Preparation and evaluation of a proton exchange membrane based on crosslinkable sulfonated poly(ether ether ketone)s

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Abstract

A series of crosslinkable sulfonated poly(ether ether ketone)s (SPEEKs) containing propenyl groups were synthesized by aromatic nucleophilic substitution reactions. ^{1}H NMR spectra were used to confirm the DS of polymers. The resulting polymers showed high molecular weights and good solubility and could be cast into tough membranes. The SPEEK membranes in acid form possessed good thermal stabilities and mechanical properties. The methanol diffusion coefficients ranged from 9.70×10^{-8} to $4.18 \times 10^{-7} \, cm^2 \, s^{-1}$, which were much lower than that of Nafion 117® $(2.38 \times 10^{-6} \, cm^2 \, s^{-1})$. The proton conductivity of the SPEEK-3 membranes $(0.072 \, S \, cm^{-1})$ was close to that of Nafion 117® $(0.083 \, S \, cm^{-1})$ at 85 °C under the same testing conditions. These results showed that the synthesized materials might have potential applications as the proton exchange membranes for PEMFCs.
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Keywords: SPEEKs; Crosslinkable; Proton exchange membrane

1. Introduction

Proton exchange membranes fuel cells (PEMFCs) have been identified as promising power sources in the fields which require clean, quiet and portable power as well as high energy conversion efficiency scalability and environmental safety [1–3]. The proton exchange membrane (PEM) is a key component in the PEMFC, which transfers protons from the anode to the cathode and prevents direct mixing of the fuel and the oxidizer. Hence, it should possess a suitable combination of the following properties: high proton conductivity, excellent mechanical properties, good thermal and chemical stability as well as low methanol diffusion. The most common commercially available proton exchange membrane is the fluorinated ionomer such as Nafion® produced by DuPont. Although this shows suitable chemical and physical properties, high cost, low conductivity at low humidity or high temperature and high methanol diffusion have limited its usage [1–4].

To meet the commercial needs for a less expensive and more versatile polymer electrolyte, intensive research has been car-

ried out on the development of new alternative PEM materials for PEMFC applications, such as sulfonated poly(ether ether ketone) (SPEEK) [5,6], sulfonated polysulfone (SPSf) [7,8], sulfonated poly(phenylene oxide) (SPPO) [9] and sulfonated polyimide (SPI) [10–12], etc. Recently, several groups [6,13–16] have reported on the synthesis of sulfonated poly(ether ether ketone)s and proven that sulfonated poly(ether ether ketone)s are a prospect for PEM applications owing to their good thermal stability and appropriate conductivity at high sulfonatation degrees (DS). However, a number of investigations have demonstrated that water uptake increased with the increase of DS.

Too much water uptake will result in the loss of mechanical strength and higher methanol diffusion. Hence the functions of these SPEEK membranes under fuel cell conditions becomes questionable.

Crosslinking is thought to be an effective approach to reduce water swelling and methanol crossover, as well as a means to enhance mechanical strength [17–19]. Therefore, we prepared crosslinkable SPEEK copolymers. In this paper, a series of crosslinkable SPEEKs containing propenyl groups were prepared by the direct copolymerizations of sulfonated monomers and were evaluated for proton exchange membrane fuel cell applications. These kind of SPEEKs has reactive double bonds, which could crosslink and be grafted by UV irradiation. In future

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work, we will further study the effect of crosslinking and grafting on the performances of the SPEEK proton exchange membranes in the FC domain.

2. Experimental

2.1. Materials

Diallyl bisphenol A was supplied by the East China University of Science and Technology. 4,4′-Difluorobenzophenone was provided by the Longjing Chemical plant. 5,5′-Carbonyl-bis(2-fluorobenzenesulfonate) was synthesized by sulfonation of 4,4′-difluorobenzophenone according to the procedure described by Wang et al. [20]. Potassium carbonate was dried at 180 °C in vacuum for 10 h before used. All the other reagents and solvents were obtained commercially and used without further purification.

2.2. Synthesis and characterization of the crosslinkable SPEEKs

2.2.1. Synthesis of polymer

Sulfonated poly(ether ether ketone)s were synthesized via nucleophilic substitution reactions of diallyl bisphenol A (monomer *l*), with 4,4′-difluorobenzophenone (monomer *k*) and 5,5′-carbonyl-bis(2-fluorobenzenesulfonate) (monomer *m*) in DMSO/toluene solvent system (Scheme 1). The reaction temperature was first kept at 140 °C for about 3 h to remove the water produced in this system, then was slowly raised to 180 °C and maintained at that temperature for 16 h. The product was purified with boiling deionized water and dried in a vacuum oven at 70 °C for 3 day.

2.2.2. Characterization of polymer

FT-IR measurements were performed with a Nicolet Impact 410 Fourier transform infrared spectrometer. The ^{1}H NMR spectra were measured on an AVANCZ 500 spectrometer at 298 K with deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent and tetramethylsilane (TMS) as the standard. The intrinsic viscosities of the polymers were measured at $5.00\,g\,L^{-1}$ in DMF at 25 °C (±1) using an Ubbelohde viscometer. Differential Scanning Calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 821e instrument at a heating rate

of $10\,°C\,min^{-1}$ under N$_2$ flow. Thermogravimetric (TGA) data were obtained on a Pyris 1TGA (Perkin Elmer). Before testing, all the polymers were preheated to 150 °C and kept at this temperature for 20 min to remove any residual moisture and solvent. After that, the samples were cooled to 100 °C and then reheated to 700 °C with a heating rate of $10\,°C\,min^{-1}$ in N$_2$ flow.

2.3. Membrane preparation and characterization

2.3.1. Membrane preparation

The dried sulfonated polymers were first dissolved in DMF to form 10–15% solutions and then filtered. The filtrates were cast onto glass substrates and dried in vacuum at 70 °C for 3 days. The resulting membranes were removed from the glass plate and were acidified in 1.0 M HCl solutions overnight, the membranes in acid form were then rinsed with deionized water to remove any excess acid.

2.3.2. Membrane characterization

The low-field signals (6.8–8.5 ppm) were characteristic resonances of the aromatic hydrogen atoms. The signal at 8.2 ppm was assigned to the aromatic hydrogen atoms (H$_1$) at the ortho position to the electron-withdrawing –SO$_3$Na groups. The DS of the polymer was estimated by ^{1}H NMR according to known references [21,22] and was calculated by the following equation:

$$\frac{DS}{14 - DS} = \frac{A_{H_1}}{\sum A_H} \tag{1}$$

where A_{H_1} was the peak area of H$_1$, $\sum A_H$ was the integral peak area of the signals corresponding to the other aromatic hydrogen.

The IEC values of the membranes were determined by classical titration and calculation method [23]. First, the membrane in acid form was transferred into the sodium form by immersing into 50 mL 1.0 M NaCl solution for 24 h. Thus, the protons of the sulfonic acid groups were exchanged with sodium ions. Then the exchanged protons were titrated with 0.01 M NaOH solution.

The titrated IEC was determined from formula:

$$IEC = \frac{C \times V}{M} \times 100 \tag{2}$$

where C was the concentration of NaOH, V the volume of NaOH, and M was the weight of the membrane.
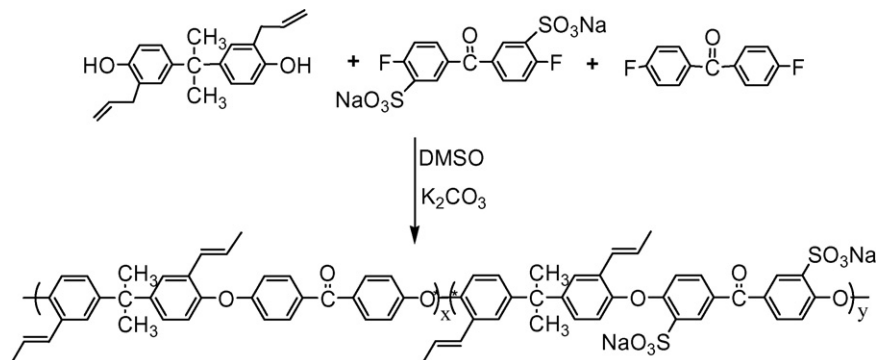
Scheme 1. The synthesis of SPEEK polymers.

The theoretical IEC value that calculated from DS was obtained by:

$$IEC = \frac{DS \times 1000}{486 + 80DS} \quad (3)$$

All the membranes in acid form were vacuum-dried at 100 °C for 24 h before testing their water uptake, then quickly weighed on a microbalance. Subsequently, the dried membranes were immersed into deionized water for 24 h at 25, 80 and 100 °C, respectively. Then the membranes were taken out, wiped with blotting paper and quickly weighed on a microbalance.

The water uptake was calculated from formula:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (4)$$

where W_{wet} and W_{dry} were the weights of wet and corresponding dried membranes, respectively.

The hydrophilicity of membrane surface was characterized based on the water contact angle measurement using a sessile drop method. Deionized water was dropped on a dry membrane with a micro syringe in atmosphere and contact angle was measured on a JC2000C1 contact angle equipment. For each sample, more than 10 contact angles were averaged to get a reliable value.

The mechanical properties of membranes were measured using SHIMADIU AG-I 1 KN at the speed of 2 mm min^{-1}. The size of membrane was 15 mm × 4 mm. For each measurement, at least five samples were used and their average value was calculated.

Methanol diffusion coefficients of membranes were measured using a liquid permeability cell described in the literature [6,24]. This cell consisted of two reservoirs, which were separated by a vertical membrane. 1.0 M methanol was placed on one side of the cell and water was placed on the other side. The magnetic stirrers were used continuously during the measurement. Prior to testing, the membranes were immersed in deionized water for 24 h. Methanol concentrations in the water cell were determined by using a SHTMADU GC-8A chromatograph. The methanol diffusion coefficient was calculated in formula:

$$C_{\text{B}}(t) = \frac{A}{V_{\text{B}}} \frac{DK}{L} C_{\text{A}}(t - t_0) \quad (5)$$

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 feed and in permeate, respectively. DK was the methanol diffusion coefficient.

Proton conductivity (σ) in water-equilibrated membranes was measured by SI 1260 + SI 1287 impedance analyzer over the frequency range from 10^2 to 10^6 Hz. A sample of membranes (2 cm × 1 cm) was clamped in a frame, providing the electrical contact with two stainless steel electrodes (the distance between two electrodes was 1 cm). Then the membrane in the frame was exposed to distilled deionized water during the experiments. The proton conductivity was calculated from the following equation:

$$\sigma = \frac{d}{Rtw} \quad (6)$$

where d was the distance between the electrodes, t and w were the thickness and width of the membranes, respectively. R was the resistance value from the impedance data.

3. Results and discussion

3.1. Characterization of the sulfonated polymers

The crosslinkable sulfonated poly(ether ether ketone)s were synthesized via nucleophilic substitution reactions (Scheme 1). FTIR and ^{1}H NMR spectra were used to confirm the chemical structure of SPEEKs. Fig. 1 shows the comparative FTIR spectra of SPEEKs with different DS. The absorption bands at 1027 and 1079 cm^{-1} were characteristic of the symmetric and asymmetric O=S=O stretching vibrations of sodium sulfonate groups, respectively. These two characteristic peaks increased with DS. No absorption peaks of allyl were found in 910 and 990 cm^{-1}. Whereas, the absorption peak at 965 cm^{-1} proved the presence of propenyl. It was because that the allyl was isomerized to the propenyl under the alkalescent situation. This phenomenon was in accordance with the studies of Price and Snyder [25] and Kesslin and Orlando [26] (Fig. 2).

The molecular structure of SPEEKs was also confirmed with ^{1}H NMR spectra [^{1}H NMR (dimethyl sulfoxide-d_6 (DMSO-d_6), d, ppm)]. The ^{1}H NMR spectra from 6.0 to 8.5 ppm for SPEEK-3 exemplified the structures of the SPEEKs, as depicted in Fig. 2. The ortho proton peak (1) to the sulfonate group appeared at the most downfield, which was attributed to electron-withdrawing –SO$_3$Na groups. The ratio of the peak areas (2 and 2′ to 3 and 3′) was about 1:1, confirming the existence of the propenyl group. In conclusion, both FTIR and ^{1}H NMR spectra showed that the crosslinkable sulfonated poly(ether ether ketone)s were synthesized as desired.

The polymerization results and the analytical data were summarized in Table 1. It can be seen from Table 1 that the polymers exhibited high intrinsic viscosity, which indicated that the polymers have high molecular weights. The higher ratio of 5,5′-carbonyl–bis(2-fluorobenzenesulfonate) to 4,4′-
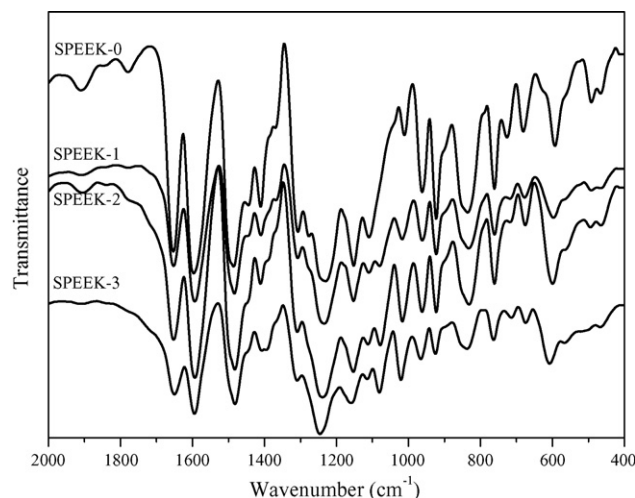

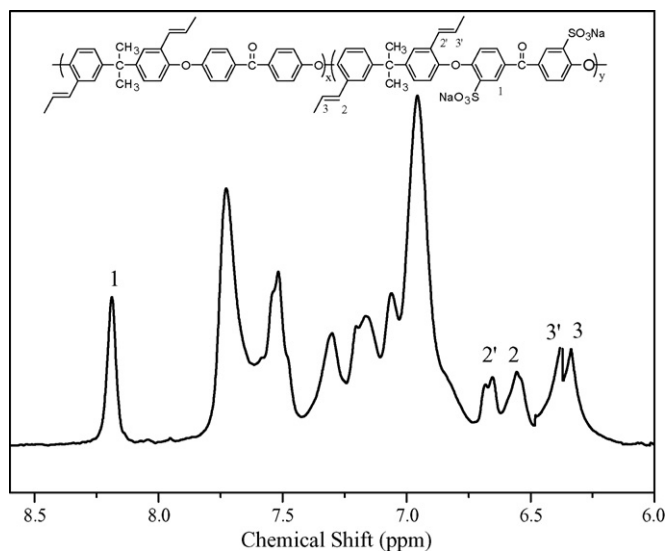Fig. 1. Comparative FT-IR spectra of SPEEKs.
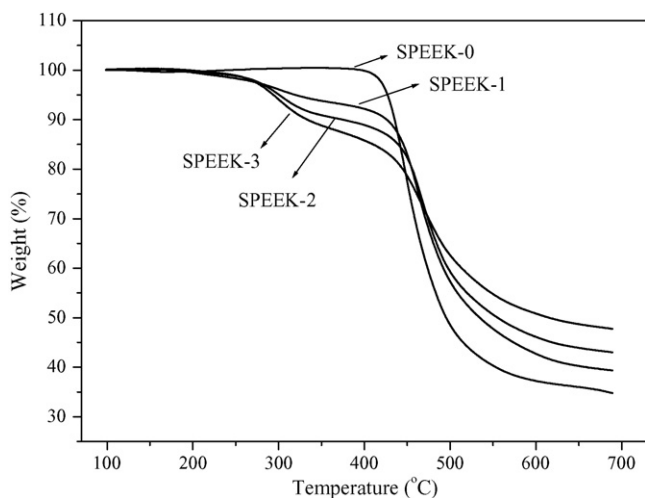
Fig. 2. ^{1}H NMR spectrum of SPEEK-3 in DMSO-d_6.

Fig. 3. TGA curves for SPEEKs in acid form.

Table 2
The solubility behavior of SPEEKs

Solvent	SPEEK-0	SPEEK-1	SPEEK-2	SPEEK-3
H$_2$O	–	–	SW	SW
Methanol	–	–	–	–
Chloroform	+	SW	–	–
DMF	+	+	+	+
DMSO	+	+	+h	+h
NMP	+	+	+	+

+: Soluble at room temperature; +h: soluble on heating; –: insoluble; SW: swelling.

the steric hindrance of sodium sulfonate groups may decrease the reactivity. The former factor may be dominant in this reaction [8]. This might also suggest that the polymer chain was not degraded during the reaction. A similar result has been mentioned in the literature [27,28].

The solubility behavior of the sulfonated polymers in selected solvents are shown in Table 2. All the polymers could be easily dissolved in a wide range of solvents, such as DMF, DMSO and NMP. Solubility of the polymers in water increased with the increase of DS: SPEEK-0 and SPEEK-1 were insoluble, yet SPEEK-2 and SPEEK-3 swelled in water. It was because that the presence of sodium sulfonate groups in the polymer chain that bring strong solvation between water and the polymer, which facilitated the dissolution of the polymer in water. The solvation became much stronger when the content of sodium sulfonate groups increased, hence the solubility of the polymers in water increased with elevation of the sulfonated degree.

DSC and TGA measurement were carried out to testify the thermal properties of the polymer. The values of the glass transition temperatures (T_g) of polymer are showed in Table 1. Obviously, the T_g values increase with the increase of DS. This is because the introduction of sodium sulfonate enhanced the intermolecular interaction through the polar ionic sites and molecular bulkiness. Both of these hinder internal rotation and further lead to the increase of the glass transition temperature [29,30]. In particular for SPEEK-3, no glass transition temperature was observed in a temperature range of 100–350 °C, probably because of strong intermolecular interaction due to the high content of sodium sulfonate groups. Similar phenomena were also observed for other sulfonated poly(ether ether ketone)s [31,32].

The thermal stabilities of this series of polymers in acid form were investigated by TGA measurement and shown in Fig. 3

difluorobenzophenone caused the higher intrinsic viscosity of the polymer. This was because two major factors may compete with each other to affect the reactivity. First, the electron-withdrawing sulfonate groups may increase the density of positive charge of the carbon atom connecting with the fluorine atom, and hence enhance the electrophilic reactivity; on the other hand,

Table 1
Data on sulfonated polymers

Polymer	m (mmol)	k (mmol)	m/k	DS[a]	DS[b]	Yield (%)	η_{sp}/c (dL g^{-1})	T_g (°C)	$T_{5\%loss}$ (°C)	$T_{10\%loss}$ (°C)
SPEEK-0	0	100	0:10	0	–	96	0.90	146	427	435
SPEEK-1	20	80	2:8	0.4	0.36	94	1.06	163	331	428
SPEEK-2	40	60	4:6	0.8	0.81	95	1.11	219	305	379
SPEEK-3	50	50	5:5	1.0	0.97	96	1.28	–	294	335

m: 4,4′-difluorobenzophenone; k: 5,5′-carbonyl–bis(2-fluorobenzenesulfonate); η_{sp}/c: measured at a concentration of 5.00 g L^{-1} in DMF at 25 ± 0.1 °C; –: not detected between 50 and 350 °C.

[a] DS, sulfonated degree obtained from monomer ratio.
[b] DS, sulfonated degree obtained from ^{1}H NMR data.

Table 3
The analytic data of SPEEK membranes

Polymer	SPEEK-1	SPEEK-2	SPEEK-3	Nafion 117®
IEC[a] (mmol g^{-1})	0.624	1.429	1.700	–
IEC[b] (mmol g^{-1})	0.699	1.489	1.736	0.92
Water uptake (%) (25 °C)	13.6	20.9	33.6	22
Water uptake (%) (80 °C)	17.3	42.7	69.2	34
Water uptake (%) (100 °C)	26.2	76.8	107.3	–
Contact angle (°)	79	59	56	–
Methanol diffusion coefficient (cm^2 s^{-1})	9.70×10^{-8}	3.09×10^{-7}	4.18×10^{-7}	2.38×10^{-6}
Proton conductivity (S cm^{-1}) (25 °C)	0.008	0.012	0.025	0.05
Proton conductivity (S cm^{-1}) (85 °C)	0.028	0.046	0.072	0.083

[a] IEC obtained by titration.
[b] IEC obtained by calculation from DS.

and Table 1. The pure SPEEK-0 showed better thermal stability than SPEEKs. SPEEK-0 had only one weight loss step with an onset at around 420 °C, whereas all of the SPEEKs in acid form exhibited two step degradation patterns. The first weight loss occurring at around 300 °C was attributed to the splitting-off of the sulfonate acid groups. The second degradation step starting at around 420 °C and corresponded to the decomposition of the main chain. The TGA curve clearly indicated that this kind of SPEEK had good thermal stability.

3.2. DS, IEC and water uptake of the SPEEK membranes

As shown in Table 1, the calculated DS values from ^{1}H NMR spectra were in agreement with the expected DS derived from the monomer ratios. This result indicated that the sodium sulfate groups were introduced to the SPEEKs quantitatively and the DS values of SPEEKs can be easily controlled by adjusting the molar ratio of monomer m to monomer k.

The IEC of the membrane played a crucial role in deciding the water uptake and proton conductivity. Table 3 lists the titrated and calculated IEC values of SPEEK-1 to SPEEK-3. The IEC determined by titration was in good agreement with the values calculated from DS, illustrating that the pendant sulfonate groups were successfully attached to the polymer chains via sulfonated monomer copolymerization without any side reactions.

It is well known that water serves the transport of protons in a proton exchange membrane and therefore influences the proton conductivity of the membrane. So the membrane must be able to absorb enough water for this purpose. However, excess water uptake can lead to the deteriorating of mechanical properties of membrane. This will limit the practical application of the membrane in fuel cells. Hence, it was very significant to determine the water uptake of SPEEK membranes. Table 3 shows the water uptake of membranes at different IECs and temperature. It is apparent that the water uptake of membranes has an increasing tendency with increment of the IEC and temperature, and the conductivity of the hydrated membrane is improved [5,33]. Due to the hydrophilic property of sulfonated groups, the water uptake increases sharply with elevated temperature in higher IEC membranes than in lower IEC membranes.

3.3. Contact angle

Water contact angle has been widely used to characterize the relative hydrophilicity/hydrophobicity of membrane surface, and is expected to govern the surface wettability. The results of the contact angle measurements are listed in Table 3. As shown in Table 3, the contact angles of all membranes were less than 90°, meaning that each membrane had a hydrophilic surface. The contact angle decreased from 79 to 56° for the membrane from SPEEK-1 to SPEEK-3, which implies that the hydrophilic property of membranes is improved [34,35]. This result was attributed to the increase of sulfonated groups at the surface of membranes. The difference in hydrophilic properties of membranes might result in different water content of membranes, which further influenced the proton conveyance in membranes.

3.4. Mechanical strength

It is essential for PEMs to possess adequate mechanical strength. The typical mechanical properties of the membranes were evaluated and listed in Table 4. For the membranes prepared from SPEEK-1 to SPEEK-3, the tensile modules were 755, 809, 876 and 766 MPa, respectively and the tensile strengths were 43–58 MPa. These data indicated that the SPEEK membranes had good mechanical properties and they were tough enough to be used as functional proton exchange membrane materials. We also noticed that the amount of sodium sulfonated groups had no obvious effect on the mechanical properties, which was different from the literature [36,37]. It might be because the mechanical properties of membranes are influenced by various factors, such as the structure, the content of sodium sulfonate

Table 4
Mechanical properties of SPEEK membranes

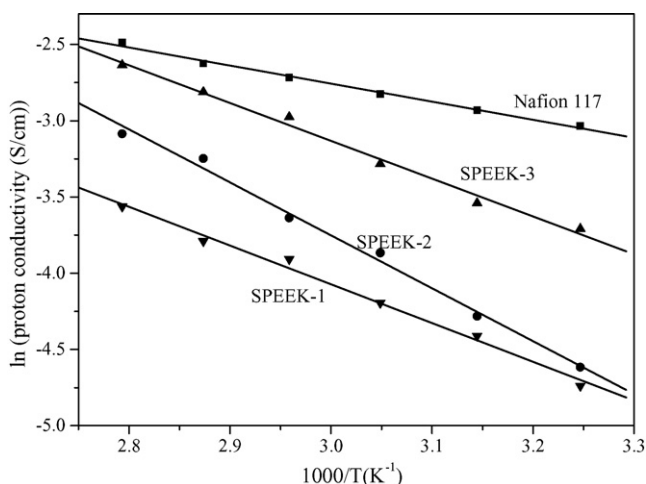| Membrane	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation (%)
SPEEK-0	755.47	58.25	7.29
SPEEK-1	809.69	43.96	10.13
SPEEK-2	876.78	47.93	8.28
SPEEK-3	766.75	46.20	7.31

Fig. 4. The proton conductivities of SPEEK membranes at different temperatures.

groups, the solvents used during membranes casting, the equality of membranes and so on.

3.5. Methanol diffusion coefficient

The methanol diffusion coefficients of the SPEEK membranes at room temperature are shown in Table 3. The membranes exhibited a methanol diffusion coefficient in the range of 9.70×10^{-8} to 4.18×10^{-7} cm^2 s^{-1} depending on the DS, which is much lower than Nafion 117® (2.38×10^{-7} cm^2 s^{-1}). The different methanol diffusion coefficient of SPEEK and Nafion® membranes can be explained by the difference in the microstructures. The sulfonate groups in SPEEK were dispersed throughout the polymer matrix and the polymer backbone had less flexibility, which made phase separation unlikely and sulfonate groups may be in the environment of "multiplets". Whereas the sulfonate groups in Nafion® were on the side chains of polymers, which may easily form hydrophobic/hydrophilic domains, especially in the presence of water, and the sulfonate groups may be mostly in the environment of a "cluster" [38,39]. Hence SPEEK may provide a smaller transport channel than Nafion®, which led to a much lower methanol diffusion coefficient. The reduction of SPEEK membrane methanol crossover could indicate a potential feasibility as an excellent electrolyte for DMFC.

3.6. Proton conductivity

One of the most essential properties of proton exchange membrane is proton conductivity. Fig. 4 and Table 3 show the proton conductivity of SPEEK membranes and Nafion 117® dependent on temperature at 100% relative humidity. In this study, the proton conductivity of Nafion 117® was obtained in our laboratory. Proton conductivities of these SPEEK membranes were strongly dependent on their IEC values. For instance, from SPEEK-1 to SPEEK-3, higher IECs tended to have higher proton conductivities at the same temperature. Although most of the membranes (SPEEK-2 and SPEEK-3) had a much larger IEC

value than Nafion 117® (0.91 mmol g^{-1}), their proton conductivities were lower than Nafion 117®. This was probably due to the different distributions of ion domains in the membrane [40,41]. Nafion® has unique ion-rich channels (clusters) which allow the ions to transport more easily than the SPEEK membranes. For all the membranes, the proton conductivity increased with the increase in temperature. Take SPEEK-3 for example, the proton conductivity increased from 0.025 to 0.072 S cm^{-1} when the temperature increased from 25 to 85 °C. The proton conductivities of the all membranes increased more quickly than the Nafion 117® membrane with increasing temperature. This is due to the higher hydrophilicity of the SPEEK polymer backbone compared with the perfluorinated backbone of Nafion® as well as the relatively strong interaction between the water molecules and the sulfonic acid groups [34]. All these would improve water absorbability and proton conductivity of SPEEK membranes at elevated temperatures.

4. Conclusions

A series of crosslinkable sulfonated poly(ether ether ketone)s containing propenyl groups were synthesized successfully by aromatic nucleophilic substitution polycondensation with 5,5′-carbonyl–bis(2-fluorobenzenesulfonate) and 4,4′-difluorobenzophenone at various ratios and were then cast into tough membranes from their solutions. ^{1}H NMR spectra were used to confirm the DS of polymers. SPEEK membranes in acid form possessed good thermal stabilities and mechanical properties. The titrated IEC values were close to the theoretical values, illustrating that sulfonate groups were successfully attached to the polymer chains via sulfonated monomer copolymerization without any side reactions. The proton conductivities of SPEEK membranes with IEC from 0.624 to 1.700 ranged from 0.008 to 0.025 S cm^{-1} at 25 °C and from 0.028 to 0.072 S cm^{-1} at 85 °C. The SPEEK membranes exhibited much lower methanol diffusion coefficients compared with a Nafion® membrane. All this suggests that the SPEEK membranes are promising in proton exchange membranes fuel cell (PEMFC) applications. In addition, these kind of SPEEKs have reactive double bonds, which could crosslink and be grafted by UV irradiation. Further investigations are in progress on the crosslinking and grafting of membranes. In the near future, we will report the performance of these membranes.

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