [12]). For the DS:C1BI:PBIO = 2:2:1 membrane, however, the first part of the

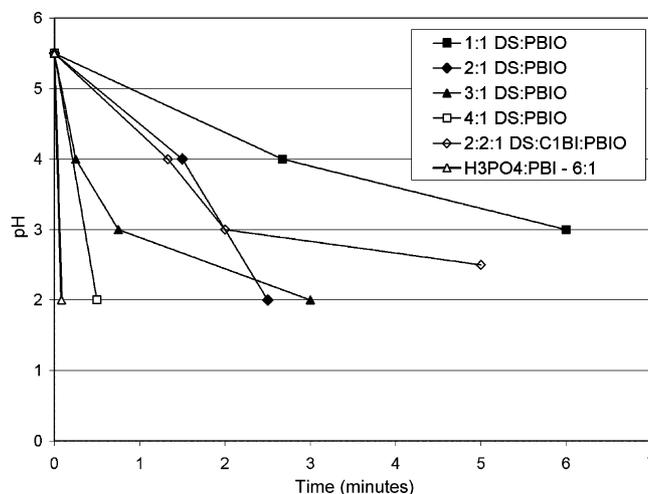


Fig. 4. pH vs. time for PBI/phosphoric acid and for PBIO with perfluorinated acids for samples immersed in deionized water.

curve was similar to that for just 2 equiv. of DS and the subsequent rate was slower. While these membranes would be subject to the same issues for loss of acid due to liquid water as commercial PBI-phosphoric acid membranes, they would be at least as good or better in this respect.

3.7. Membrane morphology after washing

Membranes made using PBI with added imide acids remained transparent after extraction of acid by soaking in water and drying. This was also the case for PBIO membranes having just a single type of acid, either DS or imide. PBIO membranes containing a mixture of imide and sulfonate acids, however, were opaque after extraction of acid following soaking in water and drying. Solvents such as isopropanol penetrated the resultant membranes readily and a porous structure was observed by scanning electron microscopy. These results showed that there was a fundamental difference in morphology for membranes that contained just a single type of acid and those that contained more than one type. While it is possible that the phase separated structure for the washed DS:C1BI:PBIO = 2:2:1 membrane did not develop until immersion in water, the good mechanical properties as indicated by DMA would be consistent with a phase separated morphology with PBIO as the continuous phase.

3.8. Conductivity as determined using ac impedance method

The conditions selected for conductivity and fuel cell evaluations, constant inlet dew point of 80 °C for 90–120 °C, were selected for screening a large number of developmental membranes over a range of increasingly challenging temperature and humidity conditions. This selection of conditions typically resulted in decreases in conductivity with increases in temperature as a result primarily of the decrease in relative humidity: 67% RH at 90 °C, 46% RH at 100 °C, 33% RH at 110 °C, and 24% RH at 120 °C.

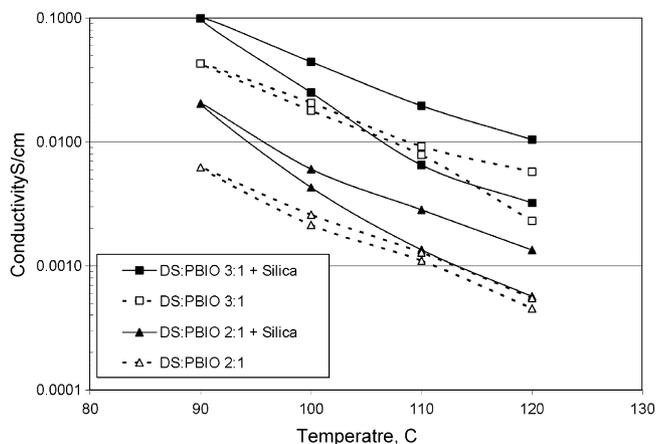


Fig. 5. Conductivity for DS:PBIO membranes with and without added silica at two ratios of acid to polymer for constant 80 °C inlet dew point.

Conductivity for DS:PBIO = 3:1 and 2:1 membranes with and without silica is given in Fig. 5 (constant 80 °C inlet dew point). As expected, conductivity was greater for the 3:1 than for the 2:1 membrane. Addition of silica increased conductivity substantially for both 3:1 (22% by weight silica) and 2:1 DS:PBIO (28% by weight silica) ratios. For the DS:PBIO = 3:1 with silica membrane, the conductivity at 90 °C was as high as typical values reported for perfluorosulfonic acid polymers such as Nafion™. While conductivity was much higher for the DS:PBIO = 3:1 membranes, they were not very strong. On the other hand, the DS:PBIO = 2:1 membranes were quite strong and conductivity with added silica was still respectable.

There was greater hysteresis between the down temperature scan and the up temperature scan for membranes with silica, which suggested that the silica helped to retain more of the water absorbed during the down temperature scan during the subsequent up temperature scan. The difference in conductivity between the down temperature scan and the up temperature scan increased with temperature. This difference indicated that the membrane did not revert quickly to the lower humidified state and conductivity observed during the down temperature scan given that the membrane was conditioned for 90 min at each temperature. Experiments were not done to determine the time required to return to the original conductivity for the down temperature scan.

A comparison of conductivity results for PBI having six moles of phosphoric acid per equivalent of basic polymer, DS:C1BI:PBIO = 2:2:1 with 16 wt.% silica, and DS:C1BI:PBIO without added silica is provided in Fig. 6. As expected, the conductivity for the PBI-phosphoric acid membrane was high and did not decrease very much as temperature increased with concomitant decrease in relative humidity (inlet dew point was held constant at 80 °C). Conductivity for the 2:2:1 membrane with 16 wt.% silica was about the same as for the DS:PBIO = 2:1 membrane with 28 wt.% silica. Similarly, conductivity for the 2:2:1 membrane without added silica was similar to that for the 2:1 membrane without silica. While these results might have been coincidental, the similarity in conductivity between 2:2:1 and 2:1 membranes suggested that the DS was the primary

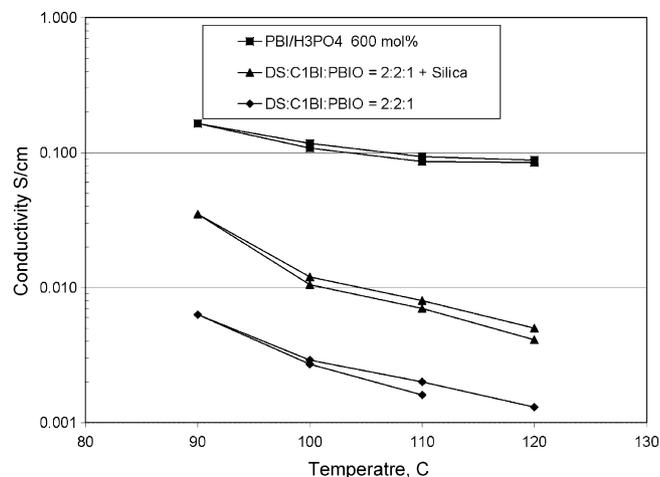


Fig. 6. Conductivity for DS:C1BI:PBIO = 2:2:1 membrane with and without added silica and for PBI with 3 equiv. of phosphoric acid (600 mol%).

source of proton conductivity. As noted above, the pH versus time curve for the 2:2:1 membrane was coincident with that for the 2:1 membrane for the first part of the curve. While conductivity for the DS:PBIO = 3:1 membrane with added silica was considerably greater, it was notably weaker. On the other hand, the 2:1 membranes and 2:2:1 membranes with or without silica were reasonably strong.

3.9. Fuel cell evaluations

Hydrogen/air fuel cell polarization results are given in Fig. 7 for DS:C1BI:PBIO = 2:2:1 with added silica (50 microns thick) and for PBI-phosphoric acid with six moles of phosphoric acid per equivalent of basic polymer at 100 °C and 110 °C (ambient pressure, constant 80 °C dew point for inlet gases). The PBI-phosphoric acid membrane was 30 μm thick. Conventional dispersed platinum electrodes having 0.4 mg cm⁻² of platinum were used. Given that membrane conductivity was significantly lower for the DS:C1BI:PBIO = 2:2:1/silica membrane than for the PBI-phosphoric acid membrane as determined by the AC

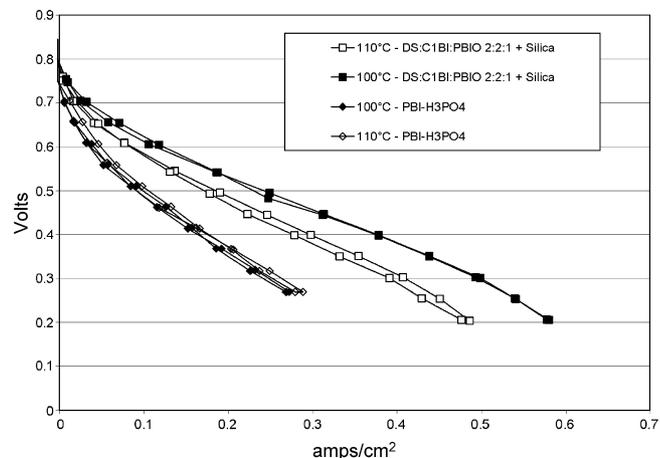


Fig. 7. Hydrogen/air fuel cell polarization for DS:C1BI:PBIO = 2:2:1 membrane/silica membrane as compared to PBI with 600 mol% of phosphoric acid.

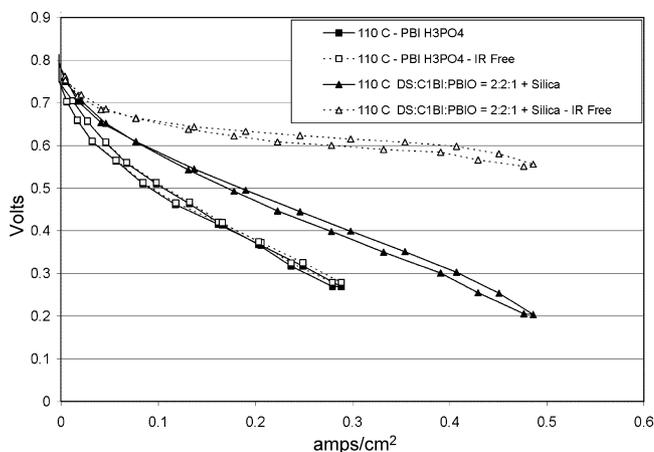


Fig. 8. IR-corrected hydrogen/air fuel cell polarization for DS:C1BI:PBIO = 2:2:1 membrane as compared to PBI with 600 mol% of phosphoric acid.

impedance method, it was surprising that fuel cell performance was significantly better for the former than for the latter. This mismatch in conductivity and fuel cell performance was most likely due to the well known poisoning of platinum by phosphate anion adsorption.

A comparison of quasi IR-corrected polarization for the 110 °C results of Fig. 7 is given in Fig. 8. The IR correction was done by calculation based on membrane thickness and ac conductivity under the same temperature and humidification conditions rather than on high frequency resistance measurements under fuel cell polarization conditions. This method of correction does not account for the electrode IR drop or gain due to greater water back diffusion for thinner membranes. For the PBI-phosphoric acid membrane, the IR-corrected polarization curve was only slightly greater than the experimental polarization curve. The increase was small due to the thinness of the membrane and due to its high conductivity. For the DS:C1BI:PBIO = 2:2:1/silica membrane, the IR correction was much greater due to both its greater thickness and much lower conductivity. The much higher performance of this MEA versus the PBI-phosphoric acid containing MEA is presumably due to lower electrode over potentials, due in turn to the lower propensity of the fluoroalkyl sulfonic acid or imide groups to adsorb to the catalyst surface compared to phosphoric acid.

4. Conclusions

Good mechanical properties, good conductivity, and good fuel cell performance above 100 °C with minimal water input were demonstrated for membranes prepared from PBIO, perfluorinated bis-acids, and silica.

Perfluorinated bis-imide acids were shown to plasticize PBI and PBIO, whereas a perfluorinated DS acid was shown to impart crystallinity to a much greater extent than for a perfluorinated bis-imide acid, which was also confirmed by XRD. For PBIO, a mixture of imide and sulfonate acids was shown to result in a phase separated morphology. Conductiv-

ity results for a DS:PBIO = 2:1 membrane with added silica was quite strong and had conductivity that was as good as a DS:C1BI:PBIO = 2:2:1 membrane with added silica, which had 4 equiv. of acid. Addition of metal oxides improved mechanical properties and improved conductivity. TGA analysis showed that the acids and membranes formed with them were stable for the most part up to about 300 °C. Differences between first heats and subsequent heats for DSC and DMA results were thought to be due in part by loss of water during the first heat, slowness of reordering, and/or the need for absorbed water for reordering.

Fuel cell results for membranes formed from PBIO, fluorinated acids, and silica were shown to be better than for the PBI-phosphoric acid membrane despite its much higher proton conductivity and lower thickness. This difference in fuel cell performance was thought to be due to the difference in anion adsorption between phosphate and the fluorinated anions. For PBI-phosphoric acid, the correction for ohmic losses were very small, which showed that polarization losses were activation over potential losses rather than ohmic. On the other hand, for DS:C1BI:PBIO = 2:2:1/silica membrane, IR-corrected results showed that ohmic losses were primarily responsible for polarization losses. While this new type of membrane showed improved performance compared to PBI-phosphoric acid membrane under the given conditions, additional increases in conductivity and/or reduction in thickness would be needed to reduce ohmic losses and thereby improve fuel cell performance.

“Nafion” is a registered trademark of DuPont.

Acknowledgements

This work was supported in part by the U.S. Department of Energy, Cooperative Agreement DE-FC36-02AL67621. DOE support does not constitute an endorsement by DOE of the views expressed in this paper.

References

- [1] S.J. Hamrock, M.A. Yandrasits, J. Macromol. Sci. Part C: Polym. Rev. 46 (2006) 219–244.
- [2] P. Staiti, M. Minutoli, S. Hocevar, J. Power Sources 90 (2000) 231–235.
- [3] M.F.H. Schuster, W.H. Meyer, Annu. Rev. Mater. Res. 33 (2003) 233–261.
- [4] L. Xiao, H. Zhang, E. Scanlon, L.S. Ramanathan, E.-W. Choe, D. Rogers, T. Apple, B.C. Benicewicz, Chem. Mater. 17 (2005) 5328–5333.
- [5] J.S. Wainwright, M.H. Litt, R.F. Savinell, Handbook Fuel Cells, vol. 3, 2003, pp. 436–446.
- [6] Q. Li, R. He, J.O. Jensen, N.J. Bjerrum, Fuel Cells 4 (3) (2004) 147–159.
- [7] O. Uensal, J. Kiefer, Canadian Patent Application 2,477,864.
- [8] W.E. O’Grady, NTIS Publication PB86201084 (U.S. Department of Commerce), 1986.
- [9] M. Razaq, A. Razaq, E. Yeager, NTIS Publication PB89178768 (U.S. Department of Commerce), 1989.
- [10] A.J. Appleby, D. DesMarteau, V. Jalan, S. Srinivasan, M.S. Gillette, J.K. Gosh, A. Parthasarathy, E.R. Gonzalez, D. Deshai, NTIS Publication DE95015701 (U.S. Department of Commerce), 1992.
- [11] E. Peled, T. Duvdevani, A. Melman, Electrochem. Solid State Lett. 1 (5) (1998) 210–211.
- [12] R.F. Savinell, M.H. Litt, US Patent 6,099,988 (2000).