

Synthesis and Characterization of High Molecular Weight Hexafluoroisopropylidene-Containing Polybenzimidazole for High-Temperature Polymer Electrolyte Membrane Fuel Cells

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ABSTRACT: A high molecular weight, thermally and chemical stable hexafluoroisopropylidene containing polybenzimidazole (6F-PBI) was synthesized from 3,3'-diaminobenzidine (TAB) and 2,2-bis(4-carboxyphenyl) hexafluoropropane (6F-diacid) using polyphosphoric acid (PPA) as both the polycondensation agent and the polymerization solvent. Investigation of polymerization conditions to achieve high molecular weight polymers was explored via stepwise temperature control, monomer concentration in PPA, and final polymerization temperature. The polymer characterization included inherent viscosity (I.V.) measurement and GPC as a determination of polymer molecular weight, thermal and chemical stability assessment via thermo gravimetric analysis and Fenton test, respectively. The resulting high molecular weight polymer showed excellent thermal and chemical stability. Phosphoric acid doped 6F-PBI membranes were prepared using the PPA process. The physiochemical properties of phosphoric acid doped membranes were characterized by measuring the phosphoric acid doping level, mechanical properties, and proton conductivity. These membranes showed higher phosphoric acid doping levels and higher proton conductivities than the membranes prepared by the conventional membrane fabrication processes. These membranes had sufficient mechanical properties to be easily fabricated into membrane electrode assemblies (MEA) and the prepared MEAs were tested in single cell fuel cells under various conditions, with a focus on the high temperature performance and fuel impurity tolerance. © 2009 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 47: 4064–4073, 2009

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INTRODUCTION

Polymer electrolyte membrane (PEM) fuel cells are becoming increasingly important as alterna-

tive energy sources for their high power density, high energy efficiency, and low environmental impact.¹ Presently, the most commonly used polymer electrolyte membranes are perfluorosulfonic acid (PFSA) ionomers, such as DuPont's Nafion[®], because of their outstanding mechanical integrity, chemical stability, and high proton conductivity. However, these membranes rely on water acting

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as the proton conductive media. Thus at higher temperatures ($>100\text{ }^{\circ}\text{C}$) or lower humidities, the membrane's proton conductivity decreases significantly. These membranes also lose their mechanical and dimensional stability at higher temperatures due to their low glass transition temperature ($80\text{--}120\text{ }^{\circ}\text{C}$). Fuel cells operated at an increased temperature ($>120\text{ }^{\circ}\text{C}$) offer many benefits including: faster electrode electrochemical reaction kinetics, higher fuel impurity resistance, both heat and water management, and so forth. To overcome the drawbacks mentioned above and utilize the advantages at higher operational temperatures, membranes which can be operated above $120\text{ }^{\circ}\text{C}$ have been investigated with great efforts to replace PFSA membranes.² A variety of approaches have been attempted such as inorganic polymer composites, nonfluorinated hydrocarbon polymers, and anhydrous proton conducting polymers.^{2,3} Among the various types of alternative high temperature polymer electrolyte membranes developed, phosphoric acid doped polybenzimidazole (PBI) was reported as a promising candidate for a low-cost and high-performance fuel cell membrane material.^{4,5} It was shown that this polymer electrolyte membrane exhibited high proton conductivity at temperatures up to $200\text{ }^{\circ}\text{C}$, low reactant permeability, high fuel impurity tolerance, excellent oxidative, and thermal stability, and nearly zero water drag coefficient.^{4,6–22} However, preparation of phosphoric acid doped PBI membranes involved multiple steps and was costly, time-consuming, and not suitable for industrial scale production. The resulting phosphoric acid doped PBI membranes had low phosphoric acid doping levels ($<10\text{ PA}$ per PBI repeat unit), low proton conductivity (0.04 S/cm at $190\text{ }^{\circ}\text{C}$), low mechanical strength at high phosphoric acid doping levels, and was made with low molecular weight (I.V. = 0.8 dL/g) PBI polymer.

A novel process to prepare phosphoric acid doped PBI membranes, named the PPA process, was developed by Benicewicz et al.^{23–25} In the PPA process, PPA was used as a solvent and condensing agent for the polycondensation reaction of tetra-amines and diacids to synthesize high molecular weight PBI polymers. After polymerization, the solution of PBI in PPA was directly cast at temperatures of $200\text{--}220\text{ }^{\circ}\text{C}$. PPA and PBI are both hygroscopic, thus absorbing moisture from the atmosphere. PPA (a good solvent for PBI) is hydrolyzed to phosphoric acid (PA, a poor solvent for PBI) and the temperature decreases to room temperature to induce the transition from the so-

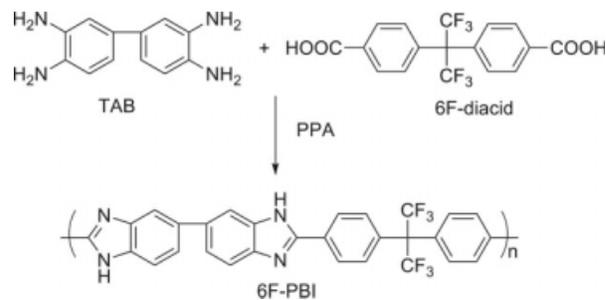


Figure 1. Synthesis of 6F-PBI in polyphosphoric acid.

lution state to the gel state. Once the gel state membranes are formed, many polymer membranes formed by this process remain in the gel state at high temperatures ($120\text{--}180\text{ }^{\circ}\text{C}$) since it is difficult to thermally convert PA to PPA at these temperatures. The PPA process is a much simpler, less costly, time-effective process, which solved many problems associated with the conventional phosphoric acid doped PBI membrane preparation process.

In this work, the synthesis of high molecular weight hexafluoroisopropylidene-containing polybenzimidazole (6F-PBI, as shown in Fig. 1) and the preparation of phosphoric acid doped 6F-PBI membranes via the PPA process are described. The hexafluoroisopropylidene group is widely used to improve high performance polymers such as polyimides and polyamides without sacrificing the high performance.²⁶ Alternate PBI approaches and new directions in fluorinated polymers for fuel cell membranes have also been explored in recent years.^{27–36} The introduction of hexafluoroisopropylidene group into the polymer backbone increases the solubility, thermal stability, flame resistance, oxidation resistance, and so forth while decreasing the crystallinity, dielectric constant, water absorption, and color. The synthesis of 6F-PBI was reported by Saegusa et al.³⁷ with low molecular weight polymers (I.V. = 0.43 dL/g , measured in 0.5 g/dL , $96\text{ wt } \%$ concentrated H_2SO_4 at $30\text{ }^{\circ}\text{C}$). The investigation of polymerization conditions to achieve high molecular weight 6F-PBI was explored in this work. The polymer was characterized by Fourier transform infrared (FTIR), inherent viscosity (I.V.) measurement, and GPC as a determination of polymer molecular weight, thermal and chemical stability assessment via thermo gravimetric analysis and Fenton test, respectively. Phosphoric acid doped 6F-PBI membranes were prepared using the PPA process.

The physiochemical properties of acid doped membranes were characterized by measuring the phosphoric acid doping level, mechanical properties, and proton conductivity. These membranes were fabricated into membrane electrode assemblies and tested in single cell fuel cells under various conditions to explore their high-temperature performance and fuel impurity tolerance.

EXPERIMENTAL

Materials

2,2-Bis(4-carboxyphenyl)hexafluoropropane was purchased from Synquest Labs (98% purity) and used as received. 3,3',4,4'-Tetraaminobiphenyl (TAB, polymer grade, ~97.5%) was donated by Celanese Ventures, GmbH and used as received. Polyphosphoric acid (115%) was used as received and supplied from FMC.

Polymer Syntheses

The general procedure for the synthesis of 6F-PBI is described as follows: A 100 mL, three-necked, round-bottom flask was equipped with an overhead mechanical stirrer, a water-cooled condenser, and nitrogen-purge inlet and outlet. 2,2-Bis(carboxyphenyl)hexafluoropropane (6F-diacid, 1.961 g, 5 mmol) and TAB (1.071 g, 5 mmol) were added, followed by 50 to 150 g of polyphosphoric acid. The reaction mixture was stirred using a mechanical stirrer at 100 rpm and purged with a slow stream of nitrogen, and the reaction temperature was controlled by a programmable temperature controller with ramp and soak features. The typical final polymerization temperatures were approximately 200–220 °C for 24 h. During the polymerization, the reaction mixture became more viscous and developed a dark brown color. A small amount of the reaction mixture was poured into water and a brown mass was isolated. The mass was pulverized, and then neutralized with ammonium hydroxide, washed thoroughly with water, and dried in a vacuum oven (2 mmHg, 110 °C) for 24 h to obtain the dry 6F-PBI powder for further polymer characterization.

Phosphoric Acid-Doped Membrane Preparation

The phosphoric acid doped 6F-PBI membranes were prepared by casting the viscous polymerization solution directly onto clear glass plates in air using a film applicator. Polyphosphoric acid was

hydrolyzed to phosphoric acid concomitant with membrane formation under different controlled conditions (for example, by placing membranes at 25 °C and relative humidity of 55% for 24 h).

Characterization

FTIR spectra were obtained using a Bio-Rad FT 3000MX Mid-IR Excalibur in transmission mode for 6F-PBI on KBr pellets in the range of 400–4000 cm^{-1} . The I.V. of the polymer was measured with a Cannon Ubbelohde viscometer at a concentration of 0.2 g dry PBI/100 mL solution of the polymer dissolved in concentrated sulfuric acid (96 wt %) at 30 °C. The polymer molecular weight was measured using a Polymer Laboratories Model 120 GPC with three Polymer Standards Service POLEFIN columns (8 × 300 mm, 10 micron linear XL) connected in series utilizing DMAc with 0.05 M LiCl at 65 °C. A refractive index detector was used to monitor the eluted polymer peaks. Thermal gravimetric analysis (TGA) thermograms were obtained using a METTLER TOLEDO TGA/SDTA 851 with a nitrogen flow rate at 20 mL/min. The temperature range was from room temperature to 900 °C and the temperature scan speed was 10 °C/min. The Fenton test was performed on both dry polymer and phosphoric acid doped membrane. Fenton's reagent, a combination of H_2O_2 and a ferrous salt, is a very effective method to generate hydroxyl and peroxy radicals. The test samples (except the phosphoric acid doped membrane) were dried in a vacuum oven at 110 °C overnight and then measured for the initial weight. The test sample and 10 mL Fenton's reagent solution (20 ppm Fe(II), 3 wt % H_2O_2) was put into a glass bottle. The bottle was sealed and then heated at 40 or 160 °C for 24 h. Subsequently, the test sample was rinsed with water, dried in vacuum oven at 110 °C overnight, and measured for the final weight. The weight loss (the difference between the final weight and the initial weight) was used to characterize the resistance to hydroxyl and peroxy free radicals. The phosphoric acid doping level of membranes was determined by titration with 0.1 M sodium hydroxide. The first equivalence point was used to determine the volume of sodium hydroxide necessary for neutralization. The samples were washed thoroughly with distilled water and dried in a vacuum oven at 110 °C for at least 8 h. The samples were allowed to cool in the vacuum oven before removal and were weighed to obtain the dry weight of the polymer. Phosphoric acid doping levels, X,

moles of phosphoric acid per mole of PBI repeat unit (X $\text{H}_3\text{PO}_4/\text{PBI}$) were calculated from the equation:

$$X = \frac{(V_{\text{NaOH}} \times C_{\text{NaOH}})}{(W_{\text{dry}}/M_{\text{polymer}})}$$

where V_{NaOH} and C_{NaOH} are the volume and concentration of the sodium hydroxide solution required to neutralize the phosphoric acid to the first equivalence point, W_{dry} is the dry weights of the polymer sample, and M_{polymer} is the molecular weights of the polymer repeat unit. The mechanical properties of the membrane were measured by cutting ASTM D683 Type V specimens from the bulk phosphoric acid doped 6F-PBI membrane. Tensile properties were measured using a United Tensile Tester (SSTM-1-PC) with a 22.2 N load cell. All measurements were made at room temperature on samples preloaded to 0.1 N with a crosshead speed of 5 mm/min. Proton conductivities of the membranes were measured by a four-probe electrochemical impedance spectroscopy method using a Zahner IM6e electrochemical workstation over the frequency range from 1 Hz to 100 kHz with amplitude of 5 mV. A two-component model with an ohmic resistance in parallel with a capacitor was employed to fit the experimental data. The conductivities of the membrane at different temperatures were calculated from the membrane resistance obtained from the model simulation with the following equation:

$$\sigma = \frac{d}{l \times w \times R_m}$$

where d is the distance between the two inner probes, l is the thickness of the membrane, w is the width of the membrane, and R_m is the ohmic resistance from the model fitting. Membrane conductivity data was recorded on the second heating scan, after the water was removed from the membrane via evaporation during the first scan at temperatures greater than 100 °C.

Membrane Electrode Assembly (MEA) Preparation and Fuel Cell Testing

The gas diffusion electrodes (GDE, acquired from BASF Fuel Cell, formerly E-Tek) with a platinum loading of 1.0 mg/cm² were used for this study. The MEA was fabricated by hot-pressing a piece of membrane between the two Kapton-framed electrodes. The MEA was then assembled into a single cell fuel cell testing hardware. The gas flow

plates were graphite plates with double serpentine gas channels. Stainless steel end plates with attached heaters were used to clamp the graphite flow plates. A commercial fuel cell testing station (Fuel Cell Technology) was used for fuel cell testing, while gases were fed to the anode and cathode without any humidification. The instrument was controlled by home-programmed Lab View Software (National Instruments, Austin, TX).

RESULTS AND DISCUSSION

Polymer Synthesis

There are several synthetic routes to synthesize polybenzimidazoles such as the melt polycondensation of dicarboxylic acid diphenyl esters with tetra-amines and the solution polycondensation of dicarboxylic acids with tetra-amines in PPA acting as condensing agent and solvent. Solution polymerization in polyphosphoric acid offers many advantages over the melt polymerization: moderate polymerization conditions, less expensive monomers, and higher polymer molecular weight. Therefore, the solution polymerization was employed to synthesize 6F-PBI from TAB and 6F-diacid in PPA, as shown in Figure 1. Previous efforts in the literature reported that the solution polymerization of 6F-PBI in PPA produced only low molecular weight polymers (I.V. = 0.43 dL/g, measured in 0.5 g/dL, 96 wt % concentrated H_2SO_4 at 30 °C).³⁷ Initial polymerization efforts in this work also gave low molecular weight 6F-PBI polymer (I.V. < 0.5 dL/g, measured in 0.2 g/dL, 96 wt % concentrated H_2SO_4 at 30 °C). During the polymerization reaction, sublimation of the 6F-diacid monomer was observed. Thus, the reason for low molecular weight polymer was attributed to the low solubility of the 6F-diacid monomer in PPA and the unequal stoichiometry of monomers caused by 6F-diacid monomer sublimation at higher polymerization temperatures. According to the Carother's equation, well-balanced monomer stoichiometry is required to obtain high molecular weight polymers from AA-BB step polymerizations. An investigation of polymerization conditions to achieve the high molecular weight 6F-PBI without loss of monomer was conducted. The experimental variables considered in this study were stepwise temperature control, initial monomer concentration in PPA, and final polymerization temperature.

A multistep temperature control profile as shown in Figure 2 was employed. The main

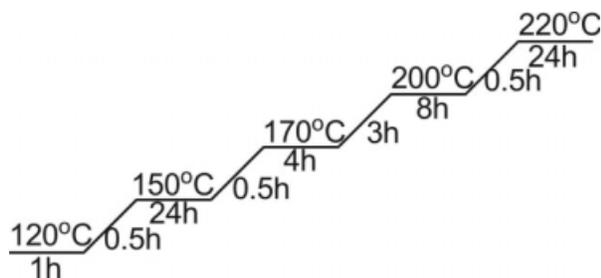


Figure 2. Stepwise temperature control profile for the synthesis of high molecularweight 6F-PBI.

difference between this multistep temperature control profile and previous temperature control profiles was the addition of intermediate temperature steps at 150 and 170 °C. The addition of intermediate temperature steps was proposed to aid the monomer dissolution in PPA. At these temperatures, the 6F-diacid monomer did not sublime, and additional longer holding time was allowed for the formation of oligomers which would not sublime at the higher polymerization temperatures. Higher molecular weight polymers with the I.V. up to 2.2 dL/g were successfully obtained using this multistep temperature control profile.

Another series of experiments was performed to determine the effects of initial monomer concentration in PPA and final polymerization temperature on the polymer molecular weight. The results are shown in Figure 3, where the polymer I.V.s are plotted as a function of monomer concentration in PPA for final polymerization temperatures of both 200 and 220 °C. The initial monomer concentration in PPA was observed to have a large effect on the molecular weight of the resulting polymer. A distinct maximum in polymer I.V. was observed at a initial monomer concentration of approximately 3 wt % in PPA for both final polymerization temperatures. Monomer sublimation was observed at initial monomer concentrations greater than 3 wt % in PPA due to the incomplete monomer dissolution even when the extended intermediate holding temperatures were used. Higher temperatures and further extension of the holding times led to enhanced sublimation of monomer, and thus lower molecular weight. For monomer concentrations lower than 3 wt % in PPA, step-growth polymerization was inhibited and thus lower polymer molecular weights were obtained. The effect of final polymerization temperature on polymer molecular weight was also investigated and shown in Figure 3. The higher final polymerization temperature (220 °C) resulted in higher polymer molecular weights

(higher polymer I.V.). Further increases in the final polymerization temperature to 240 °C were not employed due to polymer crosslinking at that temperature, and polymer solutions made under these conditions were difficult to cast.

Polymer Characterization

The FTIR spectrum of 6F-PBI was recorded and exhibited characteristic absorptions at 2800–3500 cm^{-1} , 1600 cm^{-1} , and 830 cm^{-1} corresponding to N–H bond and imidazole ring, C=N double bond, and C–F bond stretching vibrations, respectively.

The high polymer molecular weight of 6F-PBI prepared under the newly developed polymerization conditions were also analyzed via gel permeation chromatography (Polymer Laboratories Model 120 GPC, DMAc with 0.05 M LiCl, and 65 °C). The absolute molecular weights of 6F-PBIs were not measured in this work due to the lack of an absolute molecular weight detector in our high temperature GPC system. However, the determination of relative molecular weights was conducted by comparing 6F-PBI with the PMMA standards as shown in Figure 4. Polymer with an I.V. of 0.98 dL/g (curve (a) in Fig. 4) showed a relative number average molecular weight of 186,000 g/mol and weight average molecular weight of 398,000 g/mol. When compared with a previous light scattering study³⁸ of *m*-PBI (poly[2,2'-(*m*-phenylene)-5,5'-bibenzimidazole], I.V. of 1.59 dL/g, weight average molecular weight of 199,200 g/mol measured in DMAc with 4 M LiCl) that determined absolute molecular weights, it is probable

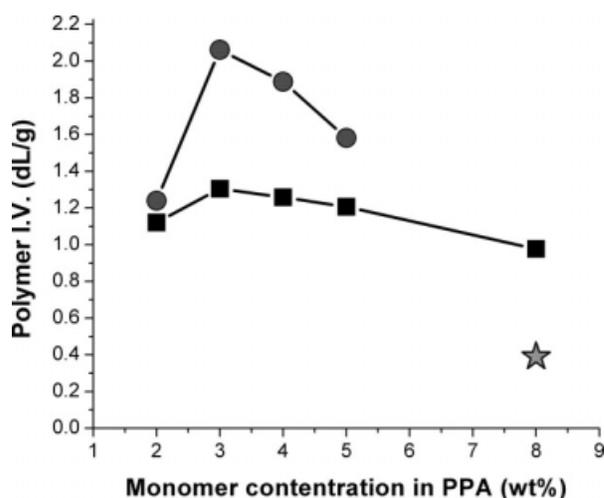


Figure 3. I.V. of 6F-PBIs at different polymerization conditions. Final polymerization temperature: 200 °C (square), 220 °C (circle); Literature value (star).²⁶

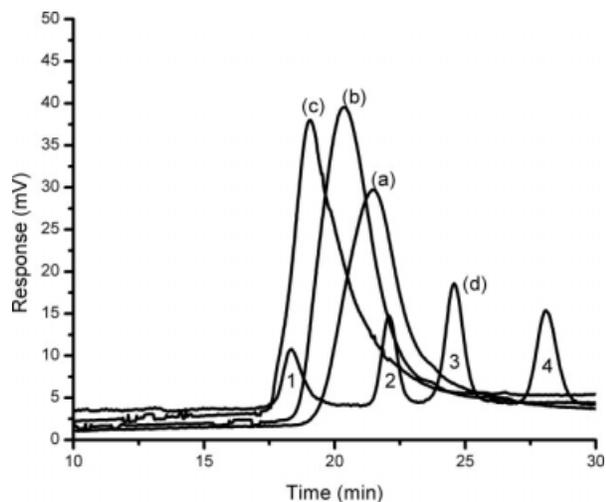


Figure 4. GPC of 6F-PBI—(a) I.V. = 0.98 dL/g, (b) I.V. = 1.12 dL/g, (c) I.V. = 1.58 dL/g, and (d) PMMA standards in DMAc with 0.05 M LiCl at 65 °C. PMMA standard molecular weights: (1) 1,944,000; (2) 281,700; (3) 79,250; and (4) 13,300.

that the GPC results based on PMMA standards overestimate the actual molecular weights of these polymers. The reason for this overestimation could be attributed to the salt (LiCl) effects on the polymer size in DMAc. Shogbon et al.³⁸ also reported that the radius of gyration of the same *m*-PBI was 43.4 nm in DMAc with 0.05 M LiCl, and 31.0 nm in DMAc with 4 M LiCl.

The thermal stability of 6F-PBI polymers was characterized using TGA. The TGA thermogram of 6F-PBI was measured in flowing nitrogen (20 mL/min) at a 10 °C/min heating rate from room temperature up to 900 °C as shown in Figure 5. The polymer was stable up to approximately 434 °C (where 0.02 wt % of original weight was lost),

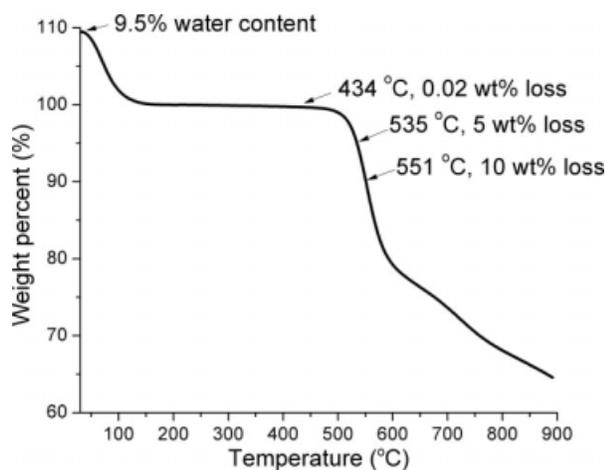


Figure 5. TGA thermogram for 6F-PBI in nitrogen.

and the decomposition temperatures TD_5 and TD_{10} (where 5 and 10% of the original weight was lost, respectively) under nitrogen were 535 and 551 °C, respectively. The polymer maintained ~65% of its original weight at 900 °C. The TGA data showed that the introduction of hexafluoroisopropylidene (HFIP) group into the polymer main chain retained the thermal stability of 6F-PBI when compared with the previously reported high thermal stability of *meta*-PBI which showed the polymer was stable up to approximately 450 °C.³⁹ Approximately 9.5% weight loss from room temperature to 120 °C was attributed to the loss of water absorbed in 6F-PBI. Despite the introduction of the hydrophobic fluorine-containing functional group into the polymer main chain, 6F-PBI remained relatively hydrophilic (for comparison: the moisture content of *meta*-PBI is 15–18 wt %).⁴⁰ The T_g of the polymer was not detectable in the DSC scans up to 400 °C.

The chemical stability of 6F-PBI polymer, or specifically the resistance to hydroxyl/peroxyl free radicals, was tested using the Fenton test. The weight losses and various testing conditions are summarized in Table 1. The initial weight of polymer in phosphoric acid doped membrane was calculated from the polymer weight percentage in the bulk membrane and initial weight of a disk-shaped membrane sample. 6F-PBI possesses excellent hydroxyl/peroxyl radical resistance regardless if the sample was in polymer powder or membrane form, with or without phosphoric acid, and at low or high temperatures. It is also confirmed that the hexafluoroisopropylidene group is stable in the polymer under the free radical conditions of the Fenton test.

Table 1. Fenton Test for 6F-PBI

| Test Sample | Weight Loss (%) | |
|---|-----------------|--------|
| | 40 °C | 160 °C |
| 6F-PBI ^a | ~0 | ~0 |
| Dry membrane (a) ^b | ~0 | ~0 |
| Dry membrane (b) ^b | ~0 | ~0 |
| Phosphoric acid doped membrane ^c | ~0 | ~0 |

^a 6F-PBI was dried polymer powder, I.V. = 2.2 dL/g.

^b Dry membrane was prepared by neutralizing phosphoric acid doped membrane with ammonium hydroxide, washing with water, then drying in a vacuum oven at 110 °C over night; (a) No phosphoric acid was used in the Fenton test, (b) 1 ml 85 % phosphoric acid was added into Fenton reagent.

^c Initial phosphoric acid-doped membrane was a disk-shaped sample cut from bulk membrane with 2 cm diameter.

Membrane Characterization

For a typical phosphoric acid doped 6F-PBI membrane prepared by the PPA process, the phosphoric acid doping levels were 30–40 mol of phosphoric acid per mole of PBI repeat unit. These values are considerably higher than any phosphoric acid doped PBI membranes prepared by the conventional membrane fabrication process,⁴ and similar to other phosphoric acid doped PBI (*meta*-PBI, *para*-PBI, etc.) membranes prepared by the PPA process. Thus, the introduction of the hexafluoroisopropylidene (HFIP) functional group into the polymer backbone does not adversely affect the ability to retain phosphoric acid in the membranes. For the phosphoric acid doped PBI membranes prepared by the conventional process, there was a tradeoff between the desired properties of the membrane, such as high phosphoric acid doping levels and proton conductivity, with high mechanical properties. High phosphoric acid doping levels usually led to high proton conductivity but also to poor mechanical properties. Li et al.⁴¹ reported one of the highest phosphoric acid doping levels (13–16 mol of phosphoric acid per mole of PBI repeat unit, using the commercially available *meta*-PBI with an I.V. of 1.0 dL/g) attained using the conventional membrane fabrication process. Mechanical strength measurements showed that such membranes with “high” phosphoric acid loading levels resulted in poor mechanical properties and were too weak to fabricate into membrane electrode assemblies. In contrast, the mechanical properties of phosphoric acid doped 6F-PBI membranes with high phosphoric acid doping levels (30–40 mol of phosphoric acid per mole of PBI repeat unit) prepared by the PPA process exhibited tensile strengths greater than 0.8 MPa and elongations at break ~100%. These membranes had sufficient mechanical properties to be easily fabricated into membrane electrode assemblies.

The measured proton conductivities of phosphoric acid doped 6F-PBI membranes were approximately 0.01 S/cm at room temperature and reached as high as 0.09 S/cm at 180 °C without humidification as shown in Figure 6. For comparison, the proton conductivity of a phosphoric acid doped 6F-PBI membrane with a phosphoric acid doping level of 3 mol PA/PBI repeat unit prepared by the conventional process was 1.7×10^{-4} S/cm at 160 °C²⁷ and the proton conductivity of a phosphoric acid doped *meta*-PBI membrane with a phosphoric acid doping level of 5 mol PA/PBI

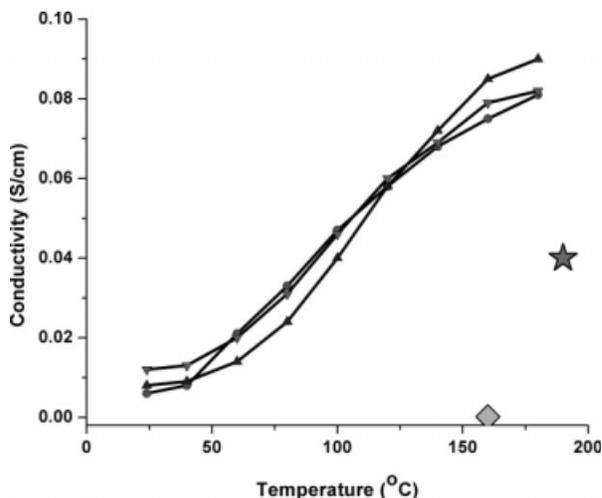


Figure 6. Proton conductivities of phosphoric acid doped 6F-PBI membranes with different I.V.—1.31 dL/g (circle), 1.58 dL/g (down triangle), 2.16 dL/g (upper triangle). Previously reported proton conductivity of phosphoric acid doped *meta*-PBI membrane—0.04 S/cm at 190 °C (star)²¹, 6F-PBI membrane— 1.7×10^{-4} S/cm (diamond)²⁷ prepared by the conventional membrane fabrication process.

repeat unit prepared by the conventional process was 0.04 S/cm at 190 °C. The proton conductivities of the phosphoric acid doped 6F-PBI membranes prepared by the PPA process were considerably higher owing to their inherently higher phosphoric acid doping levels (30–40 PA/PBI repeat unit). However, the proton conductivity of resulting 6F-PBI membranes was lower than other PBI membranes (*para*-PBI, ~0.25 S/cm at 160 °C)²⁴ prepared by the PPA process although the phosphoric acid doping level was nearly identical. This indicates a more complex relationship between the proton conductivity and membrane structure than a simple dependence on the phosphoric acid content.²⁵

Fuel Cell Testing

The high temperature fuel cell performance of phosphoric acid doped 6F-PBI membranes was investigated with polarization curves in a single cell fuel cell. Figure 7 shows the polarization curves and power density curves of a fuel cell with phosphoric acid doped 6F-PBI membrane at 160 °C, operated at atmospheric pressure and dry gases without external humidification. At a current density of 0.2 A/cm², a voltage of approximately 0.58 V was obtained with hydrogen and air supplied at 1.2 and 2.0 stoichiometric flows,

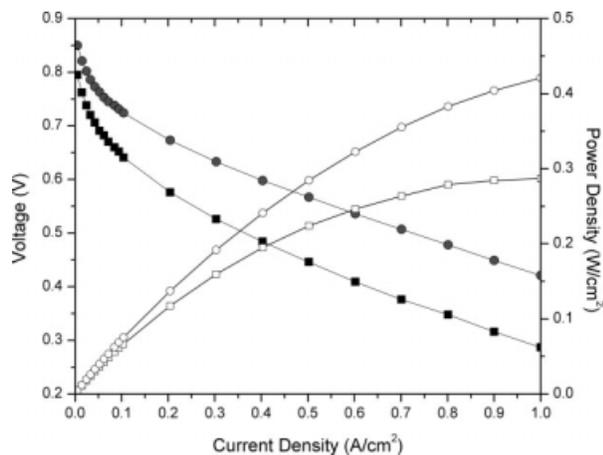


Figure 7. Typical polarization curves (filled symbols) and power density curves (unfilled symbols) of the fuel cell with phosphoric acid doped 6F-PBI membrane at 160 °C, atmospheric pressure, H₂/Air (square) or H₂/O₂ (circle), stoichiometric flows—1.2 and 2.0, respectively.

respectively. When the oxidant gas was changed from air to oxygen, the oxygen partial pressure increased from 0.21 atm to 1 atm and the cell voltage at 0.2 A/cm² increased from 0.58 to 0.67 V. According to the Nernst equation, the theoretical reversible voltage gain obtained by oxygen partial pressure change was calculated and is approximately 15 mV. However, the actual voltage gain at 0.2 A/cm² was approximately 90 mV when the oxidant changed from air to oxygen as shown in Figure 7, which was larger than expected from the calculated reversible voltage gain. This difference demonstrated that an increase in the partial pressure of oxygen results in a significant reduction in polarization at the cathode, most likely due to the phosphate absorption on platinum that is well-documented in the literature for PAFCs (phosphoric acid fuel cells).⁴² The power density was ~0.43 W/cm² at 1 A/cm² for hydrogen/oxygen fuel cell at 160 °C and atmospheric pressure. The fuel cell performance of phosphoric acid doped 6F-PBI membranes was much higher than previous results of phosphoric acid doped *meta*-PBI membranes prepared by the conventional process, whose maximum power density was only 0.25 W/cm² under the same operation conditions.²² However, the fuel cell performance of the phosphoric acid doped 6F-PBI membranes was lower compared to other PBI membranes prepared by the PPA process²⁴ (power density of 0.58 W/cm² under the same operation conditions), which can be attributed to the lower proton conductivity of the

6F-PBI membranes compared to these PBI membranes.

Low temperature PEMFCs with PFSA membranes exhibit a dramatic decrease of performance in the presence of fuel impurities.⁴³ A small amount of carbon monoxide (several ppm) will poison the catalyst and damage the fuel cell. High temperature PEMFCs with phosphoric acid doped PBI membranes are predicted to tolerate CO with high concentrations.⁴⁴ In this work, fuel cells with phosphoric acid doped 6F-PBI membranes were operated using both pure hydrogen (as reference) and reformat gas containing 40.0% hydrogen, 0.2% CO, 19.0% CO₂, and 40.8% N₂. The fuel cells were operated at 160 °C, atmospheric pressure and dry gases without external humidification. The effect of carbon monoxide on the fuel cell performance is shown in Figure 8. When the reformat gas was used as the fuel, there were mainly two effects which can decrease the fuel cell performance—carbon monoxide poisoning of the catalyst and the hydrogen dilution. The hydrogen content in the reformat gas was 40%. Thus, when this reformat gas was used as fuel, the hydrogen partial pressure on the anode side was 0.4 atm. The theoretical voltage change caused by hydrogen dilution was calculated and is ~17 mV. Comparison of the two polarization curves in Figure 8 in the current density range from 0.2 A/cm² to 0.7 A/cm² shows a voltage difference of ~20 mV, so the voltage change caused by CO poisoning effects was ~3 mV. Thus, we can conclude that the CO poisoning effect is a relatively minor effect at

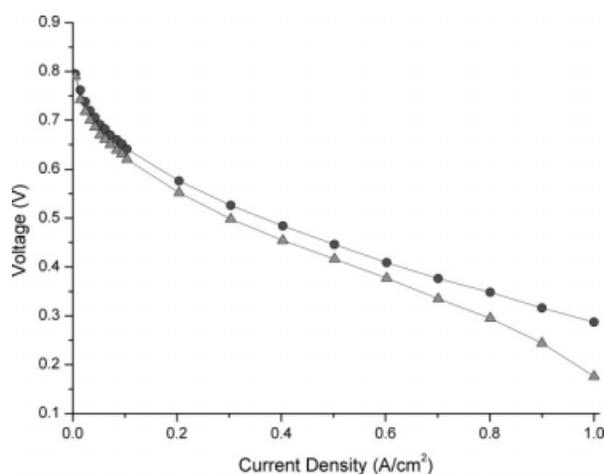


Figure 8. Polarization curves of fuel cells with phosphoric acid doped 6F-PBI membranes. Fuel cell operation conditions: 160 °C, atmospheric pressure, dry gases—hydrogen/air (circle), reformat/air (triangle).

160 °C. The increasing voltage difference between the two polarization curves at high current density $>0.7 \text{ A/cm}^2$ can be attributed to the increasing mass transport limitations.

CONCLUSIONS

A high molecular weight, thermally and chemical stable 6F-PBI was synthesized from 3,3'-diaminobenzidine and 2,2-bis(4-carboxyphenyl)hexafluoropropane in PPA. Investigation of polymerization conditions to achieve high molecular weight polymers was explored via stepwise temperature control, initial monomer concentration in PPA, and final polymerization temperature. The addition of intermediate temperature holding periods into the stepwise temperature control profile alleviated the sublimation of the 6F-diacid monomer during the polymerization. The use of newly developed polymerization conditions (3 wt % monomer concentration in PPA, 220 °C final polymerization temperature and improved stepwise temperature control profile) routinely produced high molecular weight polymer. The resulting 6F-PBI polymer showed excellent thermal stability. Fenton reagent testing on polymer and membrane, both in the presence and absence of phosphoric acid indicated very high resistance of hydroxyl/peroxyl radical attack at low and high temperatures. Phosphoric acid doped 6F-PBI membranes were prepared using the PPA process. These membranes showed high phosphoric acid doping levels and higher proton conductivities than the membranes prepared by the conventional membrane fabrication processes. The fuel cell based on the phosphoric acid doped 6F-PBI membrane showed 0.58 V at 0.2 A/cm^2 for hydrogen/air at 160 °C, operated at atmospheric pressure and dry gases. The CO tolerance test showed that at an operation temperature of 160 °C, the presence of CO at 0.2% had a relatively minor effect on the fuel cell performance.

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