

# Sulfonated Polyimide Membranes for Polymer Electrolyte Fuel Cells

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**Introduction:** Polymer electrolyte membrane (PEM) is a key component of polymer electrolyte fuel cell (PEFC). Many types of sulfonated aromatic polymer membrane (1-3) have been developed as alternatives to perfluorinated ionomer membranes (4). Sulfonated polyimides (SPIs) are one of the promising candidates for PEMs because of their low fuel permeation, good film-forming ability and excellent mechanical, thermal and chemical properties (5). However, they have a disadvantage of hydrolysis of imide ring. The SPIs derived from 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) and benzidine-2,2'-disulfonic acid (BDSA) and nonsulfonated diamines such as 4,4'-oxydianiline (ODA), which have been most investigated (1, 2), have poor water stability at temperatures above 70 °C because of relatively easy hydrolysis of imide ring (6-8). We have investigated the structure-property relationship of SPIs with different sulfonated diamine moieties, and developed SPI membranes with reasonably high water stability and PEFC performance (5, 8-12). For example, SPIs derived from 2,2'- or 3,3'-bis(3-sulfopropoxy) benzidine (BSPB) showed much better membrane stability toward hot water than the BDSA-based ones due to the higher electron density (basicity) of the former diamines (10, 11). This was also supported by the works of Watanabe's research group. They reported that the BSPB-based SPIs showed the long-term durability of 5000 h in a PEFC system operated at 80 °C with a constant current density of 0.2 A/cm<sup>2</sup> (13). However, the sulfoalkoxy groups suffer from hydrolytic cleavage of the ether-linkage especially at high temperatures above 100 °C (8), resulting in large reduction in proton conductivity especially at the lower relative humidity.

In this paper, we report on novel SPI membranes with excellent water stability and their applications for PEFCs.

**Experimental:** Typical chemical structure of SPIs is shown in Fig. 1. They were synthesized by one-step condensation polymerization of NTDA, sulfonated and non-sulfonated diamines in *m*-cresol in the presence of triethylamine (TEA) and benzoic acid. 4,4'-Bis(4-aminophenoxy) biphenyl-3,3'-disulfonic acid (BAPBDS) and 2,2'-bis(4-sulfophenoxy)benzidine (BSPOB) were used as sulfonated diamines (9, 14). 4,4'-Bis(4-aminophenoxy)biphenyl (BAPB) and 1,3'-bis(4-aminophenoxy)benzene (BAPBz) were used as non-sulfonated diamines. Membranes were prepared by casting SPI solutions in *m*-cresol onto glass plates and dried at 120 °C for 10 h. The as-cast membranes were soaked in methanol at room temperature for 48 h, followed by the proton

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exchange treatment in 1 M sulfuric acid at 50 °C for 2-5 days. The membranes were finally cured in vacuum at 150 °C for 1 h and then at 180 °C for 1 h. The membrane thickness was 30-40 μm. The dry SPI membranes in proton form were immersed into a solution of phosphorous pentoxide and methanesulfonic acid (1/10 in weight ratio; PPMA) at a given temperature for a given time to form cross-linking (15). The cross-linking is

based on the chemical reaction between sulfonic acid groups of sulfonated diamine moieties and the activated phenyl rings of non-sulfonated diamine moieties in the presence of PPMA, resulting in the very stable cross-linking through sulfonyl group.

Ion exchange capacity (IEC), water uptake (WU) for 100g dry polymer, dimensional changes in thickness and plane directions ( $\Delta t_c$  and  $\Delta l_c$ , respectively) in water at 30 °C, and proton conductivity in plane direction ( $\sigma_{\square}$ ) were measured according to the methods described previously (8, 9). The mechanical tensile strength was measured at 25 °C under 50%RH.

The active surfaces of Pt/C electrodes (Valcan XC-72, E-TEK Inc.; Pt/C load of 30 wt%; Pt load of 0.5 mg cm<sup>-2</sup>) were impregnated with a small amount of Nafion solution. A membrane-electrode assembly (MEA) was prepared by hot-pressing an electrode/membrane/electrode sandwich at 150 °C for 5 min under 60 kg/cm<sup>2</sup>. The effective electrode area was 5 cm<sup>2</sup>. The MEA was set in a single cell test fixture, and the PEFC performance was measured using a fuel cell test station (model As-510, nF Inc.).

**Results and discussion:** Table 1 lists the basic physical properties of SPIs. The SPI membranes showed anisotropic membrane swelling in water, namely, larger swelling in thickness direction than in plane direction, probably due to the anisotropic membrane morphology with orientation of polymer chains in plane direction of membrane. The anisotropy was much larger for BSPOB-based SPIs than for BAPBDS-based ones. The BSPOB-based SPIs showed the slightly larger water uptake and proton conductivity. Table 1 also lists the properties of crosslinked membranes, where, for example, -XSO<sub>2</sub> (80 °C, 5h) refers to the crosslinking conditions of temperature and time. The formation of cross-linking was judged from the insolubility of the membranes in *m*-cresol containing TEA in which the membranes were soluble before the treatment. Although all the SPI membranes were insoluble in PPMA, the cross-linking reaction could still occur by immersing them into PPMA at 30 °C for 48 h.

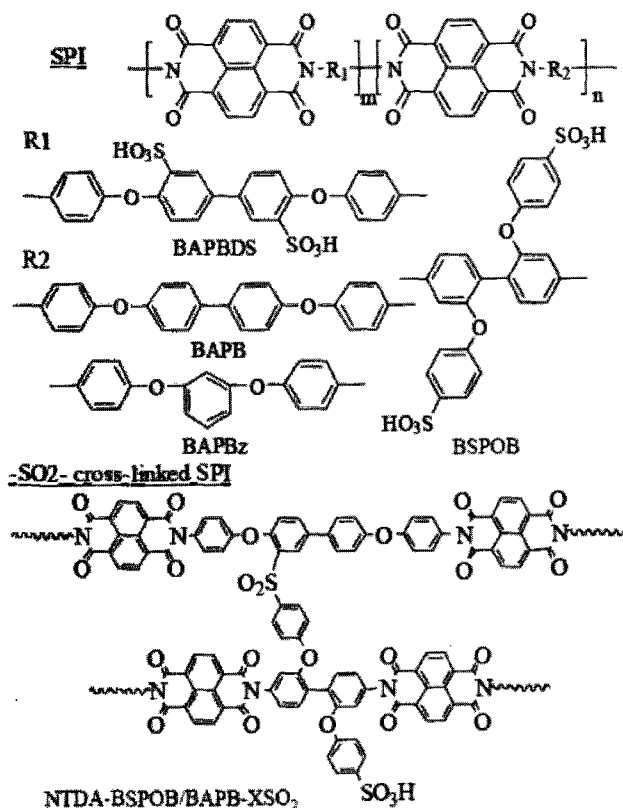


Figure 1 Chemical structure of NTDA-based SPIs.

At the higher temperature, the immersion time could be shortened, for example at 80 °C for 5 h. The optimum cross-linking condition may depend on the polymer structure and desired properties, but has not been investigated in detail. In the most cases, with the crosslinking, the IEC decreased slightly (by about Table 1 Properties of uncross- and cross-linked membranes of NTDA-based SPIs

NTDA-based SPIs	IEC <sup>a</sup> (meq/g)	WU <sup>b</sup> (g/100g)	$\Delta t_c^b$	$\Delta l_c^b$	$\sigma_{II}^c$ (mS/cm)		
					50%	70%	100%RH
BAPBDS/BAPBz(2/1)-1	1.96(1.89)	58	0.17	0.06	6.9	24	117
-XSO <sub>2</sub> (80 °C, 5h)	(1.86)	58	0.14	0.05	5.9	25	120
BSPOB/BAPB(2/1)	1.88(1.94)	78	0.39	0.02	7.0	30	168
-XSO <sub>2</sub> (80 °C, 5h)	(1.71)	80	0.20	~0	2.3	15	110
-XSO <sub>2</sub> (30 °C, 48h)		89	0.55	0.03	10	29	192
BSPOB/BAPBz(2/1)	1.96(1.82)	87	0.60	0.01	8.0	29	193
-XSO <sub>2</sub> (80 °C, 5h)	(1.69)	67	0.33	0.05	6.1	27	148
BSPOB/BAPBz(1/1)-s	1.56(1.55)	57	0.24	0.02	2.2	14	118
-XSO <sub>2</sub> (80 °C, 5h)					1.8	9	95
-XSO <sub>2</sub> (30 °C, 48h)	(1.39)	57			1.9	10	100

<sup>a</sup> Calculated data. data in parenthesis by titration. <sup>b</sup> At 30 °C. <sup>c</sup> At 60 °C; 100%RH: in water.10 %)

Table 2 Water stability results (in water at 130 °C) for uncross-linked and cross-linked membranes of NTDA-based SPIs

NTDA-based SPIs	Time h	IEC <sup>a</sup> (meq/g)	WL <sup>b</sup> %	$\sigma_{II}^c$ (mS/cm) <sup>c</sup>			$M^d$ GPa	$\mathcal{E}^e$ MPa	$\mathcal{E}^f$ %
				50	70	100%			
BAPBDS/BAPBz(2/1)-2	0	1.86		2.3	13	102	1.4	81	95
	192		7.3	2.9	13	103	1.2	55	10
BAPBDS/BAPBz(2/1)-1	0	1.86		5.9	25	120	1.4	77	91
	-XSO <sub>2</sub> (80 °C, 5h)	500	1.44	16	4.0	18	100	1.0	44
BSPOB/BAPB(2/1)	0	1.94		7.0	30	168	2.5	104	50
	192		10	6.2	31	166	2.0	76	8
	500		15	5.0	27	160	1.9	67	6
-XSO <sub>2</sub> (30 °C, 48h)	0			10	29	192	2.2	89	12
	500		17	5	24	135	1.5	45	6
BSPOB/BAPBz(2/1)	0	1.82		7.2	34	177	2.6	128	51
	500	1.68	12	8.2	35	163	1.5	52	10
-XSO <sub>2</sub> (30 °C, 48h)	0			8.0	37	148	2.7	104	18
	500		8.8	8.2	34	151	1.8	67	15
BSPOB/BAPBz(1/1)-s	0	1.55		2.2	14	118	2.3	94	50
	300		8.6	2.0	13	115	2.2	64	11
-XSO <sub>2</sub> (80 °C, 5h)	0			1.8	9	95	2.6	90	18
	300		11	1.5	8	90	2.2	73	14
-XSO <sub>2</sub> (30 °C, 48h)	0	1.39		1.9	10	100	1.8	100	40
	500		11	1.6	8	95	2.9	77	15

<sup>a</sup> By titration. <sup>b</sup> Weight loss. <sup>c</sup> At 60 °C; 100%RH: in water. <sup>d</sup> Young's modulus. <sup>e</sup> Stress at break.

<sup>f</sup> Elongation at break.

and the proton conductivity decreased slightly. The water uptake at room temperature hardly changed, but that at 100 °C decreased slightly with the cross-linking.

The mechanical tensile strength data are listed in Table 2. With the cross-linking, the Young's modulus (YM) hardly changed and was in the range of 1.0 to 2.5 GPa. The maximum stress at break (MS) hardly changed or decreased by 20% and the elongation degree at break (EB) decreased by 20-60%. The decreases in MS and EB were slightly larger with the cross-linking at 80 °C than at 30 °C. However, the cross-linked membranes showed sufficiently high mechanical strength and toughness, indicating that polymer chain scission in the crosslinking treatment with PAA occurred only to a small extent even at 80 °C.

The cross-linked SPI membranes showed reasonably high proton conductivity at high temperatures, for example, 0.25 S/cm in water and 0.03 S/cm under 50%RH at 120 °C for NTDA-BSPOB/BAPB(2/1)-XSO<sub>2</sub> (80 °C, 5h).

The water stability of SPI membranes was evaluated by means of an accelerated hydrolytic stability measurement. The membranes were aged in pressurized water at 130 °C for 192-500 h, followed by investigation of weight loss and changes in IEC, proton conductivity and mechanical properties. The results are summarized in Table 2. In the case of uncross-linked membranes, the BAPBDS-based SPIs became brittle after aging for 500 h, whereas the BSPOB-based SPIs maintained the fairly high mechanical strength and high proton conductivity. The water stability of uncross-linked membranes was much better for the BSPOB-based SPIs than the BAPBDS-based SPIs.

The cross-linking significantly enhanced the water stability. The cross-linked membranes of the BAPBDS-based and BSPOB-based SPIs maintained the reasonably high mechanical strength after aging for 500 h. Especially, in the dry state, the cross-linked membranes maintained the toughness, that is, the aged membrane sheets were folded to zero degree and then folded back but did not break. No significant reduction in proton conductivity with the aging was observed in the whole range of relative humidity. These results indicate that the cross-linked membranes have high water stability of more than 500 h at 130 °C, which corresponds to more than 6000 h at 100 °C, taking the activation energy of hydrolytic degradation of 100 kJ/mol into account (6).

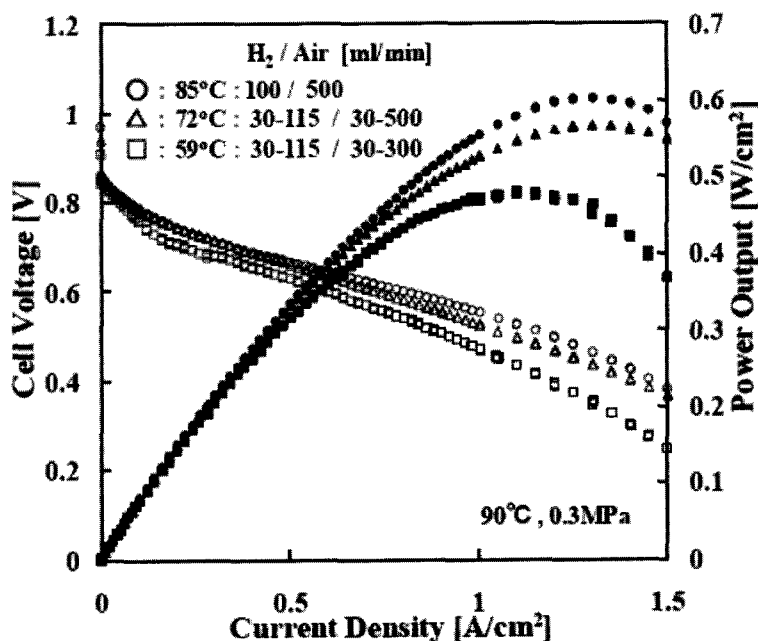


Figure 2 PEFC performance for SPI membrane under different humidification conditions.

Figure 2 shows the PEFC performances for SPI membrane with air supply and at different humidifier temperatures of 85, 72 and 59 °C (corresponding to 84, 50 and 30 %RH, respectively). With decreasing humidification, the cell performance largely decreased. However, even under a low humidification of 30 %RH, fairly high performance was still observed; for example, cell voltage of 0.63 V at current density of 0.5 A/cm<sup>2</sup>. This is because of the enhanced water content in membrane due to the back diffusion of water formed at the cathode.

For the durability test, a PEFC with cross-linked SPI membrane was operated for 1600 h under a constant current density of 0.5 A/cm<sup>2</sup>, cell temperature of 90 °C and gas humidification of 85 %RH. Open circuit voltage (OCV), cell voltage and cell resistance were monitored during the test. As shown in Fig. 3, no appreciable changes in them were observed. As shown in Fig. 4(a), the cell performance was rather enhanced with the elapsed time. This was due to the decrease in the reaction resistance at electrodes as shown in Fig. 4(b). The FTIR spectra (transmittance) were measured for the SPI membrane before and after

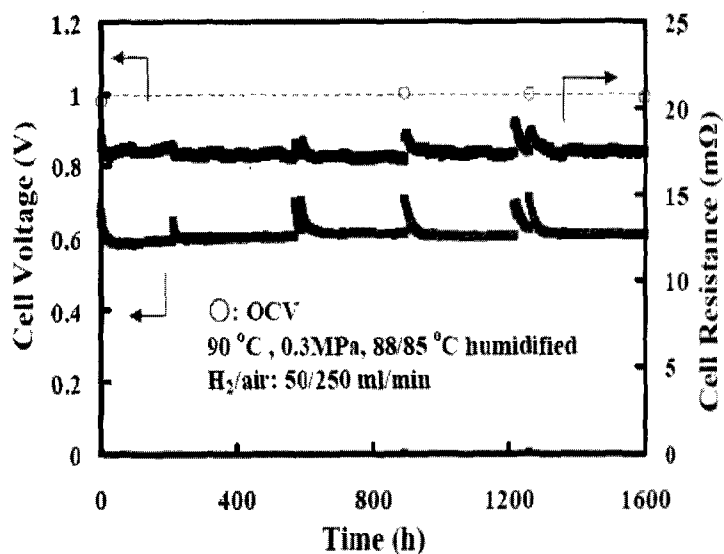


Figure 3 Durability test of PEFC with NTDA-BSPPOB/BAPB(2/1)-XSO<sub>2</sub> (80 °C, 5h).

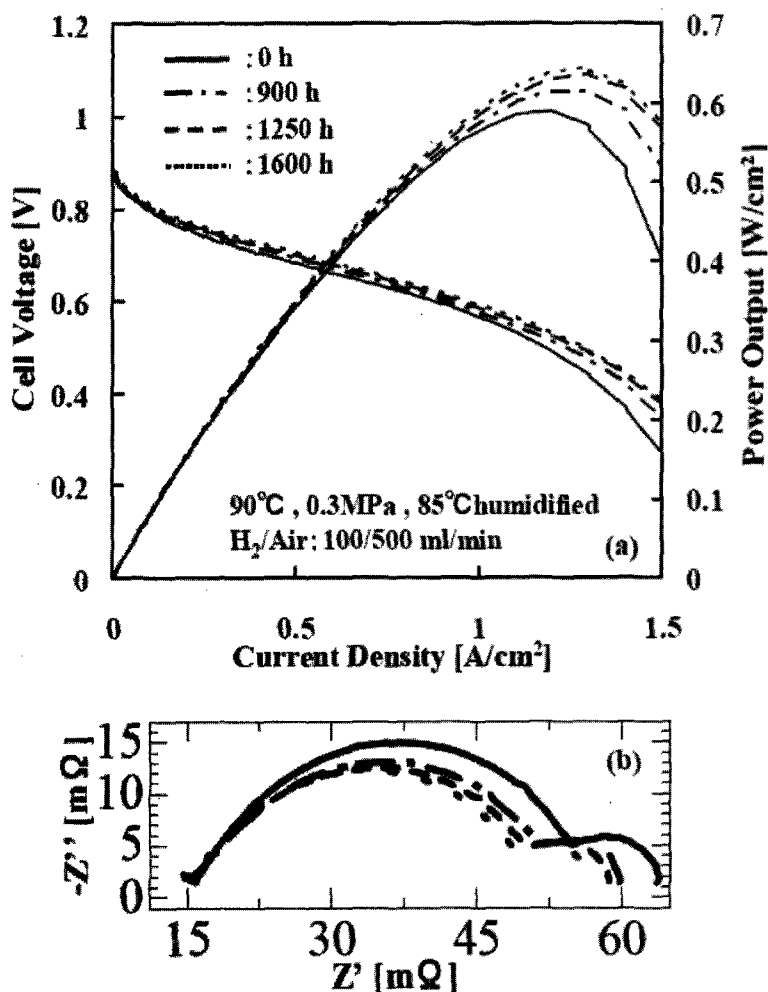


Figure 4 (a) Performance and (b) complex impedance spectra of PEFC with NTDA-BSPPOB/BAPB(2/1)-XSO<sub>2</sub> (80 °C, 5h) at different elapsed time.

the durability test. There were no significant changes in the spectra and also in the difference spectrum, indicating no appreciable chemical change in the SPI membrane by the durability test. These results indicate that the BSPOB-based SPI membranes have high potential for PEFCs at high temperatures above 80 °C.

**Conclusion:** BSPOB-based SPI membranes showed high water stability of more than 500 h in water at 130 °C. The SO<sub>2</sub>-crosslinking further improved the water stability. They showed high PEFC performances at 90 °C and 0.3 MPa with air supply; for example, cell voltages of 0.67 V and 0.63 V at 0.5 A/cm<sup>2</sup> under 85 %RH and 30 %RH, respectively. They showed high durability of more than 1600 h in PEFC operated at 90 °C, 85 %RH and 0.5 A/cm<sup>2</sup>.

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