

# Preparation and evaluation of a proton exchange membrane based on oxidation and water stable sulfonated polyimides

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Received 1 July 2007; received in revised form 26 July 2007; accepted 26 July 2007

Available online 8 August 2007

## Abstract

A series of novel oxidation and water stable sulfonated polyimides (SPIs) were synthesized from 4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BTDA), and wholly aromatic diamine 2,2'-bis(3-sulfobenzoyl) benzidine (2,2'-BSBB) for proton exchange membrane fuel cells. These polyimides could be cast into flexible and tough membranes from *m*-cresol solutions. The copolymer membranes exhibited excellent oxidative stability and mechanical properties due to their fully aromatic structure extending through the backbone and pendant groups. Moreover, all BTDA-based SPI membranes exhibited much better water stability than those based on the conventional 1,4,5,8-naphthalenecarboxylic dianhydride. The improved water stability of BTDA-based polyimides was attributed to its unique binaphthalimide structure. The SPI membranes with ion exchange capacity (IEC) of 1.36–1.90 mequiv g<sup>-1</sup> had proton conductivity in the range of  $0.41 \times 10^{-1}$  to  $1.12 \times 10^{-1}$  S cm<sup>-1</sup> at 20 °C. The membrane with IEC value of 1.90 mequiv g<sup>-1</sup> displayed reasonably higher proton conductivity than Nafion<sup>®</sup> 117 ( $0.9 \times 10^{-1}$  S cm<sup>-1</sup>) under the same test condition and the high conductivity of 0.184 S cm<sup>-1</sup> was obtained at 80 °C. Microscopic analyses revealed that well-dispersed hydrophilic domains contribute to better proton conducting properties. These results showed that the synthesized materials might have the potential to be applied as the proton exchange membranes for PEMFCs.

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**Keywords:** Proton exchange membrane; Sulfonated copolyimides; Hydrolytic stability; Oxidative stability; Proton conductivity

## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have attracted more and more attention because of their high power density and high energy conversion efficiency as well as low pollution levels [1–4]. One of the important challenges in the current fuel cell research is to develop an alternative membrane to the perfluorinated ionomers, for example, Nafion<sup>®</sup> (Du pont). Nafion<sup>®</sup> is chemically robust in oxidizing environments and has good proton conductivity when hydrated. However, some specific limitations exist for Nafion<sup>®</sup> membranes including very high cost, high gas permeability, CO poisoning, and loss of the preferable properties at high temperature (>80 °C) [5,6].

In recent years, many kinds of sulfonated aromatic polymers have been developed [7–15]. Sulfonated polyimides (SPIs) with six-membered imide rings have been identified as one of the most promising membrane materials for PEMFC application due to their low methanol permeability, excellent thermal and mechanical stabilities, and good film forming ability [16–23]. Some of them have been claimed to display higher proton conductivity than perfluorinated materials. However, aromatic polyimides tend to hydrolyze under high moisture conditions and at high temperatures, and these result in the degradation of the polymer main chain and a dramatic drop in mechanical strength. To achieve the high water stability, a variety of SPIs based on novel sulfonated diamines have been designed on the basis of knowledge acquired on the structure–property relationships. As it has been reported, polyimides with flexible structure [18,24] and high basicity of the sulfonated diamine moieties [20,25] tend to have good water stability because

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the flexibility allows easy relaxation of polymer chain and the high basicity of the sulfonated diamine moieties depresses the hydrolysis of imido rings. Recently, we have reported the synthesis of polyimides bearing sulfobenzoyl side groups based on 2,2'-bis(3-sulfobenzoyl)benzidine (2,2'-BSBB) and 1,4,5,8-naphthalenecarboxylic dianhydride (NTDA) [26]. These novel SPIs membranes showed high proton conductivity but poor water stability because of the lower basicity of sulfonated and non-sulfonated diamine. To improve the water stability and maintain other desirable properties, efforts have been made to develop membrane materials based on 4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BTDA) and 2,2'-BSBB. BTDA has two anhydride groups which are located on the two twist non-coplanar naphthalene rings [27]. As a result, the polyimides from BTDA should possess a decreased positive charge density of carbonyl groups in the naphthalimide moieties compared with that from NTDA. This is favorable to depress the hydrolysis of the imide rings. Recently, Yan and Ding et al. found that SPIs from BTDA had better water resistance than that from BTDA and the same diamines [28]. In this paper, we report the synthesis of novel polyimide ionomers from BTDA and 2,2'-BSBB. The effects of both the dianhydride and the diamines structures on the properties (including proton conductivity, oxidative and water stability, and membrane morphologies) of the copolymers were evaluated through the study of their electrolytic properties. This will be instructional in designing better membranes for improved fuel cell performance.

## 2. Experimental

### 2.1. Materials

4,4'-Binaphthyl-1,1',8,8'-tetracarboxylic dianhydride was prepared according to the method previously reported [27]. Triethylamine (TEA) was dried with 4 Å molecular sieves prior to being used. 4,4'-Diaminodiphenyl ether (ODA) and 2,2'-bis(4-aminophenyl)hexafluoropropane (BAPHF) were purchased from Aldrich and used as received. 2,2'-bis(3-sulfobenzoyl)benzidine (2,2'-BSBB) was synthesized according to the method previously reported [26]. All other reagents were used as received without further purification.

### 2.2. Polymer synthesis and membrane preparation

#### 2.2.1. Synthesis of sulfonated copolyimides

**SPI (I)-50:** To a 100 mL completely dried three-necked flask were added 0.392 g (1 mmol) of 2,2'-BSBB, 5 mL of *m*-cresol, and 0.68 mL of Et<sub>3</sub>N successively under nitrogen flow. After the 2,2'-BSBB was completely dissolved, 0.789 g (2 mmol) of BTDA, 0.200 g (1 mmol) of non-sulfonated diamine (ODA) and 0.488 g benzoic acid were added. The mixture was stirred at room temperature for a few minutes and then heated at 80 °C for 4 h and at 180 °C for 20 h. After the mixture cooled to 80 °C, additional 10 mL of *m*-cresol was added to dilute the highly viscous solution, and then the solution was poured into acetone. The fiber-like precipitate was filtered off, washed with acetone thoroughly, and dried in vacuum oven for 12 h at 150 °C to

give product with 97% of yield. FT-IR 1704 cm<sup>-1</sup> (ν<sub>sym</sub>C=O), 1658 cm<sup>-1</sup> (ν<sub>asym</sub>C=O) and 1364 cm<sup>-1</sup> (ν<sub>C-N</sub> imide).

Copolymers **SPI(I)-60**, **SPI(I)-70**, **SPI(I)-80**, **SPI(II)-70** and **SPI(II)-80** were prepared by following the same procedure as above, except that the feed ratio of the sulfonated diamine to non-sulfonated diamine was different.

#### 2.2.2. Membrane preparation

The sulfonated copolyimides were dissolved in *m*-cresol to form a 4–5 wt.% solution at 80 °C. Then the solution was filtered and cast on a glass sheet. The solvent was evaporated by heating at 120 °C for 12 h. The as-cast membranes were soaked in ethanol for 24 h to remove the residual solvent, and then treated with 1.0 mol L<sup>-1</sup> sulfonic acid at room temperature for 72 h for proton exchange. The proton exchange membranes were thoroughly washed with water and then dried in vacuum at 150 °C for 10 h.

### 2.3. Membrane characterization

#### 2.3.1. Measurements

<sup>1</sup>H NMR spectra were measured at 300 MHz on an AV 600 spectrometer in DMSO-*d*<sub>6</sub>. FT-IR spectra of the SPI membranes were obtained with a Bio-Rad digilab Division FTS-80 FT-IR spectrometer (Cambridge, MA). The inherent viscosities were determined on 0.5 g dL<sup>-1</sup> concentration of polymer in *m*-cresol with an Ubbelohde capillary viscometer at 30 ± 0.1 °C. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin-Elmer TGA-2 thermogravimetric analyzer (Inspiritech 2000 Ltd., UK) at a heating rate of 10 °C min<sup>-1</sup>. Tensile measurement was performed with a mechanical tester Instron-1211 instrument (Instron Co., U.S.A.) at a speed of 2 mm min<sup>-1</sup> at ambient conditions (at 30 °C and 50% relative humidity), and the size of specimen was 10 mm × 4 mm. Before testing, each specimen was dried at ambient conditions for 1 day. For each testing, three measurements at least were recorded and the average value was calculated.

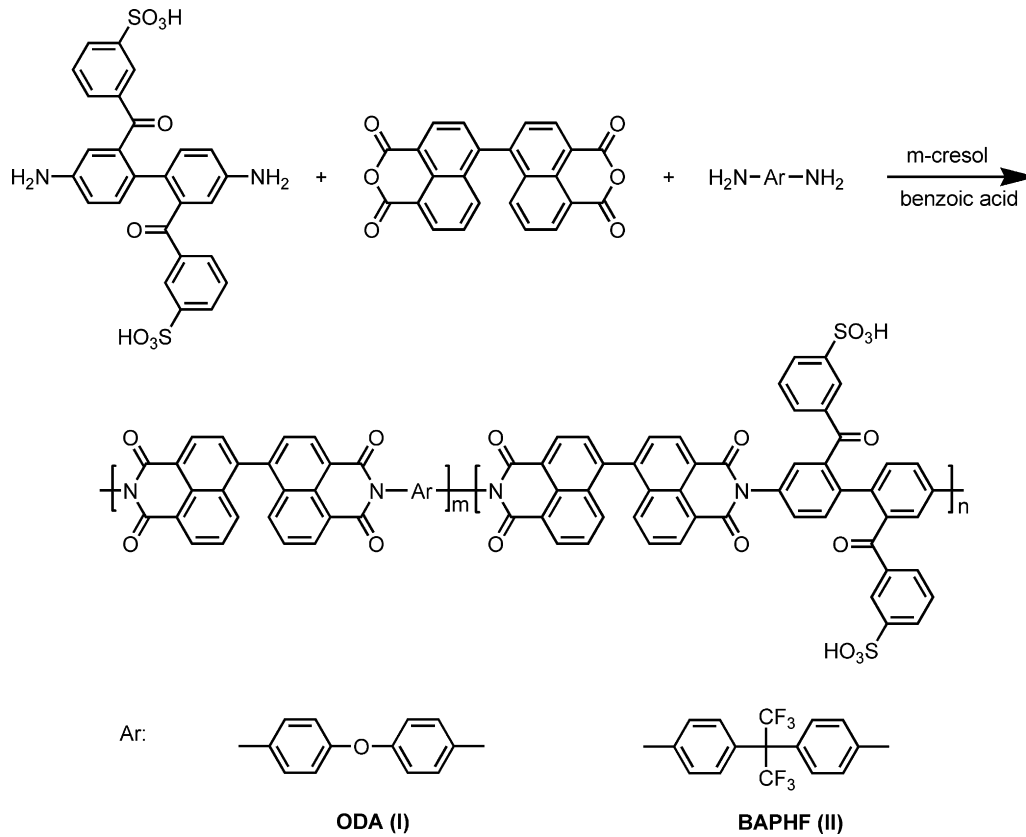
#### 2.3.2. Ion exchange capacity

Ion exchange capacity (IEC) of the membranes was determined through titration. The membranes in the H<sup>+</sup> form were immersed in a 1 mol L<sup>-1</sup> NaCl solution for 24 h to liberate the H<sup>+</sup> ions (the H<sup>+</sup> ions in the membrane were replaced by Na<sup>+</sup>). The H<sup>+</sup> ions in solution were then titrated with 0.01 mol L<sup>-1</sup> NaOH using phenolphthalein as an indicator.

#### 2.3.3. Water uptake and dimensional change

The membrane (30–40 mg per sheet) was dried at 80 °C under vacuum for 6 h until constant weight as dry material was obtained. It was immersed into deionized water at given temperature for 4 h and then quickly taken out, wiped with tissue paper, and quickly weighted on a microbalance. Use Eq. (1) to calculate the water uptake (WU):

$$WU = \frac{W_s - W_d}{W_d} \quad (1)$$



Scheme 1. The structure of sulfonated copolyimides.

where  $W_s$  and  $W_d$  are the weight of dry and corresponding water-swollen membranes, respectively.

The dimension changes of the membranes were measured in thickness and in the plane direction, which were characterized by Eq. (2):

$$\Delta T_c = \frac{T - T_s}{T_s}; \quad \Delta L_c = \frac{L - L_s}{L_s} \quad (2)$$

where  $T_s$  and  $L_s$  are the thickness and diameter of the membrane equilibrated at 70% relative humidity (RH), respectively;  $T$  and  $L$  refer to those of the membrane equilibrated in liquid water for 5 h.

The number of water molecules per ionic group ( $\lambda$ ) can be determined from water uptake and the IEC of the membrane by Eq. (3) as follows:

$$\lambda = \frac{n(\text{H}_2\text{O})}{n(\text{SO}_3^-)} = \frac{\text{water uptake}}{18 \text{ IEC}} \quad (3)$$

where  $n(\text{H}_2\text{O})$  is the  $\text{H}_2\text{O}$  mol number,  $n(\text{SO}_3^-)$  the  $\text{SO}_3^-$  group mol number, and 18 corresponds to water molecular weight ( $18 \text{ g mol}^{-1}$ ).

### 2.3.4. Oxidative stability

A small piece of membrane sample (30–40 mg) with a thickness of about  $45 \mu\text{m}$  was soaked in Fenton's reagent (30 ppm  $\text{FeSO}_4$  in 30%  $\text{H}_2\text{O}_2$ ) at  $25^\circ\text{C}$ . The stability was evaluated by recording the time when membranes began to dissolve and dissolved completely.

### 2.3.5. Hydrolytic stability

A small piece of membrane sample with a thickness  $40 \mu\text{m}$  was treated at  $140^\circ\text{C}$  and 100% RH in a pressurized closed vial for 48 h. The stability was evaluated by changes in weight and appearance of the test samples.

### 2.3.6. Proton conductivity

Proton conductivity of the SPI membranes and Nafion<sup>®</sup> 117 membrane were measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation and 0.0 V dc rest voltage. Impedance spectra were recorded using a Princeton Applied Research Model 273A Potentiostat (Model 5210 Frequency Response Detector, EG&G PARC, Princeton, NJ). The membranes were fixed in a measuring cell made of two outer gold wires to feed current to the sample and two inner gold wires to measure the voltage drops [29]. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. The proton conductivity ( $\sigma$ ) of the membranes was calculated using the following equation:

$$s = \frac{L}{RA} \quad (4)$$

where  $L$ ,  $R$ , and  $A$  denote the distance between the two inner gold wires, the resistance of the membrane, and the cross-sectional area of the membrane, respectively.

### 3. Results and discussion

#### 3.1. Polymers synthesis and characterization

A series of sulfonated copolyimides were synthesized by a one-step method in *m*-cresol in the presence of TEA and benzoic acid. TEA was used to liberate the protonized amino groups for polymerization with BTDA, and benzoic acid acted as catalyst. The degree of sulfonation (DS) of the copolymer was readily controlled through the monomer feed ratios of sulfonated diamine to non-sulfonated diamine, ODA (I), or BAPHF (II) (Scheme 1), so that a series of copolyimides with different IEC values could be obtained. The copolymers were denoted as **SPI(I)-x**, **SPI(II)-x** where **x** was the molar fraction of 2,2'-BSBB in the feed. Intrinsic viscosity values of all copolymers were higher than 1.22 dL g<sup>-1</sup> in *m*-cresol at 30 °C, which indicated successful copolymerization in producing high molecular copolymers. The solubility behavior of SPIs in polar organic solvents was listed in Table 1. All copolymers in TEA salt form are soluble in *m*-cresol, DMSO and NMP, but not soluble in DMAc and DMF. However, the polymers in acid form are less soluble in polar solvents. The <sup>1</sup>H NMR spectrum of **SPI(I)-50** in DMSO-*d*<sub>6</sub> showed peaks of aromatic protons at δ 7.31–8.74 ppm, all of which were well assigned to the supposed chemical structure (Fig. 1). Peak that appeared at δ 8.60 ppm was assigned to the chemical shifts of hydrogen of BTDA (H2 and H2'), and δ 7.31 ppm is the hydrogen of ODA (Ha). The integration ratio of H2 and H2' to Ha is very close to 1:1, as expected for the composition of **SPI(I)-50**. Fig. 2 shows the IR spectra of **SPI(I)-x**. The strong absorption bands around 1705 cm<sup>-1</sup> (*v*<sub>sym</sub>C=O), 1658 cm<sup>-1</sup> (*v*<sub>asym</sub>C=O) and 1364 cm<sup>-1</sup> (*v*<sub>C-N</sub> imide) were assigned to the naphthalenic imide rings. The bands around 1189, 1093 and 1034 cm<sup>-1</sup> were due to asymmetric and symmetric S=O stretching vibration of sulfonic acid groups. The intensity of these peaks increased with an increasing of sulfonated monomer ratio.

#### 3.2. Thermal and mechanical properties

Fig. 3 shows the thermal stability of the copolymer **SPI(I)-x** in acid form investigated by TGA. It can be seen that the SPI membranes exhibited a typical three-step degradation pattern. The first weight loss up to ca. 200 °C was ascribed to the loss of water molecules, absorbed by the highly hygroscopic

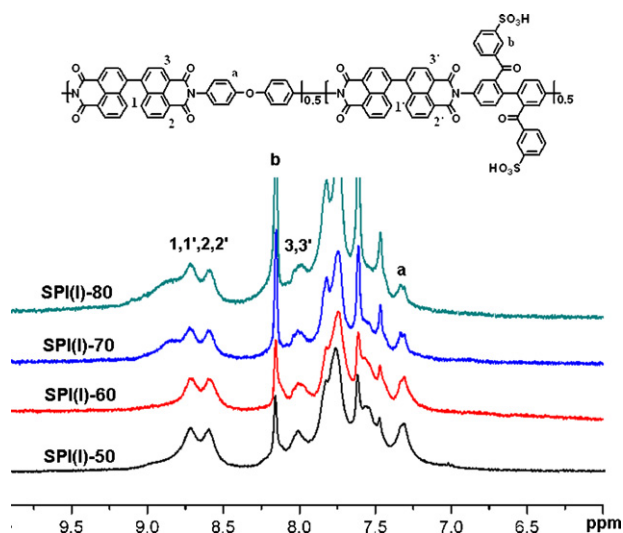


Fig. 1. <sup>1</sup>H NMR spectra of **SPI(I)-x** in DMSO-*d*<sub>6</sub>.

–SO<sub>3</sub>H groups. The second step in range of 300–350 °C was attributed to the cleavage of sulfonic acid groups. The second decomposition temperature of the polymers was much higher than that of the main-chain-type sulfonated polyimides (about 280 °C) [24], indicating that the sulfonic acid groups attached to electron deficient phenyl rings have high thermal stability

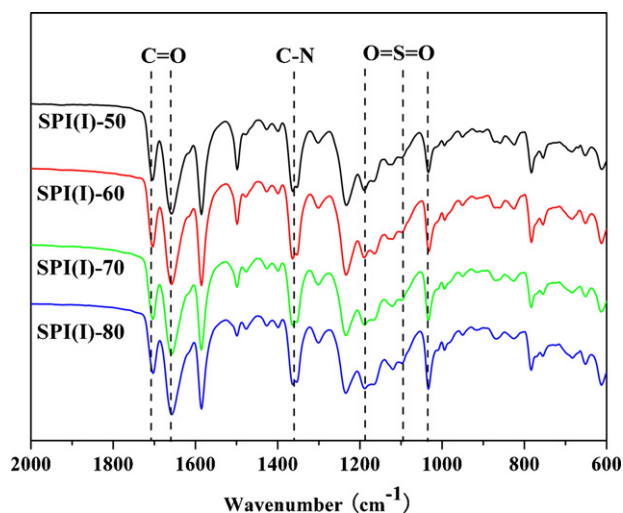


Fig. 2. FT-IR spectra of **SPI(I)-x** membranes in acid form.

Table 1  
Solubility of SPIs in TEA salt form and acid form

Membranes	$\eta^a$ (dL g <sup>-1</sup> )	<i>m</i> -Cresol	DMSO	NMP	DMF	DMAc
SPI(I)-50	1.26	++ (+)	++ (+)	+ (–)	– (–)	– (–)
SPI(I)-60	1.28	++ (+)	++ (+)	+ (–)	– (–)	– (–)
SPI(I)-70	1.25	++ (+)	++ (+)	+ (–)	– (–)	– (–)
SPI(I)-80	1.30	++ (+)	++ (+)	+ (–)	– (–)	– (–)
SPI(II)-70	1.32	++ (+)	++ (+)	+ (–)	– (–)	– (–)
SPI(II)-80	1.23	++ (+)	++ (+)	+ (–)	– (–)	– (–)

The data in parenthesis refer to the acid form. ‘++’ Easily soluble, ‘–’ insoluble, ‘+’ soluble by heating, and ‘+–’ partially soluble.

<sup>a</sup> 0.5 g dL<sup>-1</sup> in *m*-cresol at 30 °C.

Table 2

Mechanical properties of SPI membranes in dry state (samples were dried at ambient conditions for 1 day and tested at 30 °C, 50% RH)

Membranes	IEC (mequiv g <sup>-1</sup> )	Water uptake (%W/W) <sup>a</sup>	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
SPI(I)-50	1.36	8.8	202.1	1.86	44.4
SPI(I)-60	1.56	11.4	189.1	1.58	36.9
SPI(I)-70	1.74	13.5	180.0	1.83	32.8
SPI(I)-80	1.90	15.8	170.8	1.77	25.5
SPI(II)-70	1.66	12.0	112.1	1.10	29.5
SPI(II)-80	1.84	14.1	99.8	1.17	23.8

<sup>a</sup> Measured at 30 °C, 50% RH.

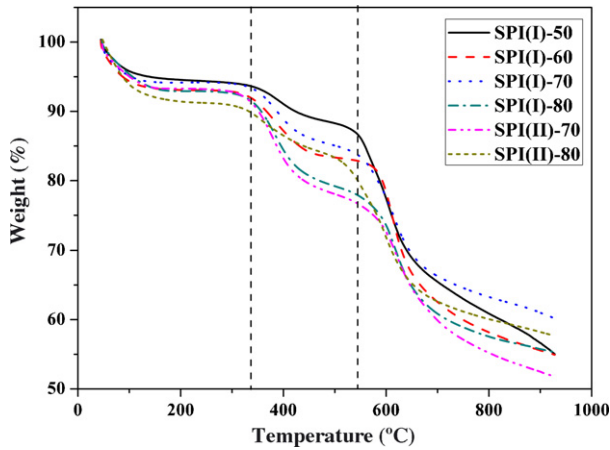


Fig. 3. TGA curves of SPI membranes in acid form in nitrogen.

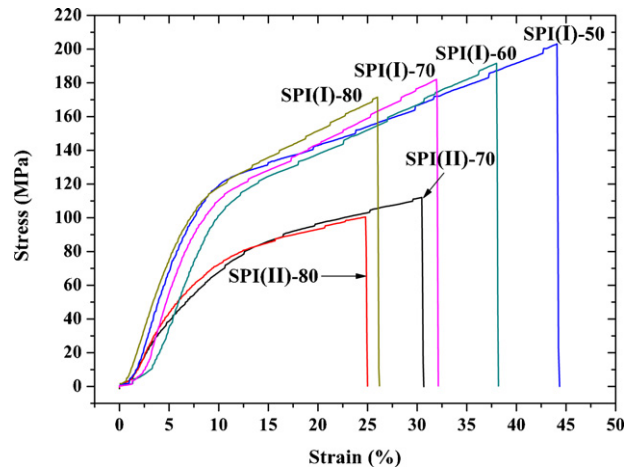


Fig. 4. Tensile stress–strain curves of SPI membranes (samples were dried at ambient conditions for 1 day and tested at 30 °C, 50% RH).

[15]. The third stage weight loss around 550 °C is assigned to the decomposition of polymer main chain. From this result, it is concluded that the **SPI(I)-x** membranes are thermally stable within the temperature range for PEMFC applications.

The mechanical properties of the SPI membranes were summarized in Table 2. The stress–strain data are shown in Fig. 4. The SPI membranes had tensile stress at maximum load of 100–202 MPa, Young's moduli of 1.1–1.9 GPa, and elongations at break of 24–44%. These SPI membranes showed higher maximum stress, Young's modulus because of their rigid molecular structure. As shown in Table 2, the tensile strength and Young's modulus of the SPI membranes are decreased with the increasing water uptake. The similar phenomenon was observed in our previous study [15]. This phenomenon is attributed to the plastic effect of the absorbed water.

### 3.3. Water uptake and dimensional change

The water uptake of the SPI membranes was mainly determined by IEC. However, the structure of polymer chain also has an obvious effect on the water uptake. Fig. 5 shows the temperature dependence of water uptake. The water uptake increased almost linearly with increasing temperature. At room temperature, the water uptake of the membranes with IEC from 1.36 to 1.90 mequiv g<sup>-1</sup> was in the range of 29.8–53.5%, which was lower than that of NTDA-based sulfonated polyimide membranes. For example, the **SPI(I)-80** membrane (IEC=1.90 mequiv g<sup>-1</sup>) showed lower WU (53.5%) than that of NTDA-based polyimide with the same sulfonated diamine (2,2'-BSBB) (64%, IEC = 1.89 mequiv g<sup>-1</sup>) [26]. The relatively lower WU of **SPI(I)-x** could be interpreted by the hydrophobic

Table 3

Ion exchange capacity, water uptake and dimensional changes of various SPI membranes

Membranes	IEC (mequiv g <sup>-1</sup> )		$\lambda$	Water uptake (%W/W)	Dimensional changes		Reference
	Calculated	Measured			$\Delta T$	$\Delta L$	
SPI(I)-50	1.36	1.32	12.2	29.8	0.11	0.01	This work
SPI(I)-60	1.56	1.55	12.6	35.5	0.14	0.01	This work
SPI(I)-70	1.74	1.71	12.9	40.5	0.18	0.01	This work
SPI(I)-80	1.90	1.87	15.6	53.5	0.24	0.02	This work
SPI(II)-70	1.66	1.59	12.5	37.5	0.13	0.01	This work
SPI(II)-80	1.84	1.80	16.6	55.0	0.19	0.01	This work
NTDA/2,2'-BSBB(70)	1.91	1.89	18.8	64.0	0.35	0.06	[26]

Table 4  
Hydrolytic stability of SPI membranes

Membranes	IEC (mequiv g <sup>-1</sup> )	90 °C in water time (h)	140 °C in water			Reference
			Time (h)	Decrease in weight (%)	Toughness	
SPI(I)-50	1.36	>1000	48	0	○	This work
SPI(I)-60	1.56	>1000	48	0	○	This work
SPI(I)-70	1.74	800	48	1	○	This work
SPI(I)-80	1.90	360	48	5	⊗	This work
SPI(II)-70	1.66	130	48	1	○	This work
SPI(II)-80	1.84	160	48	6	⊗	This work
NTDA/2,2'-BSBB(70)	1.89	24	24	NM	×	[26]

‘○’ mechanical strength was maintained; ‘⊗’ somewhat brittle; ‘×’ broken into little pieces; ‘NM’ not measured.

character of binaphthyl groups. Accordingly, the SPI membranes displayed lower dimensional changes. As shown in Table 3, the SPI membranes exhibits highly anisotropic membrane swelling in water, that is, much larger swelling in membrane thickness direction than that in plane direction. For instance, the membrane **SPI(I)-80** showed 10 times larger swelling in thickness direction (24%) than that in plane direction (2%). The similar tendency was also found in the NTDA-based membranes having other benzidine diamines, such as BSPB [21] and BSPbB [30]. The anisotropic membrane swelling is considered due to in plane polymer chain alignment.

### 3.4. Membrane stability toward water and oxidation

The water stability test for the copolymer membranes was carried out by immersing the membranes into water at 90 °C and the stability was characterized by the elapsed time when the hydrated membranes start to lose mechanical properties. The criterion for the judgment, for example, loss mechanical strength is that the membrane breaks when it is lightly bent. It is interesting to compare the stability of BTDA-based polyimide membranes with that of NTDA-based ones. As shown in Table 4, the copolymer membranes based on BTDA display much better water stability than those based on NTDA. The

copolyimide membrane (**SPI(I)-80**), for example, loses mechanical properties after being soaked in hot water for 360 h whereas the membrane based on NTDA and 2,2'-BSBB became brittle within 24 h [26]. As an accelerated hydrolytic stability testing, the polyimide ionomers were treated at 140 °C in water for 48 h, and the weight loss of the copolymers were determined. As listed in Table 4, all of the SPI membranes retained more than 94% of their original weight after the testing. Fig. 6 shows the IR spectra of **SPI(I)-70** before and after the aging. There was no appreciable change except for appearance of very weak peak of acid carbonyl at 1780 cm<sup>-1</sup> after the testing. However, the acid carbonyl peak was much smaller than the imide carbonyl peak at 1705 cm<sup>-1</sup>. Nevertheless, NTDA- and 2,2'-BSBB-based polyimides had not ensured the testing. These results confirmed that the polyimide ionomers based on BTDA exhibited much better hydrolytic stability. The improved hydrolytic stability of BTDA-based polyimides could result from its unique binaphthalimide structure. BTDA had two carbonyl groups in the separated naphthyl rings whereas NTDA had four carbonyl groups in the same naphthyl ring. Therefore, the copolymers from BTDA should possess decreased positive charge density in carbonyl groups compared with that of the copolymers from NTDA because of the electron withdrawing characteristics of carbonyl groups. In addition, the binaphthalimide groups are more hydrophobic

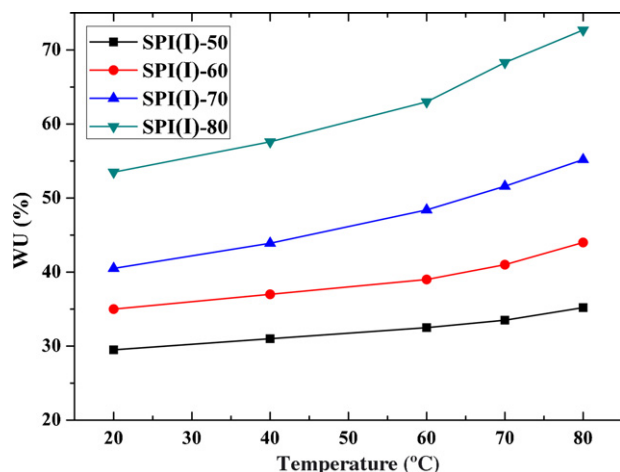


Fig. 5. Water uptake in liquid water as a function of temperature for SPI(I)-x membranes.

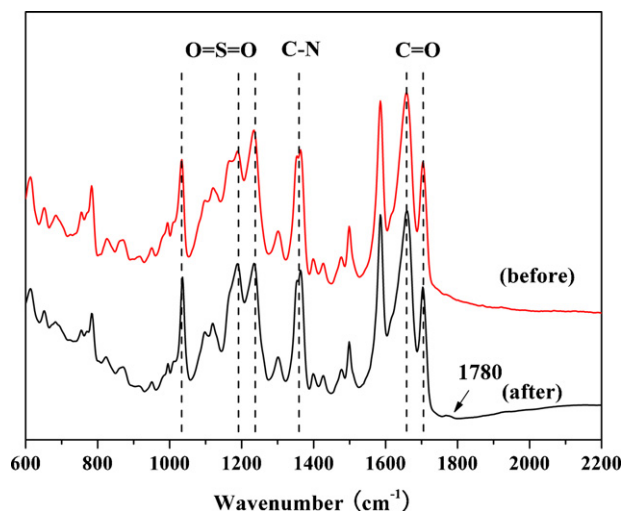


Fig. 6. IR spectra of SPI(I)-70 before and after aging in water 140 °C for 48 h.

Table 5  
Oxidative stability of SPI membranes

Membranes	IEC (mequiv g <sup>-1</sup> )	Oxidative stability <sup>a</sup>		Reference
		$\tau_1^b$ (h)	$\tau_2^c$ (h)	
SPI(I)-50	1.36	33	42	This work
SPI(I)-60	1.56	42	45	This work
SPI(I)-70	1.74	35	41	This work
SPI(I)-80	1.90	34	40	This work
SPI(II)-70	1.66	48	52	This work
SPI(II)-80	1.84	42	48	This work
NTDA/2,2'-BSBB(70)	1.89	24	89	[26]

<sup>a</sup> 30 °C in 30% H<sub>2</sub>O<sub>2</sub> containing 30 ppm FeSO<sub>4</sub>.

<sup>b</sup> The time when the membrane broke into pieces after being shaken drastically.

<sup>c</sup> The time when the membrane dissolved completely.

than the naphthalimide groups due to its decreased density of the polar carbonyl groups in the binaphthalimide groups. The highly hydrophobic nature of the binaphthalene backbone resists the approach of water to a great extent and hence prevents the rapid attack of water, which increases the overall stability of the membranes.

The stability of the polyimides to oxidation was also investigated by immersing the membranes into Fenton's reagent (30 ppm FeSO<sub>4</sub> in 30% H<sub>2</sub>O<sub>2</sub>) at 25 °C. The oxidative stability of the samples was characterized by elapsed time at which the membranes started to dissolve and dissolved completely in the solution. As shown in Table 5, all SPI membranes showed excellent oxidative stability due to the wholly aromatic sulfonated diamine. The time of the membranes started to dissolve (>33 h) larger than that of those copolyimides based on NTDA and 4,4'-diaminodiphenylether-2,2'-disulfonic acid (ODADS) [18], 9,9-bis(4-aminophenyl)fluorene-2,7-disulfonic acid (BAPFDS) [24] and 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid (BAPBDS) [31] which all are lower than 30 h. Although the SPI(I)-x membranes contain an ether bond, they show better oxidative stability than that of NTDA/2,2'-BSBB(70) [26]. The results indicated that the hydrolytic stability of sulfonated polyimides have an effect on the oxidative stability.

### 3.5. Proton conductivity and membrane morphology

The proton conductivities of SPI(I)- and SPI(II)-x copolymers along with that of Nafion<sup>®</sup> 117 were measured at 100% RH and plotted as functions of temperature in Fig. 7. The copolymer membranes showed the proton conductivities in the range of  $4.1 \times 10^{-2}$  to  $1.12 \times 10^{-1}$  S cm<sup>-1</sup> at 20 °C (Table 6). Copolymer SPI(I)-80 with 53.5% water uptake shows a conductivity of  $1.12 \times 10^{-1}$  S cm<sup>-1</sup> at 20 °C which is higher than that of Nafion<sup>®</sup> 117 ( $0.90 \times 10^{-1}$  S cm<sup>-1</sup>, WU = 33.4%) measured at the same conditions, and it is assumed that the high water uptake lead to the high proton conductivity. Furthermore, the proton conductivity of SPI(I)-80 is comparable with that of the sulfonated polyimide membranes based on BTDA and ODADS (75) ( $1.11 \times 10^{-1}$  S cm<sup>-1</sup>, IEC = 2.21 mequiv g<sup>-1</sup>, WU = 53%) [28]. The relatively higher proton conductivity of SPI(I)-80 is attributed to the higher acidity of benzoyl sulfonic acid group, as well as the larger interchain spacings which is available for water

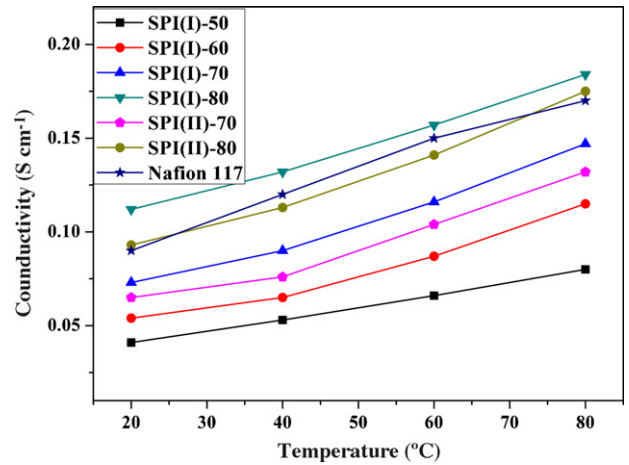


Fig. 7. Proton conductivity of SPI membranes and Nafion<sup>®</sup> 117 at different temperatures under fully hydrated conditions (in water).

to occupy. Their proton conductivities increased with IEC and water uptake, and showed a linear dependence on the temperature. Moreover, the water uptake shows a linear dependence on the temperature (Fig. 5), which indicates that the protons migrate predominantly via the vehicle mechanism in sulfonated polyimide membranes, in which only protons are mobile with the assistance of diffusible molecules, such as H<sub>3</sub>O<sup>+</sup> or H<sub>5</sub>O<sub>2</sub><sup>+</sup>. Consequently, it is not difficult to understand that the proton conductivity increased with the water uptake.

Fig. 8 shows the morphology of sulfonated copolymer. The membranes were stained with Pb<sup>2+</sup> ions; therefore, the dark areas represent hydrophilic (ionic) domains and the brighter areas represent hydrophobic domains. As it is clearly seen in Fig. 8a, SPI(I)-50 exhibited spherical ionic clusters. The similar microstructure has been reported for the other series of sulfonated polyimide [20,21] which is based on the NTDA with similar IEC value. In the TEM image of SPI(I)-80 (Fig. 8d), high density and big ionic clusters were observed. The higher IEC causes the formation of such more and bigger ionic clusters than those of SPI(I)-50 and, therefore, the better connection of proton transport pathway. By combining the microscopic observation and proton conducting behavior (Fig. 7), it is concluded that more ionic clusters and dispersed and well-distributed water molecules are likely to promote proton transport properties in the sulfonated polyimide membranes.

Table 6  
Proton conductivity of SPI membranes and Nafion<sup>®</sup> 117 under fully hydrated conditions (in water)

Membranes	IEC (mequiv g <sup>-1</sup> )	$\sigma$ (S cm <sup>-1</sup> )	
		20 °C	80 °C
SPI(I)-50	1.36	0.041	0.082
SPI(I)-60	1.56	0.054	0.115
SPI(I)-70	1.74	0.073	0.147
SPI(I)-80	1.90	0.112	0.184
SPI(II)-70	1.66	0.065	0.139
SPI(II)-80	1.84	0.093	0.175
Nafion <sup>®</sup> 117	0.91	0.090	0.170

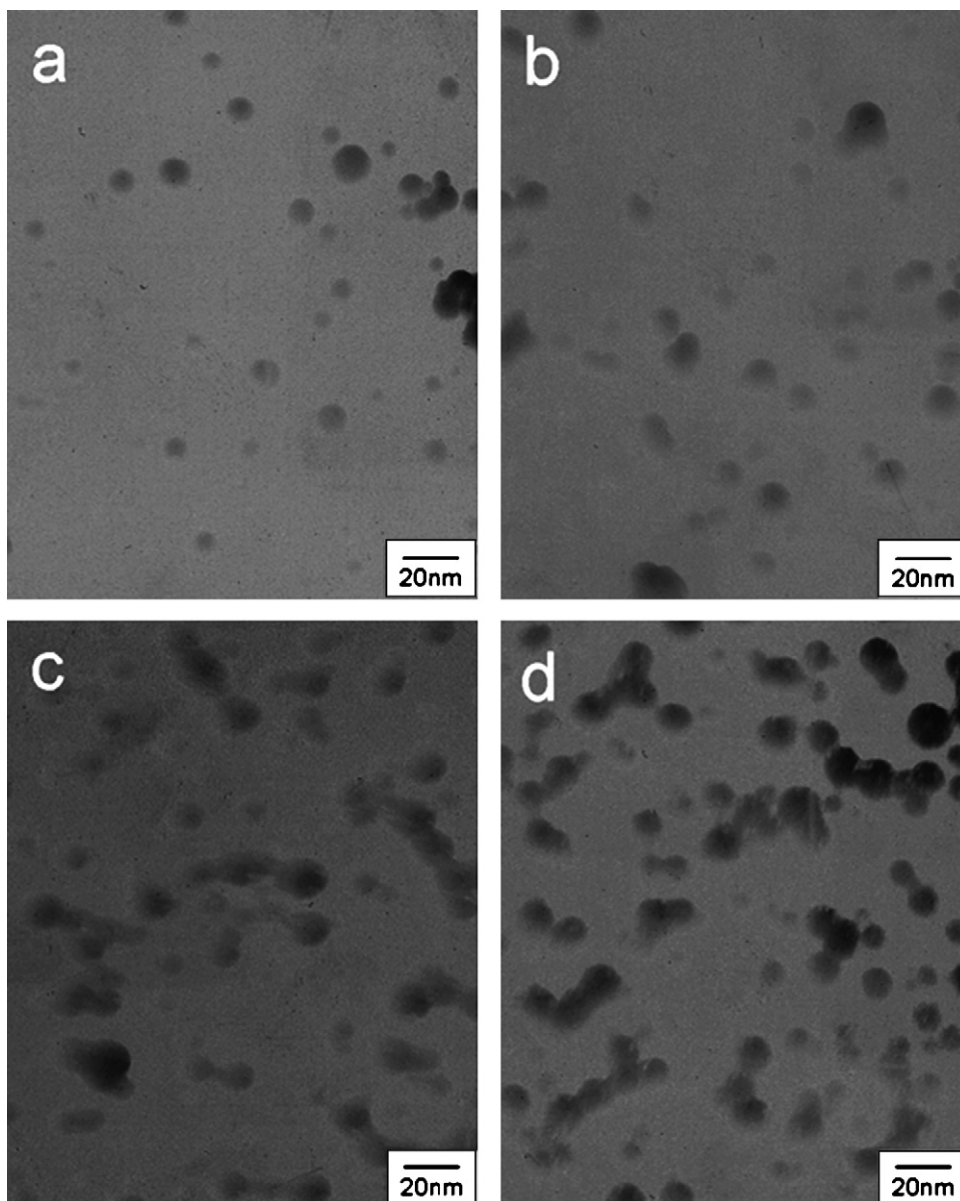


Fig. 8. TEM micrographs of SPI membranes: (a) **SPI(I)-50**; (b) **SPI(I)-60**; (c) **SPI(I)-70**; (d) **SPI(I)-80**.

#### 4. Conclusions

Proton conductive aromatic sulfonated polyimides were synthesized from 4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride and wholly aromatic diamine 2,2'-bis(3-sulfobenzoyl)benzidine (2,2'-BSBB) for proton exchange membrane fuel cells. The synthesized copolymers with  $-\text{SO}_3\text{H}$  group on the side chain of polymers possessed high molecular weights which were revealed by their high viscosity and the formation of tough and flexible membranes. The SPI membranes exhibited excellent water stability due to employing BTDA. The improved stability of BTDA-based polyimides was attributed to its unique binaphthalimide structure. The copolymer membranes exhibited excellent oxidative stability and mechanical properties due to their fully aromatic structure extending through the backbone and pendant groups. Under humidified conditions, **SPI(I)-80** membranes are highly proton conductive with

$1.12 \times 10^{-1} \text{ S cm}^{-1}$  of the conductivity at  $20^\circ\text{C}$ , which is higher than that of Nafion<sup>®</sup>117. Microscopic analyses revealed that well-dispersed hydrophilic domains contribute to better proton conducting properties. Consequently, these materials appeared to be promising as proton exchange membranes for PEMFCs.

#### Acknowledgements

We thank the National Basic Research Program of China (No. 2003CB615704) and the National Science Foundation of China (Nos. 20474061 and 50673087) for the financial support.

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