Characterization of Molecular Interaionic and Intraionic Crosslinkable Sulfonated Poly(ether ether ketone-*alt*-benzimidazole) Membrane

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ABSTRACT: A novel alternating copolymer of sulfonated poly(ether ether ketone-*alt*-benzimidazole)s (SPEEK-*alt*-BI) was synthesized by polycondensation in our previous report. In this article, we examined the properties of SPEEK-*alt*-BI membranes, such as thermal and mechanical stability, hydrolysis, and swelling properties in water, and proton conductivities at various temperatures and humidity. The experimental results showed that SPEEK-*alt*-BI membranes exhibited promising oxidative and hydrolysis stabilities. Although the base moieties in SPEEK-*alt*-BI main chain would capture proton and form reversible salt hindering the proton transfer capability, the conductivity of membrane 60SPEEK-*alt*-BI-H [Sulfonation degree (S.D.), 60% in form of proton] could achieve 22.61 mS/cm at 80°C and 100% humidity. Meanwhile, the conductivity of membrane could reach 40.12 mS/cm with phosphorus acid doping. The methanol permeation coefficient of 60SPEEK-*alt*-BI membrane is 2.3×10^{-8} cm^2/s at 20°C, which is magnitude lower than that of Nafion®117, 1.11×10^{-6} cm^2/s. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3175–3183, 2012

Key words: poly(ether ether ketone-benzimidazole)s; sulfonated polymer; proton exchange membranes
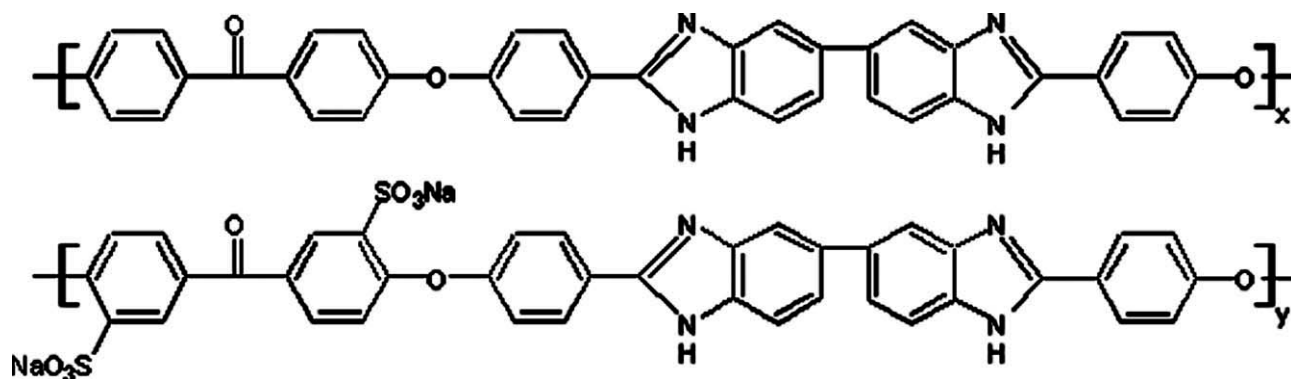
INTRODUCTION

Perfluorosulfonic acid membrane (PAM) is the most commonly used materials in the proton exchange membrane fuel cell (PEMFC), however, the pure PAM was proved not suitable for the direct methanol fuel cell (DMFC) as to its high liquid fuel crossover. Lots of work were carried out to find novel membranes to overcome the disadvantages of PAM. Sulfonated aromatic polymers (SAP) synthesized by direct polymerization or post-sulfonation were evaluated as proton transfer medium in fuel cell owing to their excellent thermal and mechanical properties. Typically, sulfonated polyether ether ketone (SPEEK) and sulfonated polyethersulfone (SPES) were considered as potential materials for high temperature proton exchange membrane fuel cell.[1–5] It was known that the conductivities of SAP membranes strongly depend on their sulfonation degrees. However, high sulfonated degrees normally induce excessive swelling of membranes in the water. The polyaromatic ether ketones (PAEKs) with a sulfonated degree more than 60% were even water-soluble, which limited its end-use in a wet surrounding. To achieve a balance between proton conductivity and mechanic properties, J. Kerres[6–9] developed an ionic crosslinking blend concept to optimize the final properties by mixing sulfonated polymer with base polymer. Because of the interaction between polymeric N-bases and polymeric sulfonic acids,[10,11] the mechanical properties and thermal stabilities could be significantly improved, as well as the swelling could be hindered. Small molecular base, for instance 1, 3-1H-dibenzimidazole-benzene, serving as an additive in sulfonated polysulfone membrane was also studied to improve the electrochemical performance of membrane in fuel cell.[12]

Polybenzimidazole (PBI) is known as an excellent high performance material due to its remarkable thermal, mechanical and chemical stability; but it has poor solvent solubility. For proton transfer, PBI membranes have to be doped with acid or base. In this case, a stable association between the benzimidazole ring and the strong acid is formed, giving a new class of proton conducting polymer membranes.[13] This kind of membranes is of particular interest for uses at high temperature (until 180°C). Another option is chemically modifying PBI by

Scheme 1   Chemical structure of SPEEK-*alt*-BI.

introducing alkylsulfonate or arenesulfonate side chain on to reactive N-H sites. Direct sulfonation of PBI membrane was also investigated on. So far, several works[14,15] were reported through direct synthesis of sulfonated PBI through copolycondensation of sulfonated aromatic diacid with aromatic tetraamine to give the sulfonated PBI. However, in these cases, the sulfonic groups seem ineffective to the proton transport due to strong interactions between the basic benzimidazole of the nonsulfonated unit and the sulfonic acid group.[16,17]

In our previous work,[18] we developed a facile synthesis of sulfonated alternating copolymers of PEEK and PBI by copolycondensation of imidazole-containing bisphenol and two difluroaromatic monomers. The preparation procedure of SPEEK-*alt*-BI is similar to PEEK or PES synthesis. The inter- and intramolecular interactions between acid and base moieties were observed as evidenced by the results of both ion exchange capacity (IEC) measurements and solubility study of SPEEK-*alt*-BI polymers. However, no knowledge about the SPEEK-*alt*-BI membrane performance was reported. In this preliminary work, membranes cast from the SPEEK-*alt*-BI have been characterized physicochemically and electrochemically and compared, performing some fundamental analyses, such as chemical (Fenton tests), mechanical (stress at break) and thermal (thermogravimetric analyses, TGA) tests, methanol permeability, hydrolysis and swollen properties in water, as well as proton conductivity. Moreover, to improve the proton transfer performance, the conductivities of phosphorus acid doped PEEK-*alt*-BI were evaluated.

EXPERIMENTAL

Materials

SPEEK-*alt*-BI (Scheme 1) was prepared following the procedure described in the previous work.[18] The monomer 4, 4′-Difluorobenzophenone (DFBP) was purchased from Songshen Chemical Company, and recrystallized from absolute ethanol before use. Sulfonated 4, 4′-difluorobenzophenone salt (SDFBP-Na) and 5, 5′-bis[2-(4-hydroxyphenyl)benzimidazole] (HPBI) were synthesized in our lab. In this paper, notation nSPEEK-*alt*-BI will be used, where n denotes for the mole percent of sulfonated difluoroaromatic monomer with respect to the total amount of mixed difluoroaromatic monomers in the feed. For instance, 60SPEEK-*alt*-BI represents the mole ratio of sulfonated difluoroaromatic monomer in the feed is 60%, which is also defined as sulfonation degree (S. D.). An ionic crosslinkable properties of SPEEK-*alt*-BI-H (acid form) were confirmed by IEC testing and solubility. N,N-dimethyl formamide (DMF), methanol, H_2O_2 aqueous solution, H_3PO_4, and $FeSO_4$ were obtained from commercial sources, and used as received.

Membrane fabrication

As mentioned before,[18] the polymer in form of acid (SPEEK-*alt*-BI-H) was insoluble in solvent, while SPEEK-*alt*-BI-Na was easily dissolved in polar nonproton solvent. Hence, sulfonated copolymer in sodium salt form (SPEEK-*alt*-BI-Na) was dissolved in DMF, and subsequently filtered through a 0.1-μm microporous Teflon membrane. The filtered solution was cast on a glass plate and dried at 50°C for 24 h. The residual solvent was evaporated at 110°C in vacuum for 12 h. The membranes in protonic acid form (SPEEK-*alt*-BI-H) were obtained by immersing SPEEK-*alt*-BI-Na film in 1.0N HCl for 24 h at room temperature. The acidified membranes were washed thoroughly with deionized water, dried at 100°C for 24 h in vacuum making them available for testing. The thickness of membranes was in the range of 40–50 μm.

Phosphoric acid-doped membrane

It is well-known that anions of phosphoric acid are proposed to be immobilized to the polybenzimidazole by strong hydrogen bonding forming a network

for proton transfer.[13] In view of the existence of base moieties in PEEK-*alt*-BI and SPEEK-*alt*-BI main chains, phosphoric acid could be doped. In this work, sulfonated PEEK-*alt*-BI (SPEEK-*alt*-BI-Na) membranes as well as unsulfonated PEEK-*alt*-BI membrane were immersed in 75% (wt/wt) phosphoric acid methanol solution for three days to get H_3PO_4-doped membranes at room temperature. The above membranes were subsequently immersed in methanol for one day followed by washing. This residual H_3PO_4 removal procedure was repeated at least three times, and then the membranes were dried to obtain phosphoric acid-doped membranes. The adsorption amounts of H_3PO_4 were evaluated by the weight gain of membranes.

Thermostability

Thermogravimetric analyses (TGA) was performed on a TGA Q50 V6.7 Instrument with a heating rate of 20°C/min in N_2 and air. Each sample was preheated from room temperature to 180°C, and held for 30 min to remove the absorbed moisture, followed by cooling to 100°C.

Water uptake and swelling ratio of the membranes

Water uptake was measured as follows: The membranes were soaked in deionized water for 24 h at desired temperature. Weights of dry and wet membranes were measured. The water uptake content was calculated from the eq. (1).

$$\text{Water uptake}(\%) = \frac{w_{\text{wet}} - w_{\text{dry}}}{w_{\text{dry}}} \times 100 \qquad (1)$$

where, w_{dry} and w_{wet} are the mass of dry and wet samples, respectively. The swelling ratio was calculated from length variation of rectangular strips (5 × 1 cm^2) by following the eq. (2):

$$\text{Swelling ratio}(\%) = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100 \qquad (2)$$

where l_{wet} and l_{dry} are the length of wet and dry samples, respectively.

The mechanic properties (maximum strength) of membrane samples (15 mm wide) were conducted by electronic controllable tensile machine (CMT5104, Shenzheng Sanxi) at room temperature with a stretching speed 2 mm/min. The distance between two clips was 25 mm.

Oxidation stability

Oxidation stability was evaluated by the Fenton test. The SPEEK-*alt*-BI membranes of 2 cm × 1 cm were immersed in 3% H_2O_2 containing 4 ppm of Fe^{2+} ($FeSO_4$) at ambient temperature. The Fenton reagent was replaced every 12 h, as there were no bubbles released. Membranes were taken out from the depleted solution to check its state every 12 h. For comparison, following a similar procedure for preparation of PEEK-*alt*-BI, sulfonated biphenol type polyether ether ketone (SPEEK) membrane synthesized by polycondensation of aromatic bisphenol and a mixture of sulfonated (20% mole ratio) and nonsulfonated difluorobenzophenones (80% mole ratio) was tested under the same oxidation condition.

Proton conductivity

Proton conductivity values were measured by using In-Plane Membrane Conductivity Test System (BEKK TECH) in a Teflon cell. The cell was placed in a thermo-controlled chamber for measurement. Hydrogen was used as test gas. The size of membrane sample was 1 cm × 3 cm. The distance between two electrodes was 0.5 cm. The test temperature of samples with different RH was from 40 to 80°C.

Proton conductivity σ (s cm^{-1}) was calculated by the following equation:

$$\sigma = \frac{L}{t \cdot w \cdot R} \qquad (3)$$

where L (cm) is the distance between the two electrodes, t (cm) and w (cm) are the thickness and width of the dry membrane without swollen, respectively, and R (Ω) is the resistance value measured. It should be noted that a conductivity calculated was based on dry dimensions of a sample at no swelling state.

Methanol permeability

The membrane permeation properties of methanol were tested according the following procedure. Before testing, the membrane was kept fully water swollen in deionized water. Preheated methanol aqueous solution (40%v/v) was loaded in feed side, respectively, to estimate their diffusion coefficients at various temperatures. To avoid concentration differential polarization, magnetic stirring was applied in the bottom of two semicells. The concentration variation of methanol was detected as a function of diffusion time by a gas chromatography technique with a FID detector (GC112A, Shanghai Analytic Instrument). According to the traditional theory, the mass transfer undergoing in dense membrane was described by a "dissolve-diffusion" model. Supposed a low permeability coefficient of methanol diffusion from the membrane, and concentration variation in feed side could be ignored in a testing period. The
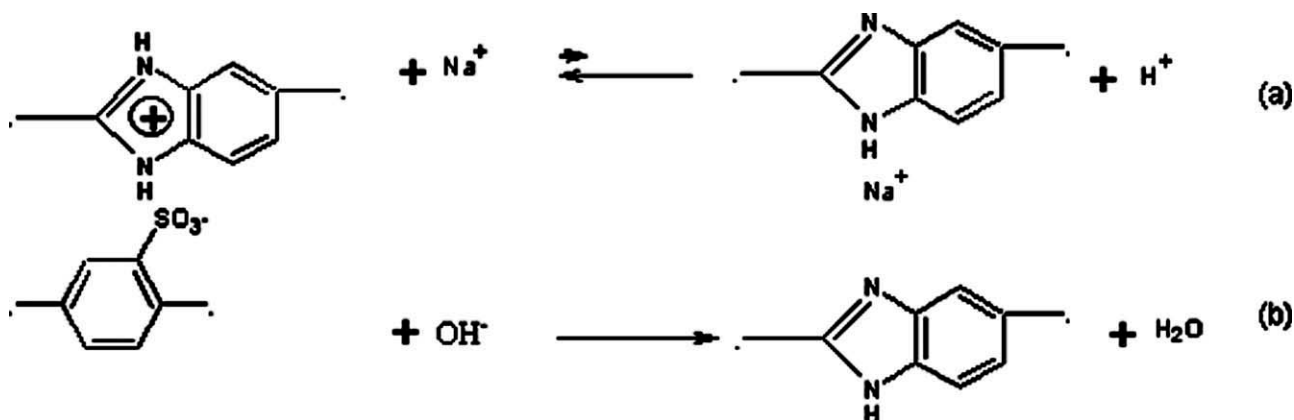
Scheme 2 Suggested restriction mechanism of proton exchange with aqueous NaCl (a) and decomposition of crosslinking by NaOH (b) in the membrane.

concentration of methanol in downside side is described by eq. (4).

$$C_B = \frac{AC_{A0}}{V_B l}\left(Pt - \frac{Hl^2}{6}\right) \quad (4)$$

where, C_B, A, C_{A0}, l, V_B, P, H are the concentration of methanol in downside (Cell B), effective membrane area, initial concentration of methanol in feedside (cell A), thickness of membrane, volume of cell B, permeability coefficient and swollen ratio, respectively. From the C_B function of time (t), the slope (S) is obtained by the following equation:

$$S = \frac{AC_{A0}}{V_B l} P \quad (5)$$

Rewriting (5), the permeation coefficient of methanol through the membranes can be calculated by the eq. (6).

$$P = S \frac{V_B l}{AC_{A0}} \quad (6)$$

RESULTS AND DISCUSSION

The reversible crosslinking and thermo-properties

For SPEEK-*alt*-BI-H (acidified membrane), a strong interaction between the H$^+$ and the benzimidazole ring has been detected by different IEC testing methods, which were suggested in our previous work.[18] Possible restriction mechanism of the direct proton exchange with Na$^+$ (Method 1, samples were immersed in NaCl solution) was illustrated in Scheme 2. In this case, only a partially amount of H$^+$ can be replaced by Na$^+$ in balance, which results in a lower experimental IEC comparing with theoretical value. It was found that SPEEK-*alt*-BI-H membrane was insoluble in polar noproton solvents, such as DMF, DMAc, and DMSO. As we know, in a pro-

ton exchange membrane fuel cell, one of the functions of the membrane is for proton transportation in a form of acid state. So it is believed that the above mentioned interaction (crosslinking) would improve the stability of the membrane in MEA.

On the contrary, while the acid membranes were treated by NaOH solution (Method 2), over-dose base which could destroy the (intra- or inter-) interaction salt and release proton would be totally neutralized. In this case, the detectable IEC value was near to the calculated one. This close value confirmed the incorporation of sulfonated monomer as feeding ratio to polymer backbone. A reversible crosslinking in the membrane is supported by the fact that the SPEEK-*alt*-BI membrane in form of sodium is soluble while insoluble in form of proton. According to this property, the membrane could be cast by SPEEK-*alt*-BI-Na and crosslinked by acidification.

TGA curves of 40SPEEK-*alt*-BI and 60SPEEK-*alt*-BI membranes in form of sodium (SPEEK-*alt*-BI-Na) or acid (SPEEK-*alt*-BI-H) in both N$_2$ and air are illustrated in Figure 1. One can see that no significant weight loss was detected for the sodium salt 40SPEEK-*alt*-BI-Na and 60SPEEK-*alt*-BI-Na either in N$_2$ or air up to ca. 420°C, whereas the first decomposition of protonic acid form was observed at much lower temperature (280°C). The first decomposition of SPEEK-*alt*-BI-H samples is attributed most likely to the decomposition of sulfonate side groups. The agreement of the calculated weight ratio of sulfonic groups to the average molecular weight of repeat units (listed in Table I) on first loss weight confirmed this suppose. Furthermore, this first decomposition underwent from 280 to 550°C, which was considerably broader than the case of SPEEK in other report[19] and because the salt (sulfonic imidazole) postponed the release of sulfonic groups from the polymer chain. In the air, both of the samples (40, 60SPEEK-*alt*-BI-H) showed almost complete decomposition with char yields near 0 at 800°C,
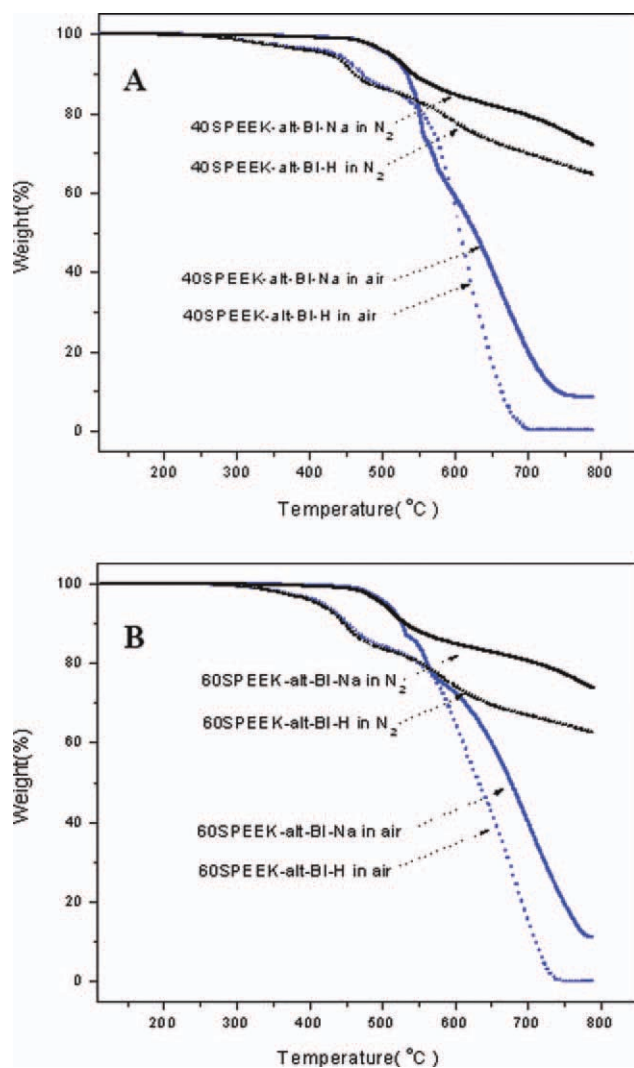
Figure 1 The TGA traces of SPEEK-*alt*-BI films: A, 40SPEEK-*alt*-BI in both N_2 and air; B, 60SPEEK-*alt*-BI in both N_2 and air. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

while the char yields in nitrogen were estimated to be 64.0% and 62.7%, respectively. In either case, the char yield of polymer salt (SPEEK-*alt*-BI-Na) was slightly higher than that of acidified polymer, probably due to nonvolatile inorganic residue of sodium

TABLE I
**Weight Loss Analysis Given by a Supposed**
Decomposition of Sulfonic Groups

S.D. of Membranes	Calculated first weight loss[a] (%)	Weigh loss at 474°C (%)
20	4.86	4.85
40	9.27	10.14
60	13.30	13.29
80	16.99	Unmeasured
100	20.38	Unmeasured

[a] This value was calculated according to the contribution of sulfonic group to molecular weight of repeat unit (g/mol) of SPEEK-*alt*-BI-H.

salt. These results suggested that all SPEEK-*alt*-BI copolymers possessed excellent thermal stability in both N_2 and air atmosphere. DSC was also applied to investigate the thermo-transform, however, no glass-transition temperature (T_g) was observed before 280°C (1st T_d).

Water uptake and swelling ratio

It has been widely reported that the proton conductivity of sulfonated polymeric membrane is associated with the water uptake and sulfoantion degree of the membrane. In the literature, blending a highly sulfonated polymer, e.g., SPEEK (S.D. = 70),[20] with base polymer can significantly reduce the water uptake. The difference of our case is that acid and base moieties were combined in a polymer chain. Water uptake and swelling ratio for various SPEEK-*alt*-BI membranes in both sodium salt and acid forms were measured as illustrated in Figures 2
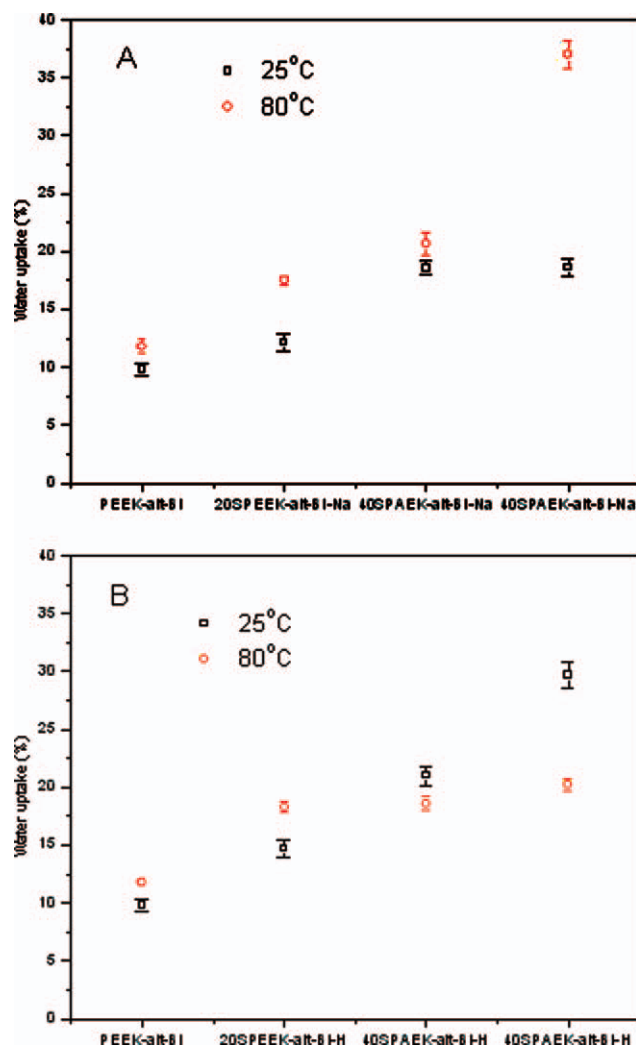
Figure 2 Water uptake of SPEEK-*alt*-BI membranes: A, Sodium form membranes; B, acid form membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
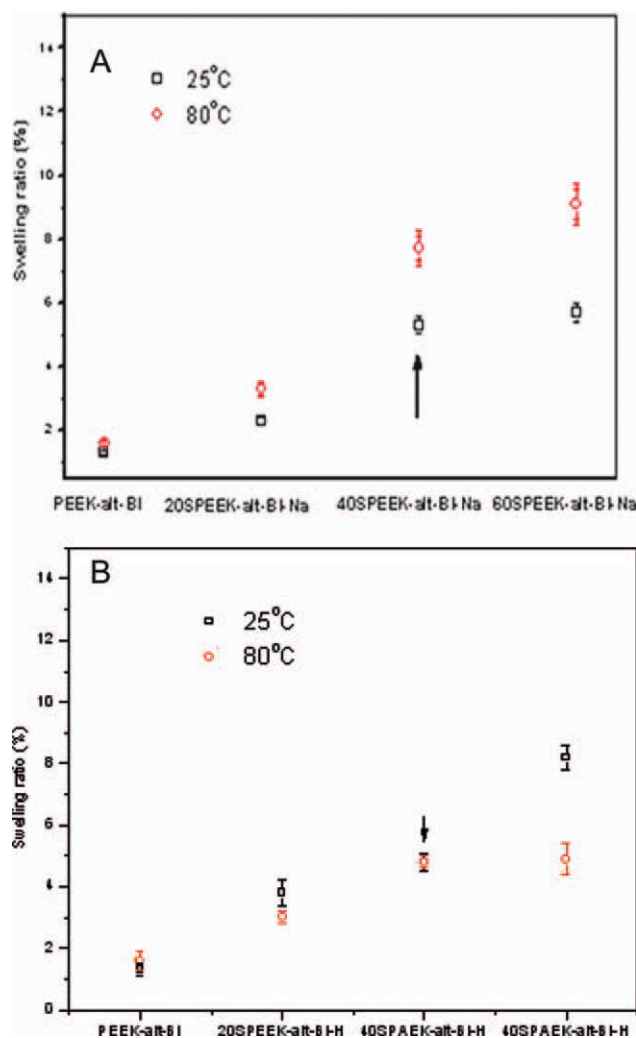
Figure 3 Swelling ratio of SPEEK-*alt*-BI membranes: A, Sodium form membranes; B, acid form membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and 3. As expected, both of these values increased with respect to the sulfonation degree. At a low temperature (25°C), water uptake values and swelling ratio of membrane samples in protonic acid form were similar to those of membrane in sodium salts. However, interestingly, at a higher temperature (80°C), samples in protonic acid form showed signif-

icantly lower water uptake and swelling ratio than those of sodium salts at high sulfonation degree (60%). Moreover, the water-takeup and swelling ratio of acidic membranes at 80°C are quite close to those values at much lower temperature (25°C). This result implies that the membranes in protonic acid form possess an unsensitive temperature-dependence of water uptake and swelling ratio. Qing and Yan et al.[14] also found the similar results from investigation of sulfonated PBI synthesized from diacid and tetraamine monomers. This could be explained by that higher temperature lead polymer chain more flexible, which resulted in better touching and entanglement between acid and base moieties. The fact that the samples of higher sulfonation degree showed larger such tendency also supports this speculation. The water uptake of 60-SPEEK-*alt*-BI was considerably lower than that of SPEEK-70.[20] Membrane swelling is a critical issue for MEA stability in fuel cells. A lower swelling ratio indicates a better stability. The much lower water uptake and dimension variation of membranes could help reduce the methanol transportation since polar liquid is known to facilitate methanol diffusion in the SPEEK membrane.[11] In the solubility testing of polymers, we can found that SPEEK-*alt*-BI-Na can be dissolved in some polar no-proton organic solvent, so that SPEEK-*alt*-BI could be casting to form membrane. Interestingly, the acidified SPEEK-*alt*-BI membranes show good solvent resistance (see Table II) due to the existence of this ionically crosslinking among the polymer chains.

Hydrolysis and oxidation stability

The membranes as proton medium in DMFC should be tolerance in high humidity and high temperature (80°C) as well as in the existence of strong oxidant. Two methods were applied to test the hydrolysis stability of SPEEK-*alt*-BI membranes (sulfonation degree from 0 to 60%). One is to put the membrane into a hot water bath (80°C) and check its flexibility by bending the samples every 12 h. No obvious crack was observed after 120 days. The other is to put the samples into 1 mol/L NaOH aqueous

TABLE II
Solubility of SPEEK-*alt*-BI-H Polymers

Polymers	HCO$_2$H	DMF	DMSO	DMAc	NMP	NB	CH$_3$OH	C$_2$H$_5$OH	H$_2$O
20SPEEK-*alt*-BI	S	–	–	–	–	–	–	–	–
40SPEEK-*alt*-BI	–	–	–	–	–	–	–	–	–
60SPEEK-*alt*-BI	–	–	–	–	–	–	–	–	–
80SPEEK-*alt*-BI	–	–	–	–	–	–	–	–	S
100SPEEK-*alt*-BI	–	–	–	–	–	–	–	–	S

–, insoluble; S, swollen; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; DMAc, *N,N*-dimethylacetamide; NB, nitrobeneze; NMP, *N*-methyl-2-pyrrolidone.

TABLE III
The Oxidative Stability of SPEEK-*alt*-BI Membranes at Room Temperature

Membranes	Oxidative time (h)
PEEK-*alt*-BI	>300
20SPEEK-*alt*-BI	140
40SPEEK-*alt*-BI	140
60SPEEK-*alt*-BI	120
80SPEEK-*alt*-BI	100
20SPEEK	70

TABLE IV
Mechanical Properties of PEEK-*alt*-BI and SPEEK-*alt*-BI Membranes in Form of Sodium

Membrane	Young's modulus (MPa)	Maximum stress (MPa)	Elongation (%)
PEEK-*alt*-BI	1427.3	70.05	5.55
20SPEEK-*alt*-BI-Na	1039.4	54.37	4.45
40SPEEK-*alt*-BI-Na	1071.9	47.49	3.80
60SPEEK-*alt*-BI-Na	1247.1	42.36	3.69
80SPEEK-*alt*-BI-Na	1085.9	31.67	3.06
100SPEEK-*alt*-BI-Na	Fragile	-	-

solution at room temperature, checking the strengthen changes every three days by bending. No apparent failure of all samples for 360 days implies a promising stability in water and strong base environment of these novel materials.

Oxidation stability was evaluated by the Fenton test. The SPEEK-*alt*-BI membranes of 2 cm × 1 cm were immersed in 3% H_2O_2 containing 4 ppm of Fe^{2+} ($FeSO_4$) at ambient temperature. As a comparison, SPEEK membrane with 20% sulfonation degree synthesized by a method similar to the preparation of SPEEK-*alt*-BI was tested under the same condition. The results were listed in Table III. Obviously, the nonsulfonated PEEK-*alt*-BI showed the longest oxidative time, while the oxidative time decreases with sulfonation degree. After two days, the comparing sample, SPEEK membrane, was destroyed and completely dissolved in the reagent. The highly sulfonated membranes, 80SPEEK-*alt*-BI, and 60SPEEK-*alt*-BI, however, displayed much poorer oxidative stability than PEEK-*alt*-BI.

Mechanical properties and methanol permeation

The tensile properties of PEEK-*alt*-BI and SPEEK-*alt*-BI-Na membranes were listed in Table IV. The maximum stretching stress of membranes decreased with sulfonation degree from 70.05 to 31.67 MPa. This phenomenon is consistent with the molecular weight decrease of polymer with the increase of mole ration of sulfonated difluoromonomer in polymerization. But those values were higher than that of Nafion as well as SPEEK synthesized in our work with the same sulfonation degree. Reduction of elongation at break and Yong's modulus indicated lower molecu-

lar weight of resulted polymer while more sulfonated units were introduced too.

For a proton exchange membrane in DMFC, it is known that an extremely low fuel crossover of membrane is required to obtain a higher operation efficiency and energy conversion.

Testing results of methanol crossover were listed in Table V. PEEK-*alt*-BI exhibits methanol diffusion coefficient at 20°C of 1.6×10^{-9} cm^2/s. The value of 60SPEEK-*alt*-BI membrane is 2.3×10^{-8} cm^2/s at the same temperature, which is magnitude lower than that of Nafion®117, 1.11×10^{-6} cm^2/s. With temperature increased from 20 to 60°C, the methanol permeability of 60SPEEK-*alt*-BI membrane increased from 2.3×10^{-8} cm^2/s to 2.3×10^{-7} cm^2/s. It is reasonable, since the more water-uptake and swelling ratio of the sample at a higher temperature must broaden the methanol transfer channel, and the increasing temperature will enhance the mass diffusion velocity. It is still to be pointed out that the methanol permeation coefficient of the sample 40SPEEK-*alt*-BI-H varied little similar to the results of water swelling testing at different temperature.

Proton conductivity

The dry membrane in form of acid (SPEEK-*alt*-BI-H) was placed in cells in a thermo-controlled chamber for conductivity measurement. The conductivity data of membranes was recorded at various temperatures (from 40 to 100°C) at 100% relative humidity (RH) (see Fig. 4). The membranes doped by phosphorus acid designated as PEEK-*alt*-BI-PA and SPEEK-*alt*-BI-PA (weight gain after doping listed in

TABLE V
Methanol Permeation Coefficient (cm^2/s) of SPEEK-*alt*-BI Membranes at Various Temperatures

T (°C)	PEEK-*alt*-BI	20SPEEK-*alt*-BI-H	40SPEEK-*alt*-BI-H	60SPEEK-*alt*-BI-H	Nafion117
			Membrane		
20	1.6E-09	2.4E-08	9.8E-08	2.3E-08	1.11E-06
40	8.0E-09	3.6E-08	9.8E-08	6.6E-08	1.85E-06
60	2.0E-08	4.0E-08	9.8E-08	2.3E-07	4.14E-06
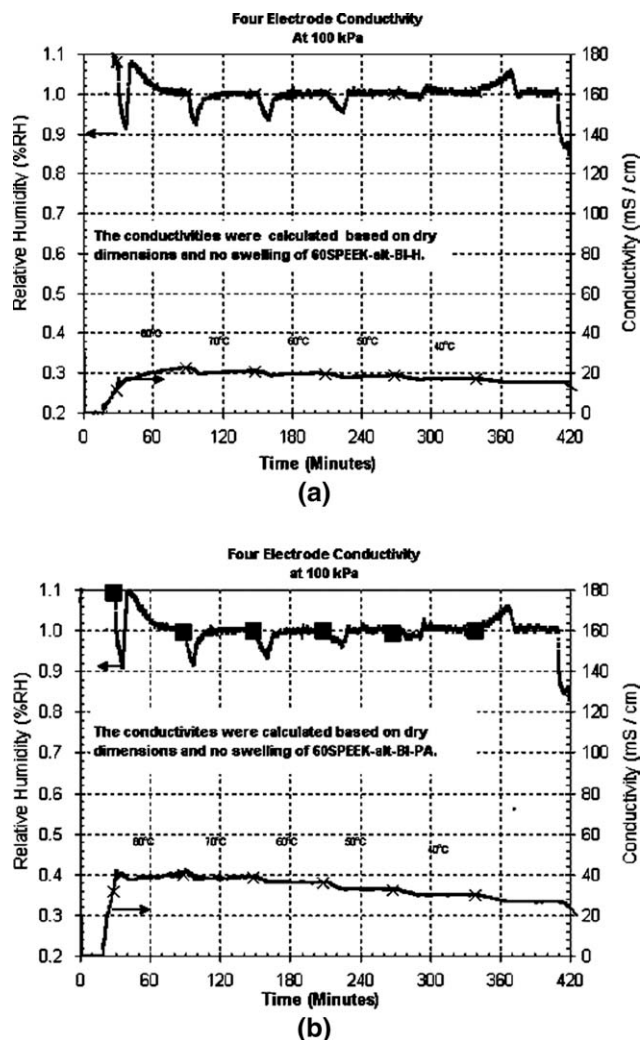
Figure 4 Variation of four electrode conductivity of membrane 60SPEEK-*alt*-BI-H and 60SPEEK-*alt*-BI-PA with testing temperature, at 100 kPa and 100% humidity.

Table VI) were tested at the same condition. The close weight gains values around 14 wt % of non-sulfonated and sulfonated membranes indicate a similar doping level in this experimental condition. It is well known that the proton conductivity of polyelectrolyte membranes is a function of sulfonated degree, temperature, and humidity. Figure 4(a,b) give the conductivity variation of membranes 60SPEEK-*alt*-BI-H and 60SPEEK-*alt*-BI-PA tracing with testing temperature decreasing from 100 to 40°C with an interval time (60 min). The two kind of samples displayed similar behavior once a humid

TABLE VI
Weight Gain of Phosphorus Acid-Doped Membranes

No.	Sample	Weight gain (wt %)
1	PEEK-*alt*-BI-PA	15.5
2	20SPEEK-*alt*-BI-PA	12.8
3	40SPEEK-*alt*-BI-PA	12.9
4	60SPEEK-*alt*-BI-PA	14.3

TABLE VII
Proton Conductivity (mS/cm^{2}of SPEEK-*alt*-BI Membranes

Membrane	Temperature (°C)				
	40	50	60	70	80
20SPEEK-*alt*-BI-H	4.29	4.67	5.02	5.28	5.29
40SPEEK-*alt*-BI-H	4.45	7.35	7.65	8.98	9.42
60SPEEK-*alt*-BI-H	16.92	18.67	19.73	21.04	22.61
PEEK-*alt*-BI-PA	17.70	20.33	23.71	24.02	27.94
20SPEEK-*alt*-BI-PA	21.90	23.67	24.70	27.23	32.11
40SPEEK-*alt*-BI-PA	27.42	29.93	31.76	35.44	35.16
60SPEEK-*alt*-BI-PA	29.61	32.68	36.22	38.81	40.12
20SPEEK-H[a]	–	–	–	–	33
40SPEEK-H[a]	–	–	–	–	67
60SPEEK-H[a]	–	–	–	–	134
Nafion®117	39.1	51.3	62.5	70.7	92.5

[a] Data adapted from Ref. 21.

atmosphere was introduced. However, phosphorus-doped membrane (60SPEEK-*alt*-BI-PA) gave a more rapid response and much higher level of conductivity than that of 60SPEEK-*alt*-BI-H. Although the base moieties will capture proton and form reversible salt hindering the proton transfer capability, the conductivity of membrane in form of proton can achieve 22.61 mS/cm at 80°C and humidity 100%.

As expected (the details of testing results were illustrated in Table VII), the conductivity of SPEEK-*alt*-BI-H increases with the sulfonation degree and temperature. For example, the conductivities of 60SPEEK-*alt*-BI-H increased from 16.92 to 22.61 mS/cm from 40 to 80°C. According to the vehicle mechanism, bound water is a result of a strong interaction between water molecules and ionic groups, including -SO$_3$H groups, in polymer matrix and is significantly responsible for proton transport.[21–24] It was not surprising to observe higher conductivity prepared by using the membrane at higher S. D, since the proton transfer facilitates more easily with increased sulfonic acid group contents. When the acid groups in the amphiphilic polymer specifically quantity, partial SO$_3$H groups may not be bonded by base moieties to some extent contributing to a sharp increase in the conductivity. This might be the reason why the conductivity value of SPEEK-*alt*-BI-H sharply increases beyond 40% S. D.

The H$_3$PO$_4$-doped membranes showed much higher conductivities than that of corresponding membranes. Because the bound water content of the membranes increased relative to that of SPEEK-*alt*-BI after doping H$_3$PO$_4$. As PBI, the unsulfonated membrane (PEEK-*alt*-BI-PA) gave conductivities, 17.70, 20.33, 23.71, 24.70, and 27.94 mS/cm at 40, 50, 60, 70, and 80°C, respectively. Obviously, the series of sulfonated membranes (SPEEK-*alt*-BI-PA) showed much higher conductivities than undoped membranes. For the sample 60SPEEK-*alt*-BI-PA, the

conductivities increased from 29.61 to 40.12mS/cm as temperature elevated from 40 to 80°C. These values are quite close to that of Nafion®117 for comparison.

CONCLUSION

Chemical (Fenton tests), mechanical (stress at break) and thermal (thermogravimetric analyses, TGA) tests of sulfonated alternating copolymer of poly(ether ether ketone-*alt*-benzimidazole)s (SPEEK-*alt*-BI) membranes were carried out. The ionic crossliking in or among the SPEEK-*alt*-BI polymer chains made the membranes much stable in protonic form. This reversible crosslinking made the polymer in form of salt processable and the membranes recyclable. The SPEEK-*alt*-BI membranes show low methanol permeability, high thermostability, and high oxidative stability. Compared with SPEEK, a lower proton transfer ability of sulfonated SPEEK-*alt*-BI was observed possibly due to the ionic interaction between sulfonic groups and imidzole units, which limited the decomposition and motion of proton. The conductivity of membrane (60SPEEK-*alt*-BI-H) can achieve 22.61 mS/cm at 80°C and humidity 100%. The doped PEEK-*alt*-BI membrane gave proton conductivity as high as 27.94 mS/cm, while the doped 60SPEEK-*alt*-BI membrane gave a value 40.12 mS/cm at the same condition.

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