



# Novel sulfonated poly(ether ether ketone)s containing nitrile groups and their composite membranes for fuel cells

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## ARTICLE INFO

### Article history:

Received 23 January 2010

Received in revised form 12 February 2010

Accepted 12 February 2010

Available online 20 February 2010

### Keywords:

Composite membranes

Methanol permeability

Fuel cells

## ABSTRACT

A series of novel sulfonated poly(ether ether ketone)s containing a cyanophenyl group (SPEEKCNxx) are prepared based on (4-cyano)phenylhydroquinone via nucleophilic substitution polycondensation reactions. To further improve their properties, novel composite membranes composed of sulfonated poly(ether ether ketone)s containing cyanophenyl group as an acidic component and aminated poly(aryl ether ketone) as a basic component are successfully prepared. Most of the membranes exhibit excellent thermal, oxidative and dimensional stability, low-swelling ratio, high proton conductivity, low methanol permeability and high selectivity. The proton conductivities of the membranes are close to Nafion 117 at room temperature. And especially, the values of SPEEKCN40 and its composite membranes are higher than Nafion 117 at 80 °C (0.17 S cm<sup>-1</sup> of Nafion, 0.26 S cm<sup>-1</sup> of SPEEKCN40, 0.20 S cm<sup>-1</sup> of SPEEKCN40-1, and 0.18 S cm<sup>-1</sup> of SPEEKCN40-2). Moreover, the methanol permeability is one order magnitude lower than that of Nafion 117. All the data prove that both copolymers and their composite membranes may be potential proton exchange membrane for fuel cells applications.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) have the potential to become an important energy conversion technology and have attracted much attention as a future source of clean energy recently [1–3]. Sulfonated perfluoropolymers, such as Nafion (DuPont), are most used as proton conducting polymers because of their high proton conductivity and high chemical stability. However, high cost, low operation temperature ( $\leq 80$  °C), high methanol crossover, and environmental recycling uncertainties of Nafion membranes are limiting their widespread commercial application in PEMFCs and DMFCs [3–5]. Currently, many efforts to design alternative Nafion have been made and intense research focus on various sulfonated polymers, such as sulfonated poly(aryl ether ketone)s, sulfonated polysulfone, sulfonated polyimides, sulfonated polybenzimidazoles, and so on [6–9], because of their high chemical, thermal stability and excellent mechanical stability. The proton conductivities intensely depend on the degree of sulfonation (DS) of these alternative random copolymers. Generally, their thermal stability and mechanical stability can be maintained at low sulfonation degree. However, the low sulfonation content will lead to the

low proton conductivity, which makes them unsuitable for using in fuel cells. To improve the proton conductive ability, the sulfonation content has to increase, which generally results in poor dimensional stability and mechanical property lost of these membranes under hot and humid circumstance. Thus, further efforts to solve this contradiction are eagerly requested and many researchers have dedicated to study in this area [1].

As we all know, chemical and structure have important effects on polymer electrolytes properties [10,11]. Acid content (ion-exchange capacity or degree of sulfonation), as chemical effects, has been reported early, and later, structure effects, such as the effects of fluorine [12], polar groups [13,14] or crosslinking [15–17], etc. are mostly concerned in recent decades. Typically, it has been found that the existence of fluorine could improve some properties of PEMs. For example, Mcgrath's group [18] has synthesized four sulfonated poly(arylene ether) copolymers derived from four structurally distinct bisphenols (4,4'-isopropylidenediphenol [BPA], 4,4'-hexafluoroisopropylidenediphenol [6F-BPA], 4,4'-biphenol and hydroquinone), and found that fluorine-containing poly(arylene ether) from 6F-BPA displayed better dimensional stability than poly(arylene ether) with the other bisphenols because of the hydrophobic nature of the hexafluoroisopropylidene connecting units. In contrast with above studies, involving polar groups and crosslinking into PEMs have aroused researchers' more interests. Polar groups are known to have strong interaction by forming hydrogen bonds [19–21]. Among these polar groups, benzonitrile

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group, who has a large dipole moment and a large polarizability, is capable of forming a stable complex through hydrogen bonds. Recently, it is found that the introduction of nitrile groups into sulfonated polymer membranes can reduce their water uptake and improves the dimensional stability when compared with the polymers that did not contain nitrile groups at similar ion-exchange capacities [22,23]. In addition, the introduction of nitrile groups into PEMs may be beneficial for promoting adhesions of interlayers during their membrane electrode assemblies (MEAs). Recently, covalent bonds or ionic crosslinking methods are adopted to improve the properties of membranes. Liu et al. [24] and Lee et al. [25] recently reported different kinds of PEMs crosslinked by an esterification reaction between  $-\text{COOH}$  and  $-\text{OH}$ , respectively. Our group also reported another crosslinking reaction between epoxy and amino groups [26], and found that the crosslinking reaction could play an important role in dimensional stability. However, both esterification reaction and epoxy crosslinking may introduce aliphatic chain, which decrease the thermal stability of membranes. Thus, acid–base composite is adopted as another simpler method to better the properties of membranes. As we reported previously [27], composite membranes could improve mechanical properties obviously without significant proton conductivities loss.

Almost all of the reported sulfonated poly(aryl ether nitrile)s were prepared from 2,6-difluorobenzonitrile (2,6-DFBN) [28–30], and some even exhibited very attractive single-cell performance [31]. It is still of interest to prepare more nitrile-containing PEMs in order to well understand the relationship of chemical structure and properties based on this kind of polymers. In this study, a new family of nitrile-containing sulfonated polymers derived from a (4-cyano)phenylhydroquinone monomer, which was previously synthesized by our group for high-performance structural materials [32], were developed. Moreover, the composite membranes, in which stronger interactions caused by acid–basic ions, cyanol and some polar groups may exist, were prepared as an attempt for the preparation of the low-swelling PEMs. The thermal stability, mechanical properties, water absorption, dimensional stability, methanol permeability and proton conducting properties of both nitrile-containing polymers and their composites were thoroughly investigated.

## 2. Experimental

### 2.1. Materials

(4-Cyano)phenylhydroquinone and (4-amino)phenylhydroquinone (4-AmPHQ) were synthesized in our lab through a two-step coupling–reduction reaction [27,32]. 1,4-Bis(4-fluorobenzoyl)naphthalene (BFBN) was synthesized in our lab according to a standard procedure [33]. 4,4'-Difluorobenzophenone (DFBP) was purchased from Yianbian Chemical Factory, China and purified by recrystallization from a mixture of ethanol and deionized water. Sodium 5,5'-carbonylbis(2-fluorobenzene-sulfonate) (SDFBP) was prepared according to procedure described by Wang et al. [34].  $\text{K}_2\text{CO}_3$  (Beijing Chemical Reagent, China) was ground into fine powder and dried at  $120^\circ\text{C}$  for 24 h before use. All the organic solvents were obtained from commercial sources and purified by conventional methods.

### 2.2. Preparation of materials

The synthesis of acidic polymer of SPEEKN40 was given as a typical example, where 40 referred to the percentage of 5,5'-carbonylbis(2-fluorobenzene-sulfonate) (SDFBP). Into a 100 mL round-bottomed flask, 4.2244 g (20 mmol) of 4-cyanophenylhydroquinone, 3.3783 g (8 mmol) of SDFBP, 2.6184 g

(12 mmol) of DFBP, 3.312 g (24 mmol) of  $\text{K}_2\text{CO}_3$ , 40 mL of DMSO and 25 mL of toluene were added. First, the mixture was heated to  $140^\circ\text{C}$  with stirring under nitrogen for 2 h to remove the produced water by azeotropic distillation with toluene, and then, the temperature was raised up to  $180\text{--}190^\circ\text{C}$  for 6–8 h. A viscous solution was obtained and poured into water. The polymer was pulverized into a powder using a blender. The polymer powder was washed several times with ethanol and hot water and dried in oven.

The basic polymer of AmPEEK-NA was prepared using our previously reported procedure [27].

The membranes of pure polymers and SPEEKN/AmPEEK-NA composite materials were prepared by solution casting. The membranes of pure copolymers in sodium-form were obtained by solution casting in N,N-dimethylacetamide (DMAc) (10%, w/v) and then transformed to acid form by ion exchange in 0.5 M  $\text{H}_2\text{SO}_4$  at  $80^\circ\text{C}$  for 2 h, and at last washed with deionized water to be neutral. For composite membranes, the sodium-form copolymer and quantitative AmPEEK-NA were dissolved in DMAc (10%, w/v), and the samples with different weight proportion of AmPEEK-NA were named as SPEEKN40-1 [AmPEEK-NA/SPEEKN40 = 0.05/1 (w/w)], SPEEKN40-2 [AmPEEK-NA/SPEEKN40 = 0.1/1 (w/w)], respectively. AmPEEK-NA was first stirred in DMAc for 1 day at  $60^\circ\text{C}$ , and then SPEEKN40 was put into this solution. After stirring for another day at  $60^\circ\text{C}$ , the clear and homogenous solution was cast onto clean glass plate and dried at  $60^\circ\text{C}$  overnight. After drying at  $120^\circ\text{C}$  in vacuum oven for 24 h, the membranes were transformed to acid form by ion exchange in 0.5 M  $\text{H}_2\text{SO}_4$  for 2 h at  $80^\circ\text{C}$ . The pure and the composite films were in the range of 47–70  $\mu\text{m}$ .

### 2.3. Characterization methods

#### 2.3.1. Characterization

The viscosities were determined using an Ubbelohde viscometer ( $\Phi = 0.8\text{ mm}$ ) in thermostatic container with the polymer concentration of  $0.5\text{ g dL}^{-1}$  in N-methyl pyrrolidone (NMP) at  $25 \pm 0.1^\circ\text{C}$ .  $^1\text{H}$  NMR experiments were carried out on a Bruker 510 spectrometer (500 MHz for  $^1\text{H}$ ) using  $\text{DMSO-}d_6$  as solvent. Differential scanning calorimeter (DSC) measurements were performed on a Mettler Toledo DSC821<sup>e</sup> instrument at a heating rate of  $20^\circ\text{C min}^{-1}$  from 50 to  $300^\circ\text{C}$  under nitrogen. Thermogravimetric analysis (TGA) was employed to assess thermal stability of membranes with a Netzch Sta 449c thermal analyzer system. Before analysis, the films were dried and kept in the TGA furnace at  $150^\circ\text{C}$  in a nitrogen atmosphere for 15 min. The samples were cooled to  $80^\circ\text{C}$  and then reheated to  $700^\circ\text{C}$  at  $10^\circ\text{C min}^{-1}$  both in nitrogen and air, and the temperatures at 5% and 10% weight loss were recorded for each sample.

#### 2.3.2. Water uptake and swelling ratio measurements

A piece of film was vacuum dried at  $120^\circ\text{C}$  to a constant weight, which was recorded as  $W_{\text{dry}}$  and then immersed in deionized water at different temperatures. During this period, the wet membrane was quickly weighed several times after removing the surface water with tissue paper until a constant weight was obtained, which was recorded as  $W_{\text{wet}}$ . The water uptake was reported using water weight percent of dry membranes as following relation:

$$\text{water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

The swelling ratio was calculated from the change of film length by

$$\text{swelling ratio (\%)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100$$

where  $L_{\text{wet}}$  and  $L_{\text{dry}}$  were the lengths of the wet and dry membranes, respectively.

### 2.3.3. Lambda number

The lambda value ( $\lambda$ ) indicated the number of water molecules absorbed per sulfonic acid groups and could be expressed as

$$\lambda_W = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times \frac{1}{M_{\text{H}_2\text{O}} \times \text{IEC}}$$

where  $M_{\text{H}_2\text{O}}$  was the molecular weight of water (18.01 g mol<sup>-1</sup>) and IEC was the ion-exchange capacity of the dry membranes in equivalent per gram. The lambda number like proton conductivity scaled with the ion-exchange capacity.

### 2.3.4. Ion-exchange capacity (IEC) of membranes

The IEC values of pure and composite membranes were determined by classical titration [29,35]. Membrane samples (about 0.06 g) were immersed in 2 M NaCl solution for at least 24 h to liberate the H<sup>+</sup> ions (the H<sup>+</sup> ions in the membranes were replaced by Na<sup>+</sup> ions). The exchanged protons within the solutions were titrated with 4 mM NaOH aqueous solution by using phenolphthalein as an indicator. For each sample, at least three measurements were carried out until the titration reached to a constant value. The IEC value was calculated from the titration result via the following formula:

$$\text{IEC (mequiv./g)} = \frac{V_{\text{NaOH}} \times C_{\text{NaOH}}}{W_{\text{dry}}}$$

where  $V_{\text{NaOH}}$  was consumed volume of NaOH,  $C_{\text{NaOH}}$  was molarity of NaOH, and  $W_{\text{dry}}$  was the weight of dry membranes.

### 2.3.5. Oxidative and hydrolytic stability

A small piece of the membrane sample was soaked in Fenton's reagent (3% H<sub>2</sub>O<sub>2</sub> containing 2 ppm FeSO<sub>4</sub>) at 80 °C. The oxidative stability was evaluated by recording the time when the membranes disappeared and the retained weights of membranes after treating in Fenton's reagent for 1 h.

### 2.3.6. Methanol permeability

The methanol diffusion coefficient is determined using a cell basically consisting of two-half-cells separated by the membrane, which is fixed between two rubber rings. Methanol solutions (10 mol L<sup>-1</sup>) are placed on one side of the cell and pure water is placed on the other side. The magnetic stirrers are used continuously during the measurement. Methanol concentrations in the water cell are periodically determined by using a GC-14C gas chromatograph (SHTMADU, Tokyo, Japan). Peak areas are converted into methanol concentration with a calibration curve. The methanol diffusion coefficient is calculated according to the following equation:

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0)$$

where  $A$ ,  $L$  and  $V_B$  were the effective area, the thickness of membrane and the volume of permeated reservoirs, respectively.  $C_A$  and  $C_B$  were the methanol concentration in methanol chamber and water chamber, respectively.  $DK$  was the methanol diffusion coefficient.

### 2.3.7. Mechanical properties of membranes

The mechanical properties of wet membranes were measured at room temperature on SHIMADU AG-1 1KN at a strain rate of 2 mm min<sup>-1</sup>. The size of samples was 20 mm × 4 mm. The samples in wet state were obtained by immersing them in water for at least 48 h.

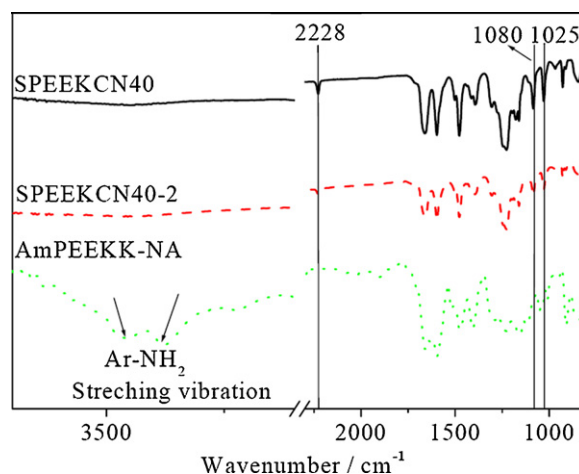


Fig. 1. FTIR spectra of SPEEKC40, SPEEKC40-2 and AmPEEK-NA.

### 2.3.8. Proton conductivity

The proton conductivity was measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation and 0.0V dc rest voltage using a Princeton Applied Research Model 2273 Potentiostat (EG&GPARC, Princeton, NJ). The membranes were fixed in a measuring cell, which was made of two outer gold wires to feed current to the sample and two inner gold wires to measure the voltage drops. The specimens were soaked in deionized water for at least 24 h prior to testing. Conductivity measurements of fully hydrated membranes were carried out with the cell immersed in liquid water, as reported in previous work [36]. The proton conductivity was calculated by the following formula:

$$\sigma = \frac{L}{RA}$$

where  $L$  was the distance between the electrodes, and  $R$  was the membrane resistance and  $A$  was the cross-sectional area of membrane.

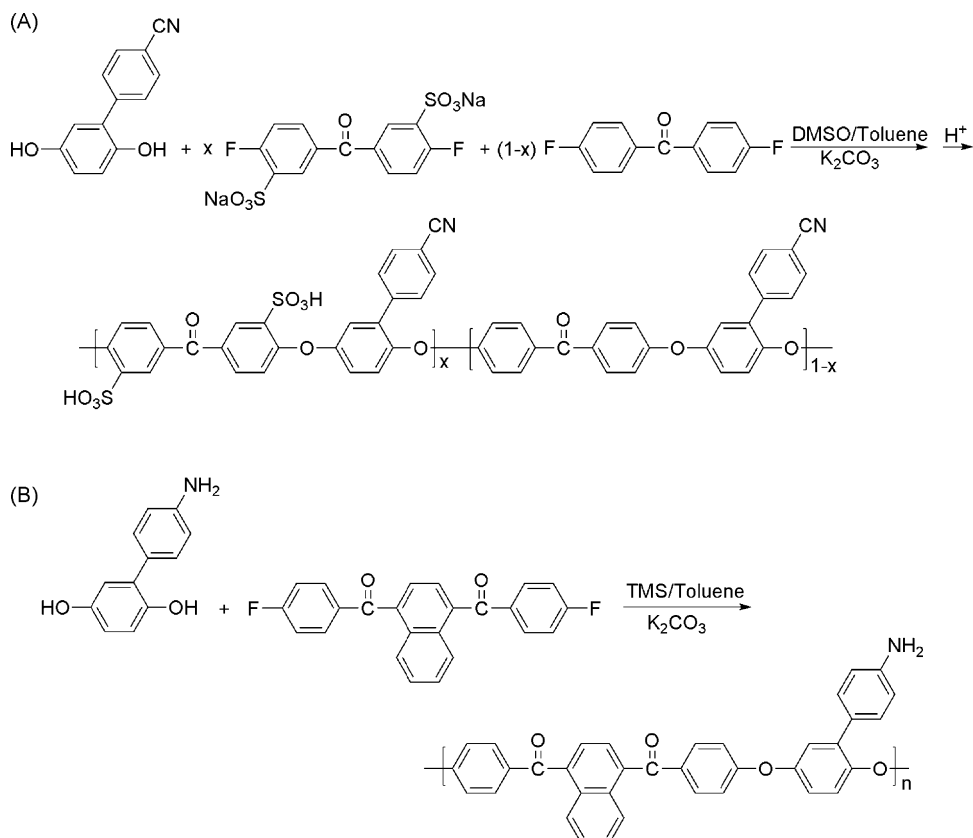
## 3. Result and discussion

### 3.1. Synthesis of the nitrile-containing sulfonated polymers

As an attempt of improving the thermal, mechanical, oxidative stability and adhesion to various substrates or interlays during their membrane electrode assemblies (MEAs), highly polar nitrile were introduced into copolymers to achieve promising results [21,31]. Because of the limitation of the cyano-containing monomers, few nitrilated aromatic polymers except the ones from commercial 2,6-DFBN have been reported so far. In this study, we synthesized a new family of nitrile-containing sulfonated poly(aryl ether ketone)s from 4-cyanophenylhydroquinone, which is the first time to be used as a monomer for the preparation of the PEMs (Shown in Scheme 1A). With proper IEC, we synthesized two kinds of copolymers, SPEEKC35 and SPEEKC40 (Section 2.2). As a result, both SPEEKC35 and SPEEKC40 had the same viscosities of 0.54 dL g<sup>-1</sup>, which indicated the success in their polymerizations.

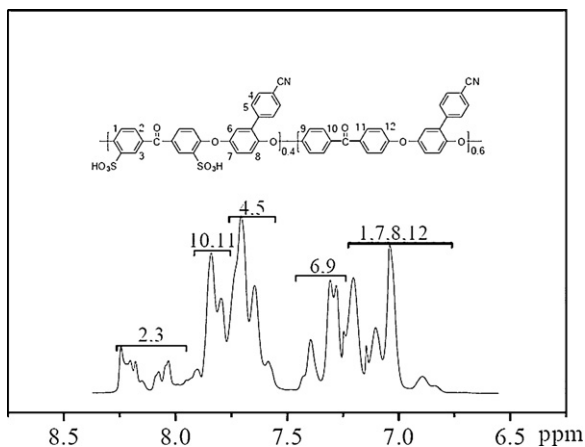
### 3.2. Characterization of copolymer structures and determination of sulfonated degree

The chemical structure of the synthesized SPEEKCxx copolymers was characterized by FTIR and <sup>1</sup>H NMR spectroscopy. FTIR is usually a convenient method to confirm the sulfonic and nitrile groups. The FTIR spectra of SPEEKC40 copolymer are illustrated in Fig. 1. In the spectra, characteristic bands of symmetric and asym-



**Scheme 1.** Synthesis route of the polymers: (A) SPEEKCNxx; (B) AmPEEKK-NA.

metric stretching vibrations of O=S=O of the aromatic sulfonic acid were observed obviously at 1025 and 1080  $\text{cm}^{-1}$  and the characteristic symmetric stretching vibration of nitrile groups at 2228  $\text{cm}^{-1}$  was also observed. This confirmed that sulfonic groups and nitrile groups were both introduced into the copolymers. Fig. 2 displayed the signal assignments in the aromatic region of  $^1\text{H}$  NMR spectrum of SPEEKCN40. The  $^1\text{H}$  NMR spectrum is usually used as the convenient method for the determination of the DS values. After assigning the  $^1\text{H}$  NMR signals of SPEEKCNxx, the DS values could be easily assessed by a simple mathematical calculation of the ratio of integral values. Taking the DS calculation of SPEEKCN40 as an example, it was derived from the ratio of integrals corresponding to the protons ortho to the carbonyl groups (H-10 and H-11 in Fig. 2) and the



**Fig. 2.**  $^1\text{H}$  NMR spectrum of SPEEKCN40.

protons adjacent to the sulfonate group and the protons ortho to the carbonyl groups (H-2 and H-3 in Fig. 2). The DS was calculated as the following equation:

$$\frac{I_{\text{H}2,3}}{I_{\text{H}10,11}} = \frac{x}{1-x}, \text{ DS} = 3x = 0.76.$$

where  $x$  was the feed ratio of SDFBP. The experimental DS value of 0.76 obtained from NMR was in close agreement with the expected DS to the feed ratio.

### 3.3. Preparation of pure and acid–basic composite membranes

Recently, the preparation of low-swelling PEMs is becoming one of the important topics in the field. In this study, the novel polymers containing nitrile groups that may enhance the interactions of the molecular chains and interlays (in MEAs) were used to prepare acid–basic composite PEMs. Base-N polymer (AmPEEKK-NA) derived from a aminated hydroquinone monomer (4-AmPHQ) was prepared by an aromatic nucleophilic substitution polycondensation according to our previous work [27], as shown in Scheme 1B. Then, composite membranes were made via a solution casting approach in DMAc. Generally, the proton conductivity decreased when high content of a second unsulfonated component was involved [27,37,38]. We selected two ratio composite membranes, which were named as SPEEKCN40-1 and SPEEKCN40-2 (Section 2.2). FTIR spectra were also used to confirm the structures of composite membranes, as shown in Fig. 1. The peaks of primary amine at 3462 and 3387  $\text{cm}^{-1}$  were assigned to the asymmetric and symmetric N–H stretching vibration absorptions, and could not be found in composite membranes (SPEEKCN40-2). It might be attributed to the interaction of the molecules in the blend membranes.

**Table 1**  
Thermal properties of copolymers and composites.

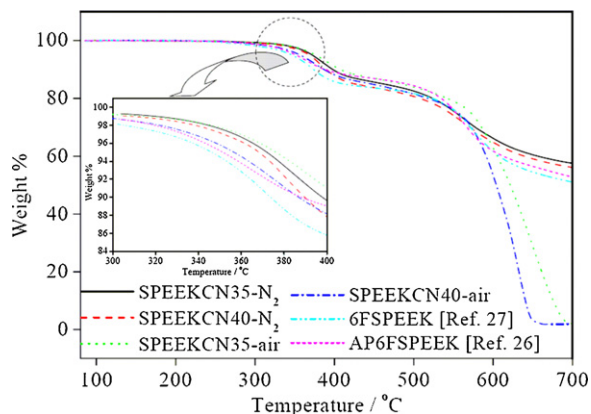
Polymer	$T_g$ (acid) (°C)	$T_d$ (5%) (°C)		$T_d$ (10%) (°C)	
		In N <sub>2</sub>	In air	In N <sub>2</sub>	In air
SPEEKC35	246	372	376	398	407
SPEEKC40	282	368	356	390	387
SPEEKC40-1	–	358	361	390	398
SPEEKC40-2	–	358	363	386	388
6FSPEEK <sup>a</sup>	233	345	–	373	–
Composite1 <sup>a</sup>	–	352	–	385	–
AP6FSPEEK <sup>b</sup>	251	351	352	388	383
AP6FSPEEK/DGBP1 <sup>b</sup>	–	323	330	372	374

<sup>a</sup> Data from Ref. [27].

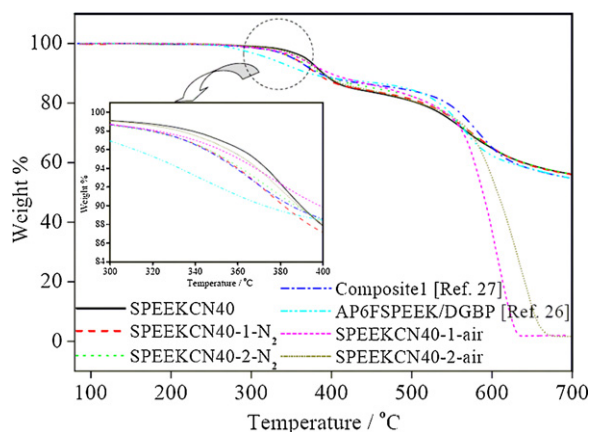
<sup>b</sup> Data from Ref. [26].

### 3.4. Thermal properties of the membranes

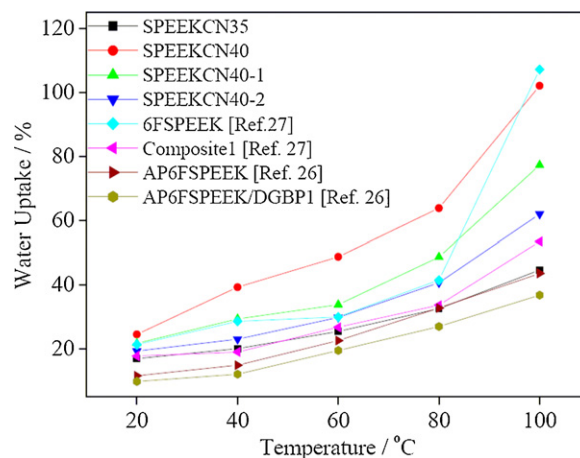
Thermal properties of SPEEKCxx copolymers and their composite materials, as one of the important factors on the usage of PEMs, were evaluated by their  $T_d$  and  $T_g$  data.  $T_d$ s were determined both in nitrogen and in air in order to detect their inherent thermal stabilities and thermal stabilities in air, and the results are shown in Table 1 and Figs. 3 and 4. In similarity with observations made previously, there were two distinct weight loss steps in the TGA curves of SPEEKCxx copolymers and their composite materials. And the first step was mainly attributed to the sulfonic groups, and the second step was on account for the polymer chains. According to the results of Table 1, we could see that the  $T_g$  of SPEEKC40 was higher than that of SPEEKC35, which could be attributed to the higher sulfonic groups in SPEEKC40. As a comparison, we also



**Fig. 3.** TGA curves of pure membranes.



**Fig. 4.** TGA curves of SPEEKC40 and composite membranes.



**Fig. 5.** Water uptake of membranes at different temperatures.

listed the testing results of 6FSPEEK and AP6FSPEEK [26,27] with the similar IEC value in Table 1. From it, we could see that both of the  $T_g$  values of SPEEKC35 and SPEEKC40 in nitrogen were higher than that of 6FSPEEK and AP6FSPEEK, respectively. This phenomenon might owe to the polar cyanophenyl groups, which may form strong intermolecular interaction and play a part in increasing  $T_g$  values. And the similar effects were also displayed in the results of  $T_{d5\%}$  and  $T_{d10\%}$  values. The  $T_d$  values of SPEEKC35 and SPEEKC40 were both higher than that of 6FSPEEK and AP6FSPEEK in nitrogen (internal diagram in Fig. 3). And the thermal stability of SPEEKC35 and SPEEKC40 in air was similar to that in nitrogen (Fig. 3). Additionally, in comparison with AP6FSPEEK/DGBP1 crosslinked with aliphatic chain [26], the thermal stability of composite membranes from SPEEKC40 and AmPEEK-NA was higher, which could be observed in Fig. 4. And similar to the tests in nitrogen, the thermal stability in air was also tested, and the results both in Figs. 3 and 4 illustrated that they all had good thermal stability in air.

### 3.5. IEC, Water uptake, swelling ratio and $\lambda$ of membranes

Water uptake plays an important role in determining the ultimate performance of proton exchange membrane materials. The existences of water molecules in sulfonated polymer membranes significantly affect the transport of protons and hydrated structures formed around sulfonic groups, and also affect the mechanical properties of the membrane by swelling [1,37]. In this study, we selected two polymers with the feed ratios of SDFBP 35% and 40%, respectively. And then, we prepared two composite membranes based on these two polymers in accordance with our previous report [27]. The theoretical and experimental IEC values are all illustrated in Table 2. We could see that the experimental IEC values were basically consistent with theoretical values. The water uptake, swelling ratio and  $\lambda$ , as shown in Table 3, Figs. 5 and 6 with functions of temperature, were similarly in agreement with the IEC values. Comparing SPEEKC35 with SPEEKC40, both water uptake and swelling ratio of SPEEKC40 were higher than that of SPEEKC35 at each testing temperature, because of the higher DS of SPEEKC40. However, the swelling ratio of SPEEKC40 was obviously lower than 6FSPEEK and AP6FSPEEK with the similar IEC (Tables 2 and 3). Comparing SPEEKC40 with AP6FSPEEK, although the water uptake of SPEEKC40 was much higher than that of AP6FSPEEK (Fig. 5), the dimensional swelling was similar for both of them (Fig. 6), which also revealed the effects of nitrile groups interaction. For further controlling the dimensional, acid–basic molecule-enhanced composite membranes were prepared. Simi-

**Table 2**  
Properties of copolymers and composites.

Polymer	IEC <sup>a</sup>	IEC <sup>b</sup>	$\eta^c$ (dL g <sup>-1</sup> )	Methanol diffusion ( $\times 10^{-7}$ cm <sup>2</sup> s <sup>-1</sup> )	Selectivity ( $\times 10^5$ S s cm <sup>-3</sup> )	Oxidative stability	
						RW (%) <sup>d</sup>	$t$ (h) <sup>e</sup>
SPEEKCN35	1.57	1.50	0.54	1.03	2.48	98	$\approx 10$
SPEEKCN40	1.76	1.69	0.54	2.62	2.25	97	3.5
SPEEKCN40-1	1.68	1.51	–	1.69	2.27	98	>10
SPEEKCN40-2	1.60	1.41	–	1.34	2.51	99	>10
6FSPEEK <sup>f</sup>	1.68	1.57	–	–	–	74	3
Composite1 <sup>f</sup>	1.60	1.41	–	–	–	>90	>6
AP6FSPEEK <sup>g</sup>	1.72	1.61	–	3.7	0.79	97	4
AP6FSPEEK/DGBP1 <sup>g</sup>	1.64	1.26	–	3.3	0.63	99	>6
Nafion 117	–	–	–	29.4	0.59	–	–

<sup>a</sup> Theoretical value (m mol g<sup>-1</sup>).

<sup>b</sup> Experimental value (m mol g<sup>-1</sup>).

<sup>c</sup> Measured in NMP at 25 °C.

<sup>d</sup> Retained weights of membranes after treating in Fenton's reagent for 1 h.

<sup>e</sup> The dissolved time of polymer membranes.

<sup>f</sup> Data from Ref. [27].

<sup>g</sup> Data from Ref. [26].

**Table 3**  
Water uptake, swelling ratio and  $\lambda$  of membranes.

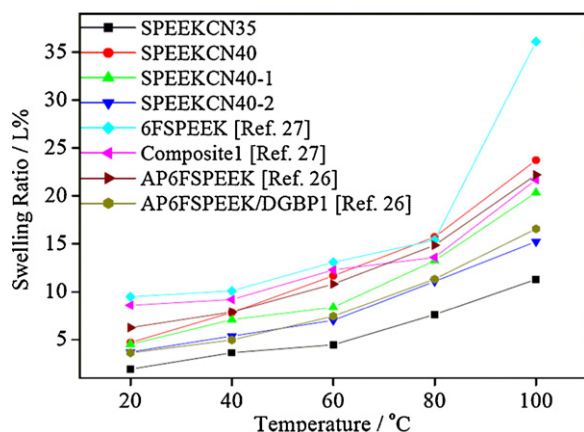
Polymer	Temperature (°C)								
	20			80			100		
	WU (%)	SR (%)	$\lambda$	WU (%)	SR (%)	$\lambda$	WU (%)	SR (%)	$\lambda$
SPEEKCN35	17.0	1.9	6.3	32.6	76	12.1	44.6	11.3	16.5
SPEEKCN40	24.5	4.7	8.1	63.9	15.7	21.0	102.1	23.7	33.6
SPEEKCN40-1	21.8	4.5	8.0	48.7	13.3	17.9	77.3	20.4	28.4
SPEEKCN40-2	19.3	3.7	7.6	40.7	11.1	16.0	62.0	15.3	24.4
6FSPEEK <sup>a</sup>	21.4	9.5	7.6	41.5	17.4	14.7	107.2	36.1	37.9
Composite1	17.8	8.6	7.0	33.7	13.6	13.3	53.5	21.7	21.1
AP6FSPEEK <sup>b</sup>	11.6	6.3	4.0	32.8	14.9	11.3	43.6	22.2	15.0
AP6FSPEEK/DGBP1 <sup>b</sup>	9.8	3.6	4.3	27.0	11.3	11.9	36.8	16.6	16.2

WU (%): water uptake (%); SR (%): swelling ratio (%);  $\lambda$ : number of water molecules absorbed per sulfonic acid groups.

<sup>a</sup> Data from Ref. [27].

<sup>b</sup> Data from Ref. [26].

larly as previous report [27,37,38], the water uptake and swelling ratio decreased with increasing the content of basic component in the same temperature, and increased with increasing the temperature. From the results of Figs. 5 and 6, we could see that to introduce a second basic component into composite materials played an important role in decreasing the water uptake and swelling ratio. And the swelling ratio of both SPEEKCN40-1 and SPEEKCN40-2 was much lower than Composite1 and AP6FSPEEK/DGBP1 (Fig. 6), which might be attributed to both nitrile groups and acid–basic interaction. The effects of introduction of a second basic com-

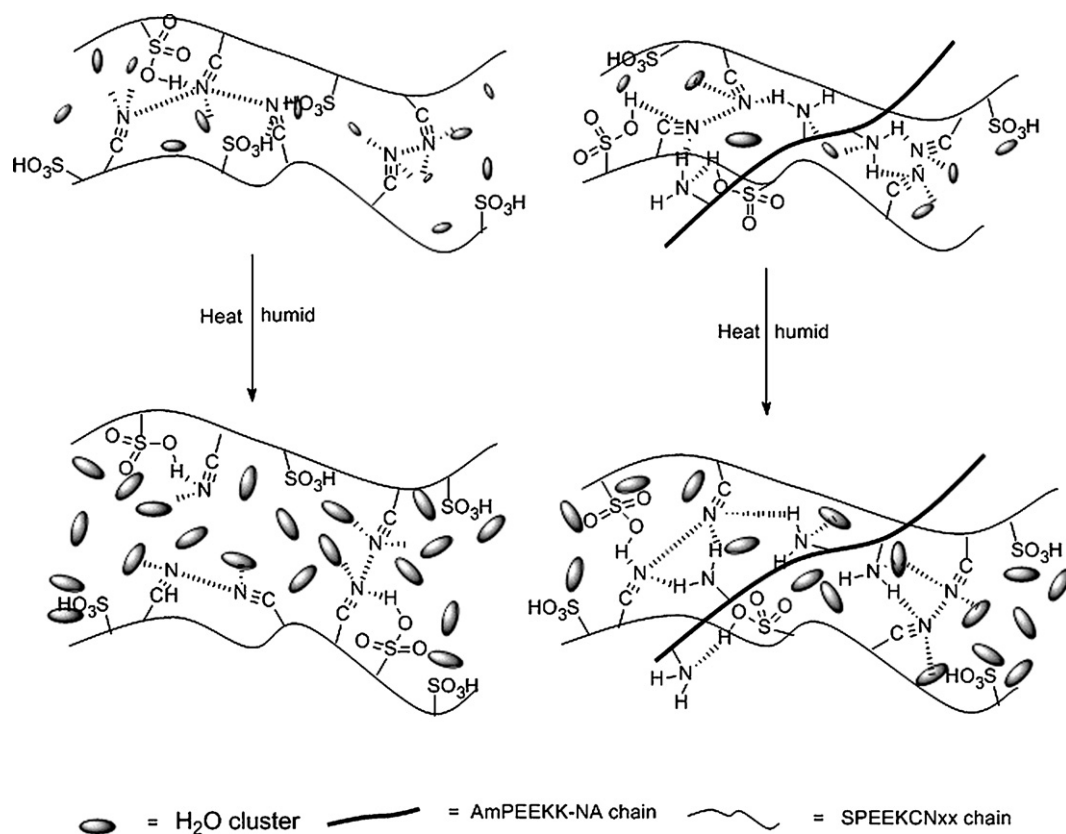


**Fig. 6.** Swelling ratio of membranes at different temperatures.

ponent could be summarized as Scheme 2. Although there was interaction between nitrile groups and nitrile groups or sulfonic groups, they were easily weakened at high temperature and humid with high dimensional swelling (Scheme 2[left]). On the other hand, in the composite membranes, the basic component bounded the movement of molecular chain by the interaction between amino and nitrile or sulfonic groups, so that dimensional stability was improved (Scheme 2[right]). Although the swelling ratio of SPEEKCN40-2 was little higher than SPEEKCN35 with the similar IEC, the values of SPEEKCN40-2 was low to 15.3% at 100 °C, which was decreased obviously compared with SPEEKCN40 of 23.7% at 100 °C. It illustrated that both the introduction of basic component and decreasing DS value could lead to the same effect in decreasing the dimensional swelling.

### 3.6. Oxidative stability and mechanical property of membranes

Oxidative stability of pure and composite membranes was examined by observing their dissolving behaviors in Fenton's reagent at 80 °C (Table 2). The series containing nitrile groups was better than the others, which displayed that nitrile groups could work well in improving oxidative stability. Among the membranes containing nitrile groups, the weight of SPEEKCN35 and composite membranes was retained above 98% after treatment in Fenton's reagent at 80 °C for 1 h, and the membranes dissolved after 10 h. All of the data were superior to SPEEKCN40, which was dissolved in 3.5 h, and this illustrated that the oxidative stability could be improved by decreasing the content of sulfonic groups and introducing a basic component. Mechanical properties were



**Scheme 2.** Water uptake and swelling illustration of nitrile-containing sulfonated polymers (left) and their composites with amino-containing polymer (right).

also important for the usage of PEMs, and the tensile results in wet state are all tabulated in Table 4. It could be seen that SPEEKCN35, SPEEKCN40, SPEEKCN40-1 and SPEEKCN40-2 exhibited good tensile strength with 44.6, 33.9, 40.7 and 43.7 MPa, respectively, which were all higher than Nafion 117 with 22.7 MPa tested at the same condition in our lab and also higher than that of 6FSPEEK and AP6FSPEEK. As reported previously [27], the tensile strength and Young's moduli of composite membranes were all higher than pure membranes, and the values increased with increasing the content of basic component. All the membranes showed the elongation at break of 42.9–50.7%, and Young's moduli were 0.31–0.54 GPa. This result indicated these membranes were strong and tough enough to be used as proton exchange membrane materials.

### 3.7. Methanol permeability, proton conductivity and selectivity of membranes

Methanol permeability and proton conductivity, which determined the fuel cell performance, were two important transport properties. Low methanol permeability and high proton conductivity

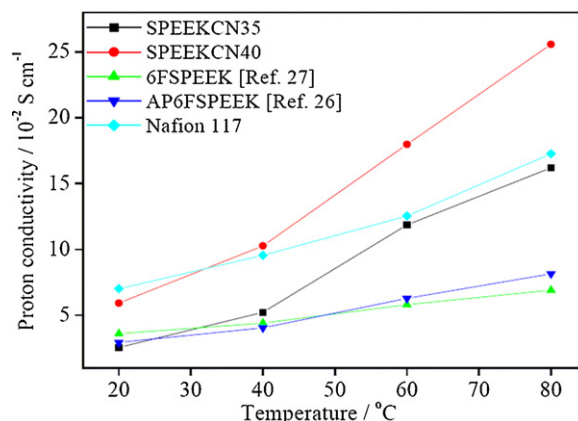
were required for direct methanol fuel cells (DMFCs) [37–39]. In DMFCs, low methanol diffusion coefficient was required because the diffusion of methanol from the anode to the cathode leads to power loss and other undesirable consequences. The methanol permeability values of membranes at room temperature were in the range of  $1.03 \times 10^{-7}$  to  $2.62 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  (Table 2), which were one order magnitude lower than the value of Nafion 117 of  $2.94 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  [26].

The proton conductivities of the membranes were estimated using impedance diagrams, and the results at different temperatures are presented in Figs. 7 and 8. The proton conductivity of an electrolyte was generally thermally stimulated, which was similar to water uptake of membranes. From the figures, we could see that the proton conductivities for each sample were a function of temperature and the values increased with elevating temper-

**Table 4**  
Mechanical properties of membranes.

Membranes	Tensile strength (MPa)	Maximum elongation (%)	Tensile modulus (GPa)
SPEEKCN35	44.6	45.9	0.53
SPEEKCN40	33.9	42.9	0.31
SPEEKCN40-1	40.7	45.8	0.35
SPEEKCN40-2	43.7	50.7	0.54
6FSPEEK <sup>a</sup>	26.2	74.8	0.37
Composite1 <sup>a</sup>	33.7	112.2	0.50
AP6FSPEEK <sup>a</sup>	25.2	41.8	0.53

<sup>a</sup> Data from Ref. [27].



**Fig. 7.** Proton conductivities of pure membranes.

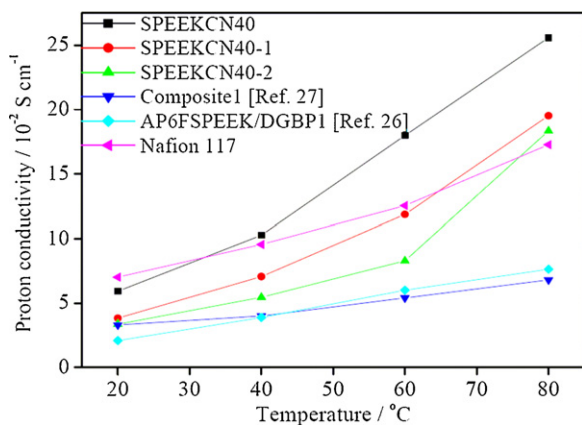


Fig. 8. Proton conductivities of composite membranes.

ature. As shown in Fig. 7, the proton conductivity of SPEEKC40 was close to Nafion 117 at 20 °C. With increasing the temperature, the proton conductivity values of the novel membranes increased faster than Nafion 117, and at 80 °C, the value of SPEEKC40 could reach to  $0.26 \text{ S cm}^{-1}$ , which was much higher than Nafion 117 of  $0.17 \text{ S cm}^{-1}$ . On the other hand, although the proton conductivities of SPEEKC35 were lower than Nafion 117 at low temperature, the value of SPEEKC35 reached to  $0.16 \text{ S cm}^{-1}$  at 80 °C, which was very close to that of Nafion 117. Both of them had higher proton conductivities than 6FSPEEK ( $0.069 \text{ S cm}^{-1}$ ) and AP6FSPEEK ( $0.087 \text{ S cm}^{-1}$ ). For the composite membranes, as shown in Fig. 8, the proton conductivities of SPEEKC40-1 and SPEEKC40-2 reached to 0.20 and  $0.18 \text{ S cm}^{-1}$  at 80 °C, respectively, which were both higher than Nafion 117, and much higher than previously reported Composite1 and AP6FSPEEK/DGBP1 [26,27].

According to previously reported study [40], we charted Fig. 9 of proton conductivity at 80 °C versus methanol resistance of membranes. The ordinate in this figure was the logarithm of the proton conductivity for membranes, and the abscissa was the logarithm of the reciprocal of methanol permeability. For comparison, we drew a line with a slope of  $(-1)$  of constant selectivity through the point of Nafion 117 according with report [40], as shown in Fig. 9. We could see that all the membranes containing nitrile groups were located in the little up right-hand corner of the figure, which meant their higher selectivity in comparison with Nafion 117, AP6FSPEEK and AP6FSPEEK/DGBP1. Meanwhile, we calculated the selectivity (defined as the ratio of proton conductivity to methanol permeability of membranes) for evaluating membrane performances considering both proton conductivity and methanol permeability.

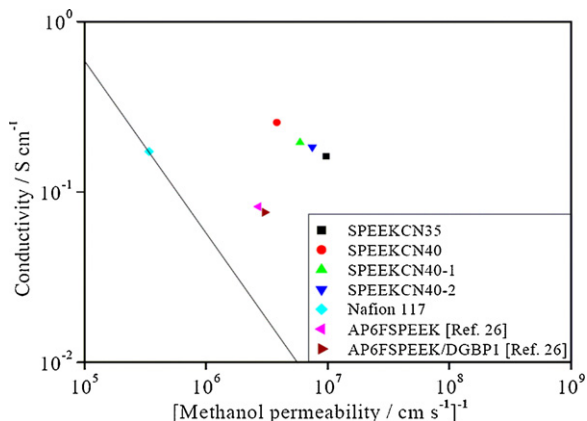


Fig. 9. Proton conductivity versus methanol resistance of membranes.

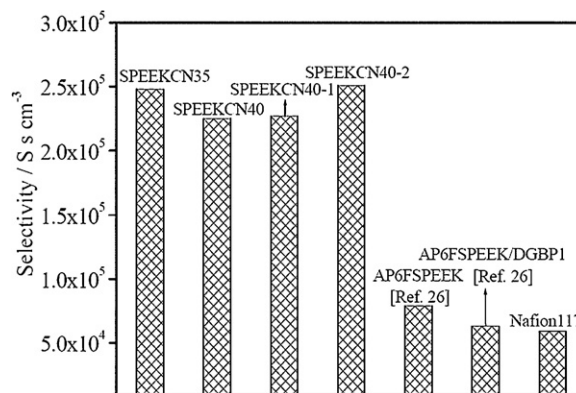


Fig. 10. Selectivity of membranes.

The results were summarized in Table 2 and Fig. 10. Although proton conductivities of the composite membranes and SPEEKC35 were lower than that of SPEEKC40 membrane, higher selectivity values were found. And its selectivity was even one order magnitude higher than Nafion 117 of  $5.87 \times 10^4 \text{ S s cm}^{-3}$ . Compared with the selectivity of AP6FSPEEK and AP6FSPEEK/DGBP1 (they had the same order magnitude as Nafion 117), we found that SPEEKC40-2 had the highest selectivity of  $2.51 \times 10^5 \text{ S s cm}^{-3}$ . All the data illustrated that both SPEEKC35 and two composite membranes might be potential in the possible future usage.

#### 4. Conclusions

A new family of nitrile-containing sulfonated poly(arylene ether ketone)s were successfully synthesized and then acid–base molecule-enhanced composite PEMs were prepared. The results illustrated that both the introducing of polar nitrile groups and the building of acid–basic composites were the effective means to prepare low-swelling PEMs. In comparison with the previously reported membranes, some of the novel membranes showed more attractive properties, such as improved oxidative and dimensional stability, lower methanol permeability and higher proton conductivity. For example, the methanol permeability of SPEEKC35 (plain sample) was  $1.03 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , which was one order lower than that of Nafion. Meanwhile, its proton conductivity was as high as  $0.16 \text{ S cm}^{-1}$  at 80 °C. For the composites, the proton conductivity values of SPEEKC40-1 and SPEEKC40-2 were up to 0.20 and  $0.18 \text{ S cm}^{-1}$  at 80 °C, respectively. Among all the evaluated membranes, SPEEKC40-2 had the best selectivity of  $2.51 \times 10^5 \text{ S s cm}^{-3}$ , and it may be a promising candidate using in DMFCs.

#### Acknowledgements

The authors thank Dr. Chengji Zhao and Dr. Dan Xu for testing proton conductivities. Furthermore, the authors acknowledge the financial support for this project provided by the National Natural Science Foundation of China (No.: 50973040) and the Science and Technology Development Plan of Jilin Province, China (No.: 20090322).

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