High-Temperature Polybenzimidazole Fuel Cell Membranes via a Sol−Gel Process

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A sol−gel process is described to produce phosphoric acid (PA)-doped polybenzimidazole (PBI) films that operate as fuel cell membranes above 150 °C for extended periods of time without the need for feed gas humidification. When solutions of high molecular weight heterocylic polymers such as polybenzimidazoles in polyphosphoric acid (PPA) were cast into films, a transition from solution state to gel state was observed during the hydrolysis of the solvent from PPA (a good solvent for PBI) to PA (a poor solvent for PBI). The resulting membranes retained high levels of phosphoric acid in the gel structure and exhibited high ionic conductivities and stable mechanical properties at elevated temperatures. Preliminary fuel cell tests have demonstrated the feasibility of such PBI membranes from the sol−gel process for operating a fuel cell at temperatures above 150 °C without any feed gas humidification or pressure requirements for more than 1000 h.

Introduction

Fuel cells based on solid polymer electrolytes have attracted much recent attention due to their promise as energy conversion devices for both mobile and stationary applications.[1] In particular, high-temperature polymer electrolyte fuel cell membranes operational above 120 °C without humidification offer many benefits including increased resistance to fuel impurities, most notably carbon monoxide (CO), fast electrode kinetics, and simplified water/thermal management.[2] For automotive applications, membranes operable at temperatures of approximately 120 °C with long-term stability would offer the largest system efficiency enhancement and reduce the radiator size by 50%. For stationary applications, operation at temperatures above 150 °C would dramatically simplify the system design by eliminating some fuel processor cleanup components owing to the substantially enhanced CO tolerance at elevated temperatures. However, state-of-the-art polymer electrolyte membranes such as the sulfonated fluoropolymers rely on the presence of water to solvate and transport the protons and therefore operate in a limited temperature range and encounter water management problems.

Great efforts have been dedicated to develop high-temperature fuel cell membranes for operation at temperatures above 100 °C. A variety of approaches have been attempted such as the attachment of sulfonic acid groups to highly stable aromatic polymers, the incorporation of hydrophilic, inorganic fillers into the ionomer membranes, and the complexation of some low vapor pressure proton conductors such as phosphoric acid (PA) or imidazole with various polymer matrixes.[3,4] Among various types of alternative high-temperature polymer electrolyte membranes developed so far, PA-doped polybenzimidazole (PBI) was reported as a promising candidate for a low-cost and high-performance fuel cell membrane material.[5] It was shown that this polymer electrolyte membrane exhibited high ionic conductivity at temperatures up to 200 °C, low gas permeability, excellent oxidative and thermal stability, and nearly zero water drag coefficient.[5−7] The conventional PA-doped PBI membranes were prepared by either imbibing the PBI membranes cast from dimethyl acetamide (DMAc) organic solvent with PA or casting directly from a solution of PBI dissolved in a mixed acid solvent such as trifluroraoacetic acid (TFA) and PA.[5−7] Another preparation approach is to introduce porosity into the PBI by leaching out a low molecular weight compound using a selective solvent for the porogen followed by soaking the film in concentrated PA.[8] However, the PA-doped PBI membranes from these methods all suffered from inferior mechanical properties at high PA-doping levels. The highly PA-doped membranes could not be tested in fuel cells and also required a tedious multistep membrane fabrication process.

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Polyphosphoric acid (PPA) has been widely used as an efficient condensation reagent for the synthesis of high molecular weight (as indicated by inherent viscosity, I.V.) PBI polymers in good yields.[9,10] Furthermore, PPA is extremely hygroscopic and will hydrolyze to PA upon absorption of moisture.[11] Hence, PPA is a promising precursor to the PA electrolyte and may serve as a solvent for the direct casting of the polymerization solution without isolation and redissolution of the PBI polymers. Although the synthesis of PBIs in PPA and aspects of the acid-doped PBI membranes for fuel cell applications have been investigated previously, no successful attempts have been made to employ PPA as both polymerization medium and film casting solvent.

Among a variety of PBI structures, only limited types of PBIs, which included primarily the commercially available PBI from the melt/solid-state polymerization process, sulfonated or phosphorylated PBI, as well as the poly(2,5-benzimidazole) (i.e., AB−PBI), have been explored for fuel cell applications.[12] No synthetic effort has been employed to systematically synthesize PBIs of different structures and study the effect of the PBI polymer molecular structure on the final film properties.

In the present study, polymerization to produce PBI polymers was carried out using PPA as both the polycondensation agent and the polymerization solvent starting from tetraaminobiphenyl (TAB) and the dicarboxylic acids (diacids). After polymerization, the PBI solution in PPA was directly cast at approximately 200 to 220 °C without isolation or redissolution of the polymers. Upon casting, hydrolysis of the PPA to PA induced a sol−gel transition that produced membranes with a desirable suite of physicochemical properties. Our work has been focused on understanding the effects of the polymer chemical structure and process variables on the stability of the gel phase envelope and properties of the resulting gels. It has been demonstrated that such membranes possess high mechanical properties at high PA-doping levels and excellent long-term stability when operating at temperatures above 150 °C. These membranes were fabricated into membrane electrode assemblies and tested in operating fuel cells under a variety of conditions.

Experimental Section

Materials and PBI Synthesis. Isophthalic acid and terephthalic acid were purchased from Amoco (99+% pure) and dried prior to use. 3,3′,4,4′-Tetraaminobiphenyl (TAB, polymer grade) was donated by Celanese Ventures, GmbH and used as received. Polyphosphoric acid (115%) was used as supplied from Aldrich Chemical Co. and FMC Corporation. The general procedure for the synthesis of polybenzimidazoles (PBIs) is described as follows: Isophthalic acid (12.460 g, 75 mmol) and TAB (16.074 g, 75 mmol) were added to a three-neck resin reaction flask in a nitrogen atmosphere glovebox, followed by 200 to 600 g of polyphosphoric acid. The reaction mixture was stirred using a mechanical overhead stirrer 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 polymerization temperatures were approximately 190−220 °C for 16 to 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 isolated as a brown mass. The mass was pulverized, neutralized with ammonium hydroxide, washed thoroughly with water, and dried in a vacuum oven for 24 h at 100 °C to obtain the PBIs for further characterization. I.V.'s of the polymer samples were measured at a polymer concentration of 0.2 g/dL in concentrated sulfuric acid (96%) at 30 °C, using a Cannon Ubbelohde viscometer. The I.V. values for the resulting PBIs polymers ranged from 1.3 to 2.0 dL/g for *meta*-PBI and 1.5 to 3.0 dL/g for *para*-PBI.

Membrane Preparation. The membranes were prepared by casting the polymerization solution directly onto untreated glass substrates in air using a film applicator with a gate thickness ranging from 0.127 mm (5 mils) to 0.635 mm (25 mils) and allowed to cool from polymerization temperature (190 to 220 °C) to room temperature in a few minutes. Hydrolysis was allowed to proceed under controlled conditions (for example, by exposing films for 24 h at 25 °C and a relative humidity of 40 ± 5%). Since both PBI polymer and polyphosphoric acid are extremely hygroscopic, moisture was absorbed from the atmosphere and hydrolyzed the polyphosphoric acid solvent to phosphoric acid. Some drain-off of water and phosphoric acid was then observed during the hydrolysis process which caused a shrinkage of membrane dimensions of 10 to 20%. The amount of water absorbed did not correlate directly with the membrane PA-doping level.

Characterization Methods. The phosphorus nuclear magnetic resonance spectra (^{31}P NMR) were recorded on a Chemagnetics CMX-360 instrument operating at a frequency of 145.71 MHz using 85% PA as external reference. Polymer films were cast onto thin glass strips and assembled into an open-ended glass NMR tube with 7.0 mm diameter. The film strips were then hydrolyzed in an environmental chamber and taken out periodically for ^{31}P NMR measurements. Dynamic mechanical analysis (DMA) was carried out on a Mettler Toledo Tritec 2000 instrument with a frequency range of 0.1−100 Hz at 25 °C. The membrane acid-doping levels were determined by titrating a preweighed piece of membrane sample with standardized sodium hydroxide solution with a Metrohm 716 DMS Titrino titrator. The samples were then washed with water and dried in a vacuum oven at 100 °C for 4 h to obtain the dry weight of polymer. The acid-doping levels, X, expressed as moles of phosphoric acid per mole of PBI repeat unit ($XH_3PO_4 \cdot PBI$) were calculated from the equation:

$$\text{acid-doping level } X = (V_{\mathrm{NaOH}}\, C_{\mathrm{NaOH}})/(W_{\mathrm{dry}}/M_{\mathrm{w}})$$

where V_{NaOH} and C_{NaOH} are the volume and the molar concentration of the sodium hydroxide titer, while W_{dry} is the dry polymer weight and M_{w} is the molecular weight of the polymer repeat unit, respectively. The composition of phosphoric acid can be determined by the acid-to-water ratio according to the equation:

$$\text{acid concentration } C_{\mathrm{acid}}\% = ((W_{\mathrm{acid}})/(W_{\mathrm{acid}} + W_{\mathrm{H_2}}\mathrm{O})) \times 100$$

Thus, most reagent grade phosphoric acid is 85% phosphoric acid and 15% water. By definition, PPAs are a continuous series of mixtures of condensed phosphoric acid oligomers of the general formula $HO[P(O)(OH)]_nH$. Most commercially available polyphosphoric acid is approximately 115% concentration and contains mostly oligomers where $n = 2-10$.

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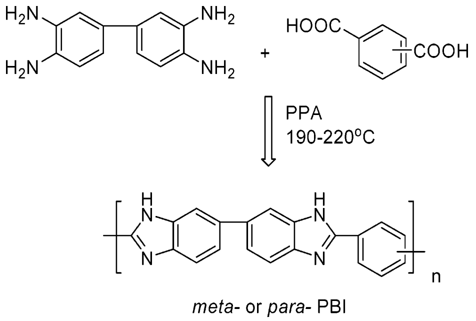
Scheme 1. Synthesis of PBI Polymers in PPA



The membrane mechanical properties were tested utilizing a United tensile tester (SSTM-1-PC) with a 22.2 N load cell. Dumbbell specimens were cut following the ASTM standard D683 (Type V specimens). Tensile properties of all film samples were measured in an air atmosphere at room temperature with a cross head speed of 5 mm per min.

Ionic conductivities were measured by a four-probe ac impedance method using a Zahner IM6e spectrometer over a frequency range from 1 Hz to 100 kHz. A rectangular piece of membrane (3.5 cm × 7.0 cm) and four platinum wire current collectors were set in a glass cell. Two outer electrodes 6.0 cm apart supply current to the cell, while the two inner electrodes 2.0 cm apart on opposite sides of the membrane measure the potential drop. The four-probe technique offers many advantages over the two-probe techniques, including measuring the bulk property of the membrane instead of the surface property and minimizing the error stemming from contact resistance and electrode resistance. The cell was placed in a programmable oven to measure the temperature dependence of the proton conductivity. The membranes were dried by first heating from room temperature to 200 °C and holding at 200 °C for 1 h. The membrane samples were then cooled in a vacuum oven and taken out just before conductivity measurement in an effort to keep the samples dry. The conductivities of the membrane samples were measured from 20 to 160 °C at intervals of 20 °C. Before the measurements at each temperature set point, the samples were held at constant temperature for at least 10 min. Repeated conductivity measurements showed that reproducible results were obtained using this temperature profile and testing procedure. A two-component model with an ohmic resistance in parallel with a capacitor was employed to fit the experimental curve of the membrane resistance across the frequency range (the Nyquist plot). The conductivities of the membrane at different temperatures were calculated from the membrane resistance obtained from the ohmic resistance of the model simulation. Proton conductivity was then calculated from the following equation:

$$\sigma = D/(LBR)$$

where D is the distance between the two current electrodes 2.0 cm apart, L and B are the thickness and width, respectively, and R is the resistance value measured.

Membrane Electrode Assembly (MEA) Fabrication and Fuel Cell Testing Conditions. The 30% Pt/C fuel cell gas diffusion electrodes acquired from E-Tek, Inc. with a Pt loading of 1.0 mg/cm^2 were used for this study. The membrane thickness was approximately 250 micrometers with a PA loading of approximately 35 mol of PA per PBI repeat unit. The MEA was fabricated by hot-pressing an electrode/membrane/electrode sandwich at 140 °C for 30 s using a manual Carver press. The MEA with an active area of approximately 44 cm^2 was then assembled into a single fuel cell testing fixture made of graphite plates with gas channels. Stainless steel end plates with attached heaters were then used to clamp the graphite flow plates. A commercial fuel cell testing station (Fuel Cell Technologies, Inc.) equipped with mass flow controllers was used for fuel cell testing, while stoichiometric gases were fed to the anode and cathode at a stoic of 1.2 and 2.5, respectively, without any feed gas humidification. All performance data were collected under atmospheric pressure with no back pressure detected. The current−voltage characteristics were recorded using a HP6050 dc electronic load, interfaced with a PC using LabView Software (National Instruments, Austin, TX).

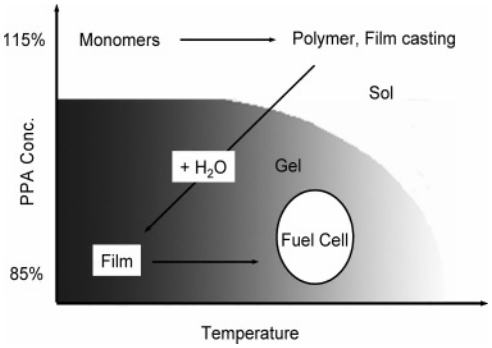


Figure 1. State diagram of the PPA sol−gel process.

Results and Discussion

As shown in Scheme 1, PBI polymers were synthesized using PPA as both the polycondensation agent and the polymerization solvent starting from tetraaminobiphenyl (TAB) and the dicarboxylic acids (diacids). The I.V. values for the resulting PBI polymers were measured in 96% sulfuric acid at 30 °C and ranged from 1.3 to 2.0 dL/g for *meta*-PBI and 1.5 to 3.0 dL/g for *para*-PBI, thus demonstrating that PPA readily serves as an efficient polycondensation agent and facilitates the synthesis of high-I.V. PBI polymers from the corresponding diacid and tetraamine monomers.

After polymerization, the PBI solution in PPA was directly cast at approximately 200 to 220 °C without isolation or redissolution of the polymers. Since both PPA and PBI polymer were hygroscopic, moisture was absorbed from the atmosphere and hydrolyzed the PPA to form PA in situ. The solution temperature also dropped from the casting temperature of approximately 200 to 220 °C to room temperature. The hydrolysis of the solvent from PPA (a good solvent for PBI) to PA (a poor solvent for PBI) combined with the temperature drop induced a transition from the solution state to the gel state that produced PBI membranes doped with PA in one step. The gels produced by such noncrosslinked transitions have been traditionally described as Flory Type III physical gels.[13,14] We identified the sol−gel transition by the formation of a stress-bearing, interconnected network, which resulted in a low-frequency plateau of the elastic modulus (Figure S1 in the Supporting Information).[15] The overall process is represented schematically in Figure 1. Our work has been focused on understanding the effects of the polymer chemical structure and process variables on the

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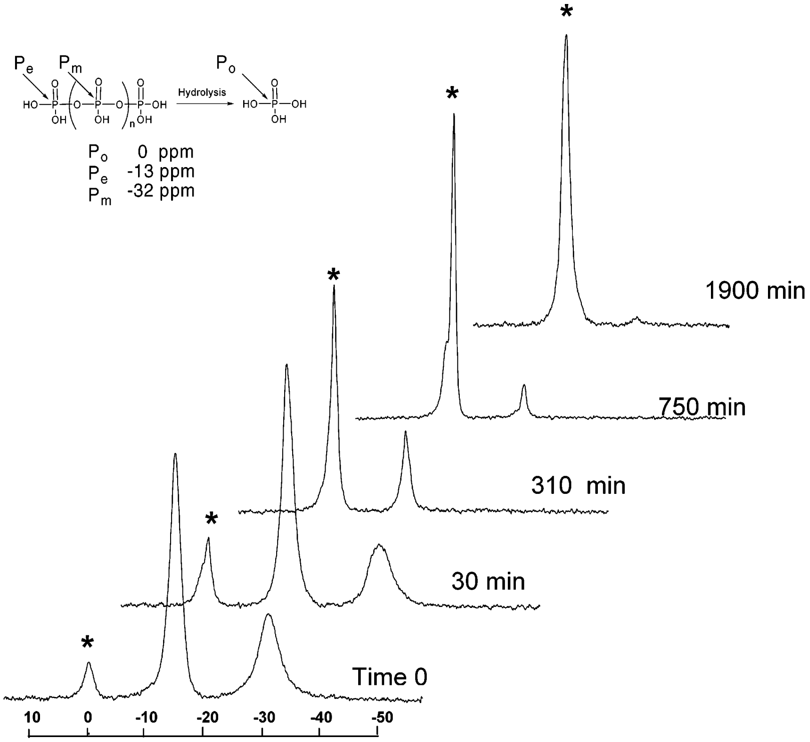

Figure 2. ^{31}P NMR spectra of cast films during the hydrolysis of PPA into PA. The 0 ppm phosphorus peak is marked ∗ for reference.

stability of the gel phase envelope and properties of the resulting gels. We have found in our continuing work that many aromatic heterocyclic polymers form gels by this process and remain stable when heated to 200 °C.

^{31}P NMR spectroscopy can distinguish the various phosphorus species in the PBI film and assist in monitoring the evolution of the phosphorus species during the hydrolysis process, as shown in Figure 2. The ^{31}P NMR spectra of the PA-doped PBI membranes at different stages of the hydrolysis process consisted of three major peaks at $\delta \approx 0$, -13, and -32 ppm, which corresponded to the phosphorus atoms at the end (P_e) and middle of the molecular chain (P_m) and to *ortho*-phosphoric acid (P_o), which is the final product of the hydrolysis reaction. The spectral components in the observed spectra are assigned to the specific phosphorus species based on the known ^{31}P chemical shift values characteristic of PA and its oligomers.[11] The increase or decrease of the intensity of the specific phosphorus NMR signals was followed as the hydrolysis proceeded. An example of the ^{31}P NMR spectra as a function of time is shown in Figure 2, for typical hydrolysis conditions of 25 °C and 25% relative humidity (RH). The relative amount of the three phosphorus species under different hydrolysis conditions was determined by integrating and normalizing the individual P_o, P_e, and P_m peaks (Figure S2 in the Supporting Information). At time 0, the PPA polymerization solution was cast onto substrates at approximately 200 °C. Initially, the PPA concentration ranged from 110% to 115% assuming the polycondensation byproduct (water) was consumed by the PPA during the polymerization. For the ^{31}P NMR spectrum at time 0, three peaks at P_o, P_e, and P_m were observed and were comparable to those in the pure PPA spectrum of similar concentration. As shown in Figure 2, the P_m peak disappeared at approximately 310 min while the P_e peak decreased gradually over approximately 1900 min. As expected, only the *ortho*-phosphoric acid species was present as the final hydrolysis product.

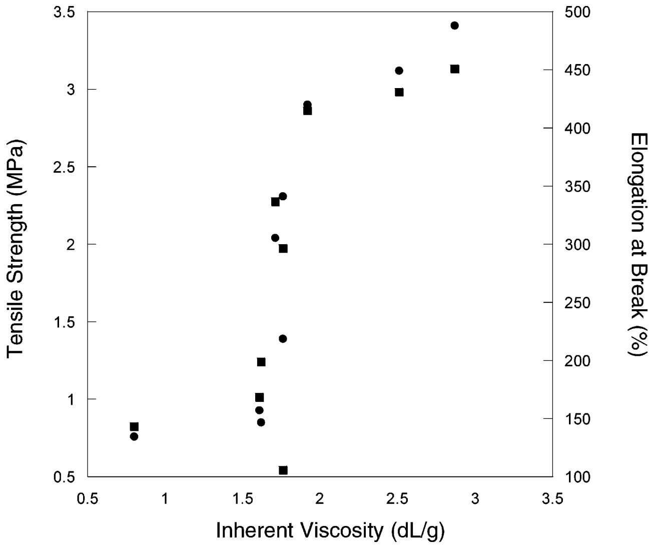

Figure 3. Tensile strength (circles) and elongation at break (squares) as a function of polymer I.V. for *para*-PBI. I.V.'s of the polymer samples were measured at a polymer concentration of 0.2 g/dL in concentrated sulfuric acid (96%) at 30 °C, using a Cannon Ubbelohde viscometer.

The PA-doping level of the membranes is defined as the molar ratio of the PA per PBI repeat unit. For a typical PBI membrane from the sol−gel process, the PA-doping level of the membrane averaged 20 to 40 mol of PA per mole of PBI repeat unit, considerably higher than that of any PA-doped PBI membranes reported previously. Furthermore, one of the major dilemmas for the PA-doped PBI membranes from the conventional imbibing method was the tradeoff between the desired properties of the membrane, such as high doping levels and high proton conductivity, with high

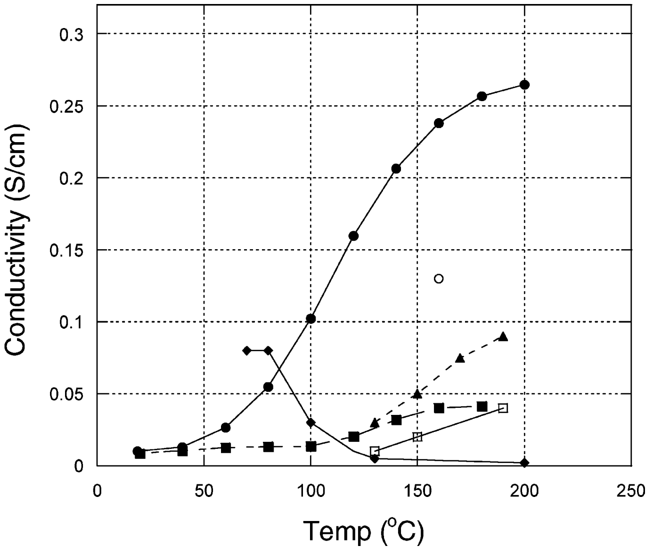

Figure 4. Conductivities of PA-doped PBI membranes from different processes: membranes made from the sol−gel process (circles, this work), conventional imbibing process (squares, this work), conventional imbibing process (unfilled circle[17]), imbibing from trifluoroacetic acid/PA solvent (triangles[19]), conventional imbibing process (unfilled squares[19]), and sulfonated fluoropolymer (diamonds[19]).

mechanical properties. Higher PA loading levels usually led to highly conductive membranes but also to poor mechanical properties.[16] Li et al. reported one of the highest PA-doping levels of 13−16 mol of PA per PBI repeat using the commercially available PBI with an I.V. of 1.0 dL/g.[17] Mechanical strength measurements showed, however, that such membranes with high PA-loading levels resulted in poor mechanical properties and were too weak to fabricate into membrane electrode assemblies (MEAs).

In contrast, the mechanical properties of PA-doped PBI membranes with high PA doping made from the sol−gel process were remarkably high with the average tensile strength and the elongation at break of about 1.0 to 3.5 MPa and 150% to 390%, respectively. Moreover, the membrane tensile strength and elongation at break were found to be critically dependent on molecular weight, as measured by the inherent viscosity (I.V.) of the PBI polymer, as illustrated in Figure 3. The data confirmed that PBIs with higher molecular weight from the PPA process contribute to high mechanical properties at high phosphoric acid-doping levels. Higher I.V.'s appeared to stabilize the gel state and produced membranes with mechanical properties suitable for MEA fabrication.

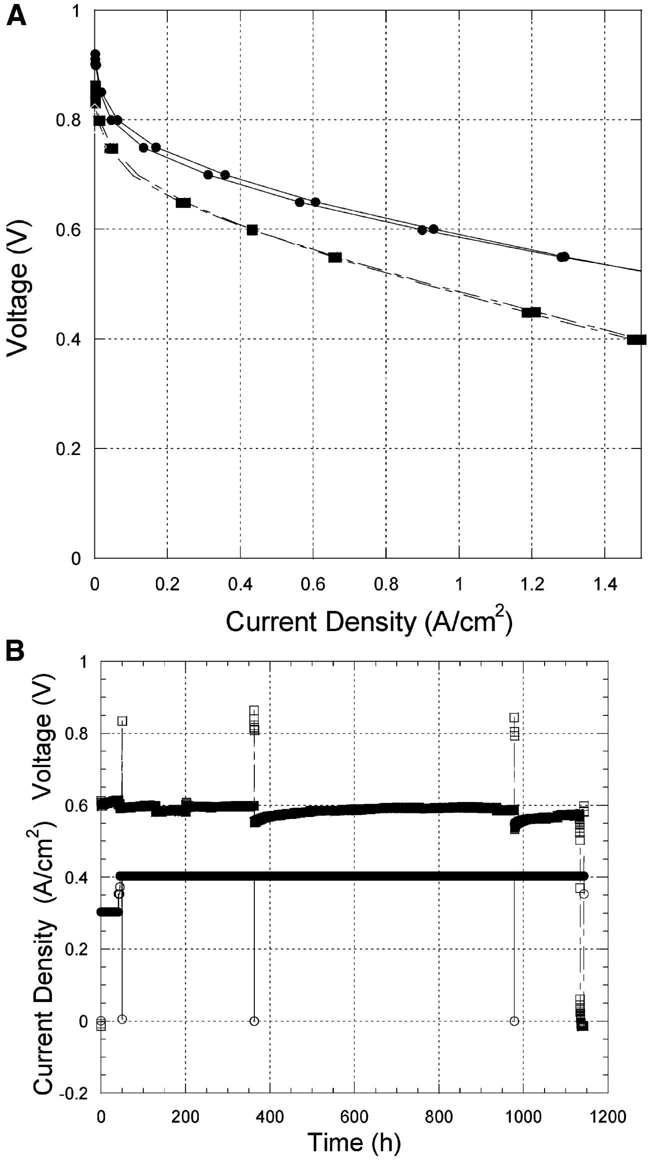

Figure 5. Fuel cell performance for the PBI membranes from the sol−gel process. (A) Performance curves of fuel cells under H_2/air (squares) and H_2/O_2 (circles), without any feed gas humidification. The membrane PA-doping level was approximately 32 mol of PA per mole PBI repeat unit. The catalyst loading in both electrodes was 1.0 mg/cm² Pt, and the cell was operated at 160 °C at constant stoichiometry of 1.2 stoic and 2.5 stoic at the anode and the cathode, respectively. (B) Long-term cell voltage (squares, upper curve) as a function of time, while drawing 400 mA/cm² of current (circles, lower curve) for >1000 h without feed gas humidification.

A key feature of a fuel cell membrane is its proton conductivity. It was reported that the proton conductivity of the PA-doped PBI membrane is greatly influenced by the presence of water and mildly dependent on the environmental humidity.[18] Operation of polymer membrane fuel cells at temperatures higher than 120 °C without any external humidification is highly desired since fuel cell systems operating at higher temperature will be simplified dramatically. Thus, our characterization efforts of the membrane proton conductivities were focused on the anhydrous condition with temperatures ranging from room temperature to 200 °C. Since PBI polymers are hygroscopic by nature due to the intermolecular hydrogen bonding between the N−H groups along the PBI backbone and water, the membranes were dried by first heating from room temperature to 200 °C and holding at 200 °C for 1 h. The membrane samples were then cooled in a vacuum oven and taken out just before testing in an effort to keep the samples dry. The proton conductivities for the PBI polymer electrolyte membranes were measured as a function of temperature, as reported in Figure 4 for a typical PA-doped PBI membrane made by the sol−gel process with approximately 32 mol of PA per PBI repeat unit. The figure also includes literature data for PBI membranes cast from organic solvents and subsequently

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imbibed with PA, as well as our own data for PBI membranes cast from DMAc and imbibed with PA.[19]

The measured conductivity at room temperature was 0.01 S/cm and reached as high as 0.26 S/cm at 200 °C. Previously reported conductivity values for the PA-doped PBI membranes ranged from 0.04 S/cm at 190 °C for a membrane with 6.0 mol PA/PBI to 0.13 S/cm at around 160 °C for a mechanically weak membrane with 13−16 mol PA/PBI.[17,20] The proton conductivities of the PA-doped PBI membranes from the PPA sol−gel process were considerably higher than those reported previously for the PA-doped PBI membranes prepared via the conventional imbibing method owing to their inherently high acid-doping levels. Simultaneously, these highly conductive PBI membranes were mechanically strong at high acid-doping levels and therefore amenable for MEA fabrication.

Preliminary fuel cell performance evaluations were performed at high temperatures without external humidification of the gases supplied to either electrode, as shown in Figure 5. The MEA active area was 44 cm^2, and noble metal (Pt) catalyst loading in both electrodes was 1.0 mg/cm^2. At a current density of 0.2 A/cm^2, a voltage of approximately 0.65 V was obtained at 160 °C. When the oxidant gas changed from air to oxygen, the voltage at 0.2 A/cm^2 increased to 0.75 V as a result of the increased oxygen partial pressure. The highest power output at ambient pressure was approximately 0.9 W/cm^2 at 2.5 A/cm^2, and mass transport limitations were not observed even at the high current density region at temperatures of 140 and 160 °C. Overall, the fuel cell performance of the sol−gel membranes with high PA content was much higher than previous results on imbibed membranes.

A long-term MEA performance stability test was performed on a typical PBI gel membrane operating at 160 °C without any humidification of either H_2 or air. Current was drawn continuously at 0.4 A/cm^2 for approximately 1200 h using stoichiometric gas flows of 1.2 stoic and 2.5 stoic for H_2 and air, respectively. Diagnostic polarization curves were collected periodically which showed as transient discontinuities on the long-term stability curve. The voltage remained nearly constant throughout the long-term testing with an average of 0.6 V at 0.4A/cm^2, and the polarization curves obtained during the long-term testing (Figure 5B) were indistinguishable. At 160 °C, the highest power output at ambient pressure reached approximately 0.8 W/cm^2 at a current density of 1.4 A/cm^2.

Conclusions

A sol−gel process has been developed to produce PA-doped PBI films that operate as high-temperature fuel cell membranes. PPA has been employed as both the polycondensation reagent to prepare high molecular weight PBI polymers and the casting solvent for film preparation in one step. Upon film casting, a transition from solution state to gel state was induced by the hydrolysis of PPA to PA combined with the temperature drop from polymerization temperature (190 to 220 °C) to room temperature (20 °C). The resulting films retained high levels of phosphoric acid in the gel structure and exhibited high ionic conductivities and stable mechanical properties at elevated temperatures. Preliminary fuel cell tests have demonstrated the feasibility of such PBI membranes from the sol−gel process for operating a fuel cell at temperatures in excess of 150 °C without any external humidification or pressure requirements for extended periods of time (>1000 h).

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Supporting Information Available: Figure S1, storage (circles) and loss (squares) moduli of the sol−gel membranes at low-frequency range; Figure S2, the normalized ^{31}P NMR peak intensities as a function of time during hydrolysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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