



## A novel sulfonated poly(ether ether ketone) and cross-linked membranes for fuel cells

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### ABSTRACT

A novel poly(ether ether ketone) (PEEK) containing pendant carboxyl groups has been synthesized by a nucleophilic polycondensation reaction. Sulfonated polymers (SPEEKs) with different ion exchange capacity are then obtained by post-sulfonation process. The structures of PEEK and SPEEKs are characterized by both FT-IR and  $^1\text{H}$  NMR. The properties of SPEEKs as candidates for proton exchange membranes are studied. The cross-linking reaction is performed at 140 °C using poly(vinyl alcohol) (PVA) as the cross-linker. In comparison with the non-cross-linked membranes, some properties of the cross-linked membranes are significantly improved, such as water uptake, methanol resistance, mechanical and oxidative stabilities, while the proton conductivity decreases. The effect of PVA content on proton conductivity, water uptake, swelling ratio, and methanol permeability is also investigated. Among all the membranes, SPEEK-C-8 shows the highest selectivity of  $50.5 \times 10^4 \text{ S s cm}^{-3}$ , which indicates that it is a suitable candidate for applications in direct methanol fuel cells.

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### 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have attracted considerable attention for transportation, distributed power, and portable power applications because of their high efficiency and environmental friendship [1–5]. In PEMFCs, a polymer electrolyte membrane (PEM) plays an important role as a core material, which requires high proton conductivity, sufficient thermal stability, low permeability of fuel and oxidant, long-term stability, as well as inexpensive operating costs [6–8]. Perfluorinated sulfonic acid ionomers such as Nafion membranes developed by DuPont brought a major breakthrough in PEMFCs. Superior proton conductivity and excellent long-term durability in fuel cells have made them as the mostly studied electrolytes. However, methanol readily migrates through Nafion membranes from the anode to the cathode, causing a serious reduction of opening voltage and poisoning the electrocatalysts at the cathode. Additionally, another major drawback of Nafion membranes is their high cost due to the difficulty in synthesizing and processing.

Recently, much research work has focused on the fabrication of novel alternative proton conductive membranes based on non-fluorinated aromatic ionomers [9–18]. Generally, membranes

based on these polymers only reach high proton conductivity at high IEC values. However, high IEC values usually lead to high water uptake, large dimensional variations as well as inadequate mechanical properties, which render the membranes unsuitable for applications in PEMFCs. To overcome this problem, several methods have been developed, such as optimizing the polymer structure [19–23], preparing composite membranes [24–29] and cross-linked membranes [30–34]. The cross-linking method is promising because of its easy preparation. Moreover, the resulting cross-linked membranes exhibit improved mechanical and chemical stabilities, reduced water uptake and methanol permeability compared with the non-cross-linked membranes.

In this study, we synthesized a novel poly(ether ether ketone) (PEEK) bearing pendant carboxyl groups which could be widely used in the cross-linking reaction as reported previously [35]. Post-sulfonation process was then performed to obtain SPEEKs. Cross-linked SPEEKs were obtained by an esterification reaction using poly(vinyl alcohol) (PVA) as the cross-linker. Lin et al. reported PVA used as PEM can effectively suppress the methanol permeability and improve the selectivity [36]. Furthermore, PVA is a macromolecular cross-linker, which may result in a higher cross-linking density compared to some small molecules, such as diols [37]. The properties of cross-linked membranes were studied in detail compared to the non-cross-linked membranes, and the influence of cross-linker content on PEM properties was also investigated.

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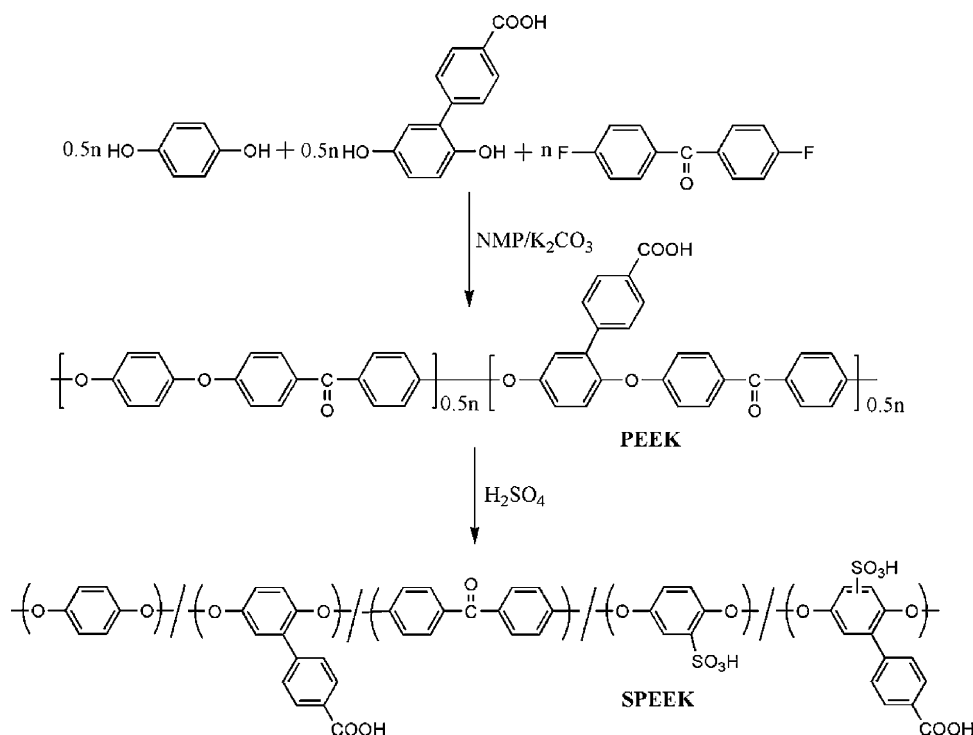


Fig. 1. Synthesis and structures of PEEK and SPEEK.

## 2. Experimental

### 2.1. Materials

4,4'-Difluorobenzophenone was purchased from Longjing Chemical plant, poly(vinyl alcohol) (a molecular weight of 105400–111600) was purchased from Sigma–Aldrich Ltd. 4-Carboxylphenyl hydroquinone was synthesized according to a previous reference [38]. Other reagents were commercially available grade and used without further purification.

### 2.2. Characterization

<sup>1</sup>H NMR spectrum was recorded on a Bruker 510 spectrometer (<sup>1</sup>H, 500 MHz) by using deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>) as the solvent. FT-IR spectra were recorded on a Nicolet Impact 410 Fourier transform infrared spectrometer using KBr disc. The T<sub>g</sub> of polymers was measured using differential scanning calorimeter (DSC) measurement performed on a Mettler Toledo DSC821<sup>e</sup> instrument at a heating rate of 10 °C min<sup>-1</sup> from 20 to 300 °C under nitrogen. The specific viscosities ( $\eta_{sp}/c$ ) of the obtained polymers were determined by using Ubbelohde viscometer in thermostatic container with a polymer concentration of 5.0 g L<sup>-1</sup> in DMF at 25 °C.

### 2.3. Synthesis of PEEK bearing pendant carboxyl groups

As shown in Fig. 1, PEEK was synthesized via a nucleophilic aromatic substitution reaction. A detailed polymerization procedure was described as follows: in a 250 mL three-necked flask equipped with a mechanical stirrer, a Dean-Stark trap, and a nitrogen inlet, 4-carboxylphenyl hydroquinone (3.45 g, 0.015 mol), hydroquinone (1.65 g, 0.015 mol), 4,4'-difluorobenzophenone (6.54 g, 0.03 mol), K<sub>2</sub>CO<sub>3</sub> (5.52 g, 0.04 mol), N-methyl pyrrolidone (37 mL) and toluene (15 mL) were placed. The mixture was firstly refluxed at 140 °C about 3 h to remove the water produced in this system. After removing toluene, the reaction temperature was raised up to 200 °C and kept at this temperature for another 4 h. The viscous solution

was then poured into a mixture of concentrated hydrochloric acid and water. Finally, the polymer powder was washed thoroughly with hot water and dried at 120 °C for 24 h (yield: 92%,  $\eta_{sp}/c$ : 0.82, T<sub>g</sub>: 184 °C).

### 2.4. Post-sulfonation

Post-sulfonation was carried out in concentrated sulfuric acid at 80 °C for several hours. The procedure was described as follows: 1 g PEEK was dissolved in 10 mL sulfuric acid and the solution was stirred for 5, 7 or 8 h at 80 °C. After cooling to room temperature, the polymer solution was isolated in an excess amount of deionized water and the resulting solid was washed thoroughly with deionized water until the water was neutral. The product was then dried in a vacuum oven at 80 °C for 24 h (yield: 78–89%).

### 2.5. Preparation of covalently cross-linked membranes

1 g SPEEK-1 and the cross-linker PVA (2, 4, and 8 wt%) were dissolved in 10 mL dimethyl sulfoxide at 70 °C, and the membranes were prepared using solution-casting and evaporation method. The cross-linking reaction was performed by heating these membranes at 140 °C for 4 h to obtain cross-linked membranes. The schematic illustration of cross-linking network structure is shown in Fig. 2.

### 2.6. Thermal stability

The thermal stability was measured using a Pyris 1 TGA (PerkinElmer) equipment. Before testing, all membranes were pre-heated at 120 °C for 5 min to remove any residual moisture and solvent, and then the samples were cooled to 100 °C and reheated to 700 °C at a heating rate of 10 °C min<sup>-1</sup> in N<sub>2</sub> flow.

### 2.7. Mechanical properties

The mechanical properties of membranes were measured on a SHIMADZU AG-I 1KN equipment. Membrane specimens of

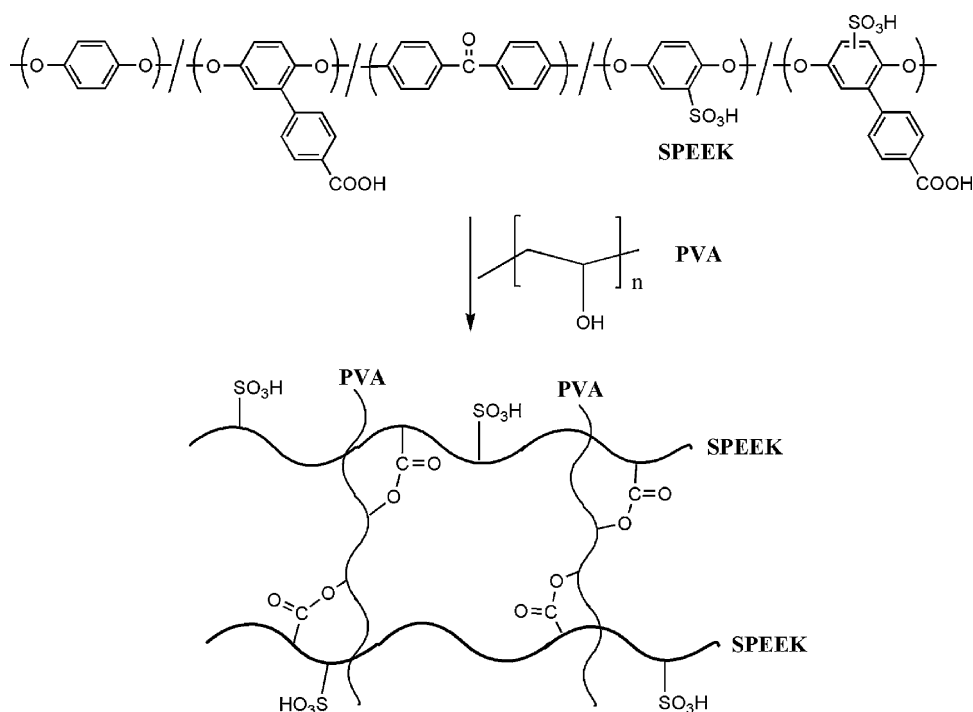


Fig. 2. Schematic representation of the cross-linking network structure.

15 mm × 4 mm were placed between the grips of the testing machine at a tensile rate of 2 mm min<sup>-1</sup>.

### 2.8. Oxidative stability

Small pieces of membranes were 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 characterized by recording the time when the membranes began to break into pieces and dissolved completely.

### 2.9. Ion exchange capacity (IEC)

The IEC of membranes was determined by a classical titration method: acid-form membranes were immersed in 2 M NaCl solution for 48 h, and the solution was titrated with 0.01 M NaOH solution using phenolphthalein as an indicator. The titrated IEC was obtained from the following formula:

$$\text{IEC} = \frac{\text{consumed NaOH (ml)} \times \text{molarity of NaOH}}{\text{weight of dried membrane}} (\text{mequiv. g}^{-1}) \quad (1)$$

### 2.10. Water uptake and swelling ratio

The dried square membranes were immersed into deionized water at the desired temperature for 24 h. Then the membranes were taken out and wiped with tissue paper quickly. The weight and the length (or thickness) were quickly measured. The water uptake and the swelling ratio were calculated by the changes in weight and length between fully hydrated and dry membranes as follows:

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (2)$$

$$\text{Swelling ratio (\%)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (3)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the masses of wet and dry membranes,  $L_{\text{wet}}$  and  $L_{\text{dry}}$  are the lengths (or thickness) of wet and dry membranes, respectively.

### 2.11. Proton conductivity

Fully hydrated membranes (4 cm × 1 cm) were measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation and 0.0 V dc rest voltage using a Princeton Applied Research Model 273A Potentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ) [31]. The measurement was carried out with the cell (Fig. 3) immersed in the constant temperature water, and the proton conductivity was determined by the equation:

$$\sigma = \frac{L}{R \times S} \quad (4)$$

where  $L$  is the distance between the two electrodes,  $R$  is the membrane resistance and  $S$  is the cross-sectional area of membranes.

### 2.12. Methanol permeability

A glass diffusion cell was used to measure the methanol permeability as described in the literature [24]. The cell was consisted of two reservoirs, which were separated by a mem-

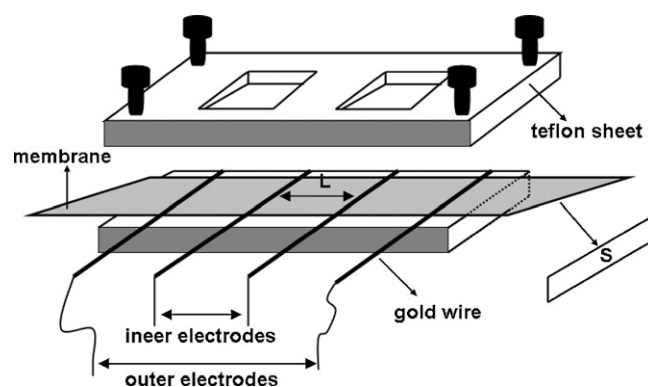


Fig. 3. Test cell for proton conductivity measurement.

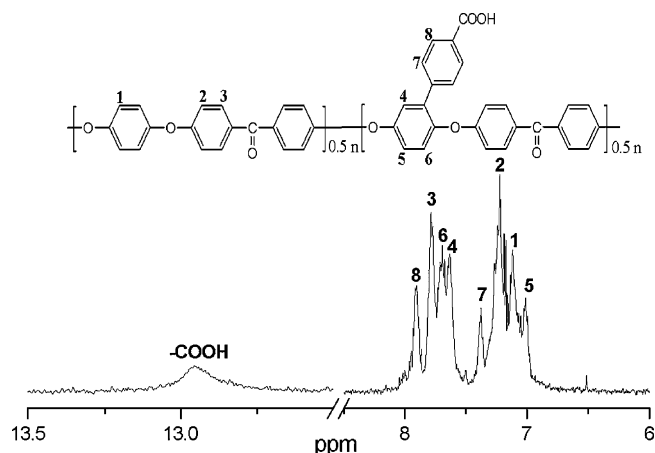


Fig. 4.  $^1\text{H}$  NMR spectrum of PEEK.

brane. 10 M methanol solution and deionized water were placed on each side. Magnetic stirrers were used on each compartment to ensure uniformity. The concentration of the methanol in water reservoir was determined by using a SHIMADZU GC-8A chromatograph. The methanol permeability was calculated as follows:

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - T_0) \quad (5)$$

where  $A$  ( $\text{cm}^2$ ) and  $L$  (cm) are the effective area and the thickness of the membrane, respectively,  $V_B$  ( $\text{cm}^3$ ) is the volume of diffusion reservoir,  $C_A$  and  $C_B$  ( $\text{mol L}^{-1}$ ) are the methanol concentration in methanol reservoir and water reservoir, respectively,  $DK$  is the methanol permeability ( $\text{cm}^2 \text{s}^{-1}$ ).

### 3. Results and discussion

#### 3.1. Synthesis and characterization of PEEK and SPEEK

To synthesize a PEEK with pendant carboxyl groups, hydroquinone was introduced into the polymerization reaction due to the poor solubility of 4-carboxylphenyl hydroquinone. The mole ratio of hydroquinone to 4-carboxylphenyl hydroquinone was fixed at 1:1. The structure of PEEK was confirmed by  $^1\text{H}$  NMR spectroscopy (Fig. 4). Post-sulfonation of PEEK was performed in concentrated sulfuric acid at  $80^\circ\text{C}$  for 5, 7 or 8 h, respectively. A slight degradation was observed after a long post-sulfonation time because the membranes became brittle in dry state. The  $^1\text{H}$  NMR spectrum of SPEEK is shown in Fig. 5. Compared to the spectrum of PEEK, several new

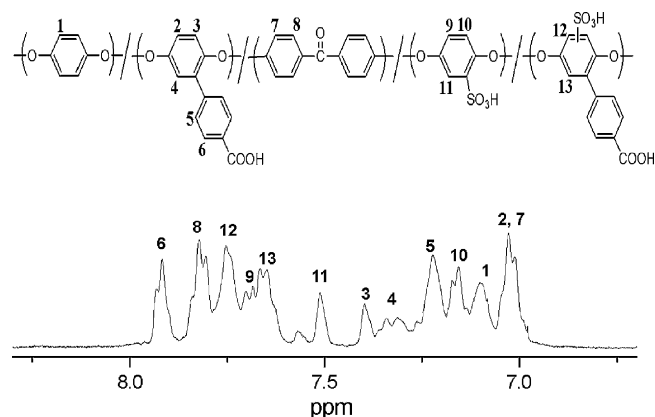


Fig. 5.  $^1\text{H}$  NMR spectrum of SPEEK.

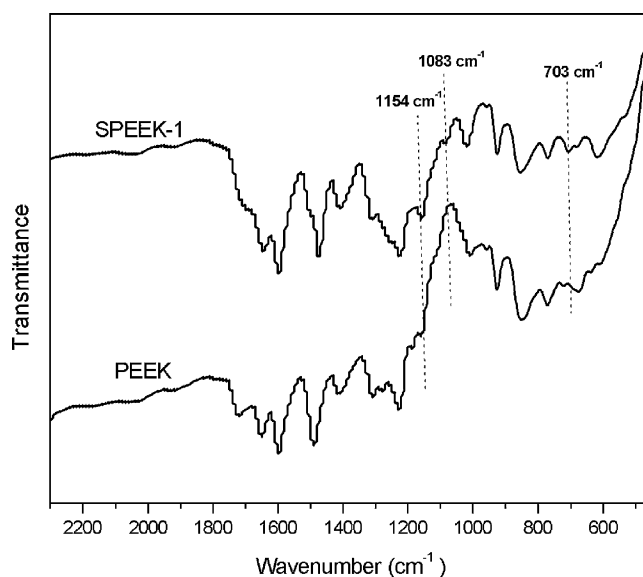


Fig. 6. FT-IR spectra of PEEK and SPEEK.

peaks appeared in Fig. 5. The peak at 7.5 ppm was assigned to the hydrogen atom adjacent to the sulfonic group in hydroquinone, and the peak at 7.75 ppm was assigned to the hydrogen atom adjacent to the sulfonic group in 4-carboxylphenyl hydroquinone. Fig. 6 shows the FT-IR spectra of PEEK and SPEEK-1. Compared to the PEEK, the peak at  $703 \text{ cm}^{-1}$  was assigned to the S–O stretching of  $-\text{SO}_3\text{H}$  groups, and the peaks at  $1083$  and  $1154 \text{ cm}^{-1}$  could be assigned to O=S=O stretching vibrations of SPEEK-1. Therefore, both FT-IR and  $^1\text{H}$  NMR spectra indicated that the SPEEK was synthesized successfully.

#### 3.2. Gel fraction of cross-linked membranes

The pristine SPEEK membranes can be easily dissolved in common organic polar solvents, such as dimethylformamide (DMF), while the cross-linked membranes cannot be dissolved in this solvent. Gel fraction which can be considered as an indirect measurement of cross-linking density, was obtained from the ratio of the weight of the cross-linked membranes after extraction from DMF and the initial weight. From Table 1, gel fraction increased with increasing the content of PVA, which means an increment of cross-linking density.

#### 3.3. Thermal stability, mechanical properties and oxidative stability

The TGA curves of both pristine SPEEKs and cross-linked polymers are shown in Fig. 7. The SPEEK samples showed slight degradation at around  $210^\circ\text{C}$ , which was associated with the thermal degradation of the sulfonic acid groups. As reported by many groups, the sulfonic groups in post-sulfonated polymer were not as chemically stable as those in the pre-sulfonated polymer [39]. The cross-linked SPEEK showed its first-stage weight loss at  $205^\circ\text{C}$ , which may be due to the loss of sulfonic acid groups or the degradation of PVA. From the results of TGA test, we can conclude that the thermal stability of SPEEKs and cross-linked membranes was adequate for use in fuel cells.

It is essential for electrolyte membranes to have good mechanical strength to be used in fuel cells. As shown in Table 2, the SPEEK-1 had a Young's modulus of  $1368.7 \text{ MPa}$ , a tensile strength of  $51.7 \text{ MPa}$  and an elongation at break of 9.9%. With the increment of sul-

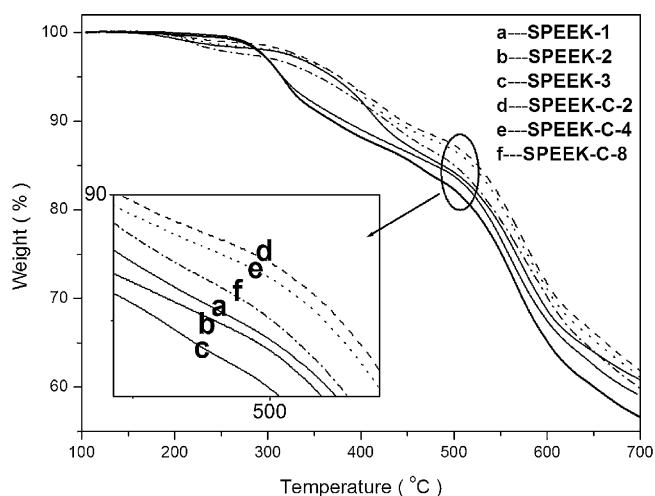
**Table 1**  
The polymer description,  $\eta_{sp}/c$ , gel fraction, IEC and oxidative stability.

Polymer	Sulfonation time (h)	$\eta_{sp}/c$	Gel fraction (%) <sup>a</sup>	IEC (mequiv · g <sup>-1</sup> )	Oxidative stability	
					$t_1^b$ (min)	$t_2^b$ (h)
SPEEK-1	5	0.71	0	1.67	35	>48
SPEEK-2	7	0.58	0	1.81	32	32
SPEEK-3	8	0.51	0	2.03	19	25
SPEEK-C-2	– <sup>c</sup>	–	24.4	1.62	46	>48
SPEEK-C-4	– <sup>c</sup>	–	39.8	1.57	51	>48
SPEEK-C-8	– <sup>c</sup>	–	53.5	1.49	58	>48

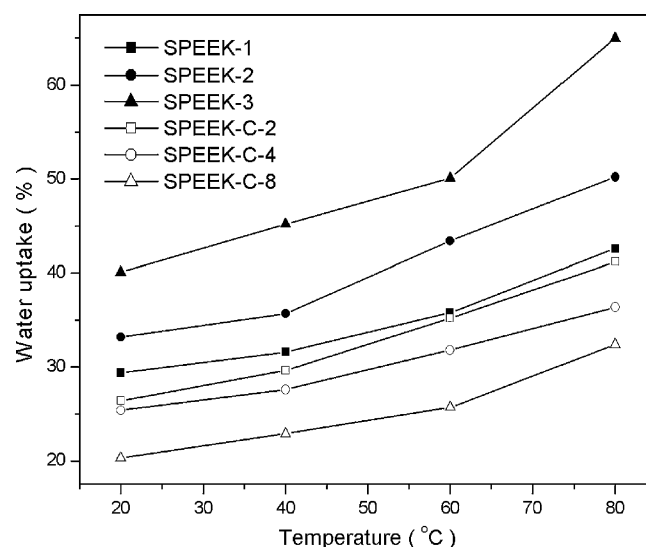
<sup>a</sup> Gel fraction was obtained from the ratio of the weight of the cross-linked membranes after extraction from DMF and the initial weight.

<sup>b</sup> The expended time that the membranes started to break and disappeared in the solution.

<sup>c</sup> Cross-linked membrane of SPEEK-1 with the cross-linker content of 2%, 4%, 8%, respectively.



**Fig. 7.** TGA curves of SPEEK and cross-linked membranes.



**Fig. 8.** Water uptake of membranes as a function of temperature.

**Table 2**  
The mechanical properties of membranes.

Membranes	Young's modulus (MPa)	Tensile strength (MPa)	Maximum elongation (%)
SPEEK-1	1368.7	51.7	9.9
SPEEK-2	624.2	25.3	7.7
SPEEK-3	– <sup>a</sup>	– <sup>a</sup>	– <sup>a</sup>
SPEEK-C-2	1318.4	75.7	15.5
SPEEK-C-4	1420.3	67.8	13.5
SPEEK-C-8	1630.0	64.8	15.6

<sup>a</sup> Not applicable: membrane was too brittle to be tested in dry state.

fonation time, the SPEEK membranes displayed poor mechanical properties, which may be attributed to the degradation in post-sulfonation process. Because the film was too fragile in dry state, the mechanical properties of SPEEK-3 could not be obtained. However, after cross-linking, the membranes possessed markedly improved mechanical properties, they had Young's modulus, tensile strength, and elongation at break in the range of 1318–1630, 64.8–75.7 MPa, and 13.5–15.6%, respectively.

The oxidative stability of membranes was evaluated by the expended time that the membranes started to break and disappeared in Fenton's reagent. As shown in Table 1, the oxidative stability of membranes reduced with the increment of IEC. SPEEK-1 membrane began to break after 35 min and did not disappear even after two days. SPEEK-3 membrane had the worst oxidative stability. After cross-linking, the oxidative stability of membranes was better improved and SPEEK-C-8 exhibited the best oxidative stability.

### 3.4. Ion exchange capacity

The ion exchange capacity is an important property of membranes since it determines proton conductivity, water uptake, and dimensional stability. The IEC of the membranes was determined by titration, which was commonly used to determine IEC of sulfonated polymers. As shown in Table 1, SPEEK-1 showed the IEC of 1.67 mequiv · g<sup>-1</sup>, and with the increment of sulfonation time, the IEC of sulfonated polymers increased. Because the introduction of the cross-linker diluted the concentration of the sulfonic acid groups, the cross-linked membranes displayed slightly reduced IEC compared with the non-cross-linked membrane.

### 3.5. Water uptake and swelling ratio

The water uptake is a fundamentally important property of proton conducting membranes and determines the level of conductivity to a great extent. Generally, the post-sulfonated polymers absorb more water molecules than the pre-sulfonated polymers with similar IEC. As shown in Fig. 8 and Table 3, the water uptake and swelling ratio of sulfonated polymers increased with the increment of sulfonation time. SPEEK-1 had the water uptake of 29.4%, swelling ratio in length of 8.9% and in thickness of 5.7% at 20°C. SPEEK-3 membrane had the most water uptake of 40.1% at 20°C. Compared with the results of Peckham et al. [40], our SPEEK displayed lower water uptake with similar IEC, which may be due to the introduction of carboxyl groups. The cross-linked membranes displayed reduced water uptake and swelling ratio compared with SPEEK-1. SPEEK-C-8 exhib-



**Table 3**  
The proton conductivity, methanol permeability, water uptake and swelling ratio of membranes.

Membranes	Proton conductivity ( $S\text{ cm}^{-1}$ )		Methanol permeability ( $\times 10^{-7}\text{ cm}^2\text{ s}^{-1}$ )	Water uptake (%)		Swelling ratio (%)			
						In length		In thickness	
	20 °C	80 °C		20 °C	80 °C	20 °C	80 °C	20 °C	80 °C
SPEEK-1	0.035	0.068	1.98	29.4	42.6	8.9	12.2	5.7	8.9
SPEEK-2	0.046	0.075	2.24	33.2	50.2	10.3	13.6	6.6	9.2
SPEEK-3	0.050	0.082	7.09	40.1	65.0	14.5	18.7	7.2	12.5
SPEEK-C-2	0.031	0.061	1.62	26.4	41.2	7.8	11.9	5.4	8.5
SPEEK-C-4	0.027	0.055	1.04	25.4	36.3	7.5	9.8	5.5	7.6
SPEEK-C-8	0.020	0.047	0.40	20.7	32.4	6.1	8.4	4.3	6.8

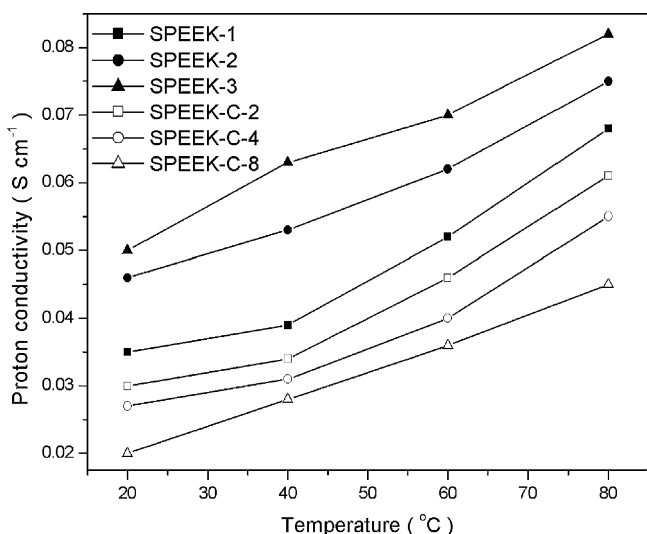
ited the lowest water uptake due to the cross-linking network structure.

### 3.6. Proton conductivity

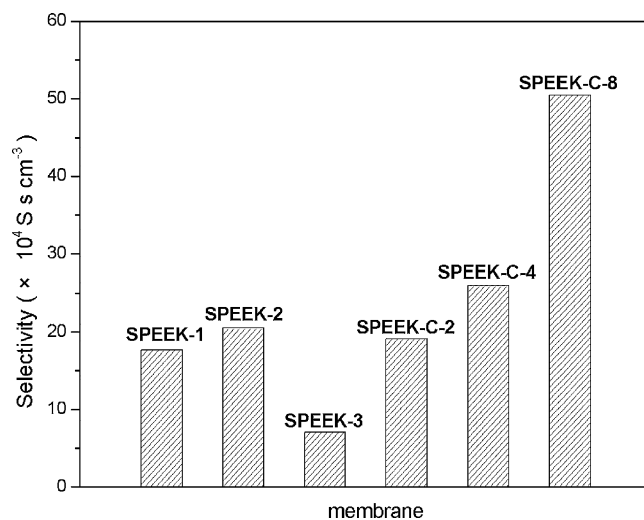
The proton conductivity of membranes at 100% RH was measured and the results are shown in Fig. 9. As seen, the proton conductivity of the membranes increased in proportion to the measuring temperature. The membranes with higher IEC displayed higher proton conductivity. SPEEK-3 with the highest IEC showed the highest proton conductivity of  $0.082\text{ S cm}^{-1}$  at  $80\text{ °C}$ . The cross-linked membranes displayed reduced proton conductivity because of the lower water uptake and IEC. The SPEEK-C-8 had the lowest proton conductivity of  $0.047\text{ S cm}^{-1}$  at  $80\text{ °C}$ , but it was still above  $10^{-2}\text{ S cm}^{-1}$ .

### 3.7. Methanol permeability

To prevent fuel from penetrating and energy efficiency loss, the proton exchange membranes used in direct methanol fuel cells (DMFCs) should possess well methanol resistance property. Table 3 indicated that all the membranes possessed excellent methanol resistance property. The methanol permeability of SPEEK-1 membrane was  $1.98 \times 10^{-7}\text{ cm}^2\text{ s}^{-1}$ , and with the increment of IEC, the methanol permeability of membranes extended to  $7.09 \times 10^{-7}\text{ cm}^2\text{ s}^{-1}$ . The cross-linked membranes showed remarkably reduced methanol permeability due to the cross-linking network structure. SPEEK-C-8 had the lowest methanol permeability which was five times lower than that of SPEEK-1.



**Fig. 9.** Proton conductivity of membranes as a function of temperature.



**Fig. 10.** Selectivity of SPEEK and cross-linked membranes.

### 3.8. Selectivity

The selectivity, that is, the ratio of proton conductivity to methanol permeability, is a crucial factor for polymer electrolyte membrane to be used in direct methanol fuel cells. Accordingly, higher selectivity could allow superior membrane performance. As seen in Fig. 10, for pristine sulfonated membranes, SPEEK-2 exhibited the highest selectivity while SPEEK-3 showed the lowest selectivity. After cross-linking, SPEEK-C-8 showed the highest selectivity of  $50.5 \times 10^4\text{ S s cm}^{-3}$ , which was three times higher than that of SPEEK-1. The result indicated that the cross-linking method can greatly improve the selectivity of membranes. The improvement of selectivity could be resulted from that cross-linking effectively hindered the polymer chain mobility and suppressed the swelling of membranes, which may be responsible for the reduced methanol permeability and the improved selectivity.

## 4. Conclusions

In summary, we synthesized a series of novel sulfonated poly(ether ether ketone)s with pendant carboxyl groups via a post-sulfonation process. The sulfonated polymers were characterized by both FT-IR and  $^1\text{H}$  NMR spectroscopy. In order to improve their dimension stability in water, we prepared a series of cross-linked PEMs using PVA as a cross-linker. Compared to the pristine membranes, the cross-linked membranes exhibited better mechanical properties, improved oxidative stability, much lower water uptake and swelling ratio. Though the proton conductivity of the membranes was slightly reduced after cross-linking, the cross-linked membranes showed much lower methanol permeability compared to the pristine membranes. Combined with their high selectivity,

this type of cross-linked membranes may be applicable as PEMs for PEMFCs.

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### References

- [1] R. Perrin, M. Elomaa, P. Jannasch, *Macromolecules* 42 (2009) 5146–5154.
- [2] C. Bi, H.M. Zhang, Y. Zhang, X.B. Zhu, Y.W. Ma, H. Dai, S.H. Xiao, *J. Power Sources* 184 (2008) 197–203.
- [3] K. Miyatake, Y. Chikashige, E. Higuchi, M. Watanabe, *J. Am. Chem. Soc.* 129 (2007) 3879–3887.
- [4] C.H. Min, *J. Power Sources* 195 (2010) 1880–1887.
- [5] T.J. Peckham, J. Schmeisser, S. Holdcroft, *J. Phys. Chem. B* 112 (2008) 2848–2858.
- [6] S. Matsumura, A.R. Hlil, C. Lepiller, J. Gaudet, D. Guay, A.S. Hay, *Macromolecules* 41 (2008) 277–280.
- [7] D.S. Kim, G.P. Robertson, M.D. Guiver, *Macromolecules* 41 (2008) 2126–2134.
- [8] J. Weber, K.D. Kreuer, J. Maier, A. Thomas, *Adv. Mater.* 9999 (2008) 1–4.
- [9] J.B. Hou, H.M. Yu, L. Wang, D.M. Xing, Z.J. Hou, P.W. Ming, Z.G. Shao, B.L. Yi, *J. Power Sources* 180 (2008) 232–237.
- [10] H.S. Lee, O. Lane, J.E. McGrath, *J. Power Sources* 195 (2010) 1772–1778.
- [11] Y.Á. Gallego, S.P. Nunes, A.E. Lozano, J.G. Campa, J. Abajo, *Macromol. Rapid Commun.* 28 (2007) 616–622.
- [12] J.H. Fang, X.X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kitan, K. Okamoto, *Macromolecules* 35 (2002) 9022–9028.
- [13] N. Asano, M. Aoki, S. Suzuki, K. Miyatake, H. Uchida, M. Watanabe, *J. Am. Chem. Soc.* 128 (2006) 1762–1769.
- [14] K. Miyatake, M. Watanabe, *J. Mater. Chem.* 46 (2006) 4465–4467.
- [15] M.A. Hofmann, C.M. Ambler, A.E. Maher, E. Chalkova, X.Y. Zhou, S.N. Lvov, H.R. Allcock, *Macromolecules* 35 (2002) 6490–6493.
- [16] Y.Y. Shao, G.P. Yin, Z.B. Wang, Y.Z. Gao, *J. Power Sources* 67 (2007) 235–242.
- [17] C.H. Fujimoto, M.A. Hickner, C.J. Cornelius, D.A. Loy, *Macromolecules* 38 (2005) 5010–5016.
- [18] J. Jouanneau, R. Mercier, L. Gonon, G. Gebel, *Macromolecules* 40 (2007) 983–990.
- [19] Ken Yoshimura, Katsuhiko Iwasaki, *Macromolecules* 42 (2009) 9302–9306.
- [20] E.M.W. Tsang, Z.B. Zhang, Z.Q. Shi, T. Soboleva, S. Holdcroft, *J. Am. Chem. Soc.* 129 (2007) 15106–15107.
- [21] F. Zhang, N.W. Li, S.B. Zhang, S.H. Li, *J. Power Sources* 195 (2010) 2159–2165.
- [22] C. Terraza, J.G. Liu, Y. Nakamura, Y. Shibasaki, S. Ando, M. Ueda, *J. Polym. Sci. Part A: Polym. Chem.* 46 (2008) 1510–1520.
- [23] Y. Zhang, Y. Wan, C.J. Zhao, K. Shao, G. Zhang, H.T. Li, H.D. Lin, H. Na, *Polymer* 50 (2009) 4471–4478.
- [24] D. Wu, R.Q. Fu, T.W. Xu, L. Wu, W.H. Yang, *J. Membr. Sci.* 310 (2008) 522–530.
- [25] N.Y. Arnett, W.L. Harrison, A.S. Badami, A. Roy, O. Lane, F. Cromer, L.M. Dong, J.E. McGrath, *J. Power Sources* 72 (2007) 20–29.
- [26] U. Sen, S.U. Celik, A. Ata, A. Bozkurt, *Int. J. Hydrogen Energy* 33 (2008) 2808–2815.
- [27] S. Reichman, L. Burstein, E. Peled, *J. Power Sources* 179 (2008) 520–531.
- [28] O. Acar, U. Sen, A. Bozkurt, A. Ata, *Int. J. Hydrogen Energy* 34 (2009) 2724–2730.
- [29] B. Smitha, D.A. Devi, S. Sridhar, *Int. J. Hydrogen Energy* 33 (2008) 4138–4146.
- [30] S.L. Zhong, T.Z. Fu, Z.Y. Dou, C.J. Zhao, H. Na, *J. Power Sources* 162 (2006) 51–57.
- [31] S.L. Zhong, X.J. Cui, T.Z. Fu, H. Na, *J. Power Sources* 180 (2008) 23–28.
- [32] D.S. Phu, C.H. Lee, C.H. Park, S.Y. Lee, Y.M. Lee, *Macromol. Rapid Commun.* 30 (2009) 64–68.
- [33] L.Y. Jang, O.H. Kweon, K.E. Kim, G.J. Hwang, A.B. Moon, A.S. Kang, *J. Power Sources* 181 (2008) 127–134.
- [34] K. Matsumoto, T. Hirabayashi, T. Harada, H. Matsuoka, *Macromolecules* 38 (2005) 9957–9962.
- [35] D.S. Kim, M.D. Guiver, S.Y. Nam, T.I. Yun, M.Y. Seo, S.J. Kim, H.S. Hwang, J.W. Rhim, *J. Membr. Sci.* 281 (2006) 156–162.
- [36] C.W. Lin, R. Thangamuthu, C.J. Yang, *J. Membr. Sci.* 253 (2005) 23–31.
- [37] M.A.J. Van Der Mee, J.G.P. Goossens, M. Van Duin, *J. Polym. Sci. Part A: Polym. Chem.* 46 (2008) 1810–1825.
- [38] H.T. Li, Z.M. Cui, C.J. Zhao, J. Wu, T.Z. Fu, Y. Zhang, K. Shao, H.Q. Zhang, H. Na, W. Xing, *J. Membr. Sci.* 343 (2009) 164–170.
- [39] S. Takamuku, K. Akizuki, M. Abe, H. Kanesaka, *J. Polym. Sci. Part A: Polym. Chem.* 47 (2009) 700–712.
- [40] T.J. Peckham, J. Schmeisser, M. Rodgers, S. Holdcroft, *J. Mater. Chem.* 17 (2007) 3255–3268.