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### Preparation and characterization of novel pyridine-containing polybenzimidazole membrane for high temperature proton exchange membrane fuel cells



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#### 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) operated at 100-200 °C have numerous advantages including high tolerance to fuel impurities, well controllability of thermal and water issues, and fast electrochemical reaction kinetics [1–3]. Acid-base polymer membranes [1], especially a basic polymer imbibed with an inorganic acid or blended with a polymeric acid, used for high temperature PEMFC, include polyethyleneoxide (PEO), polyethyleneimine (PEI), polyacrylamide (PAAM), poly (vinylpyrrolidone) (PVP), and others, as summarized by lasségues [4]. The basic polymer acts as a proton acceptor and the acid molecules are brought in due to acid-base interactions [1,5]. Most of these polymers taking in high level of acid will be too soft to have any practical uses [1]. A big improvement was obtained when using polybenzimidazole (PBI) as the acid-doped membranes [6].

Phosphoric acid (PA) doped PBIs as high temperature proton exchange membranes for use in fuel cells have recently attracted extensive attention, owing to the high proton conductivity with no or low humidification and promising fuel cell performance above 100 °C [5-13]. However, one of the main problems associated with polybenzimidazoles seems to be their poor solvent solubility,

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#### ABSTRACT

A novel pyridine-containing polybenzimidazole (PDA-PBI) membrane was developed as a candidate for high-temperature polymer electrolyte membrane fuel cells. Aiming to improve the solubility and proton conductivity of the ionomer, a diacid monomer, 4,4'-(pyridine-2,6-diylbis(oxy))dibenzoic acid (PDA), was synthesized and condensation polymerized with 3,3'-diaminobenzidine (DAB) to prepare a polymer containing ether groups and pyridine rings. The soluble PDA-PBI membranes were prepared by solution casting method and then soaked in phosphoric acid solution. The polymers were characterized by Fourier transform infrared spectroscopy, element analysis and thermogravimetric analyses. The PDA-PBI has good thermal stability with onset decomposition temperature up to 350 °C. The proton conductivity of the prepared membrane is 11 mS cm<sup>-1</sup> at 25 °C and 83 mS cm<sup>-1</sup> at 160 °C without any humidification. The evaluations of fuel cell performance were conducted using the PDA-PBI membranes and a peak power density of 460 mWcm<sup>-2</sup> was obtained at 160 °C with unhumidified hydrogen and oxygen.

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which results from the high degree of molecular rigidity in the backbone and the strong intra-interchain hydrogen bonding interactions, coming in the way of development of new applications [14–16]. Attempts [17–21] have been made to modify the properties of PBI by incorporating flexibilizing groups or other bulky units in main or side chain to overcome the restricted polymer solubility. Hergenrother et al. [17] prepared poly (arylene ether benzimidazole)s, containing ether groups, by the aromatic nucleophilic displacement reaction of three new bis[(4-hydroxyphenyl)benzimidazole] compounds with activated aromatic difluoro compounds. Qian et al. [21] had synthesized PFCB-PBI which contains 6 fluorines per repeated unit. They found the polymer could dissolve in N,N-dimethyl acetamide (DMAc) without high pressures or high temperatures and didn't require lithium chloride as stabilizer [22].

In addition, it seems that proton conductivities of the phosphoric acid-doped PBI membranes increase with increasing PA doping levels, which is incorporated at the proton acceptor sites of the polybenzimidazole. More N atoms or NH groups can enhance the base content of the polymer and thus improve the acid doping and proton conductivity [1,5]. So recently, large efforts to change the base monomer structure of PBIs, like nitro containing PBIs [23], PBIs bearing pendant phenoxyamine groups [24] and pyridine based PBIs [25,26], were also reported. However, the mechanical strength of PBI type membranes is sacrificed with the high acid contents [8,26]. In order to solve this problem, high molecular PBIs [12], introduction of inorganic fillers [8] and cross-linked polymers[2] have been investigated.

In this work, the preparation of pyridine-containing polybenzimidazoles (PDA-PBI) from novel diacid monomer, containing a pyridine unit and ether groups, namely, 4,4'-(pyridine-2,6-diylbis(oxy))dibenzoic acid (PDA), and 3,3'-diaminobenzidine (DAB) in phosphorous pentoxide/methanesulfonic acid (PPMA) is reported. The imparting of ether groups aims to boost the polymer solubility and flexibility. The introduction of pyridine ring is designed to increase the density of basic sites favoring the acid doping and hence improvement in proton conductivity. The new diacid was characterized by NMR, FT-IR and element analysis. The polymer structure characterization included FT-IR and element analysis, inherent viscosity (I.V.) determination as a measurement of polymer molecular weight and thermal stability assessment via thermogravimetric analysis. It is found that this polymer could be easily dissolved in dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF) and dimethylacetamide (DMAc) to facilitate casting of membranes. The membrane was studied with respect to doping level, ion conductivity, mechanical properties, as well as oxidative stability. Finally, the synthesized membrane was fabricated into MEA and the fuel cell performance was evaluated at temperatures up to 160 °C.

#### 2. Experimental

#### 2.1. Materials

4-Hydroxybenzoic acid (99%), 2,6-Dichloropyridine (98%), 3,3'-Diaminobenzidine (DAB, 99%) and Methanesulfonic acid (MSA, 99%) were purchased from J&K Chemical Co., Ltd. and used as received. Potassium carbonate, Acetone, Phosphorus pentoxide, sulfuric acid, phosphoric acid (PA), hydrochloric acid, methanol, N, N-dimethylformamide (DMF), N,N-dimethyl acetamide (DMAc), N-methyl-2-pyrrolidone (NMP), tetrhydrofuran (THF), trichloromethane (CHCl<sub>3</sub>) and Dimethyl sulfoxide (DMSO) were commercially obtained from China National Medicines Co., Ltd. These reagents were used without further purification. Deuterated dimethylsulfoxide (DMSO-d<sub>6</sub>) was supplied by Merck, Germany. The solution phosphorus pentoxide/methanesulfonic acid (PPMA, w/w: 1/10) was premade according to the literature [27]. Deionized water was used throughout.

#### 2.2. Polymer synthesis

The PDA-PBI was produced by two steps. At the first step, PDA was obtained from potassium 4-hydroxybenzoate and 2,6-

dichloropyridine by nucleophilic substitution (Scheme 1). At the second step, PDA-PBI was synthesized based on PDA and DAB by condensation polymerization (Scheme 2).

# 2.2.1. Synthesis of 4,4'-(pyridine-2,6-diylbis(oxy))dibenzoic acid (PDA)

The 4,4'-(pyridine-2,6-diylbis(oxy))dibenzoic acid (PDA) was synthesized through two steps and the details are as follows. Step one. 4-Hydroxybenzoic acid (20.7 g, 0.15 mol) and potassium carbonate (10.35 g, 0.075 mol) were mixed in 100 ml deionized water, according to the scheme shown in Scheme 1. The reaction system consisted of a round bottomed flask equipped with a carbon dioxide outlet tube. Then the mixture was magnetically stirred at 90 °C and cooled down after 10 h of reaction. The potassium 4-hydroxybenzoate was then extracted from the aqueous solution by reduced pressure distillation and dried in vacuum oven at 50 °C for 24 h. Step two. A 250 ml, three-necked, round bottomed flask was equipped with an overhead reflux condenser, nitrogen inlet and gas outlet. Potassium 4-hydroxybenzoate (17.86 g, 0.05 mol), 2,6-dichloropyridine (3.7 g, 0.025 mol), potassium carbonate (14 g, 0.1 mol) and DMSO (100 ml) were added into it. The reaction mixture was heated to 190 °C under a steam of nitrogen and stirred at this temperature for 10 h. As the reaction proceeded, the mixture turned into dark tawny. After cooling down to room temperature the mixture was slowly poured into excessive deionized water and acidified with hydrochloric acid solution until the pH was about 2. The slurry was filtered and dried up at 120 °C inside an oven. Then, the crude solid was ultrasonic washed with an excess of acetone three times to obtain the white insoluble 4,4'-(pyridine-2,6-diylbis(oxy))dibenzoic acid (PDA). Finally, the PDA was rinsed into deionized water until the pH was constant and dried up in an oven.

#### 2.2.2. Synthesis of pyridine-containing polybenzimidazole (PDA-PBI)

A general procedure for the synthesis of the pyridine-containing polybenzimidazole (PDA-PBI) is given in the following. 4,4'-(Pyridine-2,6-diylbis(oxy))dibenzoic acid (PDA, 1.19 g, 3.4 mmol), 3,3'-Diaminobenzidine (DAB, 0.74 g, 3.4 mmol) and PPMA (27.6 g) were charged into a 100 ml, three necked flask, which was equipped with an overhead mechanical stirrer and nitrogen-purge inlet and outlet. The reaction mixture was stirred using a mechanical stirrer at 100 rpm and the reaction temperature was controlled at 80 °C for 0.5 h, 120 °C for 1 h, and 140 °C for 8 h. Once the time elapsed, the dark purple reaction mixture was directly poured into DI water so as to isolate the polymer which was later soaked in 5 wt% potassium hydroxide at 60 °C for 10 h. Afterwards, the polymer was washed thoroughly with deionized water until neutral in pH, and then dried in a vacuum oven at 80 °C for 24 h.



Scheme 1. Synthesis of 4,4'-(pyridine-2,6-diylbis(oxy))dibenzoic acid (PDA) by nucleophilic substitution.



Scheme 2. Synthesis of PDA-PBI by the condensation polymerization of PDA with 3,3'-diaminobenzidine (DAB).

Finally, the polymer was ground to a fine gold-brownish PDA-PBI powder for further usage.

#### 2.3. Film casting

The membranes were prepared by the solution-casting and evaporation method. PDA-PBI powder (0.6 g) and 15 ml DMSO were placed in the reaction flask, and then gradually heated up to 80 °C under stirring for 24 h. After filtered, the obtained homogeneous solution was poured onto a clear glass plate and evaporated in a vacuum oven at 80 °C until completely dried. Then the glass plate was cooled slowly and the polymer film was removed from the glass plate automatically. The film was then dried to a constant weight at 120 °C for 12 h in the vacuum oven to remove small traces of the organic solvents. The thickness of the membrane is controlled between 60–80  $\mu$ m.

#### 2.4. Characterization

#### 2.4.1. Structural analysis

The <sup>1</sup>H NMR and <sup>13</sup>C NMR experiments were carried out on an Advance II 400 (Varian Corporation, U.S.A). The PDA powder was analyzed using deuterated dimethylsulfoxide (DMSO-d<sub>6</sub>) as the solvent. The FT-IR spectra of 4,4'-(pyridine-2,6-diylbis(oxy))dibenzoic acid (PDA) and PDA-PBI were scanned using a Nicolet Avatar 330 (Thermo Electron Corporation, U.S.A). The sample powder was dispersed in KBr powder and compressed into pellets. The inherent viscosity (I.V.) of the polymer was determined on 0.4 g dL<sup>-1</sup> concentration of dry PDA-PBI dissolved in DMSO solvent with an Ubbelohde capillary viscometer at  $30 \pm 0.1$  °C. Elemental analyses were performed on a Vario EL III Elemental analyzer (Elementar Analysen Syetem GmbH, Germany).

#### 2.4.2. Thermal stability

The thermogravimetric analysis (TGA) thermograms of the PDA-PBIs were obtained under a flowing nitrogen atmosphere or a flowing air atmosphere with a TG209F1 system (NETZSCH, Germany) at a heating rate of 10 °C min<sup>-1</sup> over the temperature range of 30-900 °C.

#### 2.4.3. Acid doping

To measure the H<sub>3</sub>PO<sub>4</sub> uptake, membranes were immersed in phosphoric acid solutions of different molar concentrations for various time intervals at room temperature. After doping for a

suitable time, the membrane was taken out from acid, and the  $H_3PO_4$  on the film surface was removed with filter paper, then the membrane was dried at 110 °C under vacuum for 24 h; after that, the membrane was withdrawn from the oven and rinsed in excessive ethanol for an appropriate period of time and thereafter dried at 80 °C under vacuum until a constant weight was reached. The acid uptake in wt% was calculated by the equation bellow:

$$H_3PO_4 \text{ uptake}(wt\%) = \frac{W_d - W_u}{W_u} \times 100\%$$

Where  $W_u$  is the weight of the dried sample without doping and  $W_d$  is the weight of membrane sample taken from the oven at the second time.

#### 2.4.4. Proton conductivity

The proton conductivity of the membranes was estimated from four-probe electrochemical impedance spectroscopy using a Parstat 263 electrochemical equipment (Princeton Advanced Technology, USA) over the frequency range from 1 Hz to 100 kHz. The conductivity of the membrane was calculated by the equation below:

$$\sigma = \frac{L}{R \times A}$$

Where  $\sigma$  (s cm<sup>-1</sup>) is the proton conductivity, *L* (cm) is the distance between the two inner probes, *R* ( $\Omega$ ) is the ohmic resistance through the plane of the membrane, and *A* is the surface area of the membrane exposed to the electric field, as described in our previous studies [28–30]. A programmable oven was used to measure the temperature dependence of the proton conductivity. The measurements were conducted from 30 to 160 °C under anhydrous conditions at intervals of 20 °C with a 15 min pause at each temperature intervals for thermal equilibrium.

#### 2.4.5. Mechanical properties

The tensile strength and elongation at break of the membrane were tested by Universal material testing machine (SUN 2500, Italy).

#### 2.4.6. Oxidative stability

The oxidative stability was studied by estimating the weight changes of the membrane before and after immersing the films into Fenton's reagent (3%  $H_2O_2$  solution containing 4 ppm FeSO<sub>4</sub>). A small piece of the undoped membrane sample (2 cm × 2 cm) was immersed into Fenton's reagent at 70 °C under stirring. The

sample was taken out of the solution at regular intervals and washed thoroughly with deionized water several times, then dried at 120 °C for more than 10 h in a vacuum oven before the weight was measured. The degradation of the undoped membranes was measured by the weight loss. After weighted, the undoped membrane samples were then placed into fresh Fenton solutions again for continued testing.

# 2.4.7. Membrane Electrode Assembly (MEA) fabrication and fuel cell test

The catalyst slurry ink for both anode and cathode was prepared by mixing Pt/C powders (40 wt% Pt, Johnson Matthey) with the ionomer solution (5 wt% PDA-PBI in DMSO) and isopropyl alcohol under ultrasonic vibration. The catalyst ink was sprayed onto the microporous gas diffusion layer (GDL) giving a Pt loading of 0.6 mgcm<sup>-2</sup> to prepare the electrodes, and dried in a vacuum oven at 150 °C for 3 h. The GDL coating with the catalyst layer was dipped in a 10 wt% phosphoric acid aqueous solution at room temperature for 24 h, and then dried in vacuum oven at 80 °C for 4 h. After that, the phosphoric acid impregnated membranes were sandwiched between two catalyst-loaded carbon papers  $(2 \text{ cm} \times 2 \text{ cm})$  by using a hot-press under a pressure of 1 MPa for 8 min at 130 °C to obtain the MEA. The MEA was assembled into a single fuel cell apparatus with serpentine flow channels. The performances of single fuel cell were tested at a temperature range of 120–160 °C under ambient pressure by a fuel cell testing system (GE/PEM-10 FCT, Guangdong Electronic Technology Institute, Guangdong, China.) Pure and dry hydrogen and oxygen gases were fed to the anode and cathode compartments, respectively.

#### 3. Results and discussion

3.1. Structural analysis from NMR, FT-IR, inherent viscosity and

#### elemental analysis. Synthesis of PDA

Scheme 1 shows the synthesis route of PDA monomer from 4-hydroxybenzoic acid with 2,6-dichloropyridine. Due to the electronegative nitrogen, the pyridine ring is relatively electron deficient (especially at the 2 and 6 sites), so the two chloride ions of 2,6-dichloropyridine are activated. They can undergo nucleophilic displacement by phenolic groups of potassium 4-hydroxybenzoate to form the diacid monomer in the presence of potassium carbonate and the product yield was up to 68%.

Fig. 1 shows <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra of 4,4'-(pyridine-2,6-diylbis(oxy))dibenzoic acid (PDA). The two protons of carboxyl groups appear at 12.89 ppm. The triple peak at 7.97 ppm is assigned to the contribution of proton at the fourth site of pyridine ring. The other two protons of pyridine ring appear at 6.85 ppm and the aromatic protons in the region 7.20–7.92 ppm show the expected multiplicity and integration values [Fig. 1(A)].

The <sup>13</sup>C-NMR spectrum of 4,4'-(pyridine-2,6-diylbis(oxy))dibenzoic acid (PDA) shows carbons of pyridine ring at 161.09, 144.48 and 107.147 with expected multiples. Two carbons of carboxyl groups appear at 167.09 ppm while the aromatic carbons at 157.82, 131.55 127.21 and 120.64 [Fig. 1(B)].

The FT-IR spectra of the PDA and PDA-PBI powder are shown in Fig. 2. The PDA emerges several peaks. The band at 3433 cm<sup>-1</sup> is the O–H stretching due to absorbed water [31]. The peak at 1692 cm<sup>-1</sup> is assigned to the stretching vibration of the carbonyl group in carboxylic acid and those several peaks between 2500 and 3000 cm<sup>-1</sup> are owing to the presence of carboxylic acid group [2,31]. The absorption at 3079 cm<sup>-1</sup> is due to the C–H of phenyl ring and the bands at 1602, 1582, 1510 and 1435 cm<sup>-1</sup> correspond to the existence of benzene ring while the peak appearing at 860 cm<sup>-1</sup> confirms the presence of p-substituted benzene ring [2,31]. Band due to C–O–C linkage appears at the region of 1205–1289 cm<sup>-1</sup> [23]. The absorption peak at 1165 cm<sup>-1</sup> is ascribed to the stretching vibration of C=N [2]. For the PDA-PBI, the



Fig. 1. <sup>1</sup>H-NMR (A@and <sup>13</sup>C-NMR (B) spectra of 4,4'-(pyridine-2,6-diylbis(oxy))dibenzoic acid (PDA).



Fig. 2. FT-IR spectra of PDA and PDA-PBI.

absorption due to N–H stretching of imidazole ring is observed at 3400 cm<sup>-1</sup> [2]. The peaks at 1633, 1168, 1005 correspond to amine and imine groups. The absorption peak owing to the carboxylic acid group at 1692 is present in PDA but disappears in the spectrum of the PDA-PBI. The presence of absorption peaks for the secondary amine and imine groups and the disappearance of carboxylic acid group in the PDA-PBI demonstrate the successful polymerization of PDA-PBI.

Inherent viscosity value of PDA-PBI was measured to be  $1.6-1.9 \text{ dL g}^{-1}$  in dimethyl sulfoxide solvent at 30 °C, which provided a qualitative inference of reasonably high molecular weight of the polymer and indicated successful polymerization.

The calculated weight percentages of C, N and H for PDA  $(C_{19}H_{13}NO_6)$  are 64.9, 3.98 and 3.73, respectively. Elemental analysis of the synthesized PDA found the contents of C, N and H were 64.74, 3.69 and 3.92, respectively, which were consistent with the theoretical values. Elemental analysis of the PDA-PBI powder revealed the weight percentage of C and N were 67.52 and 12.50, respectively. Therefore the relative number of C and N was 6.3, which conforms to the polymer structure.

Thus, chemical structure of new compound 4,4'-(pyridine-2,6diylbis(oxy))dibenzoic acid (PDA) was established by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FT-IR and elemental analysis, while PDA-PBI was testified by FT-IR and elemental analysis.

#### 3.2. Solubility behavior

It is generally known that solubility of the PBI in organic solvents is poor due to the rigid structure and strong intermolecular hydrogen bonding [15,16]. The dissolution of the polymer could be improved by introducing the flexible segment. Table 1 lists the polymer solubility behavior in some conventional solvents. The PAD-PBI polymer was studied by dissolving 5 mg of the novel synthesized polymers in 0.5 ml solvent. It can be readily soluble at room temperature in strong acids like H<sub>2</sub>SO<sub>4</sub>, and methane

Solubility behavior of PDA-PBI.

sulfonic acid (MSA), etc. It also can be easily dissolved in some strong polar organic solvent, such as dimethyl sulphoxide (DMSO) and N-methyl pyrrolidone (NMP) at the ambient temperature. The PDA-PBI is partially soluble in N,N-dimethylformamide (DMF) and dimethylacetamide (DMAc) at room temperature but the solubility increases with heating. Heated to 80 °C under refluxing with frequent agitation, the PDA-PBI polymer can be completely dissolved in DMF and DMAc without any auxiliary additives. However, it is insoluble in tetrahydrofuran (THF), toluene, and chloroform even at elevating temperature. In comparison with commercial PBI reported by Lobato et al. [32], which could only dissolve in aprotic solvents such as DMAc by heating for a long time using lithium chloride as stabiliser, the solubility of PDA-PBI polymer is significantly improved by incorporating aryl ether linkages and pyridine aromatic heterocycle in the polymer backbone. This may result from the decrease of rigidity by introduction of ether group and the protonation effect at the nitrogen atom of pyridine ring with some polar solvents. The improvement of solubility leads to the homogeneous and transparent PDA-PBI membranes could be easily fabricated by solution casting method with DMSO, DMAc or DMF as the solvent.

#### 3.3. Thermogravimetric analysis

The thermal stability of the PDA- PBI polymers was studied by thermogravimetric analysis (TGA), as shown in Fig. 3. The black curve shows that the initial decomposition temperature is approximately 350-380 °C in nitrogen and the residue weight is about 65 wt% up to 900 °C. Roughly 1.8 wt% weight loss from room temperature to 120 °C was ascribed to the evaporation of water or solvents [21,31]. The onset decomposition temperature  $(T_d)$  is around 380 °C, which might be associated with the degradation of the C–O–C group, because the benzene ring and the pyridine unit are stable at least above 400 °C according to the literature [5,33]. The red curve demonstrates the thermal stability of PDA-PBI is high with a decomposition temperature of 360 °C in air. These TGA curves verify the excellent thermal stability of the PDA- PBI polymers below 350 °C, which are suitable for use as electrolytes in high temperature fuel cells. The results also manifest that the incorporation of ether units and pyridine rings into the polymer backbone maintains the high thermo-oxidative stability of polybenzimidazoles.

#### 3.4. Acid doping study

Fig. 4 shows the weight increase for PDA-PBI membranes after immersing in 2–14 molar phosphorous acid at room temperature for a suitable period of time until total saturation. The doping level is defined as the wt% of  $H_3PO_4$  of the polymer. It is seen that a steady increase in acid uptake with increase in concentration. In the acid concentration range from 2 to 10 M, the doping level increases slightly. There is a huge jump between 10 and 12 M, where a doping level of 115 wt% and 237 wt% of  $H_3PO_4$  is achieved, respectively. Thus, the doping level in mole/repeat unit is around 23.5 mol of  $H_3PO_4$  by immersing in 12 M acid solution. It was previously reported by Li and coworkers that the acid doping level

Sample		Solvent								
	MSA	H <sub>2</sub> SO <sub>4</sub>	DMSO	NMP	DMF	DMAc	Methanol	THF	chloroform	toluene
PDA-PBI	++	++	++	++	+	+	-	-	-	_

(++) Soluble at the room temperature; (+) soluble by heating; (-) Insoluble.





Fig. 4. Doping level of phosphoric acid (wt%) in PDA-PBI as a function of the  $\rm H_3PO_4$  molar concentration.

of PBI membrane was about 6 mol of  $H_3PO_4$  in 12 M acid solution [34]. The improvement is probably due to the introduction of the base pyridine, which aids in the retention of phosphorous acid. It has been also reported that the doped membranes were too soft to have any practical uses when the  $H_3PO_4$  concentration was higher than 13 M [34]. However a doping level around 249 wt% of  $H_3PO_4$ , about 40 PA repeat unit, is achieved in this work by using the 14 M  $H_3PO_4$  solution. In the subsequent process of MEA preparation, the acid doped membranes remain intact after being hot-pressed at 1 MPa for 8 min at 130 °C, indicating that the doped membranes have sufficient strength and flexibility for use in fuel cells.

Fig. 5 is the curve of weight increase versus time for PBI membranes by soaking in 85% H<sub>3</sub>PO<sub>4</sub> solution at room temperature. The total saturation is quickly reached with time up to 9–10 h and the ultimate acid uptake of PDA-PBI membrane is 255 wt%, about 40 mol H<sub>3</sub>PO<sub>4</sub> per unit. It is much faster compared with previous literatures [2,32]. It is ascribe to the N atoms and NH groups which could enhance the acid affinity and facilitate the diffusion of phosphoric acid in the membrane.

#### 3.5. Proton conductivity

The proton conductivity of the PDA-PBI film, doped with 85% phosphoric acid for 12 h, were measured in the temperature range of 30–160 °C without humidification. A programmable oven was used to house the cell, so the temperature dependence of the proton conductivity for the membrane could be obtained. As can



Fig. 5. Acid doping level of PDA-PBI membranes as a function of time at room temperature.



Fig. 6. Proton conductivity of the PDA-PBI membranes as a function of temperature without humidification.

be seen in Fig. 6, the proton conductivity of the acid doped membrane increases linearly with temperature. The proton conductivity increases significantly as the temperature rises from 30 to 140 °C with an increment of 20 °C. It is 11 mS cm<sup>-1</sup> at 30 °C and reaches 79 mS cm<sup>-1</sup> at 140 °C. However, the proton conductivity increases slightly when temperatures ranging from 140 to 160 °C with an increment of 10 °C. The nitrogen atom in the pyridine group of PBI can provide the opportunity for the protonation of PA molecules [35,36]. Therefore, both the doping level and conductivity can be increased after the incorporation of pyridine rings into the polymer backbone.

The results indicate that the proton conductivity of the PDA-PBI membrane meets the basic requirement for fuel cell application, it can be used as the polymer electrolyte in high temperature proton exchange membrane fuel cells under anhydrous condition.

#### 3.6. Mechanical properties

The mechanical properties of the acid doped PDA-PBI membrane were measured at room temperature. As can be seen in Table 2, after doped in 85 wt% PA solution at room temperature for 12 h, the PDA-PBI membrane with high doping level also shows a

Table 2		
Mechanical properties of	f acid doped PDA-PBI membra	ane.
Mombrano camplo	Topsilo strongth (MPa)	Elongation at bra

Membrane sample	lensile strength (MPa)	Elongation at break (%)
Acid doped PDA-PBI	12.3	40.5

tensile strength of 12.3 MPa. The relatively good mechanical strength can be attributed to the high molecular weight and improved flexibility of the synthesized PDA-PBI.

#### 3.7. Oxidative stability

The lifetime at operational conditions is an important index of the polymer electrolyte membrane. It is generally believed that membrane degradation caused by radicals, such as hydroxyl (HO•) and hydroperoxy (HOO•), is one of the major durability issues for polymer electrolyte membrane fuel cells [37]. Experimentally, Fenton's reagent is extensively employed to simulate the practical operational environment of fuel cells. In this work, the undoped membrane was immersed in Fenton's reagent at 70 °C under stirring for 7 days. The degradation of the membrane was evaluated by determining the weight loss. Fig. 7 showed the weight loss as a function of time. As can be observed, the weight of the membrane was almost unchanged (less than 1%) within 60 h in Fenton's reagent test. However, the weight of the membrane decreased gradually as the time went on. After 168 h of Fenton reagent test, the membrane remained intact and displayed a weight loss of less than 9 wt%, showing relatively good oxidative stability.

#### 3.8. Fuel cell test

Due to the relatively higher ion conductivity and good oxidative stability of PDA-PBI membrane, a single fuel cell was assembled employing PA doped membrane (75  $\mu$ m) which doped with 85% phosphoric acid for 12 h. Pt/C was used as a catalyst with a loading of 0.6 mg cm<sup>-2</sup>. The performance of the H<sub>2</sub>/O<sub>2</sub> cell was tested under 0% relative humidity (RH) at temperature of 120, 140 and 160 °C. Fig. 8 shows the polarization curves (dashed lines) and power density (solid lines) for MEA equipped with PA doped PDA-PBI membrane. As can be seen, the open circuit voltage (OCV) of the H<sub>2</sub>/O<sub>2</sub> fuel cell was about 0.91 V, indicating that the membrane was dense, as well as a good barrier between H<sub>2</sub> and O<sub>2</sub> gases. The voltage of cell declined sharply after an initial increase in current density because of the activation loss. The cell exhibited increased performance at higher temperature, which benefited from the improved electrode kinetics and higher electrolyte conductivity.



Fig. 7. Fenton test results of undoped PDA-PBI membrane.



Fig. 8. Polarization curves (dashed lines) and power densities (solid lines) of single fuel cell.

The maximum power density was found to be 460 mWcm<sup>-2</sup> at 160 °C, 420 mWcm<sup>-2</sup> at 140 °C, 333 mWcm<sup>-2</sup> at 120 °C, respectively. The relatively high performance of the single cell could be preliminarily attributed to the high ion conductivity of the acid doped membrane because the MEA fabrication had not yet been optimized. Compared with the state of the art PBI MEAs, the performance is very promising, indicating the potential of this membrane to be used in high temperature PEM fuel cell applications.

The durability test of the single cell based on acid doped PDA-PBI membrane was carried out under continuous steady state operation at a constant load of 300 mA cm<sup>-1</sup> at 140 °C without humidification. The variation of cell voltage (V) was plotted against testing time and the result was shown in Fig. 9. During the initial 100 h operation, the cell voltage increased from 0.56 to 0.58 V, which may due to the activation effect of MEA [10]. The MEA based on acid doped PDA-PBI membrane had operated for 900 h and showed good stability. After a voltage-stabilized period, the cell performance exhibited an average voltage decrease rate of about 2.67 × 10<sup>-5</sup> V h<sup>-1</sup> from 150 to 900 h.



Fig. 9. Durability test in terms of the cell voltage under a constant load of 300 mA cm $^{-2}$  at 140  $^\circ\text{C}.$ 

#### 4. Conclusions

A novel PDA-PBI polymer incorporating ether groups and pyridine units was successfully synthesized in pentoxide/methanesulfonic acid (PPMA) by polycondensation of 3,3'-diaminobenzidine and 4,4'-(pyridine-2,6-diylbis(oxy))dibenzoic acid (PDA). Incorporation of the ether group and pyridine unit in the macromolecular structures resulted in the synthetic polymer with high molecular weights and good solubility. Homogeneous membranes were prepared by solution casting method and displayed high proton conductivity after doped in PA with high doping level. The TGA measurements confirm the good thermal stability of the PDA-PBI polymers below 350 °C. Fenton test results show the undoped membrane possesses reasonable oxidative stability. Fuel cell tests employing the synthesized membranes were carried out at temperatures of 120,140 and 160 °C with unhumidified hydrogen and oxygen. The single fuel cell had reached to the maximum power outputs of 333, 420 and 460 mW/cm<sup>-2</sup> when the fuel cell operating temperatures were at 120, 140 and 160 °C, respectively. The MEA durability test showed a stable performance without any noticeable degradation for 900 h. These results indicate that the novel PDA-PBI membrane is a promising candidate for high-temperature polymer membrane fuel cells.

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