HIGH TEMPERATURE POLYMER ELECTROLYTE FUEL CELLS

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ABSTRACT

Recently, we reported the use of phosphoric acid-doped polybenzimidazole (PBI) membrane as a solid polymer electrolyte for fuel cell applications. The advantages of PBI include: (i), good protonic conductivity at elevated temperatures; (ii), near zero electro-osmotic drag, which means that the proton transport through the PBI membrane does not involve water transport, (iii), low gas permeability, and (iv) low methanol crossover. The purpose of this paper is to present details of polymer processing and methods used to cast acid doped PBI films. Also, we will report and compare the electrical and mechanical properties of these films. A second PBI-like polymer synthesized in our laboratory is introduced with some preliminary characterization that indicates promise for fuel cell applications.

INTRODUCTION

In recent years there has been intense research interest in the development of proton electrolyte membrane (PEM) fuel cells for transportation and portable power applications. Typically, the polymer electrolyte used is a hydrated perfluorosulfonic acid polymer. This type of polymer requires water for proton conductivity; therefore operating temperature is limited to below the boiling point of water. The maximum conductivity of Nafion occurs at about 80 °C at atmospheric pressure. Fuel cell operation at high current densities is complicated by the water drag accompanying proton transport. A water transport imbalance results, leading to dehydration near the anode and cathode flooding with liquid water.

A high temperature polymer electrolyte, which conducts protons with low water content, should ameliorate the water balance problem. There is also increasing interest in the development of a direct methanol/oxygen polymer electrolyte fuel cell [1-4]. The use of methanol as a fuel has several advantages as compared to hydrogen. Methanol is a liquid fuel available at low cost that can be easily handled, stored, and transported. Fuel cell operation at temperatures above 80°C will improve electrode kinetics, improve tolerance to catalyst poisons, and may reduce fuel crossover. A polymer capable of proton conduction at 200 °C opens up the possibility of directly coupling endothermic methanol reforming with the exothermic fuel cell. This could lead to efficient energy integration and reduce size and complexity of the overall fuel cell system. For example, consider a 10% excess over stoichiometric feed of a 50:50 by mole mixture of liquid
methanol and water fed to a reformer/fuel cell combination operating at 200 °C. Assuming a fuel cell electrical efficiency of 40%, energy balance calculations show that 10% of the energy in methanol will be utilized in the reformer, 22% will be used to preheat and vaporize the feed streams, and 28% will need to be rejected as waste heat.

A high temperature PEM fuel cell will assist in simplifying fuel cell systems designed to operate on higher molecular weight fuels as well. Tolerance to relatively high CO levels (on the order of mole percents) will reduce the need for extensive prox CO clean-up and other polishing reactor schemes. An example is shown in Figure 1 for a PBI (see below) fuel cell with platinum catalysts operated at 150 °C with 1 % CO in H₂ as the fuel. The excess overpotential of the hydrogen anode is only about 5 mV as compared to operation on pure H₂. Low platinum loading anodes, comparable to those of Nafion PEM fuel cells with high platinum utilization, give excellent performance in the presence of CO at the higher temperatures.

Recently, we reported the use of phosphoric acid-doped polybenzimidazole (PBI) membrane as a solid polymer electrolyte for fuel cell applications [5]. The advantages of PBI include: (i), good protonic conductivity at elevated temperatures; (ii), near zero electro-osmotic drag, which means that the proton transport through the PBI membrane does not involve water transport, (iii), low gas permeability, and (iv) low methanol crossover. In addition, it was shown that acid doped PBI membrane exhibits excellent oxidative and thermal stability [6], and good mechanical flexibility at elevated temperature (200°C) [7]. These properties of PBI membranes offer excellent prospects for the application of acid-doped PBI membranes as a superior polymer electrolyte in fuel cells. The demonstration of PBI in an H₂/O₂ fuel cell [8] and a methanol/O₂ fuel cell [9] have been reported.

The purpose of this paper is to present details of polymer processing and methods used to cast acid doped PBI films. Also, we will report and compare the electrical and mechanical properties of these films. A second PBI-like polymer synthesized in our laboratory is introduced with some preliminary characterization that indicates promise for fuel cell applications.

EXPERIMENTAL RESULTS AND DISCUSSION

PBI Powder and Acid Doping

Polybenzimidazole (PBI) is commercially manufactured by Hoechst-Celanese with primary use in fabrics for fire protection clothing. The polymer is high temperature resistant and is chemically stable. It has a glass transition temperature of about 450 °C because of its all aromatic structure. The benzimidazole group has a pKa of about 5.5, which facilitates its absorption of acid, which can act as a plasticizer. The structure of PBI is shown below in Figure 2.

PBI polymer can be synthesized with a broad range of molecular weights, as shown in Table 1. One measurement often used to characterize the molecular weight of a polymer in the inherent viscosity (I.V.). The I.V. is found by measuring the viscosity
of a 0.5 wt% solution of the polymer dissolved in a solvent (concentrated sulfuric acid for PBI). The equation for calculating the I.V. is given below:

\[
\text{I.V.} = \frac{\ln \left( \frac{\text{viscosity of the solution}}{\text{viscosity of the solvent}} \right)}{(\text{solution concentration in g/dL})}
\]

Table 1 shows the I.V. and molecular weight distribution for low, medium, and high molecular weight polymer. The low molecular weight material was purchased from Aldrich Co. The material normally available from Hoechst-Celanese is the medium molecular weight with an I.V. of about 0.7, but some high molecular weight material with an I.V. of about 0.91 has been made available to us. As will be shown later, high molecular weight material is necessary for good mechanical properties following film formation. As it turns out, the I.V. = 0.3 material could not be made into free-standing films. Our understanding is that the high I.V. material is currently a byproduct in PBI manufacturing, but could be the primary product via process adjustments.

Table 1: Characteristics of Commercially Available PBI

| Polymer | I.V. (dL/g) | M_n | M_w | MWD (M_w/M_n) |
|---------|-------------|-----|-----|---------------|
| Low     | 0.3         | 6700| 11200| 1.7           |
| Medium  | 0.68        | 18000| 27200| 1.5           |
| High    | 0.97        | 26300| 50300| 1.9           |

all I.V. values for 0.5 wt% solution in sulfuric acid

In order to increase the average molecular weight of polymer for high quality films, the lower MW components can be extracted by fractionation in dimethyl acetamide (DMAc). Typical extraction results for the yield of undissolved polymer are shown in Table 2. For example, when material initially having an I.V. = 0.91 is extracted at 94 °C, a yield of 69% of the original material is obtained. The I.V. of the extracted material has been increased to 1.14. The yield decreases as the average molecular weight of the material after extraction increases. The yield of these high I.V. fractions would be significantly less for a starting material of 0.71 I.V.

Table 2: PBI Extraction Results using DMAc
Initial I.V. = 0.91

| Trial | Fractionation Temperature °C | Yield (%) of undissolved polymer | I.V. (dL/g) of undissolved polymer |
|-------|-----------------------------|---------------------------------|----------------------------------|
| A     | 94                          | 69                              | 1.14                             |
| B     | 110                         | 53                              | 1.19                             |
| C     | 130                         | 41                              | 1.28                             |
| D     | 160                         | 23                              | 1.42                             |
Due to the basic nature of the benzimidazole group, PBI readily absorbs acid. Oxo-acids are required to achieve proton conductivities commensurate with fuel cell operation. Sulfuric acid was originally investigated, but poor film mechanical properties led us to consider phosphoric acid. However, further investigation with different I.V. materials and casting methods may warrant another look at this system. P$^{31}$ NMR indicates that the first two phosphoric acids per repeat unit protonate the two benzimidazole groups, as shown in Figure 3. However, additional phosphoric acid is needed for high levels of conductivity. The additional phosphoric acid is more weakly tied into the PBI structure, but relatively immobile. Still the polymer-acid system is single-phase.

**Film Forming Methods and Film Properties**

In Figure 4 a schematic of two methods that were investigated for forming films of PBI with phosphoric acid is shown. In the first method, the polymer is dissolved in DMAc and 1-2 wt% LiCl is added to maintain solution stability. A film is cast onto a glass plate, the solvent is evaporated, and then the film is washed in boiling water to remove the residual LiCl. Doping of the film is accomplished by immersion in phosphoric acid solutions. The molarity of the acid determines the final acid loading in the membrane. For example, immersion in 5M acid solution gives a doping level of about 3 moles of acid per PBI repeat unit (this is called 300 mol% doping level). This technique yields a maximum doping level of 520 mol% phosphoric acid by immersion in 11M acid solution.

In the second method, PBI and acid are directly cast together from a co-solvent, trifluoroacetic acid (TFA). The solvent is evaporated and the film is ready for use. Even though the compositions are similar, the properties of the film formed by this process are substantially different than those formed by the DMAc method.

The mechanical properties of DMAc cast films are compared to TFA cast films in Table 3. Films formed by the DMAc casting method are normally stronger and tougher. The TFA films require a polymer of higher I.V. in order to generate films of reasonable strength. The TFA films have much more crystallinity as compared to the DMAc films, and the surface texture is different. The TFA films are more rubbery and softer.

| Table 3: Comparison of Mechanical Properties of DMAc and TFA Films |
|---------------------------------------------------------------|
| **DMAc Cast, IV = 1.0**                                      | **TFA Cast, IV = 0.91**                                  |
| Modulus 10⁹ Pa     | Toughness 10⁹ Pa   | Modulus 10⁹ Pa     | Toughness 10⁹ Pa   |
| Dry               |                   | Dry               |                   |
| 1.94              | 105.0             | 1.27              | 50                |
| doped H₃PO₄ 100 mol% |                   | doped H₃PO₄ 100 mol% |                   |
| 3.53              | 48.5              | 1.88              | 35                |
In the case of TFA films, the toughness of the acid free polymer increases to about 150 MPa for 1.42 I.V. material as compared to 50 for 0.91 I.V. material. The addition of 50 mol% phosphoric acid drops the toughness to about 100. As acid concentration increases, the toughness increases because of ionic bonding to a maximum value of about 140 MPa. However, once the acid concentration exceeds 200 mol% the excess acid acts as a plasticizer and the toughness decreases (e.g. it drops to about 70 MPa with 500 mol% acid).

Although the mechanical properties of the TFA cast films are not as good as the DMAc cast films, the method of casting is simpler and as shown in Figure 5, the proton conductivity is greater. The proton conductivity of TFA films under dry conditions and temperatures exceeding 180 °C is greater than that of Nafion (for Nafion’s optimum operating conditions of 100% RH, 80 °C).

Several techniques have been used to measure the methanol permeability across PBI films [9,10,11]. These techniques include closed receiving volume membrane diffusion cells, limiting current methods, and mass spectroscopy methods. All techniques gave similar results. The crossover equivalent current (50 mol% of methanol in vapor feed at 1 atm pressure) for DMAc cast film is about 5-10 mA/cm², which is a factor of 10-20 times less than that reported for Nafion 117. For TFA cast films, the crossover is larger by a factor of 3, but still considerably less than Nafion 117. Of course, the low crossover is reasonable considering that the methanol activity is low in the gas phase at high temperatures and that PBI is a homogeneous system.

Poly (2,5-benzimidazole) (AB-PBI)

AB-PBI is the second PBI-type polymer investigated at CWRU. The polymer is relatively simple to synthesize by a condensation reaction. Figure 6 shows the synthesis route and the chemical structure of the AB-PBI repeat unit. The presence of polyphosphoric acid scavenges the water produced and helps to form high molecular weight material, as shown below in Table 5. Although the DABA starting material is available commercially, purification is critical for high molecular weight polymer. The highest I.V. we have obtained is 7.1 and the preferred reaction conditions were 200 °C for 2 hours with DABA/P₂O₅/H₃PO₄ of 1/7/3.22. (an I.V. of 4.1 corresponds to a M.W. of 71,000.) Reports in the literature indicate that much higher molecular weights are achievable (I.V. up to 12-25). Thermogravimetric (TGA) measurements indicate stability at temperatures below 600 °C in an inert atmosphere.

Table 5: Effect of excess phosphoric acid on AB-PBI molecular weight synthesis at 160 °C

| Excess P₂O₅, % | I.V. of a 0.5 wt% solution |
|---------------|--------------------------|
| 50            | 0.84                     |
| 150           | 1.28                     |
| 300           | 3.31                     |
Doping of acid into AB-PBI is accomplished by submersion into phosphoric acid solution. The mechanical properties of the resulting films are given in Table 6. By drying the film at 140 °C before submersion, a higher doping level can be achieved. Annealing the doped film at temperatures of 150 °C improves film strength to levels about that of PBI/TFA films. We expect better film properties with higher molecular weight material. A remarkable property of this material is the amount of strain before break. Some films have been stretched by a factor of 10 before breaking. Thus the toughness of the AB-PBI films is ca. 100X greater than that of PBI films we have cast.

| Soln. H₃PO₄ Molar | H₃PO₄/Repeat | Annealing Temp.°C | Modulus Gpa | Strain at Break,% |
|-------------------|-------------|-------------------|-------------|-------------------|
| 0                 | 0           | 25                | 1.47        | 256               |
| 3                 | 1.29        | 25                | 1.77        | 161               |
| 6                 | 1.79        | 25                | .25         | 437               |
| 6*                | 3.29        | 25                | .069        | 872               |
| *                 |             | 100               | .33         | 767               |
|                   |             | 150               | 1.75        | 548               |

* Film dried at 140 °C before acid doping

The conductivity of AB-PBI was measured in one atmosphere water pressure in the temperature range of 150-200 °C. The results are given in Table 7 and it should be noted that temperature effects were not significant. The conductivity of AB-PBI is greater than that of the PBI/DMAc films and nearly equivalent to that of PBI films cast from TFA. To compare acid loadings, a value of 1.3 Acid/Repeat in AB-PBI is equivalent to 2.6 Acid/Repeat in PBI.

| H₃PO₄/Repeat | Conductivity, S/cm |
|--------------|--------------------|
| 1.3          | .022               |
| 2.5          | .05                |
| 3.29         | .086               |

AB-PBI is an attractive polymer for fuel cell applications considering its high conductivity, its good mechanical properties for film formation, and its ease and control of synthesis. We have only begun to develop the PBI-type polymers for fuel cell applications. Further work is needed to understand the conduction mechanism and to optimize the properties for film formation and electrode attachment. These polymers may also find other applications. Some examples include sensors and electrochemical reactors for destruction of toxic volatile organic compounds, among others.
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Figure 1: Effect of 1% CO on hydrogen anode performance at 150 C.
Electrode: 1mg/cm² Pt black. H₂ and H₂ w/ 1% CO, 1 atm, humidified at 65C.
Electrolyte: PBI/TFA membrane, 600 m/o H₃PO₄

Figure 2: Chemical structure of the PBI repeat unit.
poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole]

Figure 3: Five phosphoric acids per PBI repeat unit.

PBI FILM FORMATION METHODS

I. Cast then doped with acid

PBI 1 g

250 C
60 - 100 psi

DMAc w/ 1-2 wt% LiCl 9 g

FILTERED

CONCENTRATED

CAST FILM

SOLV.EVAP. 140 G

WASH IN BOILING WATER

DOPED FILM

ACID DOPING

FILM

II. Direct casting with acid in TFA

PBI 1 g
TFA 20 g

STIRRED/REFLUXED
4-6 HOURS

H$_2$PO$_4$ - 6 equiv/PBI repeat

MIX

FILTER

CAST

SOLVENT EVAP.
VAC/RM TEMP

DOPED FILM

Figure 4: Schematics of two methods to cast PBI films.
Figure 5: Measured conductivity of PBI doped with 600 m\% phosphoric acid for two casting methods as compared to Nafion 117 at 1 atm pressure and .5 atm water partial pressure.

Figure 6: Synthesis route for ABPBI.

\[
\begin{align*}
\text{H}_2\text{N} & \quad \xrightarrow{\text{PPA}} \quad \text{H}_n\text{N} \\
\text{H}_2\text{N} & \quad \text{COOH} \\
\text{P}_2\text{O}_5 & \quad \xrightarrow{2 \text{H}_2\text{O}} \quad \text{H}_4\text{P}_2\text{O}_7 \\
\end{align*}
\]

3,4 diaminobenzoic Acid (DABA)
Purified

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