Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 3090–3097

polymer

www.elsevier.com/locate/polymer

Blend membranes based on disulfonated poly(aryl ether ether ketone)s (SPEEK) and poly(amide imide) (PAI) for direct methanol fuel cell usages

Chengji Zhao [a], Zhe Wang [b], Dawu Bi [a], Haidan Lin [a], Ke Shao [a], Tiezhu Fu [a], Shuangling Zhong [a], Hui Na [a,*]

[a] *Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, PR China*
[b] *Changchun University of Technology, Jilin 130012, PR China*

Received 10 December 2006; received in revised form 23 March 2007; accepted 29 March 2007
Available online 4 April 2007

Abstract

Highly disulfonated poly(aryl ether ether ketone)s (SPEEK-70) copolymer was synthesized via direct polymerization to precisely control the degree of sulfonation ($D_s = 1.40$), which was confirmed and estimated by ^{1}H NMR. As expected, the proton conductivity of SPEEK-70 membrane is 0.084 S/cm at 25 °C and increases to 0.167 S/cm at 80 °C, surpassing that of Nafion® 117. However, the relatively high methanol crossover and excessively swelling properties limited its usage in DMFC. Poly(amide imide) was blended with SPEEK-70 to improve the methanol resistance and mechanical properties. These blend membranes were characterized as a function of weight fraction of PAI in terms of ion exchange capacity (IEC), water uptake, water desorption, proton conductivity and methanol permeability in detail. Although the proton conductivities decreased upon the addition of PAI, higher selectivity values defined as the ratio of proton conductivity to methanol permeability were found for the blend membranes. Therefore, the SPEEK/PAI blend membranes are promising for usage in DMFC.

Keywords: Fuel cells; Proton exchange membrane; Disulfonated copolymers

1. Introduction

Proton exchange membrane fuel cells (PEMFC), particularly direct methanol fuel cell (DMFC), are receiving considerable attention on account of their promising applications as electric power sources for automobile (cars, trucks, buses) or portable (cell phones, laptops) devices owing to the high efficiency, simply design, low emissions and low operating temperatures [1]. Proton exchange membrane as proton conductive material is the vital component in DMFC for transferring protons from anode to cathode as well as providing a barrier to fuel gas cross-leads between the electrodes. For the proton exchange membranes, suitable membranes with high proton conductivity, low swelling and methanol permeability are required to satisfy the application in DMFC [2,3]. Nafion® is by far the most studied and commercially available proton exchange membrane. Although it shows good performance in PEMFC, the high cost, low conductivity at low humidity and high methanol permeability of Nafion® limited its usages for practical DMFC applications. As a result, many researchers have been rendered to develop high performance and low cost alternative conductive materials.

Recently, several new classes of proton-conducting materials based on aromatic polymers have been formed into membranes and their properties investigated [4]. The polymers studied include sulfonated poly(ether sulfones) [5,6], sulfonated poly(arylene ether)s [7], sulfonated poly(*p*-phenylene) [8,9], sulfonated polyimide [10,11] and sulfonated poly(arylene ether ketones) [12–14]. In our previous study [15–18], the preparation and characterization of a new type of proton exchange membrane based on SPEEK or SPEEKK, which was obtained by directly synthesis from sulfonated monomer, have been described. The conductivity values for the SPEEK copolymers at a degree of sulfonation around 1.2 were 0.07 S/cm at 25 °C and 0.13 S/cm at 80 °C,

---

* Corresponding author. Tel.: +86 431 85168870; fax: +86 431 85168868.
E-mail address: huina@jlu.edu.cn (H. Na).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.03.064

indicating that they are promising candidates for PEM materials [15]. However, the brittleness of the membranes at evaluated temperatures, excessively swelling properties and the relatively high methanol crossover in membranes at high sulfonated degrees have limited their usages. In order to solve these problems and improve selected PEM properties, acid–base composite membranes were widely investigated [19–22]. Kerres et al. prepared several acid–base blend membranes mainly from sulfonated poly(ether sulfone) or poly(ether ether sulfone) and different kinds of basic polymers, such as polybenzimidazole, aminated polysulfone, and polyethylenimine [19–21]. They observed that the blend membranes show high decomposition temperature, low swelling ratio and reduced methanol permeability as expected. Weiss and co-workers have proposed that SPEEK based blends using alternatives to poly(ether imide) (PEI) restrict the high swelling of the blend without significantly diminishing the conductivity [22]. In our former work, PANI and polypyrrole were, respectively, blended with SPEEK copolymers to form acid–base composite membranes [23,24]. These blends have been proposed as promising materials for applications in DMFC.

In this paper we have prepared SPEEK/PAI composite membranes. PAI is a kind of high-temperature, engineering thermoplastic that was selected because of the possibility of forming the hydrogen bond between the sulfonated acid groups and amine groups. Moreover, an intermolecular, electron donor–acceptor complex between the imide groups and the sulfonic groups of SPEEK also exists in the SPEEK/PAI blends reported by Karcha and Porter [25].

It is well known that the incorporation of basic polymers into sulfonated poly(arylene ether ketone)s could lower the proton conductivity as well as the water uptake, so it is necessary to use highly sulfonated copolymers. The present paper firstly reported the directly condensation copolymerization of SPEEK with D_s reaching up to 1.31. Then the SPEEK/PAI composite membranes were prepared and characterized in detail.

2. Experimental

2.1. Materials and reagents

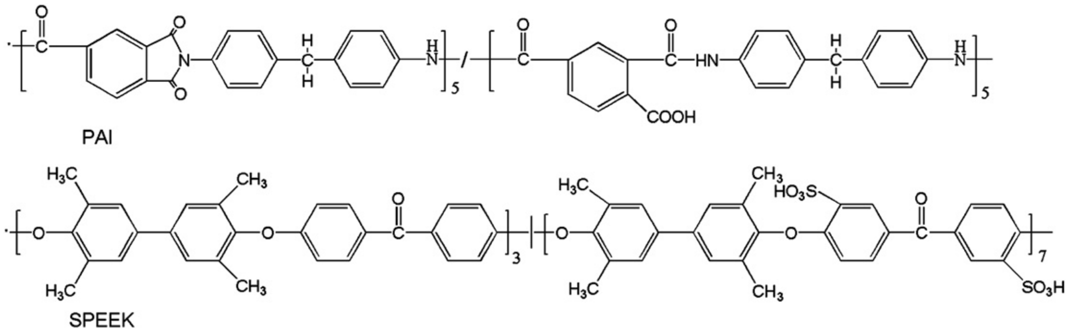
Poly(amide imide) Torlon® AI-10 was purchased from Solvay Advanced Polymers with the structural formulas shown in Scheme 1. Sodium 5,5′-carbonybis(2-fluorobenzene-sulfonate) was synthesized according to a previously reported procedure [15]. 3,3′,5,5′-Tetramethyl diphenyl-4,4′-diol was prepared in our lab and recrystallized from acetone before use. Potassium carbonate was dried at 180 °C for 10 h prior to use. All other chemicals were obtained commercially and used as received.

2.2. Synthesis and characterization of SPEEK-70 copolymer

SPEEK-70 copolymer, which has 70 mol% sulfonated polymer unit incorporated in the SPEEK copolymer composition, was prepared by direct aromatic nucleophilic substitution with the following monomers: 4,4′-difluorobenzophenone (0.015 mol), sodium 5,5′-carbonylbis(2-fluorobenzene-sulfonate) (0.035 mol), 3,3′,5,5′-tetramethyl diphenyl-4,4′-diol (0.050 mol) and potassium carbonate (0.055 mol) according to the reported literatures [15]. After mixing the monomers in DMSO/toluene system, the mixture was stirred at 140 °C for 4 h and then raised to 170 °C for 6 h. The reaction mixture was cooled to room temperature and poured into acetone. The inorganic salts were removed by washing with boiling water several times. The product was immersed in 0.5 M HCl solution for 48 h to convert into H^+ form and then dried at 100 °C under vacuum. The structure of SPEEK-70 is also shown in Scheme 1. The degree of sulfonation of SPEEK-70 was estimated by ^1H NMR (in DMSO-d_6) using a 500 MHz Bruker Avance 510 spectrometer. The chemical shift of tetramethylsilane was used as the internal standard. Intrinsic viscosity of SPEEK-70 was measured in a concentration of 5.00 g/l DMF solution at 25 °C using an Ubbelohde viscometer.

2.3. Preparation of SPEEK/PAI blend membranes

The SPEEK (in acidic form) mixed with the various amounts of PAI by weight (5–20 wt.%) were firstly dissolved in DMF to afford a mass fraction of 10% solution. Then the pure SPEEK-70 and the SPEEK/PAI blend membranes were prepared by casting their viscous solutions onto clean glass plates. The glass plate was heated at 80 °C for 6 h and 120 °C for another 12 h until most of the solvent was removed. These membranes were detached from the glass plates by immersing into deionized water for several minutes.



Scheme 1. The structure of PAI and SPEEK copolymers for preparing the blend membranes.

2.4. Membrane characterization

FT-IR spectra were recorded between 4000 and 400 cm^{-1} on a Bruker Vector 22 FT-IR spectrometer with thin, homogeneous cast films. UV–vis spectra were performed on UV-2501 PC spectrometer (Shimadzu) with the SPEEK/PAI blend membranes.

A Pyris TGA (Perkin–Elmer) was used to study the thermal stability behaviors of the blend membranes. About 5–10 mg samples were heated to 150 °C and kept at this temperature for 20 min to remove any residual water or solvent remaining in N_2 flow, then cooled to 80 °C and reheated to 700 °C at a heating rate of 10 °C/min.

Small angle X-ray scattering (SAXS) measurement was performed on swollen SPEEK-70 and its blended membranes. The membranes in swollen state were prepared by immersing in water for 24 h at room temperature. All the measurements were collected with Kratky small-angle X-ray scattering, with Cu Kα (Philips) radiation.

The water uptake of the membrane was determined by measuring the change in the weight between the dry and swollen membranes. A detailed procedure was reported previously [15]. The IEC values were measured by a classical titration method. Firstly, the membranes in the acid form (H^+) were immersed into a 50 ml 1 M NaCl solution for 24 h in order to completely exchange the H^+ ions with Na^+ ions. Then, the released H^+ ions within the solutions were titrated with a 0.1 M NaOH solution, using a phenolphthalein indicator. The IEC values were recorded in unit of millimole NaOH per gram of the membrane samples (mequiv./g) as an average value for each sample. The formula for calculating theoretical IEC values of blend membranes is

$$\mathrm{IEC_{blend}} = \frac{(\mathrm{IEC_{sp}} \times W_{\mathrm{sp}}) + (\mathrm{IEC_{pai}} \times W_{\mathrm{pai}})}{W_{\mathrm{sp}} + W_{\mathrm{pai}}} \tag{1}$$

where $\mathrm{IEC_{sp}}$ and $\mathrm{IEC_{pai}}$ are the IEC values of SPEEK (sulfonic acid groups) and PAI (carboxylic groups), respectively, while W_{sp} and W_{pai} are the weights of SPEEK and PAI, respectively.

The water desorption measurement was made by Pyris 1TGA (Perkin Elmer), which was used to record the weight changes of the samples with time. The membranes were firstly immersed in deionized water at room temperature for 48 h. Then the wet membranes were quickly swabbed to remove the superficial water before measurement. During the process of measurement, the temperature was kept at 80 °C for 60 min.

Methanol diffusion coefficient was measured using a home-made glass diffusion cell, which consisted of two compartments divided by a membrane sample. Pure methanol (100 ml) was placed on one side of the diffusion cell (cell A) and 100 ml water was placed on the other side (cell B). The solution in each compartment was continuously stirred to ensure uniformity. The concentration of the methanol in cell B was measured using Shimadzu GC-8A chromatograph. Peak areas were converted to methanol concentration with a calibration curve. The methanol diffusion coefficient was calculated by the reference report [16].

The proton conductivity was measured by AC impedance spectroscopy over a frequency range of $10-10^7$ Hz with 50–500 mV oscillating voltage using an impedance/gain-phase analyzer (*Solatron* 1260, Solatron Analytical, UK) in combination with an electrochemical interface (*Solatron* 1287). Conductivity measurement of fully hydrated membranes was carried out with the cell immersed in liquid water. The proton conductivity was calculated by Eq. (2):

$$\sigma = L/RA \tag{2}$$

where σ is the proton conductivity in S/cm, L is the distance between the two electrodes, and A is the cross-sectional area of membrane. R is derived from the low intersection of the high frequency semicircle with the Re(Z) axis on a complex impedance plane.

3. Results and discussion

3.1. Polymer synthesis and characterization

According to the reported work of others [26], the incorporation of PAI into post-sulfonated SPEEK lowered proton conductivity as well as methanol permeability, so it is necessary to obtain copolymers with high concentration of ionic sites. Disulfonated poly(aryl ether ether ketone) of theoretical D_s 1.40 (SPEEK-70) was synthesized accordingly to a similar procedure described in previous work. The D_s was controlled by varying the ratio of sulfonated to unsulfonated dihalide monomer. The inherent viscosity value of SPEEK-70 was 0.93 dl/g in DMF at a concentration of 5.00 g/l, which indicated high molecular weight of the resulting polymer and ease formation of ductile, tough membrane by casting from DMF solution.

Fig. 1 represents the ^{1}H NMR spectrum and the chemical constituents of SPEEK-70 copolymer. Derived from the following Eq. (3), a calculated D_s of 1.31 was measured by NMR technique [27].

$$\frac{D_s}{12 - 2D_s} = \frac{i_1}{i_R} \tag{3}$$

where i_1 is the intensity of H_1 (8.15–8.36 ppm) and i_R is the intensity of the remaining aromatic signals (6.33–7.91 ppm).

3.2. Membrane preparation and characterization

Blend membranes composed of 5, 10, 15 and 20 wt.% of PAI in SPEEK-70 were prepared by dissolving the polymers in DMF and solution casting. Prior to this, SPEEK-70 was converted to its sulfonic form by immersing in acid solutions. In this paper, blend membranes obtained with different weight ratios (5%, 10%, 15% and 20%) are referred to SPEEK/PAI-1, SPEEK/PAI-2, SPEEK/PAI-3 and SPEEK/PAI-4, respectively.

FT-IR and UV–vis spectra were performed to confirm the incorporation of PAI in blend membranes. Fig. 2 shows the FT-IR of the SPEEK-70, PAI and SPEEK/PAI blend membranes. For the blend membranes, the symmetric and

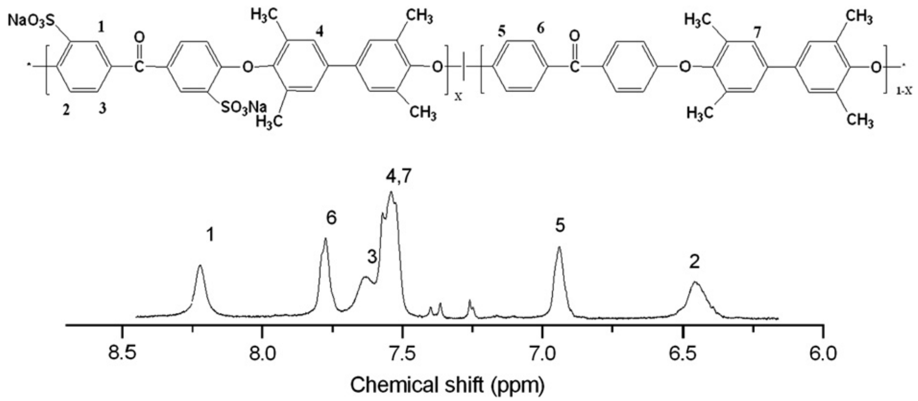


Fig. 1. ^{1}H NMR spectrum in DMSO-d_6 and the chemical constituents of SPEEK-70 ($D_s = 1.31$).

asymmetric stretches of the sulfonate groups appeared at 1089 and 1026 cm^{-1}, respectively. The strong absorptions at 1725 cm^{-1} were due to the symmetric stretches of the imide group. The asymmetric stretch vibration of imide group was observed around 1779 cm^{-1}. With the increment of PAI content in the blend membranes, the intensities of these two characteristic peaks increased, which confirmed the successful incorporation of the PAI and the trend of the weight ratio of PAI in the blend membranes.

The UV–vis spectra of the pure SPEEK-70 and SPEEK/PAI blend membranes are shown in Fig. 3. All the membranes showed absorption peaks at 210 nm, 267 nm and 370–440 nm. The peaks at 210 nm and 267 nm corresponded to the stretching of the benzene ring. The broad absorption at 370–440 nm was induced by the π–π* transition of the benzenoid rings. It can be observed that the last peaks had shifted from 440 nm to the lower wavelength 370 nm in the blend membranes, which may be caused by the hydrogen bond between the sulfonated acid groups and amine.

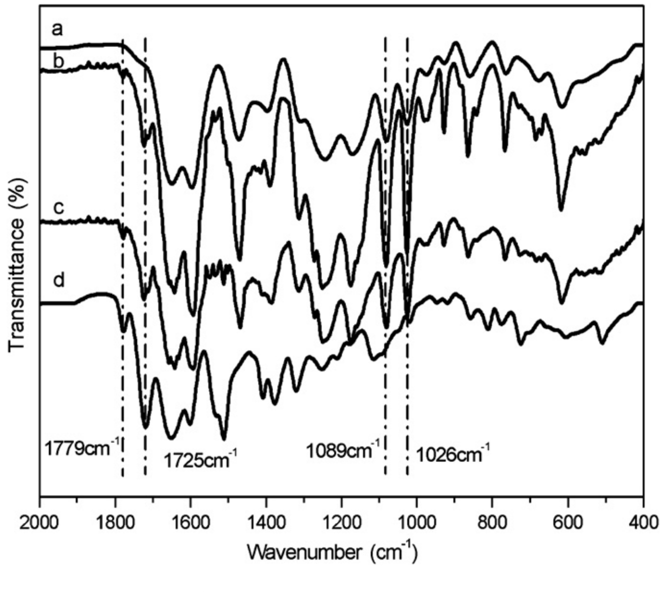


Fig. 2. FT-IR spectra of (a) SPEEK-70, (b) SPEEK/PAI-1, (c) SPEEK/PAI-4, and (d) PAI.

3.3. The thermal stability of membranes

TGA measurement was performed to evaluate the thermal properties of the composite membranes. Fig. 4 shows that the TGA curves of the SPEEK/PAI blend membranes in nitrogen are very similar to that of SPEEK-70 copolymers. In each TGA curve one can observe two distinct weight loss steps, of which the initial one at around 300 °C was mainly associated with the splitting-off of sulfonic acid groups of SPEEK. The second weight loss region at about 450 °C was attributed to the decomposition of the main chain of the copolymers. These results indicated that all the membranes are thermally stable at about 300 °C, which is good enough for usage as proton-conducting materials. However, it is important to note that for the blend membranes, the temperatures corresponding to the onset of thermal degradation were relatively higher than the pure SPEEK membrane, especially for the PAI weight content up to 20% in the blend membranes. The weight remaining after the polymer decomposition also depended on the content of the PAI. When SPEEK-70 copolymers lost about 45% by weight at 650 °C after thermal decomposition, the SPEEK/

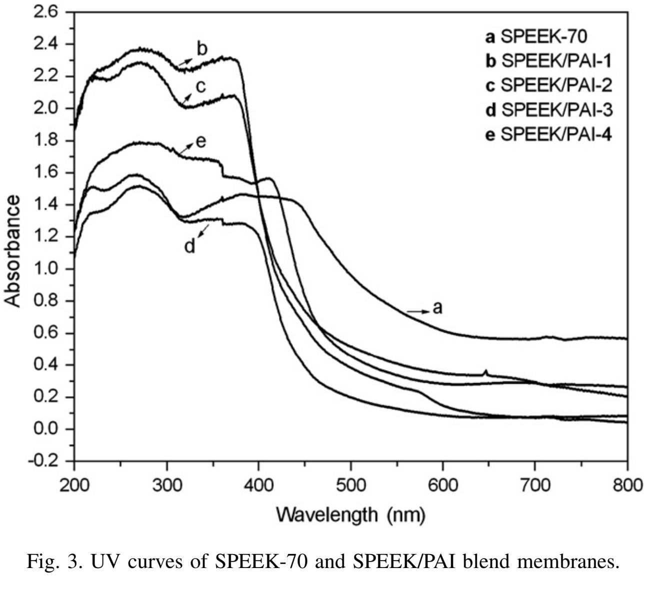


Fig. 3. UV curves of SPEEK-70 and SPEEK/PAI blend membranes.

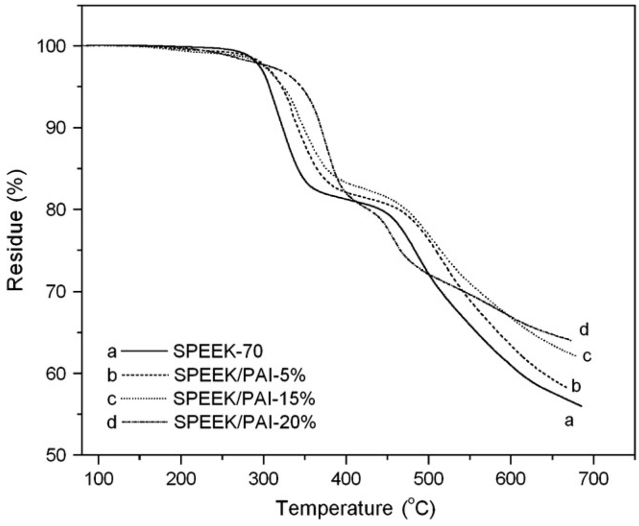


Fig. 4. TGA curves of SPEEK/PAI blend membranes under nitrogen.

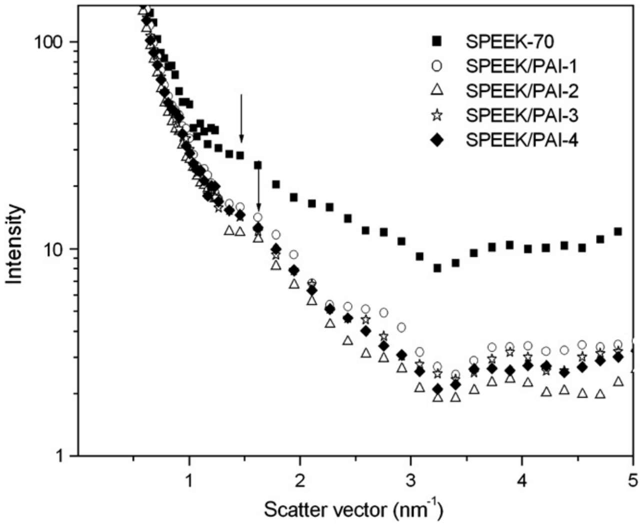


Fig. 5. The SAXS profiles of membranes.

PAI blend membranes lost about 30–35% by weight at the same temperature. TGA results can provide the information that the thermal stabilities are enhanced as a result of the incorporation of PAI into the highly charged SPEEK membranes, which is due to the restriction of the SPEEK hydrophilic cluster's mobility caused by the intermolecular interaction between SPEEK and PAI.

3.4. SAXS analyses

As reported in the literatures, the electrochemical behaviors of proton exchange membranes are closely associated with their morphology [28]. In the case of SPEEK membranes, the sulfonic groups may aggregate into large hydrophilic clusters, which are embedded in the hydrophobic polymer matrix, leading to the nano-phase separation [29]. To investigate the hydrophilic clusters in the membrane structure, SAXS measurements were carried out for SPEEK-70 and its blend membranes under fully hydrated conditions. As mentioned previously, many models based on SAXS studies were supposed, such as a core–shell model and a phase separation model [30]. The phase separation between the hydrophilic and hydrophobic domains of SPEEK membranes may lead to the scattering maximum (so-called ‘‘ionomer peak’’) at large angles [17,23,30]. From the results of SAXS profiles (Fig. 5), the ionomer peaks of SPEEK/PAI blend membranes shift to larger scattering vectors (q) compared to the SPEEK-70 membrane, which reveals the relatively smaller ‘‘center to center distance’’ between two clusters in the blend membranes. These results indicate that the hydrophilic cluster in the SPEEK/PAI blend membranes is smaller in size to that of SPEEK-70 membrane, resulting in a considerable amount of a smaller hydrophilic domain presenting in the blend membranes [23].

3.5. Water uptake, water desorption and IEC of blend membranes

It has been widely reported in the literatures that the proton conductivity of sulfonated polymers is associated with the water uptake and IEC of the membranes [31,32]. In general, proton conductivity depends on the number of available sulfonic acid groups and their dissociation capability in water. Water uptake is an important parameter in studying PEMs, because the water resides in the hydrophilic domains and can facilitate the transport of protons, but too much water absorption results in loss of mechanically stability. Li et al. reported water uptake and IEC increase with increasing D_s [16]. SPEEK-70 membrane showed high IEC of 2.11 mequiv./g and water uptake of about 60% at 25 °C due to its high D_s value of 1.31. The IECs and water uptake values of SPEEK/PAI blend membranes are shown in Table 1 and Fig. 6 as functions of SPEEK

Table 1
The properties of blend membranes

Samples	IEC (mmol/g)		Water uptake (%)		Water diffusion coefficient (m^2/s)	Methanol diffusion (cm^2/s)	Proton conductivity (S/cm)	
	Cal[a]	Exp[b]	25 °C	80 °C			25 °C	80 °C
SPEEK-70	2.50	2.11	59.56	93.27	8.65×10^{-9}	2.61×10^{-6}	0.084	0.167
SPEEK/PAI-1	2.44	1.96	54.52	87.72	4.62×10^{-9}	2.02×10^{-6}	0.066	0.148
SPEEK/PAI-2	2.38	1.86	50.83	82.62	2.60×10^{-9}	1.41×10^{-6}	0.055	0.137
SPEEK/PAI-3	2.33	1.70	43.44	71.99	1.46×10^{-9}	1.17×10^{-6}	0.051	0.115
SPEEK/PAI-4	2.27	1.65	39.28	60.80	1.38×10^{-9}	8.47×10^{-7}	0.040	0.098

[a] IEC values calculated from the content of sulfonic acid groups and carboxylic groups per membrane weight.

[b] IEC values measured using titration method.

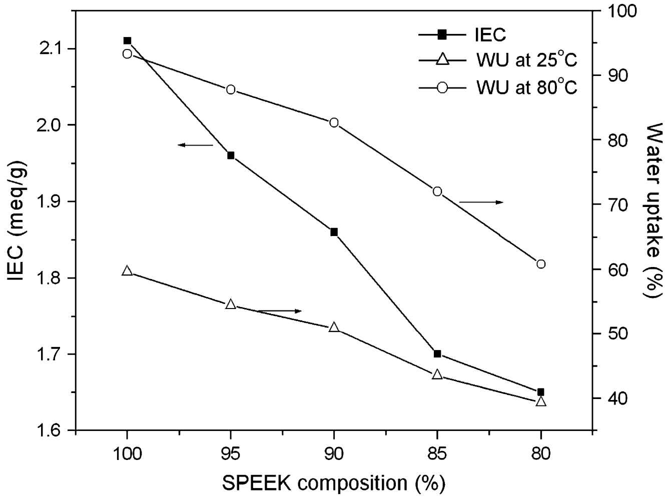


Fig. 6. Variation of IEC and water uptake values with SPEEK composition in the blend membranes. (WU is the abbreviation for water uptake).

weight composition. As compared to theoretical IEC values calculated from the content of sulfonic acid groups and carboxylic groups per membrane weight, the experimentally determined IECs of the blend membranes were lower because sulfonic acid or carboxylic protons of the ionomers were partially consumed by acid–base interaction between the sulfonic acid groups and amine groups of PAI component.

As expected, the water uptake values decreased with increases in the weight fraction of PAI in the membrane matrix. For example, the water uptake of pure SPEEK-70 membrane is nearly 60%, whereas, SPEEK/PAI blend membranes show the water uptake of 54.4%, 50.8%, 43.4% and 39.2%, respectively, at 25 °C with the content of PAI increasing from 5 wt.% to 20 wt.%, while IEC of blend membranes decreases from 2.11 to 1.65 mequiv./g. Since PEMs in fuel cells are generally operated at temperatures close to 80 °C, water uptake of these membranes were measured at each SPEEK proportion as functions of temperature. The results are shown in Fig. 7. The shapes of the water uptake versus temperature curves for the blend membranes were found to be similar. The water uptake values increase sharply with temperature. At elevated temperatures, the polymer chain mobility and the free volume for water absorption increase. As a result, the pure SPEEK membrane swelled much at 80 °C, which showed a water uptake of 95%. While the PAI weight content reached up to 20 wt.%, the water uptake values decreased sharply to 60%. This decrease in the water absorption may be due to the incorporation of PAI into the SPEEK matrix, which resulted in the formation of the intermolecular, electron donor–acceptor complex and hydrogen bonding. These specific interactions between the blend components may be the reasons for the reduction of swelling of SPEEK component. Therefore, the mechanical stability of blend membranes could be reinforced by the incorporation of PAI component, which is favorable for PEM to be used in DMFC.

Water retention and diffusion properties of proton exchange membranes have significant effects on their proton conductivities, especially at high temperatures and low relative humidity. They are very important in view of their practical application in proton exchange membrane fuel cells. The velocity of water evaporation in membranes may give the information about water retention of membranes. Water desorption isotherms of the pure SPEEK and its composite membranes are shown in Fig. 8. M_t and M_∞ refer to the mass desorbed at time t and infinite time, respectively. Plots of M_t/M_∞ versus $t^{1/2}$ initially were linear for Fickian diffusion [33]. Diffusion coefficients for desorption (D) were determined from the initial slopes according to Eq. (4).

$$\frac{M_t}{M_\infty} = 4\left(\frac{D_t}{\pi l^2}\right)^{1/2} \tag{4}$$

where l is the film thickness. It can be observed that the water in composite membranes evaporates more slowly than SPEEK

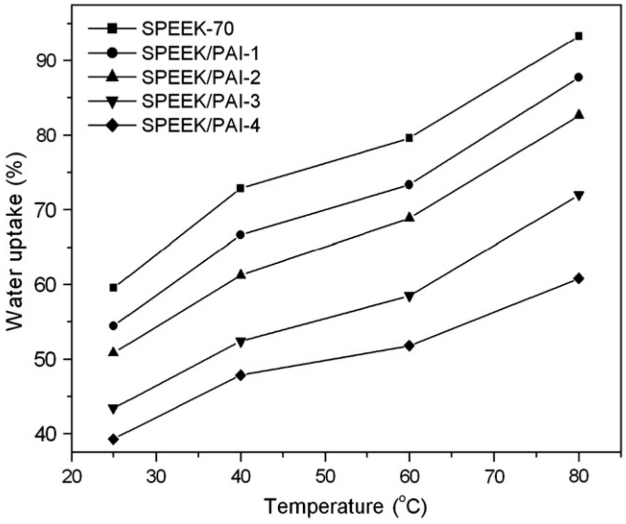


Fig. 7. Water uptake of SPEEK/PAI blend membranes at different temperatures.

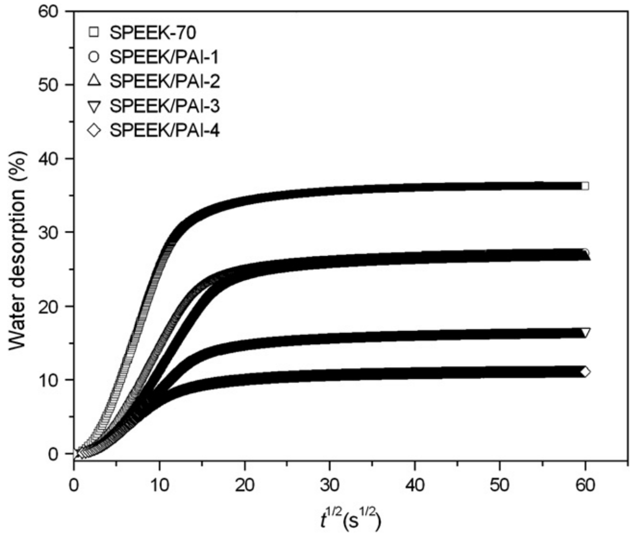


Fig. 8. Water desorption of SPEEK-70 and SPEEK/PAI blend membranes.

membranes, which may be resulted from the interaction between the SPEEK and PAI. The water diffusion coefficients of pure SPEEK-70 and its composite membranes calculated from the slope of the line were 8.65×10^{-9}, 4.62×10^{-9}, 2.60×10^{-9} and 1.38×10^{-9} m^2/s, respectively. From the result it is clear that the velocity of water volatilization decreased with increasing PAI content. In another words, the water retention of the composite membranes at relative high temperatures improved after the introduction of PAI component.

3.6. Proton conductivity and methanol permeability

The proton conductivities of the membranes at different temperatures were estimated using resistance measurements, acquired in the frequency range of 10–100 kHz. The conductivity data were analyzed in terms of Arrhenius plot, as reported in Fig. 9. It is well known that the proton conductivity of ionomer membranes is a function of D_s, temperature and water content. Indeed, high D_s results in high water content and higher proton conductivity. In addition, proton conductivity is in general a thermally stimulated process. For example, the proton conductivity of SPEEK-70 membrane ($D_s = 1.31$) was 0.084 S/cm at 25 °C and increased to 0.167 S/cm at 80 °C, surpassing that of Nafion® 117 and other SPEEK membranes reported by our groups previously.

As seen in Fig. 9, the conductivities of all the SPEEK/PAI blend membranes at room temperature are higher than 1×10^{-2} S/cm, which is conventionally regarded as the lowest value of practical interest for use as PEMs in fuel cells. With the increase in PAI, proton conductivities measured at 25 °C showed a decreasing tendency. They were in the range of 0.040–0.066 S/cm, which were lower than that of pure SPEEK-70 membrane (0.084 S/cm) and were still comparable to that of Nafion® 117 membrane measured under the same condition. The decreasing tendency in proton conductivity was mainly influenced by the introduction of hydrophobic PAI into the hydrophilic SPEEK matrix. As described in Section 3.4, for SPEEK membranes, the hydrophilic sulfonic groups may aggregate into hydrophilic ionic clusters, which are embedded in the hydrophobic polymer matrix [29]. When the density of sulfonic groups is low, these ionic clusters are isolated in the continuous hydrophobic domain. However, when the density of sulfonic groups increases to a certain value, these ionic clusters aggregate and lead to a random distribution of ion channels with good connectivity and proton can transport fast in these channels [34]. The introduction of hydrophobic PAI component reduced the density of sulfonic groups in the SPEEK membranes, further led to the more dense microstructures due to the interaction between them. Compared to the pure SPEEK membranes, the mobility and the size of the ionic clusters in the blend membranes could be restricted, resulting in the low proton conductive ability of the blend membranes, which was confirmed by SAXS study.

Membranes for the practical usage in DMFC must both possess high proton conductivity and low methanol permeability [35]. The high methanol crossover for Nafion® membrane in the DMFC application is one of the most significant drawbacks that makes them unpractical for large-scale production. The methanol permeability of SPEEK-70 and its blend membranes is shown in Table 1. The methanol permeability of the blend membranes decreased obviously compared to the pure SPEEK membranes. With the increase of the content of PAI, the methanol permeability of the blend membranes decreased. The pure SPEEK membrane showed the methanol diffusion coefficient of 1.57×10^{-6} cm^2/s at room temperature, whereas, the blend membranes, which contain 5, 10, 15 and 20 wt.% of PAI showed the coefficient of 2.02×10^{-6}, 1.41×10^{-6}, 1.17×10^{-6} and 8.47×10^{-7} cm^2/s, respectively. As above-mentioned, the transport of methanol in membranes also requires channels with good connectivity formed by the

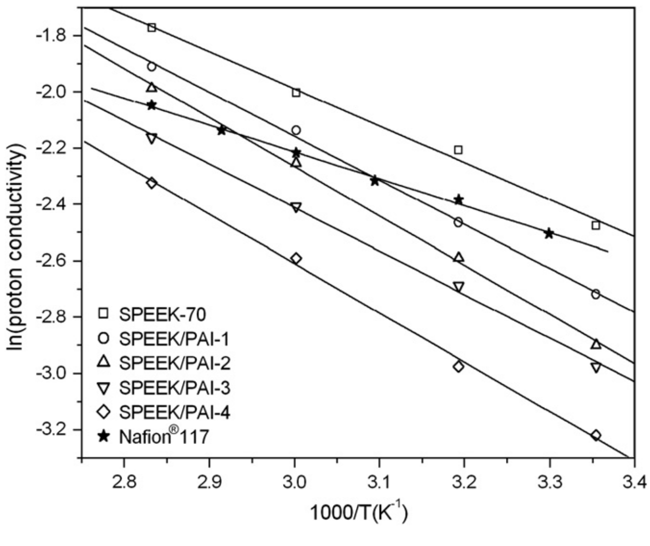


Fig. 9. Proton conductivity of SPEEK/PAI blend membranes and Nafion® 117 immersed in liquid water as a function of temperature.

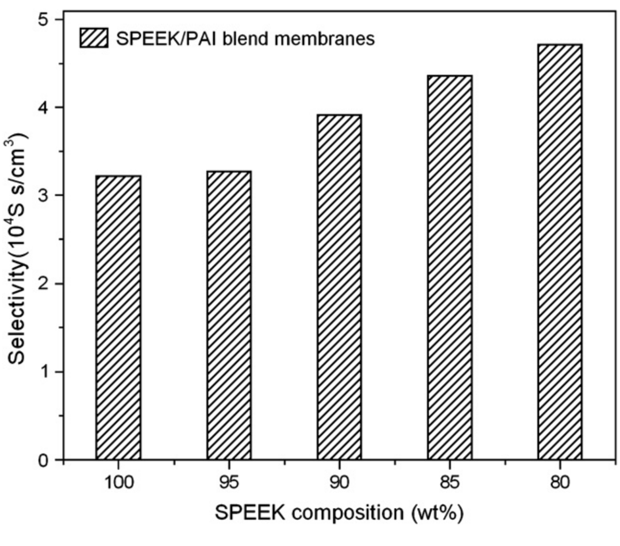


Fig. 10. The selectivity of SPEEK/PAI blend membranes at different SPEEK compositions.

aggregation of hydrophilic clusters. The interaction between the SPEEK and PAI restricts the formation of large ionic clusters or transport channels in the blend membranes, and further contributes to the decreasing of methanol diffusion, which can be explained by the SAXS study.

The selectivity, which is defined as the ratio of proton conductivity to methanol permeability [36], is often applied to evaluate the potential performance in DMFCs. Fig. 10 shows the selectivity of the pure SPEEK-70 and SPEEK/PAI blend membranes, which is based on their conductivities and methanol permeability measured at room temperature. The blend membranes showed a gradually increasing tendency with the increase of PAI content. The selectivity ranged from 3.22×10^4 to 4.72×10^4 S s/cm^3, which is attractive for DMFCs.

4. Conclusion

Highly disulfonated poly(aryl ether ether ketone) was prepared via direct polymerization of sulfonated dihalide monomers. The degree of sulfonation of SPEEK-70 determined by ^{1}H NMR was 1.31. The proton conductivity of it was comparable to that of Nafion® 117. SPEEK/PAI blend membranes were prepared with varied weight ratio of PAI component and characterized for DMFC application. The water uptake of the blend membrane was significantly reduced and ranged from 59.56% to 39.28% along with IEC values decreasing from 2.11 to 1.65 mequiv./g. The water diffusion coefficients for desorption fell as the PAI content increases since the water swelling behavior was restricted. Although the proton conductivities decreased upon the addition of PAI, higher selectivity values defined as the ratio of proton conductivity to methanol permeability were found for the blend membranes. Therefore, considering these results, it can be concluded that, the SPEEK/PAI blend membranes are promising for usage in DMFC.

References

[1] Steele BCH, Heinzel A. Nature 2001;414:345.
[2] Rikukawa M, Sanui K. Prog Polym Sci 2000;25:1463.
[3] Kreuer KD. J Membr Sci 2001;185:29.
[4] Hickner MA, Ghassemi H, Kim YS, Einsla BR, McGrath JE. Chem Rev 2004;104:4587.
[5] Wang F, Hickner MA, Kim YS, Zawodzinski TA, McGrath JE. J Membr Sci 2002;197:231.
[6] Li Y, Wang F, Yang J, Liu D, Roy A, Case S, et al. Polymer 2006;47:4210.
[7] Ghassemi H, McGrath JE, Zawodzinski TA. Polymer 2006;47:4132.
[8] Wu SQ, Qiu ZM, Zhang SB, Yang XR, Yang F, Li ZY. Polymer 2006;47:6993.
[9] Ghassemi H, McGrath JE. Polymer 2004;45:5847.
[10] Genies C, Mercier R, Sillion B, Cornet N, Gebel G, Pineri M. Polymer 2001;42:359.
[11] Chen S, Yin Y, Tanaka K, Kita H, Okamoto K. Polymer 2006;47:2660.
[12] Xing PX, Robertson GP, Guiver MD, Mikhailenko SD, Kaliaguine S. Macromolecules 2004;37:7960.
[13] Mikhailenko SD, Wang KP, Kaliaguine S, Xing P, Robertson GP, Guiver MD. J Membr Sci 2004;233:93.
[14] Shang X, Li X, Xiao M, Meng Y. Polymer 2006;47:3807.
[15] Gil M, Ji XL, Li XF, Na H, Hampsey JE, Lu YF. J Membr Sci 2004;234:75.
[16] Li XF, Zhao CJ, Lu H, Wang Z, Na H. Polymer 2005;46:5820.
[17] Zhao CJ, Li XF, Wang Z, Dou ZY, Zhong SL, Na H. J Membr Sci 2006;280:643.
[18] Li XF, Wang Z, Lu H, Zhao CJ, Na H, Zhao C. J Membr Sci 2005;254:147.
[19] Kerres J, Ullrich A, Meier F, Häring T. Solid State Ionics 1999;125:243.
[20] Cui W, Kerres J, Eigenberger G. Sep Purif Technol 1998;14:145.
[21] Zhang W, Tang CM, Kerres J. Sep Purif Technol 2001;22–23:209.
[22] Swier S, Shaw MT, Weiss RA. J Membr Sci 2006;270:22.
[23] Li XF, Chen DJ, Xu D, Zhao CJ, Wang Z, Lu H, et al. J Membr Sci 2006;275:134.
[24] Li XF, Liu CP, Xu D, Zhao CJ, Wang Z, Zhang G, et al. J Power Sources 2006;162:1.
[25] Karcha RJ, Porter RS. J Polym Sci Part B Polym Phys 1993;31:821.
[26] Wu HL, Ma CM, Li CH, Lee TM, Chen CY, Chiang CY, et al. J Membr Sci 2006;280:501.
[27] Zaidi SMJ, Mikhailenko SD, Robertson GP, Guiver MD, Kaliaguine S. J Membr Sci 2000;173:17.
[28] Yang YS, Shi ZQ, Holdcroft S. Macromolecules 2004;37:1678.
[29] Eisenberg A. Macromolecules 1970;3:47.
[30] Fujimura JM, Hashimoto TJ, Kawai H. Macromolecules 1981;14:1309.
[31] Xing P, Robertson GP, Guiver MD, Mikhailenko SD, Wang K, Kaliaguine S. J Membr Sci 2004;229:95.
[32] Kim YS, Einsla B, Sankir M, Harrison W, Pivovar BS. Polymer 2006;47:4026.
[33] Watari T, Fang JH, Tanaka K, Kita H, Okamoto KI, Hirano T. J Membr Sci 2004;230:111.
[34] Won J, Park HH, Kim YJ, Choi SW, Ha HY, Ha IH. Macromolecules 2003;36:3228.
[35] Kim DS, Liu BJ, Guiver MD. Polymer 2006;47:7871.
[36] Pivovar BS, Wang YX, Cussler EL. J Membr Sci 1999;154:155.