High-temperature fuel cell membranes based on mechanically stable *para*-ordered polybenzimidazole prepared by direct casting

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Abstract

Poly[2,2′-(*p*-phenylene)-5,5′-bibenzimidazole] (pPBI) is synthesized by mixing 3,3′-diaminobenzidine tetrahydrochloride and terephthalic acid in polyphosphoric acid (PPA) at 240 °C for 12 h. pPBI can be cast in membrane form directly from a polymerization solution (direct casting) or from a methanesulfonic acid solution (MSA casting). Membranes obtained by direct casting are almost amorphous and have much higher acid doping levels and larger water uptake values than those prepared by MSA casting. As a result, the pPBI membrane from direct casting has a high proton conductivity of 0.15 S cm^{-1} (at 180 °C and 1% relative humidity) at an acid doping level of 8.78 mol H_3PO_4 per mole of polymer repeat unit. Moreover, this membrane has good mechanical stability (tensile strength of 57 MPa at 22 °C and 24% relative humidity) even at this high doping level.
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Keywords: Fuel-cell membrane; Poly[2,2′-(*p*-phenylene)-5,5′-bibenzimidazole]; Direct casting method; Proton conductivity; Mechanical stability

1. Introduction

High-temperature polymer electrolyte membrane fuel cells (PEMFCs) that are operational above 100 °C without humidification offer many advantages including anode tolerance to significant quantities of CO, performance relatively independent of humidity, fast cathode kinetics, elimination of cathode flooding, and simplified thermal management [1–3]. Therefore, much effort has been devoted to the development of high-temperature polymer electrolyte membranes, that can preserve proton conductivity above 100 °C. Among the various approaches developed to date, acid-doped polybenzimidazoles (PBIs) have emerged as promising materials because of their high proton conductivity in low humidity and the fuel cell performance at high temperatures. The most commonly reported PBI used as a proton exchange membrane is based on poly[2,2′-(*m*-phenylene)-5,5′-bibenzimidazole] (mPBI), which was first introduced by Savinell and co-workers [4]. Numerous studies have been performed on acid-doped mPBI membranes concern-

ing its proton conductivity [4–8], thermal stability [9], water drag coefficient [10,11], methanol crossover [11], and fuel cell tests [6,10]. The proton conductivity of mPBI membranes increased when the acid doping level increased, while the mechanical strength of the membranes decreased significantly at the same time [10,12]. Therefore, a doping level of around 5 (5 mol of H_3PO_4 per mole of polymer repeat unit) is reported to be the maximum to maintain reasonable mechanical strength of mPBI membranes for PEMFC applications. Lifetime tests of mPBI-based fuel cells showed that mechanical degradation of the membranes under operational conditions is one of the major reasons for the performance degradation of phosphoric acid-doped mPBI fuel cells [13,14].

Poly[2,2′-(*p*-phenylene)-5,5′-bibenzimidazole] (pPBI) was first synthesized in the 1960s [15,16]. The wholly *para*-structured pPBI exhibits superior mechanical properties, including a high degree of tensile strength and unusually high stiffness, compared with the *meta*-structured mPBI [17,18]. Thus, pPBI might sustain its mechanical strength with a higher acid doping level. However, there have been no such studies or reports on pPBI membranes to the best of our knowledge; Xiao et al. [17,19] briefly mentioned the possible application of pPBI for fuel cell membranes. This lack of apparent interest in pPBI

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may be due to its low processability caused by poor solubility, since pPBI is only soluble in strong acids such as sulfuric acid and methanesulfonic acid (MSA).

PBI films for fuel cell applications have generally been fabricated by solution-casting methods using solvents such as DMAc, TFA, or MSA [10,20,21]. In the solution-casting method, PBI powder is first obtained from the polymerization solution through precipitation and purification processes, and then redissolved in solvent to prepare the casting solution. Recently, Xiao et al. [17] developed a sol-gel process, in which PPA polymerization solution was directly cast on a glass plate and acid doping was achieved through hydrolysis of PPA to phosphoric acid during the casting process. They obtained PBI membranes that had very high acid doping levels of 20–40 (20–40 mol of phosphoric acid per mol of PBI repeat unit) and good mechanical properties at high temperatures. We believe that the doping level of membranes in this process depends highly on the hydrolysis conditions such as humidity, temperature and reaction time. In this study, we prepare acid-doped pPBI membranes using a polyphosphoric acid (PPA) direct-casting method developed by our group and then compared their properties with those of mPBI. By this method, we can eliminate the extra isolation, purification and redissolution procedures needed in the traditional solution-casting process. It is found that pPBI thus prepared has an inherent viscosity as high as 3.22 dL g^{-1} and that the pPBI membrane can maintain its mechanical strength at an acid doping level greater than 5. The effects of casting process variables on membrane properties are also examined.

2. Experimental

2.1. Materials

Isophthalic acid (99%) was purchased from Aldrich and purified by recrystallization in ethanol to obtain white needle-like products. 3,3′-Diaminobenzidine tetrahydrochloride dihydrate (DABIT) was prepared by adding 3,3′-diaminobenzidine (97%, Tokyo Kasei TCI) to hydrochloric acid solution and recrystallized from water and hydrochloric acid as brown needles. Terephthalic acid (99%, Aldrich), phosphorous pentoxide (97%, Aldrich), polyphosphoric acid (116% H_3PO_4, Junsei), phosphoric acid (85 wt.% solution, Aldrich) and other solvents were used as received. All the monomers were dried under vacuum at 60 °C for 2 days before use.

2.2. PBI synthesis

mPBI and pPBI were synthesized by condensation polymerization of DABIT with isophthalic acid and terephthalic acid, respectively, with a molar ratio of 1:1 in polyphosphoric acid (PPA). The general procedure for the synthesis of PBIs is as follows. A 250 mL three-neck reactor equipped with a mechanical stirrer, a nitrogen inlet and a calcium chloride drying tube was charged with PPA, and then heated to 150 °C. Purified DABIT (5.139 g, 12.97 mmol) was added gradually to this reactor, and then the solution was stirred for 4 h at 150 °C to remove hydro-

gen chloride from the DABIT under a slow stream of nitrogen. 12.97 mmol (2.155 g) of terephthalic acid (or 2.155 g of isophthalic acid) was added to this solution. This mixture was heated to 240 °C then stirred for 30 min. 51.11 mmol (7.254 g) of phosphorous pentoxide was added and heating was continued at 240 °C for 12 h. PPA (187 and 67 g) were used for the preparation of 2 wt.% pPBI and 5 wt.% of mPBI solutions, respectively. These polymer concentrations were calculated by a comparison of the estimated amounts of the resulting polymers (generated from the condensation reaction of monomers) and PPA solution (initial PPA amount and the amount of phosphorous pentoxide and water eliminated during the polymerization). More PPA was used for the preparation of pPBI due to the poor solubility of terephthalic acid and pPBI in PPA [22]. When PPA (87 g) was employed to prepare 4 wt.% of polymer concentration, the resulting polymer precipitated during the polymerization process [19]. A portion of the hot polymerization solution was used to prepare direct-cast membranes; the detailed procedures are described below. The rest of the polymerization solution was poured into distilled water (800 mL) and the precipitate was washed several times with distilled water to remove PPA. The polymer was powdered by a pulverizer (A11 basic, IKA) and any remaining phosphoric acid in the polymer powder was further removed by extraction with distilled water in a Soxhlet extractor. Finally, the powder product was dried at 70 °C under vacuum for 3 days.

2.3. Film fabrication

The PBI films were prepared by a solution-casting method and a direct-casting method. In the former method, pPBI films were fabricated using MSA as a casting solvent, while mPBI films were produced using both MSA and DMAc with 2 wt.% of LiCl. The typical procedure of the solution-casting method using MSA for the fabrication of pPBI and mPBI films is described as follows. 0.6 g of pPBI (or mPBI) powder was dissolved in 15 g of MSA at 80 °C, then the solution was cast on to a clean flat glass surface and the solvent was evaporated slowly at 140 °C for 12 h under a ventilated hood. After cooling to room temperature, the resulting brown coloured film was soaked in distilled water and peeled off from the substrate. The film was boiled in distilled water for 24 h to remove traces of the solvent and then dried at 70 °C under vacuum for 3 days. The thickness of mPBI and pPBI films prepared by solution-casting was in a range from 40 to 80 μm in the dry state.

pPBI films were prepared using a direct-casting method by casting the hot polymerization solution directly on to a stainless-steel plate or a glass substrate in air and flattening the solution evenly using a film applicator at 100 °C and then quenching it to −20 °C immediately. The obtained film was immersed in a water bath to remove the acid and dried at room temperature under vacuum for 48 h. It was found that these quenching and washing procedures prohibit the formation of pPBI crystals and make the film hazy. Transparent amorphous pPBI films were obtained. Each film was detached from the substrate and treated with boiling water to remove the residual acid. Finally, the pPBI films were dried at 70 °C under vacuum condition. The thickness

and size of the films was varied by controlling the volume and concentration of the solution. In the present work, the thickness of pPBI films was in a range from 40 to 80 μm in the dry state.

2.4. Acid doping and water uptake

The PBI films were cut into 1 cm × 5 cm portions and dried at 70 °C under vacuum for 2 days. The films were doped by immersion in phosphoric acid solutions of different concentration at 30 °C for 5 days. The weight gain due to both water and phosphoric acid was obtained by comparing the weight change before and after the doping process. In order to obtain the acid doping levels and water uptake values, these samples were dried at 70 °C under vacuum for 2 days. The water content in the doped membranes was obtained by measuring the weight loss, and then the doping levels of the membranes were determined by comparing the weight changes before and after doping. The acid doping level was quantified by the number equal to the number of absorbed H_3PO_4 molecules per repeat unit of PBI.

2.5. Analysis

Inherent viscosities were measured by means of an Ubbelode viscometer in a water bath at 30 °C. 0.125 g of a polymer dried under vacuum at 70 °C for 2 days was placed in a 25 mL volumetric flask and dissolved in 96% H_2SO_4 (concentration 0.5 g dL^{-1}). Fourier transform infrared spectroscopy (FT-IR) spectra were collected between wave numbers that ranged from 4000 to 400 cm^{-1} with a Perkin-Elmer Spectrum 2000 Fourier transform infrared spectrometer using films about 10 μm thick. All samples were measured at room temperature after being dried at 70 °C under vacuum for 24 h. UV–vis spectra were measured with an Agilent 8453 E spectrometer in MSA. The X-ray patterns of powders and films were collected via wide-angle X-ray scattering (WAXS) with a general area detector diffraction system (GADDS) ($\lambda = 1.5406$ Å, Cu Kα) at 2θ between 0° and 40°. TGA analyses were performed on a TA instruments Thermogravimetric Analyzer 2050. Measurements were carried out over a temperature range from 50 to 990 °C at a heating rate of 10 °C min^{-1} under nitrogen atmosphere.

The mechanical properties of the membranes were measured utilizing a universal testing machine (Lloyd LR-10K). Dumbbell specimens were prepared using the ASTM standard D638 (Type V specimens). The tensile properties of film samples were measured in an air atmosphere at 22 °C under 25% relative humidity with a gauge length of 15 mm and a cross-head speed of 5 mm min^{-1}.

Conductivity measurements were made using the four-probe technique. Impedance measurements were carried out in potentiostat mode with a perturbation amplitude of 10 mV over a frequency range from 1 Hz to 1 MHz, using a ZAHNER IM-6ex impedance analyzer. The impedance of a membrane sample at controlled humidity and temperature can be measured via a Nyquist plot. For the Nyquist plot, both the real (Z') and imaginary parts (Z'') of the components of impedance in the membrane sample were measured simultaneously over the defined frequency range. The real Z'-axis intercept is close to the ohmic resistance (R) of a membrane sample. The proton conductivity (σ) was calculated using the relation $\sigma = d/RS$, where d is the distance between the reference electrode and the sensing electrode and S is the cross-sectional area (thickness × width) of a doped membrane. All conductivity measurements were performed in the longitudinal direction in a thermally controlled, stainless-steel vessel equipped with a temperature and humidity transmitter (HMT 338, Vaisala). The temperature of the measurement cell was controlled by heating or cooling the stainless-steel vessel which was placed in an oil-bath. Membranes of 5 cm × 1 cm having different doping levels were introduced in the conductivity cell and heated to 180 °C, stabilized at this temperature for 30 min, and then measurements were carried out while cooling down the cell at 10 °C steps to 80 °C. The relative humidity at each temperature was controlled by injecting deionized water and blowing dry nitrogen gas into the sealed stainless-steel vessel.

3. Results and discussion

3.1. Polymer synthesis

Poly[2,2'-(p-phenylene)-5,5'-bibenzimidazole] (pPBI) and poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (mPBI) were synthesized from DABIT and the dicarboxylic acids, isophthalic acid and terephthalic acid, respectively, in PPA as shown in Fig. 1. The inherent viscosity of pPBI, 3.22 dL g^{-1}, was higher than that of mPBI, 2.45 dL g^{-1} (Table 1). The molecular weight of pPBI may also be higher than that of mPBI as previously reported [15,17]. mPBI was soluble in several organic solvents and acids, as shown in Table 1. The solubility of mPBI especially increased with increasing temperature and with the addition of LiCl. For example, a homogeneous 5 wt.% mPBI solution was
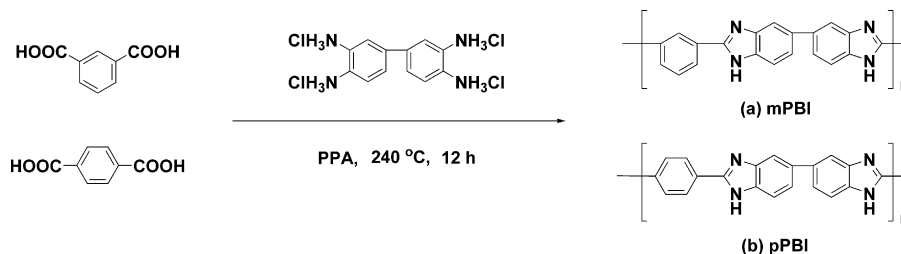

Fig. 1. Scheme of synthetic route for production of (a) poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (mPBI) and (b) poly[2,2'-(p-phenylene)-5,5'-bibenzimidazole] (pPBI).

Table 1
Inherent viscosity and solubility data of PBIs

Polymer	$\eta_{inh.}$ (dL g^{-1})	Solubility[a]					
		DMAc/2 wt.% LiCl	DMSO/2 wt.% LiCl	Trifluoro-acetic acid	Formic acid	95% sulfuric acid	MSA
mPBI	2.45	++	++	++	+	++	++
pPBI	3.22	+	−	+	−	++	++

[a] ++ denotes soluble at room temperature or by heating; + denotes partially soluble or swelling; − denotes insoluble.

obtained by dissolving 0.25 g of the polymer in 4.75 g of DMAc containing 2 wt.% LiCl at 250 °C. By contrast, pPBI was not practically soluble in any organic solvent except MSA. mPBI and pPBI were indistinguishable according to their FT-IR spectra. Both polymers exhibit characteristic absorption bands at 3450–3250 and 1630 cm^{-1} due to the stretching vibration of N−H and C=N groups. The UV spectra of pPBI and mPBI show different absorption peaks; pPBI has maximum absorption wavelengths at 382 and 258 nm, while mPBI has these at 341 and 254 nm (Fig. 2). The UV spectra agree very well with those reported by Iwakura et al. [15] and Vogel and Mawel [16].

3.2. Film fabrication

In this study, pPBI films were prepared by direct casting of the PPA polymerization solution on to stainless-steel plates. This method eliminated the extra isolation, purification and redissolution procedures needed in the traditional solution-casting process. A stainless-steel plate was used as a substrate because the polymer film can easily separate from the glass substrate during the washing procedure; the film that separated from the glass plate shrank severely, particularly in the drying process. When using a stainless-steel plate as a substrate, the polymer film remains attached during the washing and drying processes and the dimensions of the film are preserved without any wrinkles forming on the film surface. The level of acid doping of pPBI membranes was controlled by immersing the films in solutions with various concentrations of phosphoric acid. It is considered that pPBI membranes with higher acid doping levels can be obtained using the sol-gel process reported by Xiao et al. [17]. However, we intentionally doped the pPBI films with phosphoric acid solutions to control the doping level, so that the effects of the casting method on the doping levels and conductivities of
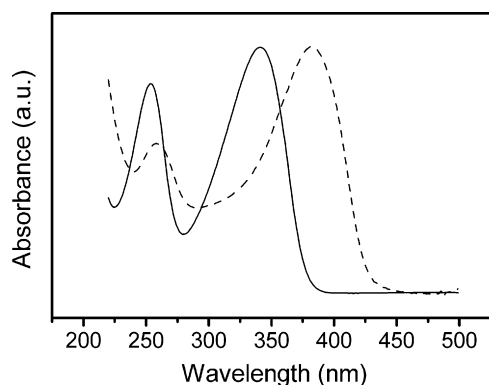
the polymers could be studied systematically. For comparison, pPBI and mPBI films were also prepared by the solution-casting method using MSA and/or DMAc with 2 wt.% LiCl as the casting solvent. Attempts were also made to produce mPBI films by direct casting, but uniform polymer films could not be obtained. Rather, film shrinkage and wrinkles were observed in the resulting polymer films. The lower viscosity (or lower molecular weight) of mPBI may have caused this result. Therefore, a comparison could not be made of the properties of mPBI membranes prepared by solution-casting and direct-casting methods.

3.3. X-ray diffraction

The X-ray diffraction patterns of PBI powders and films prepared by different casting methods are presented in Fig. 3. pPBI powder has two broad peaks at around 11° and 25°. This observation agrees very well with previous results by Iwakura et al. [15]. mPBI powder has a very similar X-ray pattern, as shown in Fig. 3(f). The peak at around 25° has been attributed [23] to parallel orientation of the benzimidazole rings. It is concluded that the origin of the two peaks from pPBI powder in Fig. 3(c) is the same as that for those from mPBI because the two polymers have very similar chemical structures. The pPBI film from MSA casting has one relatively sharp peak at 26.3°, which indicates that ordering of the parallel orientation of the benzimidazole rings increases with respect to the film surface. For the pPBI film from direct casting, a broad amorphous halo at 23–28° is observed
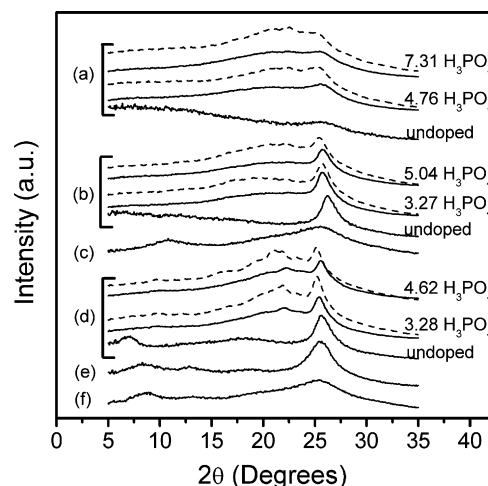

Fig. 2. Ultraviolet spectra of mPBI; solid line and pPBI; dotted line.

Fig. 3. X-ray diffractions of PBI sample: (a) pPBI membranes from direct casting, (b) pPBI membranes from MSA casting, (c) prisitine pPBI powder, (d) mPBI membranes from MSA casting, (e) mPBI film from solution-casting using 2 wt.% LiCl-DMAc solution, (f) pristine mPBI powder. Dashed lines denote annealed membranes at 200 °C.

in Fig. 3. Therefore, the solution-casting procedure produces a semi-crystalline film, while the direct-casting procedure gives an amorphous pPBI film in spite of the semi-crystalline character of pPBI powder. The mPBI films prepared from MSA solution and from LiCl/DMAc solution has a relatively sharp peak at 25.6°, again indicating an increased in the ordering of the parallel orientation of the benzimidazole rings compared with that of mPBI powder.

X-ray diffraction patterns of phosphoric acid-doped PBI membranes were obtained to study the effects of doping on the membrane structures. The acid-doped pPBI and mPBI membranes from MSA casting display X-ray peaks with lower intensity and larger width compared with those of undoped membranes, which agrees very well with previous reports by other investigators [21,24]. For pPBI membranes, the amorphous halo observed for the undoped film changes to broad peaks at around 20–25 °C. The almost amorphous structure formed during the quenching process in the direct-casting method changes to a slightly crystalline structure during the doping process. Nevertheless, the crystallinity of the acid-doped membranes obtained by direct casting is lower than that of acid-doped membranes from MSA casting. The diffraction patterns of acid-doped membranes annealed at 200 °C for 1 h were also investigated since these membranes are normally used at elevated temperatures in fuel cell operations. The annealing process slightly increases the intensity of the peaks around 20–25° of all membranes including pPBI membranes from direct casting. Wainright et al. [25] have found that heating of acid-doped mPBI membranes increases their crystallinity. Again, the membrane crystallinity from direct casting is lower than that of the membranes made by MSA casting, as determined by the peak intensities in Fig. 3(a) and (b), (d). This difference has considerable effects on membrane properties including acid doping level, water uptake and proton conductivity, as discussed below.

3.4. Acid doping level and water uptake

Fig. 4 shows the acid doping levels of pPBI and mPBI films in various phosphoric acid concentrations at 30 °C. As expected, the doping level increases as the acid concentration is increased. The pPBI film from direct casting had the highest acid doping
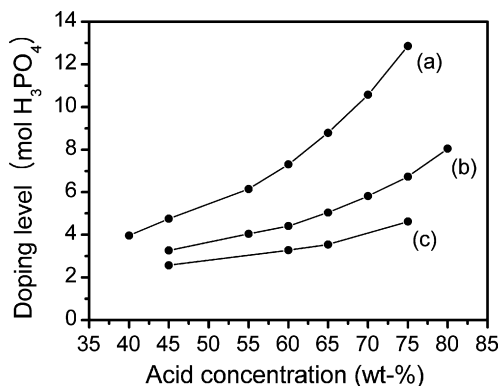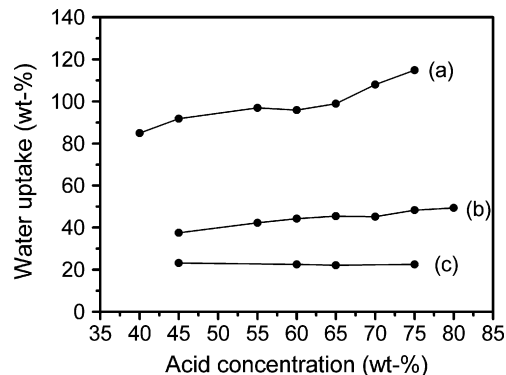

Fig. 5. Water uptake values of pPBI membranes from: (a) direct casting and, (b) MSA casting, and (c) mPBI membranes from MSA casting.

level. X-ray results indicate that the pPBI film made by direct casting is almost amorphous. The acid can therefore penetrate the totally amorphous pPBI film more easily than it can the semi-crystalline pPBI and mPBI films. It is known [26] that polymers with more amorphous contents have higher permeability of gas and liquid than those with less amorphous contents. For pPBI and mPBI films prepared from the same MSA solution-casting method, the former films show higher acid doping levels than the latter. Since these two polymers have similar crystallinity according to the X-ray results (Fig. 3), the difference in doping level between the polymers cannot be explained by their crystallinity differences. Polymer with different chemical structures can have different permeability values for many reasons that include solubility, chain mobility, free volume and polarity [26]. For some reason, although we do not have a clear answer, the linear backbone structure of pPBI can absorb more acid than the curved backbone structure of mPBI.

Fig. 5 shows water uptake results for PBI membranes after immersion in various concentrations of phosphoric acid solution. The water uptake of mPBI membranes from MSA casting are almost constant at about 20 wt.%, which agrees well with earlier findings [27]. For pPBI membranes, the water uptake increases slightly with the concentration of the acid solution; the values are always larger than those of mPBI membranes. In particular, the amorphous pPBI membrane made by direct casting has a very large water uptake, for example, around 95 wt.% is achieved using a 60 wt.% H_3PO_4 solution at 30 °C. Therefore, pPBI membranes from direct casting can have very large doping levels and water uptake values that, in turn, can exert a considerable effect on the conductivities of the membranes, as will be discussed below.

3.5. Mechanical strength

As the doping level is increased, the tensile strength decreases for all pPBI and mPBI membranes, as shown in Fig. 6. As mentioned in the Introduction, a doping level of around 5 mol of H_3PO_4 is about the maximum to maintain a reasonable mechanical strength for mPBI membranes for PEMFC applications. It is also found that when the doping level is much greater than 5 mol H_3PO_4, the mechanical stability of mPBI membranes becomes very poor, and reproducible conductivity studies are not possi-

Fig. 4. Acid doping levels of pPBI membranes from: (a) direct casting and, (b) MSA casting, and (c) mPBI membranes from MSA casting.
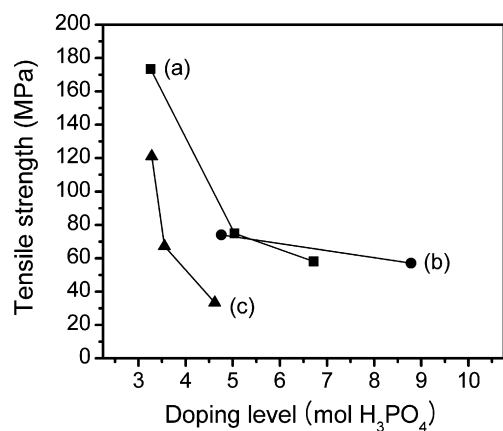
Fig. 6. Tensile strength at break of pBBI membranes from: (a) MSA casting, and (b) direct casting, and (c) mPBI membranes from MSA casting.

ble; the tensile strength of mPBI membrane doped with 4.62 mol H_3PO_4 is 33 MPa (22 °C, 25% relative humidity). pPBI membranes have reasonably good mechanical stability, however, even though the acid doping levels of these membranes are higher than 5 mol H_3PO_4; tensile strengths of about 60 MPa are observed for pPBI membranes from MSA casting and direct-casting methods that have acid doping levels ranging from 6 to 9 mol. One possible reason for the improved mechanical strength of pPBI membranes at doping levels greater than 5 mol H_3PO_4 is the increased viscosity (or molecular weight); the inherent viscosity values for mPBI and pPBI are 2.45 and 3.22 dL g^{-1}, respectively. The stiffer backbone structure of pPBI due to its wholly *para*-ordered molecular orientation may also improve the mechanical stability [18].

3.6. Proton conductivity

In Fig. 7 the proton conductivities of pPBI and mPBI membranes made by MSA casting as a function of doping level and temperature at 1% relative humidity. Because the measurements were performed under relatively wet conditions (1% or
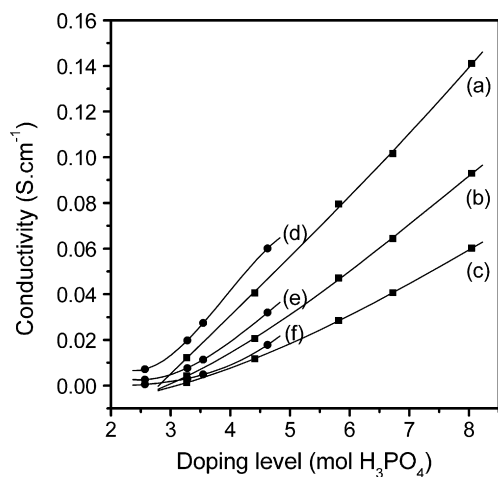

Fig. 7. Proton conductivity (1% relative humidity) of pPBI membranes from MSA casting at: (a) 180 °C, (b) 150 °C, (c) 120 °C and mPBI membranes from MSA casting at (d) 180 °C, (e) 150 °C, and (f) 120 °C, in humidified N_2.
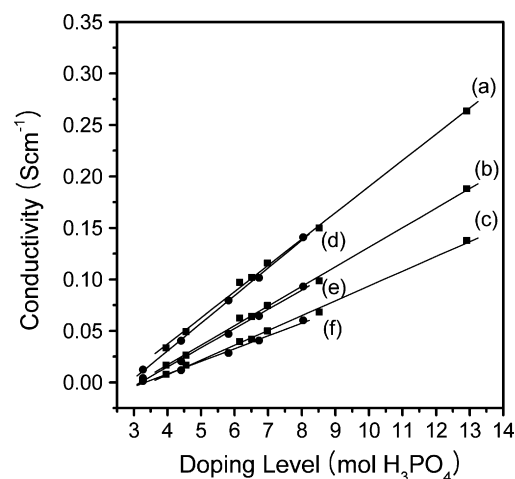

Fig. 8. Proton conductivity (1% relative humidity) of pPBI membranes from direct casting at (a) 180 °C, (b) 150 °C, (c) 120 °C and pPBI membranes from MSA casting at (d) 180 °C, (e) 150 °C, and (f) 120 °C, in humidified N_2.

5% relative humidity) to prevent self-dehydration of phosphoric acid at high temperature, the conductivity values obtained in this work are comparatively higher than others available in literature [12,20]. Nevertheless, the humidity was evenly controlled for all membranes, and the conductivity results are highly reproducible. The membrane conductivity increased as the doping level and temperature increased. The conductivity of pPBI at 180 °C increases from 0.012 to 0.141 S cm^{-1} as the doping level is increased from 3.27 to 8.05 mol H_3PO_4. The conductivity of mPBI at 180 °C increases from 0.0071 to 0.060 S cm^{-1} as the doping level is raised from 2.57 to 4.62 mol H_3PO_4. Therefore, the conductivity of mPBI is larger than that of pPBI at the same doping level. Nevertheless, the maximum conductivity (0.060 S cm^{-1} at 180 °C) of mPBI membrane is lower than that (0.141 S cm^{-1} at 180 °C) of pPBI because the maximum doping level of the mPBI membrane is much lower than that of the pPBI membrane. When pPBI membranes are prepared by the direct-casting method, the conductivity increases further because the direct-casting method can increase the acid doping level, as shown in Fig. 4. Figs. 8 and 9 show the proton conductivities of pPBI membranes prepared by both MSA solution-casting and direct-casting as a function of the doping level at 1% and 5% relative humidity, respectively. The proton conductivities of pPBI membranes made by direct casting are almost identical to those from MSA casting at 1% relative humidity, within experimental error. At 5% relative humidity, pPBI membranes prepared by direct casting have larger conductivities than those from MSA casting. Because pPBI membranes from direct casting have much larger water uptake values than those from MSA casting, as shown in Fig. 5, the greater relative humidity can obviously increase the water uptake value, and thus the conductivity, much more for membranes from direct casting. It should be noted that the conductivity values, 0.15 S cm^{-1} (180 °C and 1% relative humidity) and 0.18 S cm^{-1} (180 °C and 5% relative humidity), of pPBI membranes from direct casting with a doping level of 8.78 mol are very large. These values are much larger than those for mPBI membranes prepared by the conventional method.
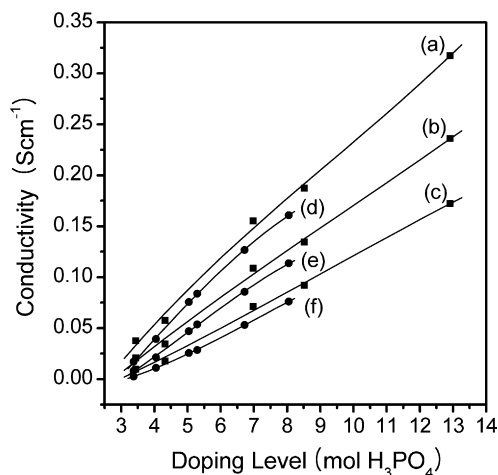
Fig. 9. Proton conductivity (5% relative humidity) of pPBI membranes from direct casting at (a) 180 °C, (b) 150 °C, (c) 120 °C and pPBI membranes from MSA casting at (d) 180 °C, (e) 150 °C, and (f) 120 °C, in humidified N_2.

Fig. 10 summarizes the conductivity and mechanical strength of acid-doped PBI membranes with various acid doping levels. For comparison, a poly[2,5-benzimidazole] (ABPBI) membrane was prepared by direct casting [28]. Obviously, it can be seen that mPBI and ABPBI membranes lose their mechanical strength more rapidly than pPBI membranes with increasing proton conductivity. On increasing the doping level of mPBI membranes from 3.28 to 4.62 mol H_3PO_4, the proton conductivity increases from 0.020 to 0.060 S cm^{-1}, but the tensile strength simultaneously decreases from 121 to 33 MPa. The ABPBI membrane also shows very low tensile strength (12 MPa) despite of its large inherent viscosity (5.45 dL g^{-1}) at a proton conductivity of 0.14 S cm^{-1}. By contrast, the tensile strength of pPBI membranes decreases from 173 to 58 MPa on increasing proton conductivity from 0.012 to 0.10 S cm^{-1}, which means pPBI membranes can preserve large tensile strength even at high proton conductivity. Therefore, acid-doped pPBI membranes have very good prospects for use in high-temperature fuel cells

because they have reasonably high proton conductivity and better physical strength compared with most mPBI and ABPBI membranes. Preliminary fuel cell tests using the pPBI membranes are now in progress.

4. Conclusions

Poly[2,2′-(p-phenylene)-5,5′-bibenzimidazole] (pPBI) with high inherent viscosity is prepared through the polycondensation reaction of 3,3′-diaminobenzidine tetrahydrochloride and terephthalic acid using polyphosphoric acid as a solvent. The pPBI membranes have higher acid-doping levels and larger water uptake values than mPBI membranes. The pPBI membranes prepared by direct casting have an almost amorphous structure and much higher acid-doping levels and larger water uptake values than pPBI membranes prepared by the solution-casting method using methanesulfonic acid. The tensile strength of pPBI membranes is remarkably higher than that of mPBI membranes at the same doping level. Therefore, pPBI membranes maintain their excellent mechanical stability even at very high acid-doping levels above 5 mol H_3PO_4. As a result, the membranes can have both high proton conductivity (0.15 S cm^{-1} at 180 °C and 1% relative humidity) and good mechanical stability (tensile strength of 57 MPa at 22 °C and 24% relative humidity) at a high acid doping of 8.78 mol.
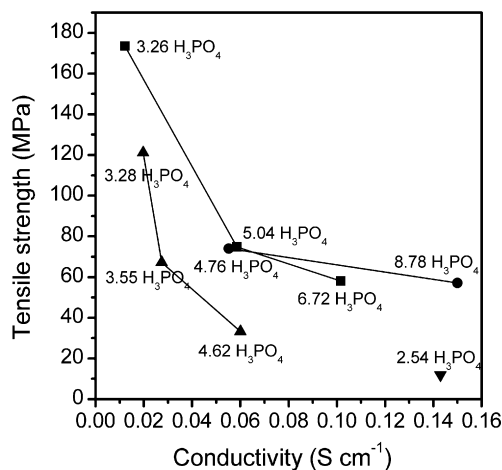
Fig. 10. Mechanical strength vs. proton conductivity (180 °C, 1% RH) of (■) pPBI membranes from MSA casting, (●) pPBI membranes from direct casting, (▲) mPBI membranes from MSA casting and (▼) poly[2,5-benzimidazole] (ABPBI) from direct casting [25].

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