Polym. Bull. (2012) 68:1369–1386
DOI 10.1007/s00289-011-0638-1

ORIGINAL PAPER

Covalently and ionically crosslinked sulfonated poly(arylene ether ketone)s as proton exchange membranes

Pei Chen · Xinbing Chen · Zhongwei An

Received: 8 June 2011 / Revised: 21 September 2011 / Accepted: 21 September 2011 /

Abstract A series of covalently and ionically crosslinked sulfonated poly(arylene ether ketone)s (SPAEKs) were prepared via the cyclocondensation reaction of crosslinkable SPAEKs with 3,3′-diaminobenzidine to form quinoxaline groups, where crosslinkable SPAEKs were synthesized by copolymerization of 4,4′-biphenol with 2,6-difluorobenzil, 4,4′-difluorobenzophenone, and 5,5′-carbonylbis(2-fluorobenzene sulfonate). The SPAEK membranes had high mechanical properties and the isotropic membrane swelling. The covalent and ionical crosslinking significantly improved the membrane performance, i.e., the crosslinked membranes showed the lower membrane dimensional change, lower methanol permeability, and higher oxidative stability than the corresponding uncrosslinked membranes, with keeping the reasonably high proton conductivity. The crosslinked membrane (**CK3**) with measured ion exchange capacity of 1.62 mequiv g^{-1} displayed a reasonably high proton conductivity of 110 mS/cm with water uptake of 33 wt% at 80 °C, and exhibited a low methanol permeability of 1.7×10^{-7} cm^2 s^{-1} for 32 wt% methanol solution at 25 °C. The covalently and ionically crosslinked SPAEK membranes have potential for polymer electrolyte membrane fuel cells and direct methanol fuel cells.

Keywords Covalently and ionically crosslinked sulfonated poly(arylene ether ketone) · Proton exchange membrane · Quinoxaline groups · Methanol permeability

---

P. Chen · X. Chen (✉) · Z. An
Key Laboratory of Applied Surface and Colloid Chemistry (Shaanxi Normal University),
Ministry of Education, School of Materials Science and Engineering, Shaanxi Normal University,
Xi'an 710062, People's Republic of China
e-mail: chenxinbing@snnu.edu.cn

Z. An
Xian Modern Chemistry Research Institute, Xi'an 710065, People's Republic of China

Introduction

In the past decades, considerable attentions have been focused on polymer electrolyte membrane (PEM) fuel cells (PEFCs) and direct methanol fuel cells (DMFCs) as clean energy sources for transportation, stationary and portable power applications due to their high efficiency and low pollution to environment [1, 2]. PEM is one of the key components in PEFC and DMFC systems, and serves as a proton conductor and a fuel separator between anode and cathode. Perfluorosulfonate polymer membranes such as DuPont's Nafion membranes are the state-of-art PEMs commercially available with features of high proton conductivity and excellent chemical stability [3]. However, the shortcomings such as large fuel crossover, lower operating temperature below 80 °C, and high cost critically limit their widespread application [4]. Therefore, extensive efforts have been devoted to develop alternative PEMs based on sulfonated aromatic polymers [4–25].

Sulfonated poly(arylene ether)s (SPAEs), such as sulfonated poly(arylene ether sulfone)s (SPAESs) [13–19] and sulfonated poly(arylene ether ketone)s (SPAEKs) [20–22], are one of the promising candidates for fuel cell applications due to their good thermal and chemical stability. Unfortunately, most of SPAEs with high levels of sulfonation (or ion exchange capacity, IEC) makes them excessively swell and even soluble in water, resulting in a lower membrane stability. To overcome this problem, several methods have been developed, such as covalently crosslinked membranes [26–32], ionically crosslinked acid/base blend membranes [33–35], and layer-by-layer membranes [36–39], in which the formation of strong and stable crosslinking bonds is a common and powerful method to suppress membrane swelling and to improve the membrane durability.

Recently, we have developed a facile crosslinking method based on the cyclocondensation reaction of benzil moieties in polymer chains with 3,3′-diaminobenzidine (DAB) to form quinoxaline groups [40]. However, in order to clearly investigate the effects of the crosslinking on the membrane properties, the IECs of the studied SPAEK membranes were limited to be higher than 2.0 mequiv g^{-1}, which made the crosslinked SPAEK membrane swell strongly at 80 °C. Meanwhile, the side-chain type of nonsulfonated monomer, 2,6-Difluorobenzil (DFB), was not helpful for increasing the mechanical property of the SPAEK membranes due to the rigid structure of the formed nonsulfonated parts. In the present study, we present crosslinkable SPAEKs composed of benzil moieties and flexible sulfonated and nonsulfonated monomers, and prepare a series of quinoxaline-based covalently and ionically crosslinked SPAEKs with IECs less than 2.0 mequiv g^{-1} via the developed method [40]. For the crosslinked membranes with different quinoxaline capacity, the properties including water uptake, membrane swelling, proton conductivity, mechanical property, oxidative stability, and methanol permeability are investigated, compared with the corresponding precursor membranes. It is postulated that this approach can lead to high dimensional stability and low methanol crossover membranes with acceptable proton conductivity.

Experimental

Materials

4,4′-Biphenol (BP) and DAB were purchased from Aladdin-reagent Co. and BP was purified by vacuum sublimation prior to use. 4,4′-Difluorobenzophenone (DFBP) were purchased from Aldrich and used as received. Dimethyl sulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), and 1-methyl-2-pyrrolidone (NMP) were purchased from Sinopharm Chemical Reagent Co. and dehydrated with molecular sieve 4A. Fuming sulfuric acid (20% SO_3), calcium hydride, and other materials were purchased from Sinopharm Chemical Reagent Co. and used as received. NMP was dehydrated by calcium hydride, distilled under reduced pressure, and then dried with molecular sieve 4A prior to use. 5,5′-Carbonyl-bis(2-fluorobenzene sulfonate) (CBFBS) was prepared by sulfonation of DFBP at 120 °C using fuming sulfuric acid. DFB was prepared according to the literature [40].

Polymerization

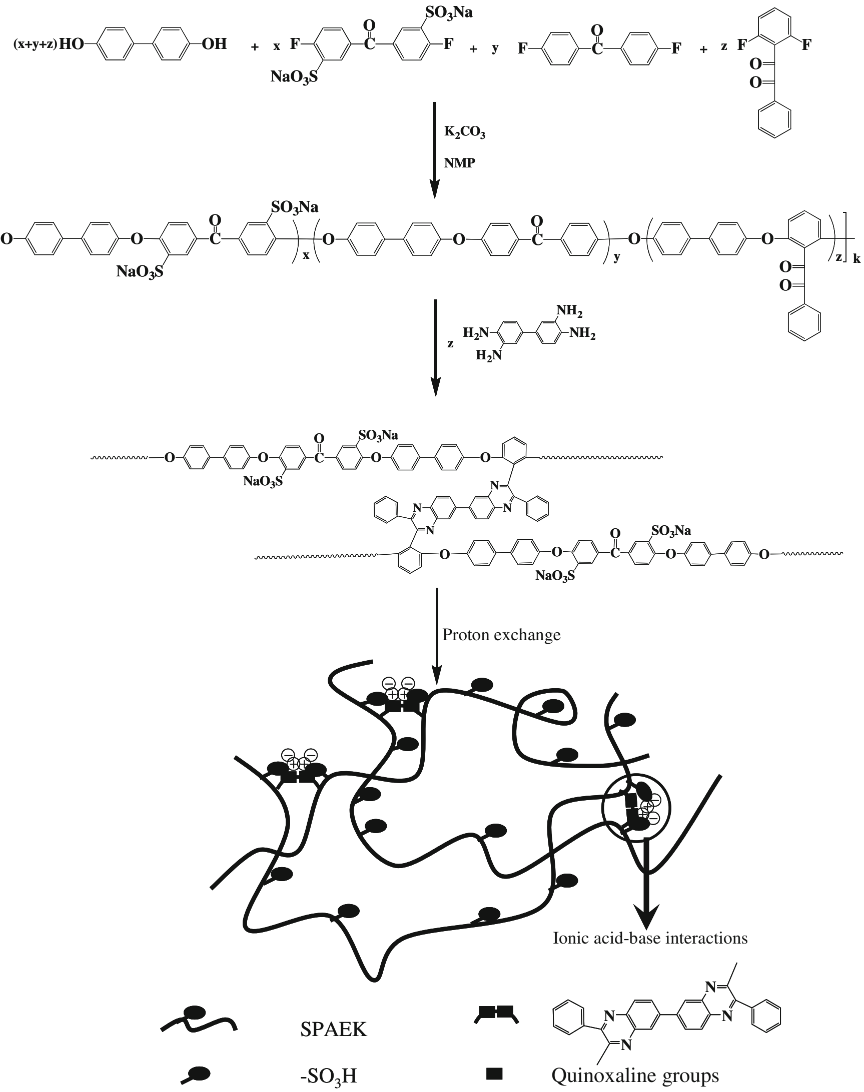
SPAEK copolymer BP–CBFBS/DFBP/DFB(*x*/*y*/*z*), where the data in parenthesis refer to the molar ratio of CBFBS:DFBP:DFB, was prepared by a one-pot high temperature polymerization method, as shown in Scheme 1. As an example, the preparation procedure of BP–CBFBS/DFBP/DFB(1/0.5/0.5), **K1** in Table 1, is described.

To a 100 mL dry three-neck flask equipped with a Dean-Stark trap and a condenser, 2.111 g (5.0 mmol) of CBFBS, 0.546 g (2.5 mmol) of DFBP, 0.616 g (2.5 mmol) of DFB, 1.862 g (10.0 mmol) of BP, 1.588 g (11.5 mmol) of anhydrous potassium carbonate, 26 mL of NMP, and 15 mL of toluene were added under nitrogen flow with stirring. The reaction mixture was heated to 140 °C. Water and toluene were evaporated as the azeotrope and collected in the Dean-Stark trap. After water was completely evaporated (the Dean-Stark trap became clear), the reaction temperature was raised to 160 °C and the polymerization was continued at this temperature for 10 h. The resulting highly viscous solution was slowly poured into water. The resulting fiber-like precipitate was thoroughly washed in water with stirring at 50 °C overnight, and then washed with methanol, and dried at 120 °C in vacuum.

Membrane formation and proton exchange

Uncrosslinked SPAEK membrane

A 7 wt% SPAEK solution in DMSO was prepared and filtrated. The filtrate was cast onto glass plates at 80 °C, and dried at 100 °C for 12 h. The as-cast membranes were soaked in water at 40 °C for 48 h, and proton-exchanged with 1 M hydrochloric acid at 50 °C for 48 h. The proton-exchanged membranes were thoroughly washed with deionized water till the rinsed water became neutral, followed by drying in vacuum at 120 °C for 15 h. The membranes obtained were 40–60 μm in thickness.



Scheme 1 Preparation of crosslinkable SPAEKs and corresponding crosslinked membranes

Crosslinked SPAEK membrane

Crosslinked SPAEK membrane, BP–CBFBS/DFBP/DFB/DAB(*x*/*y*/*z*/*w*), where the data in parenthesis (*x*/*y*/*z*/*w*) refer to the molar ratio of CBFBS:DFBP:DFB:DAB, was prepared by using the cyclocondensation reaction of benzil groups in DFB moieties and DAB to form quinoxaline, as shown in Scheme 1. Here, the molar content of DAB was set as 30 mol% based on DFB for the crosslinked membranes except **CK5**, that is, $w = 0.3z$. As an example, the crosslinked membrane of BP–CBFBS/DFBP/DFB/DAB (1/0.5/0.5/0.15), **CK1** in Table 1, is described.

Table 1 Basic properties of SPAEK membranes

Code	Membranes	η_r[a] (dL g^{-1})	IEC[b] (mequiv g^{-1})	QC (mequiv g^{-1})	WU (%)		λ[c]		Size change[d]		$\Delta_{t/l}$[d]
					25 °C	80 °C	25 °C	80 °C	Δt_c	Δl_c	
K1	BP–CBFBS/DFBP/DFB(1/0.5/0.5)	1.0	2.11(2.08)	–	44	73	12	19	0.20	0.22	0.91
CK1	BP–CBFBS/DFBP/DFB/DAB(1/0.5/0.5/0.15)	–	2.06(1.84)	0.31	35	54	11	16	0.16	0.15	1.07
K2	BP–CBFBS/DFBP/DFB(1/0.7/0.5)	1.2	1.96(1.94)	–	40	60	11	17	0.17	0.16	1.06
CK2	BP–CBFBS/DFBP/DFB/DAB(1/0.7/0.5/0.15)	–	1.92(1.71)	0.29	25	44	8	14	0.14	0.13	1.08
K3	BP–CBFBS/DFBP/DFB(1/0.5/0.7)	1.1	1.95(1.94)	–	37	59	11	17	0.16	0.16	1.00
CK3	BP–CBFBS/DFBP/DFB/DAB(1/0.5/0.7/0.21)	–	1.90(1.62)	0.40	22	33	8	11	0.11	0.10	1.10
K4	BP–CBFBS/DFBP/DFB(1/0.7/0.8)	1.0	1.76(1.74)	–	28	48	9	15	0.15	0.14	1.07
CK4	BP–CBFBS/DFBP/DFB/DAB (1/0.7/0.8/0.24)	–	1.71(1.41)	0.41	18	25	7	10	0.081	0.083	0.98
K5	BP–CBFBS/DFBP/DFB(1/1/0.5)	1.3	1.77(1.74)	–	26	46	8	15	0.13	0.14	0.93
CK5	BP–CBFBS/DFBP/DFB/DAB (1/1/0.5/0. 23)	–	1.72(1.43)	0.40	19	29	7	11	0.082	0.084	0.98
CK3-2	BP–CBFBS/DFBP/DFB/DAB(1/0.5/0.7/0.30)	–	1.87(1.42)	0.56	19	26	7	10	0.081	0.084	0.96
CK4-2	BP–CBFBS/DFBP/DFB/DAB (1/0.7/0.8/0.32)	–	1.69(1.27)	0.54	14	21	7	9	0.073	0.071	1.03
R1	BP–CBFBS/DFB(1/1)	1.5	2.08(2.06)	–	42	63	11	17	0.21	0.21	1.00

The experimental errors for IEC, MU, SU, WU, and size change were ±1, ±2, ±2, ±2, and ±3%, respectively

[a] At 0.5 g dL^{-1}, DMSO solution of SPAEK in sodium salt form at 35 °C

[b] Calculated value; The data in parentheses are obtained by a titration method

[c] Based on measured IEC, $\lambda = WU \times 10/(18 \times IEC)$

[d] At 80 °C

A 7 wt% BP–CBFBS/DFBP/DFB(1/0.5/0.5) solution in DMSO was prepared and filtrated. A given amount of DAB was added into the filtrate and the mixture was stirred at 140 °C for 4 h, and then 160 °C for 4–5 h (the gelation took place if the reaction was continued for a longer time). The mixture was cooled and cast onto glass plates at 80 °C, and dried at 100 °C for 4 h, 120 °C for 2 h, and then cured at 180 °C in vacuum for 5 h to promote the crosslinking reaction. The as-cast membranes were post-treated as mentioned above.

Characterization and measurements

FT-IR spectra were recorded on a Bruker Equinox 55 spectrometer. ^{1}H NMR spectra were recorded on a Bruker AV 300 (300 MHz) instrument. Thermogravimetric analysis (TGA) was carried out with a TA 600SDT in helium (flow rate: 100 $cm^3 min^{-1}$) at a heating rate of 10 °C min^{-1}, standing at 150 °C for 0.5 h. Mechanical tensile tests were performed on a universal testing machine (CTM6001) at 25 °C and about 30% relative humidity at a crosshead speed of 5 mm min^{-1}. Solubility tests were carried out in DMAc, DMF, NMP, and DMSO with a concentration of 5% (w/v) at room temperature. The reduced viscosity (η_r) was measured with an Ubbelohde viscometer using 0.5 g dL^{-1} DMSO solution of SPAEK in sodium salt form at 35 °C.

Ion exchange capacity (IEC) was calculated from the molar ratio of sulfonated difluoride monomer to nonsulfonated one in feed, and also evaluated by a titration method. A sample membrane in proton form was soaked in a 15 wt% NaCl solution at 40 °C for 72 h and the released proton was titrated with a 0.05 M NaOH solution, using phenolphthalein as an indicator. The titration was carried out for the solutions containing the sample membranes within a few minutes.

Quinoxaline capacity (QC) defined as the molar amount of quinoxaline groups per unit weight (mequiv g^{-1}) was calculated from the molar ratio of crosslinking reagent DAB to nonsulfonated difluoride monomer DFB in feed.

Water uptake (WU) of membrane was obtained by calculating the weight difference between the dry and wet membranes. The completely dried membrane samples were weighed, and then soaked into deionized water until the weight remained constant. Then, the samples were taken out, wiped with tissue paper, and quickly weighted on a microbalance. The WU was calculated, using the following equation:

$$\mathrm{WU} = [(W_\mathrm{s} - W_\mathrm{d})/W_\mathrm{d}] \times 100\% \tag{1}$$

where W_s and W_d are the weights of swollen and dry membranes, respectively.

Dimensional change of membrane was measured by soaking more than two sample sheets in water at different temperatures. The *through-plane* and *in-plane* dimensional changes (Δt_c and Δl_c) and the membrane swelling ratio ($\Delta_{\mathrm{t/l}}$) were calculated from Eq. 2:

$$\begin{aligned} \Delta t_\mathrm{c} &= [(t - t_\mathrm{d})/t_\mathrm{d}] \times 100\% \\ \Delta l_\mathrm{c} &= [(l - l_\mathrm{d})/l_\mathrm{d}] \times 100\% \\ \Delta_{\mathrm{t/l}} &= \Delta t_\mathrm{c}/\Delta l_\mathrm{c} \end{aligned} \tag{2}$$

where t_d and l_d are the thickness and length of the dry membrane, respectively; t and l refer to those of the membrane immersed in water.

Proton conductivity of membrane was determined using an electrochemical impedance spectroscopy technique over the frequency from 100 Hz to 100 kHz (Hioki 3532-80). A single cell with two platinum plate electrodes was mounted on a Teflon plate at 0.5 cm distance. A membrane swollen in water at 25 °C was set in the cell. The cell was placed in deionized water. Proton conductivity was calculated from Eq. 3:

$$\sigma = d/(t_s w_s R) \qquad (3)$$

where d is the distance (or membrane length) between the two electrodes, t_s and w_s are the thickness and width of the membrane in deionized water, respectively, and R is the measured resistance value. The d, t_s, and w_s values at different temperatures were evaluated from the temperature dependence of dimensional change of membrane.

Oxidative stability was determined using Fenton's reagent (3 wt% H_2O_2 + 2 ppm $FeSO_4$) at 80 °C. The membranes (50–60 μm in thickness) were immersed in Erlenmeyer flasks containing Fenton's reagent. The flasks were shaken vigorously once every 10 min until the membranes begin to break.

Methanol permeability (P_M) measurement was carried out using a liquid permeation cell composed of two compartments, which were separated by a vertical membrane. The membrane was first immersed in water for 2 h to get the water-swollen sample, and then set into the measurement cell (effective area: 16 cm^2). One compartment of the cell ($V_a = 400$ mL) was filled with 32 wt% methanol feed solution, and the other compartment ($V_b = 90$ mL) was filled with deionized water. The compartments were stirred continuously during the permeability measurement. The methanol concentrations of the two compartments were analyzed with a Shimadzu GC2014C gas chromatography apparatus. Methanol permeability, P_M, was calculated from Eq. 4:

$$P_M = kV_b L/(AC_a) \qquad (4)$$

where k is the slope of the straight-line plot of methanol concentration in permeate versus permeation time, C_a refer to the methanol concentration in feed, V_b is the solution volume of the permeate. L and A refer to the thickness and effective area of the swollen membrane, respectively.

Results and discussion

Characterization of crosslinkable SPAEK

Table 1 lists crosslinkable SPAEK copolymers prepared in this study (**K1**–**K5**) and their fundamental properties. The molar ratio of sulfonated monomer to nonsulfonated one was set in the range of 1/1–1/1.5 to ensure the copolymers with calculated IECs of 1.76–2.11 mequiv g^{-1}. The copolymers were prepared with high

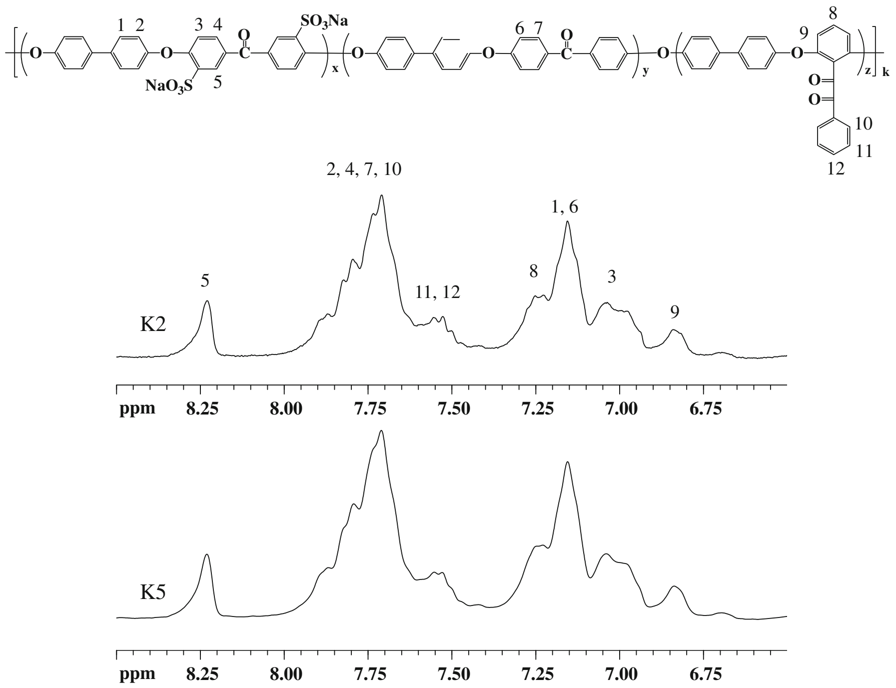


Fig. 1 ^{1}H NMR spectra of SPAEK membranes (**K2** and **K5**) in proton form in DMSO-d_6

yields and had high reduced viscosities ranged from 1.0 to 1.3 dL g^{-1}, indicating the high molecular weights. The IEC values determined by the titration method were as large as 98% of the corresponding theoretical values, which indicates that the proton exchange was almost complete for SPAEKs.

The chemical structure was identified by ^{1}H NMR and IR spectra. Figure 1 shows the ^{1}H NMR spectra of **K2** and **K5**. The signal at 8.23 ppm was assigned to the aromatic hydrogen atom H5 at the *ortho* position to the electron-withdrawing –SO_3H group. Comparing the ^{1}H NMR spectra of the copolymers with those of DFB and DFBP, the other peaks were assigned, as shown in Fig. 1.

Integration of ^{1}H NMR signals was used to calculate the sulfonation content which represents the actual mole percentage of sulfonated unit per average repeat unit in the obtained copolymers. The ratio of the integration value of proton H9 to H5 was used for the calculation. The sulfonation content determined by the ^{1}H NMR method was in good agreement with the one calculated from the feed molar ratio within the difference of ±1 mol%, which implied that the polymerization was performed completely.

Figure 2 shows the IR spectrum of **K1**. The absorption bands at 1658 cm^{-1} was assigned to symmetric stretching vibrations of C=O. The symmetric and asymmetric vibration of O=S=O bond of sulfonic acid group and sulfone group appeared at 1020, 1080, and 1165 cm^{-1}. The 1238 cm^{-1} peak was attributed to the vibrations of C–O–C group in aryl ether backbone.

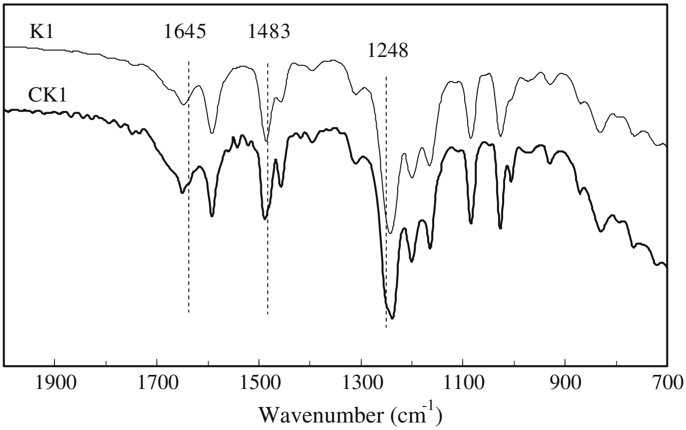


Fig. 2 IR spectra of SPAEK membranes

Crosslinked SPAEK

Table 1 also lists crosslinked SPAEK membranes (**CK1**–**CK5**) and their fundamental properties. The formation of crosslinking was confirmed by IR measurement and also judged by the reduced solubility of the crosslinked membranes in common aprotic solvents in which the corresponding uncrosslinked membranes were well soluble. Figure 2 shows the IR spectra of the uncrosslinked and crosslinked membranes (**K1** and **CK1**, respectively) in proton form. Although the two spectra were similar, the following differences were observed for **CK1.** The strong shoulder peak appeared at 1248 cm^{-1} was assigned to the characteristic stretching vibration of C–N. Although overlapping with that of phenyl ring (1490 cm^{-1}), the characteristic absorption bands of quinoxaline ring resulted in a strong shoulder peak at 1483 cm^{-1}. In addition, compared with **K1**, the shoulder peak at 1645 cm^{-1} for **CK1** was attributed to the vibration of C=N of quinoxaline ring. These indicated the formation of quinoxaline ring. The characteristic absorption bands of amino group at 3000–3400 cm^{-1} was not detected for **CK1** in sodium salt form as well as in proton form, indicating the absence of the unreacted diamino-phenyl end-groups. It was confirmed that the crosslinking of SPAEK was performed well with the formation of the quinoxaline cross-linkage.

As listed in Table 1, the IEC values determined by titration method were very close to the calculated IEC values for the uncrosslinked SPAEK membranes (**K1**–**K5**), whereas they were 11–18% smaller than the calculated ones for the crosslinked membranes (**CK1**–**CK5**). This was due to the formation of acid–base complex between sulfonic acid groups and quinoxaline moieties. For example, **CK1**, with calculated IEC of 2.06 mequiv g^{-1} and QC of 0.31 mequiv g^{-1}, exhibited a titrated IEC value of 1.84 mequiv g^{-1}. If sulfonic acid groups form the acid–base complex with all the quinoxaline groups to become unexchangeable with Na^+ ions, the titrated IEC value will be close to the value subtracted QC from the calculated IEC. In the case of **CK1**, this value was 1.75 mequiv g^{-1}, which was slightly smaller than the titrated IEC value. Therefore, the titrated IEC value is considered as the effective IEC value.

Solubility, mechanical properties, thermal and oxidative stability

The solubility properties of SPAEKs are listed in Table 2. The uncrosslinked SPAEKs generally showed good solubility to the polar aprotic solvents such as DMSO, NMP, and DMF, both in sodium salt and in proton form. In general, crosslinking reduces the solubility. The crosslinked SPAEKs (**CK1**–**CK5**) in sodium salt form revealed reduced solubility in polar aprotic solvents, indicating the construction of the covalent crosslinking. After the proton exchange treatment, the crosslinked SPAEK membranes became partially soluble only at elevated temperature in all the tested polar aprotic solvents. This suggests that the crosslinking of the crosslinked SPAEK membranes was further improved by the ionic acid–base crosslinkage between sulfonic acid groups and quinoxaline groups. The present uncrosslinked membranes (**K1**–**K5**) containing nonsulfonated side-chain and main-chain difluoride monomers showed good solubility to the polar aprotic solvents, as similarly observed for **R1** containing nonsulfonated side-chain difluoride monomer. However, the crosslinked SPAEK membranes were partially soluble in solvents in proton form, even soluble in sodium salt form. This indicated that, for quinoxaline-based crosslinking method, the present crosslinking degree was not enough to ensure the formation of perfect network in the membranes, although crosslinking reaction was well performed. In our previous report [41], crosslinked SPAEKs composed of side-chain type of nonsulfonated monomer (DFB) were partially soluble in most of tested solvents in sodium salt form with QCs of 0.36–0.40 mequiv g^{-1}. The high solubility for present crosslinked

Table 2 Solubility properties of SPAEK membranes

Code	DMSO	NMP	DMAc	DMF
K1	++(++)	++(++)	++(++)	++(++)
CK1	+−(++)	+−(++)	+−(+)	+−(+)
K2	++(++)	+(++)	+(++)	+(++)
CK2	+−(++)	+−(+)	+−(+)	+−(+)
K3	++(++)	+(++)	+(++)	+(++)
CK3	+−(++)	+−(++)	+−(+)	+−(+)
K4	+(++)	+(++)	+(++)	+(++)
CK4	+−(++)	+−(++)	+−(+)	+−(+)
K5	+(++)	+(++)	+(++)	+(++)
CK5	+−(++)	+−(+)	+−(+)	+−(+)
CK3-2	−(+−)	−(+−)	−(+−)	−(+−)
CK4-2	−(+−)	−(+−)	−(+−)	−(+−)
R1	++(++)	++(++)	++(++)	++(++)

The data in parentheses refer to sodium salt form and others refer to proton form

++ soluble at room temperature, + soluble at elevated temperature, +− partially soluble at elevated temperature, − insoluble

Table 3 Mechanical properties of SPAEK membranes

Code	*M* (GPa)	*S* (MPa)	*E* (%)
K1	1.16	63	88
CK1	1.52	69	76
K2	1.07	59	73
CK2	1.22	63	60
K3	1.01	45	60
CK3	1.20	55	50
K4	0.99	54	39
CK4	1.22	69	28
K5	1.06	50	30
CK5	1.61	62	19
R1[a]	1.20	41	90

M Young's modulus, *S* Maximum stress, *E* Elongation at break

[a] Measured at 25 °C and about 70% RH

membranes may be attributed to the introduction of flexible main-chain type of nonsulfonated monomer (DFBP) and the slightly low QC values. To investigate the effect of QC on solubility, crosslinked SPAEK membranes **CK3-2** and **CK4-2** with high QCs (above 0.50 mequiv g^{-1}) were prepared. **CK3-2** and **CK4-2** were partially soluble in sodium salt form and insoluble in proton form. This indicated that QC value above 0.50 mequiv g^{-1} was requirement for the formation of perfect network in quinoxaline-based crosslinked SPAEK membranes.

The mechanical properties of SPAEK membranes are listed in Table 3, which are characterized by Young's modulus (*M*), maximum stress (*S*), and elongation at break (*E*). All the present SPAEK membranes had much higher Young's modulus and maximum stress than Nafion 112 (*M* of 0.24 GPa, *S* of 40 MPa, and *E* of 380%) and **R1**, indicating their excellent mechanical properties. Compared with the uncrosslinked membranes (**K1–K5**), the crosslinked ones (**CK1–CK5**) showed the higher Young's modulus and maximum stress, but the smaller elongation at break. This indicates that the crosslinked SPAEK membranes were slightly stiffer than the uncrosslinked ones. All the SPAEK membranes were tough even in the dry state.

The thermal stability of SPAEKs in proton form was examined by TGA. Above 150 °C, the two-step degradation profile was observed for all of the membranes, as shown in Fig. 3. The weight loss below 400 °C was attributed to the cleavage of sulfonic acid groups, whereas the weight loss above 500 °C was attributed to the decomposition of polymer backbone. Obviously, **CK1** exhibited better thermal stability than **K1**, which was attributed to the acid–base interaction between sulfonic acid groups and quinoxaline groups. Although **K1** showed the slightly lower thermal stability than **R1** in the first degradation step, the corresponding crosslinked membrane displayed the higher thermal stability than **R1** due to the acid–base interactions.

The oxidative stability for peroxide radical attack was investigated by measuring the elapsed time that a membrane became broken after immersing the membrane sample into Fenton's reagent (3 wt% H_2O_2 + 2 ppm $FeSO_4$) at 80 °C. The results are listed in Table 4. The crosslinked SPAEK membranes exhibited the higher oxidative stability than those of the corresponding uncrosslinked ones. This is

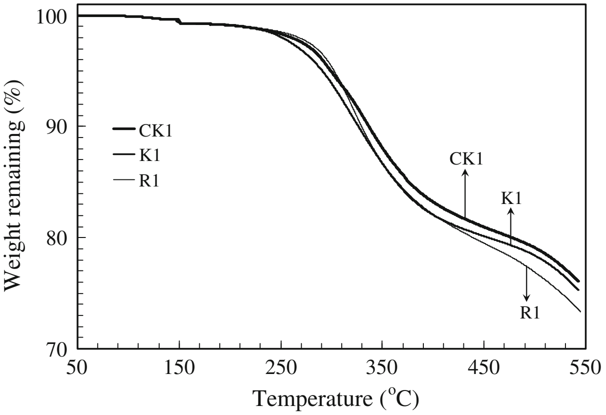


Fig. 3 TGA curves of SPAEK membranes

Table 4 Proton conductivity, oxidative stability, methanol permeability, and the selectivity of SPAEK membranes

Code	σ^a (mS cm^{-1})		τ_1^b (min)	P_M^c (10^{-7} cm^2 s^{-1})	φ^c (10^4 S cm^{-3} s)
	25 °C	80 °C			
K1	62	187	180	4.9	12.7
CK1	44	155	245	2.8	15.7
K2	58	174	210	4.2	13.8
CK2	33	127	300	2.1	15.7
K3	59	163	220	4.0	14.8
CK3	27	110	335	1.7	15.9
K4	40	140	320	2.7	14.8
CK4	19	80	410	0.73	26.0
K5	38	138	335	2.5	15.2
CK5	19	81	415	0.71	26.8
R1	60	152	143	13.2	4.6

[a] In water

[b] τ_1: oxidative stability, refers to the elapsed time that the membranes became broken

[c] At 32 wt% methanol solution and 25 °C

attributed to their lower water uptake as well as the covalent and ionical crosslinking. It was noted that **K1** had the slightly higher oxidative stability than **R1**, indicating that main-chain type of nonsulfonated monomer (DFBP) was useful to achieve the better oxidative stability than the side-chain type (DFB).

Water uptake and dimensional change

In general, the higher water uptake leads to the higher proton conductivity, because the water uptake of sulfonated polymers has a profound influence on the proton

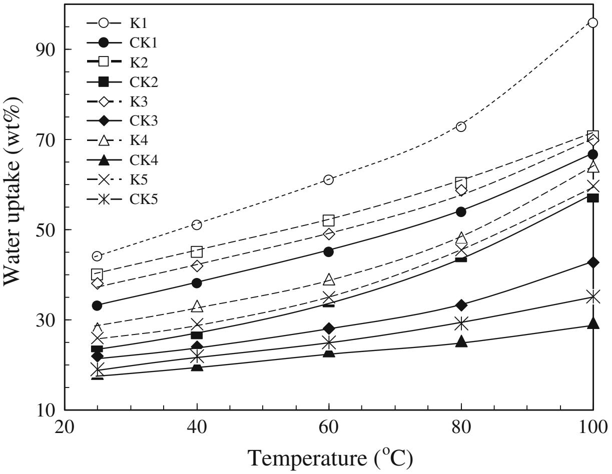


Fig. 4 Temperature dependence of water uptake of SPAEK membranes

conductivity where sulfonic acid groups need to dissociate for protons to become mobile and transportable in membrane. However, excessive water uptake will result in unacceptable dimensional change or loss of dimensional shape and the dilution of the proton concentration in the membrane, which will cause a dimensional mismatch and a decrease in the proton conductivity. Therefore, a proper level of water uptake should be maintained in sulfonated polymer membranes in order to guarantee both the dimensional stability and the high proton conductivity.

The water uptake data of the uncrosslinked and crosslinked SPAEK membranes at different temperatures are summarized in Table 1 and Fig. 4. With increasing temperature from 25 to 100 °C, the water uptake increased largely especially for the membrane with the higher IEC. It is noted that **K1** displayed slightly higher water uptakes than **R1** in spite of almost the same IEC values, which indicated that the nonsulfonated monomer with benzil moiety was useful to reduce the water uptake. Although the crosslinked membranes had the slightly lower calculated IECs than the corresponding uncrosslinked ones, the former displayed the much lower water uptakes than the latter, especially at elevated temperatures. For example, **CK3** showed reasonably low water uptakes of 22 and 33% at 25 and 80 °C, respectively, whereas **K3** showed fairly high values of 37 and 59%, respectively. It is noted that the covalent and ionical crosslinking suppressed the polymer chain relaxation in water, resulting in the reduced water uptake. As the WU significantly depends on the IEC, the comparison of water uptake among membranes with different IECs is often performed in terms of the number of sorbed water molecules per sulfonic acid group (λ). The λ values were calculated using the IEC values measured by the titration method as the effective ones, and are listed in Table 1. The crosslinked SPAEKs showed the λ values of 7–11 at 25 °C and 10–16 at 80 °C, which were smaller than those (8–12 and 15–19, respectively) of the uncrosslinked ones. The λ values of the present crosslinked SPAEKs with measured IEC of 1.41–1.84 mequiv g^{-1} were comparable with those (12–15) of the reported crosslinked SPAEKs at 80 °C with the high IEC of

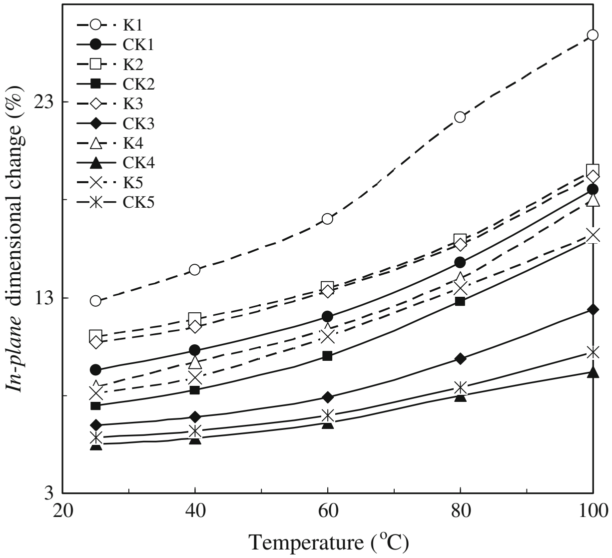


Fig. 5 Temperature dependence of *in-plane* dimensional change of SPAEK membranes

1.68–2.19 mequiv g^{-1} [30, 31, 40], and those (10–21) of the reported crosslinked SPAESs at 80 °C with the similar IEC of 1.32–1.62 mequiv g^{-1} [32, 41].

Through-plane and *in-plane* membrane dimensional changes at different temperatures were measured and the results are summarized in Table 1 and Fig. 5. The uncrosslinked and crosslinked SPAEK membranes showed the isotropic membrane swelling with $\Delta_{t/l}$ values close to unity. This is similar to the case of Nafion and SPAEs [13, 17], but different from the case of sulfonated polyimides (SPIs) with the larger *through-plane* dimensional change than the *in-plane* one [10, 23]. The dimensional change increased with an increase in temperature and also with an increase in IEC, as similarly observed for the water uptake. It is noted that **K1** and **R1** displayed the same dimensional change due to their similar IEC, as similarly observed for the water uptake. Compared with the uncrosslinked SPAEK membranes, the crosslinked ones had the much lower dimensional change. The crosslinked membranes such as **CK3**, **CK4**, and **CK5** showed the low *in-plane* dimensional changes less than 0.11 at 80 °C, which are reasonably low for fuel cell applications.

Proton conductivity

The proton conductivity (σ) data are summarized in Table 4 and Fig. 6. The conductivity significantly depended on IEC, water uptake, and temperature. The SPAEK membrane with the higher IEC showed the higher proton conductivity. **K1** had the highest proton conductivity of 187 mS cm^{-1} at 80 °C because of the highest IEC and water uptake. With increasing measured IEC from 1.41 to 2.08

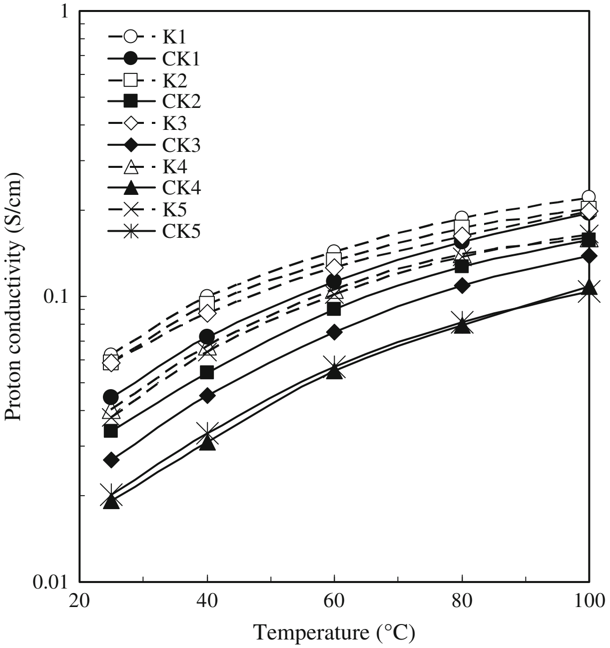


Fig. 6 Temperature dependence of proton conductivity of SPAEK membranes

mequiv g^{-1}, the proton conductivity increased largely. It is noted that **K1** displayed slightly higher proton conductivity at 25 °C and much higher at 80 °C than **R1** in spite of the same IEC value, as similarly observed for the water uptake, this indicated that the main-chain type of nonsulfonated monomer (DFBP) was useful to achieve the higher water uptake which resulted in a higher conductivity than the side-chain type (DFB). The crosslinked membranes displayed the lower proton conductivity than the corresponding uncrosslinked ones, especially at low temperature, due to the lower measured IEC. For example, **CK3** showed low proton conductivities of 27 and 110 mS cm^{-1} at 25 and 80 °C, respectively, whereas **K3** showed high values of 59 and 163 mS cm^{-1}, respectively.

The reported values of size change Δl_c and proton conductivity in water at 80 °C for Nafion 117 and 1135 membranes were in the range of 0.20–0.24 and 83–125 mS/cm, respectively [18, 19, 42]. The corresponding values for the present crosslinked membrane (**CK3**) were 0.10 and 110 mS cm^{-1}, respectively. It is noted that **CK3** showed the much smaller size change and the comparable proton conductivity compared with Nafion membranes.

The present covalently and ionically crosslinked membranes, such as **CK3**, **CK4**, and **CK5**, showed more than two times larger conductivity in spite of the lower water uptake than the crosslinked SPAEK membranes (water uptakes of 39–50% with conductivities of 22–32 mS/cm) [30, 31]. On the other hand, a few crosslinked SPAES membranes have been reported to have the much larger conductivities (245 mS/cm) with the much lower water uptakes (23%) [32], compared with the present crosslinked membranes.

Methanol permeability

The methanol permeability (P_M) and the ratio of proton conductivity to methanol permeability (selectivity, φ), which is an effective parameter to evaluate the performance of membrane in a DMFC system, are summarized in Table 4. **K1** with the highest IEC (2.08 mequiv g^{-1}) showed the highest P_M of 4.9×10^{-7} cm^2 s^{-1} and the lowest φ of 12.7×10^4 S cm^{-3} s. For the crosslinked SPAEK membranes, with decreasing measured IEC, the methanol permeability decreased more largely than the proton conductivity, and as a result the selectivity φ increased. **CK5** showed the lowest P_M of 0.71×10^{-7} cm^2 s^{-1} and the largest φ of 26.8×10^4 S cm^{-3} s among the present SPAEK membranes. This performance was fairly high, taking the high feed methanol concentration (32 wt%) into account. It is noted that **K1** displayed much lower P_M than **R1** in spite of the same IEC value and the similar water uptake as well as dimensional change at 25 °C, which indicated that the proper introduction of DFBP into polymer chain to instead of part of DFB was useful to achieve the better balance of water uptake and P_M. Compared with **R1**, **K1** composed of both main-chain and side-chain type of DFBP and DFB nonsulfonated monomer should has a more compact structure, which was corresponded to their densities (1.2615 and 1.2554 g cm^{-1} in the dry state for **K1** and **R1**, respectively). Where this kind of structure was helpful to enhance the mechanical properties and reduce the methanol permeability.

Some comparisons are made between the present crosslinked membranes and the representative SPAEs reported in literatures [15, 16, 18, 19, 32] in terms of P_M and φ values. As the feed concentration of methanol was different from literature to literature, the rough comparison among the PEMs is preferable. The present crosslinked membranes exhibited low P_M and high φ in the range of $0.71–2.8 \times 10^{-7}$ cm^2 s^{-1} and $15.7–26.8 \times 10^4$ S cm^{-3} s, respectively, which were slightly higher than those of the reported membranes. They have potential for DMFC application.

Conclusions

Crosslinked SPAEK membranes were prepared by the cyclocondensation reaction of the benzil moieties in polymer chain with DAB to form quinoxaline groups acting as covalent and ionical crosslinking. The crosslinked SPAEK membranes showed the high mechanical properties and the isotropic membrane swelling. They showed the lower water uptake, lower dimensional change, lower methanol permeability, and higher oxidative stability than the corresponding uncrosslinked membranes, with keeping the reasonably high proton conductivity. **CK3** showed a reasonably high proton conductivity of 110 mS/cm, a low water uptake of 33 wt% at 80 °C, a low P_M of 1.7×10^{-7} cm^2 s^{-1}, and a large φ of 15.9×10^4 S cm^{-3} s for 32 wt% methanol solution at 25 °C, suggesting the potential application as PEMs in DMFC and PEFC.

Acknowledgments The authors would like to thank the Key Technologies R&D Program of Shaanxi Province (No. 2009K06-08), Program for Changjiang Scholars and Innovative Research Team in

University (IRT1070), the Fundamental Research Funds for the Central Universities (No. GK200902002, GK201002002), and the Scientific Research Foundation for Returned Scholars, Ministry of Education for financial support of this work.

References

1. Kamarudin S, Achmad F, Daud W (2009) Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices. Int J Hydrogen Energy 34:6902–6916
2. Ahmad H, Kamarudin S, Hasran U, Daud W (2010) Overview of hybrid membranes for direct-methanol fuel-cell applications. Int J Hydrogen Energy 35:2160–2175
3. Mauritz K, Moore R (2004) State of understanding of Nafion. Chem Rev 104:4535–4585
4. Rikukawa M, Sanui K (2000) Proton-conducting polymer electrolyte membranes based on hydrocarbon polymers. Prog Polym Sci 25:1463–1502
5. Mehta V, Cooper J (2003) Review and analysis of PEM fuel cell design and manufacturing. J Power Sources 114:32–53
6. Jones D, Roziere J (2008) Advances in the development of inorganic-organic membranes for fuel cell applications. Adv Polym Sci 215:219–264
7. Higashihara T, Matsumoto K, Ueda M (2009) Sulfonated aromatic hydrocarbon polymers as proton exchange membranes for fuel cells. Polymer 50:5341–5357
8. Aslan A, Bozkurt A (2011) Proton conducting properties of ionically cross-linked poly(1-vinyl-1,2,4 triazole) and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) electrolytes. Polym Bull 66: 1099–1110
9. Hickner M, Ghassemi H, Kim Y, Einsla B, McGrath J (2004) Alternative polymer systems for proton exchange membranes (PEMs). Chem Rev 104:4587–4612
10. Yin Y, Yamada O, Tanaka K, Okamoto K (2006) On the development of naphthalene-based sulfonated polyimide membranes for fuel cell applications. Polym J 38:197–219
11. Chen X, Chen P, Okamoto K (2009) Synthesis and properties of novel side-chain-type sulfonated polyimides. Polym Bull 63:1–14
12. Marestin C, Gebel G, Diat O, Mercier R (2008) Sulfonated polyimides. Adv Polym Sci 216:185–258
13. Lee H, Roy A, Lane O, Lee M, McGrath J (2010) Synthesis and characterization of multiblock copolymers based on hydrophilic disulfonated poly(arylene ether sulfone) and hydrophobic partially fluorinated poly(arylene ether ketone) for fuel cell applications. J Polym Sci A 48:214–222
14. Einsla M, Kim Y, Hawley M, Lee H, McGrath J, Liu B, Guiver M, Pivovar B (2008) Toward improved conductivity of sulfonated aromatic proton exchange membranes at low relative humidity. Chem Mater 20:5636–5642
15. Miyatake K, Chikashige Y, Higuchi E, Watanabe M (2007) Tuned polymer electrolyte membranes based on aromatic polyethers for fuel cell applications. J Am Chem Soc 129:3879–3887
16. Bae B, Yoda T, Miyatake K, Uchida H, Watanabe M (2010) Proton-conductive aromatic ionomers containing highly sulfonated blocks for high-temperature-operable fuel cells. Angew Chem Int Ed 49:317–320
17. Matsumoto K, Higashihara T, Ueda M (2009) Locally and densely sulfonated poly(ether sulfone)s as proton exchange membrane. Macromolecules 42:1161–1166
18. Kim D, Robertson G, Guiver M (2008) Comb-shaped poly(arylene ether sulfone)s as proton exchange membranes. Macromolecules 41:2126–2134
19. Kim D, Robertson G, Kim Y, Guiver M (2009) Copoly(arylene ether)s containing pendant sulfonic acid groups as proton exchange membranes. Macromolecules 42:957–963
20. Hu H, Xiao M, Wang S, Meng Y (2010) Poly (fluorenyl ether ketone) ionomers containing separated hydrophilic multiblocks used in fuel cells as proton exchange membranes. Int J Hydrogen Energy 35:682–689
21. Liu B, Robertson G, Kim D, Guiver M, Hu W, Jiang Z (2007) Aromatic poly(ether ketone)s with pendant sulfonic acid phenyl groups prepared by a mild sulfonation method for proton exchange membranes. Macromolecules 40:1934–1944
22. Li X, Zhao C, Lu H, Wang Z, Na H (2005) Direct synthesis of sulfonated poly(ether ether ketone ketone)s (SPEEKKs) proton exchange membranes for fuel cell application. Polymer 46:5820–5827
23. Bi H, Chen S, Chen X, Chen K, Endo N, Higa M, Okamoto K, Wang L (2009) Poly(sulfonated phenylene)-block-polyimide copolymers for fuel cell applications. Macromol Rapid Commun 30:1852–1856

24. Asano N, Aoki M, Suzuki S, Miyatake K, Uchida H, Watanabe M (2006) Aliphatic/aromatic polyimide ionomers as a proton conductive membrane for fuel cell applications. J Am Chem Soc 128:1762–1770
25. Qiu Z, Wu S, Li Z, Zhang S, Xing W, Liu C (2006) Sulfonated poly(arylene-co-naphthalimide)s synthesized by copolymerization of primarily sulfonated monomer and fluorinated naphthalimide dichlorides as novel polymers for proton exchange membranes. Macromolecules 39:6425–6432
26. Kerres J, Zhang W, Haering T (2004) Covalently cross-linked ionomer (blend) membranes for fuel cells. J New Mater Electrochem Syst 7:299–309
27. Fang J, Zhai F, Guo X, Xu H, Okamoto K (2007) A facile approach for the preparation of cross-linked sulfonated polyimide membranes for fuel cell application. J Mater Chem 17:1102–1108
28. Mikhailenko S, Robertson G, Guiver M, Kaliaguine S (2006) Properties of PEMs based on cross-linked sulfonated poly(ether ether ketone). J Membr Sci 285:306–316
29. Gu S, He G, Wu X, Guo Y, Liu H, Peng L, Xiao G (2008) Preparation and characteristics of crosslinked sulfonated poly(phthalazinone ether sulfone ketone) with poly(vinyl alcohol) for proton exchange membrane. J Membr Sci 312:48–58
30. Zhong S, Cui X, Cai H, Fu T, Zhao C, Na H (2007) Crosslinked sulfonated poly(ether ether ketone) proton exchange membranes for direct methanol fuel cell applications. J Power Sources 164:65–72
31. Ding F, Wang S, Xiao M, Li X, Meng Y (2007) Fabrication and properties of cross-linked sulfonated fluorene-containing poly(arylene ether ketone) for proton exchange membrane. J Power Sources 170:20–27
32. Feng S, Shang Y, Xie X, Wang Y, Xu J (2009) Synthesis and characterization of crosslinked sulfonated poly(arylene ether sulfone) membranes for DMFC applications. J Membr Sci 335:13–20
33. Kerres J, Ullrich A, Haring T, Baldauf M, Gebhardt U, Preidel W (2000) Preparation, characterization and fuel cell application of new acid-base blend membranes. J New Mater Electrochem Syst 3:229–239
34. Sen U, Bozkurt A, Ata A (2010) Nafion/poly(1-vinyl-1,2,4-triazole) blends as proton conducting membranes for polymer electrolyte membrane fuel cells. J Power Sources 195:7720–7726
35. Li H, Zhang G, Ma W, Zhao C, Zhang Y, Han M, Zhu J, Liu Z, Wu J, Na H (2010) Composite membranes based on a novel benzimidazole grafted PEEK and SPEEK for fuel cells. Int J Hydrogen Energy 35:11172–11179
36. Lin H, Zhao C, Ma W, Li H, Na H (2009) Layer-by-layer self-assembly of in situ polymerized polypyrrole on sulfonated poly(arylene ether ketone) membrane with extremely low methanol crossover. Int J Hydrogen Energy 34:9795–9801
37. Yang M, Lu S, Lu J, Jiang S, Xiang Y (2010) Layer-by-layer self-assembly of PDDA/PWA-Nafion composite membranes for direct methanol fuel cells. Chem Commun 46:1434–1436
38. Kharlampieva E, Kozlovskaya V, Sukhishvili S (2009) Layer-bilayer hydrogen-bonded polymer films: from fundamentals to applications. Adv Mater 21:3053–3065
39. Taylor M, Sekol R, Podsiadlo P, Ho P, Kotov N, Thompson L (2007) High-performance nanostructured membrane electrode assemblies for fuel cells made by layer-by-layer assembly of carbon nanocolloids. Adv Mater 19:3859–3864
40. Chen X, Chen P, An Z, Chen K, Okamoto K (2011) Crosslinked sulfonated poly(arylene ether ketone) membranes bearing quinoxaline and acid-base complex cross-linkages for fuel cell applications. J Power Sources 196:1694–1703
41. Tripathi B, Chakrabarty T, Shahi V (2010) Highly charged and stable cross-linked 4, 4′-bis(4-aminophenoxy) biphenyl-3, 3′-disulfonic acid (BAPBDS)-sulfonated poly(ether sulfone) polymer electrolyte membranes impervious to methanol. J Mater Chem 20:8036–8044
42. Pang J, Zhang H, Li X, Jiang Z (2007) Novel wholly aromatic sulfonated poly(arylene ether) copolymers containing sulfonic acid groups on the pendants for proton exchange membrane materials. Macromolecules 40:9435–9442