Crosslinked SPEEK/AMPS blend membranes with high proton conductivity and low methanol diffusion coefficient for DMFC applications

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Abstract

The crosslinked sulfonated poly (ether ether ketone)/2-acrylamido-2-methyl-1-propanesulfonic acid (SPEEK/AMPS) blend membranres were prepared and evaluated as proton exchange membranes for direct methanol fuel cell (DMFC) applications. The structure and morphology of SPEEK/AMPS membranes were characterized by FTIR and SEM, respectively. The effects of crosslinking and AMPS content on the performance of membranes were studied and discussed in detail. The proton conductivity and methanol diffusion coefficient of SPEEK/AMPS membranes increased gradually with the increase of AMPS content. Most SPEEK/AMPS membranes exhibited higher proton conductivity than Nafion® 117 ($0.05 \, S \, cm^{-1}$ at $25\,°C$). However, all the membranes possessed much lower methanol diffusion coefficient compared with Nafion® 117 ($2.38 \times 10^{-6} \, cm^2 \, s^{-1}$) under the same measuring conditions. Even the methanol diffusion coefficient ($8.89 \times 10^{-7} \, cm^2 \, s^{-1}$) of SPEEK/AMPS 30 sample with the highest proton conductivity ($0.084 \, S \, cm^{-1}$ at $25\,°C$) was only about one third of that of Nafion® 117. The selectivity of all the SPEEK/AMPS membranes was much higher in comparison with Nafion® 117 ($2.8 \times 10^4 \, S \, s \, cm^{-3}$). In addition, the SPEEK/AMPS membranes possessed relatively good thermal and hydrolytic stability. These results suggested that the SPEEK/AMPS membranes were particularly promising to be used as proton exchange membranes in DMFCs, and the high proton conductivity, low methanol diffusion coefficient and high selectivity were their primary advantages for DMFC applications.
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1. Introduction

The direct methanol fuel cells (DMFCs) are promising energy conversion devices by virtue of their high energy efficiency, stable and simple operating conditions at a relatively low temperature, and no requirement of fuel reforming process [1–3]. The proton exchange membrane (PEM) is one of the most important components in DMFC. The PEMs with high proton conductivity have huge potential in DMFC applications. Nevertheless, while the PEMs possess high proton conductivity, they usually show poor methanol barriers [4–6]. Currently, perfluorinated copolymers such as Nafion® are the most common PEMs used in DMFCs owing to their excellent chemical and physical stabil-ity and high proton conductivity. However, the expensive cost, high methanol crossover and difficulty in synthesizing and pro-cessing have limited their wide applications [7,8]. In particular, the high methanol crossover causes not only catalyst poison-ing but also fuel consumption and energy efficiency loss [9,10]. In order to obtain high proton conductivity and mitigate the effects of methanol crossover on DMFC performance, many efforts have been devoted to modify Nafion® membranes or to develop new proton exchange membranes [11–13]. In recent years, some new PEMs have been successfully proposed such as sulfonated aromatic membranes [14,15], graft membranes [16], crosslinked [17,18] and blend membranes [19,20]. Among them, sulfonated poly (aryl ether ketone)s have attracted considerable attention because of their good mechanical strength and high chemical and thermal stabilities [21,22]. In our previous study, the synthesis and properties of a series of sulfonated poly (ether ether ketone)s (SPEEKs) containing propenyl groups have been

reported [23]. Like other sulfonated aromatic main-chain polymers, these SPEEKs require a certain acidic groups to achieve high proton conductivity. However, too high loading of acidic groups induces excessive water swelling and methanol diffusion, which will weaken the membranes and limit their practical application in DMFCs. Crosslinking is a feasible and effective method to reform proton exchange membranes, which cannot only suppress water swelling and methanol diffusion but also improve stability and mechanical strength of membranes. Nevertheless, these good properties are obtained usually by sacrificing proton conductivity [24,25]. Considering cost and availability, one of the preferred routes to resolve this problem is to incorporate another inexpensive material with acidic groups into crosslinkable SPEEK. Thus, it is possible to improve the performance of membranes by choosing a suitable additive and crosslinking.

The main aim of this study is to obtain the PEMs with high proton conductivity and low methanol diffusion coefficient for DMFC applications. To achieve this objective, the cheap and easily available 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) was introduced into the SPEEK matrix containing propenyl groups. By introducing AMPS, the proton conductivity of membrane would be improved greatly due to the superior ability of sulfonic acid groups originated from AMPS in supporting proton conduction [26]. By crosslinking, the water swelling and methanol diffusion could be restricted and stability of membranes can be enhanced owing to the formation of compact network structure.

In this paper, several properties of the crosslinked SPEEK/AMPS blend membranes were amply described to evaluate their feasibility as proton exchange membranes in DMFCs, including water uptake, methanol diffusion coefficient, proton conductivity, selectivity, thermal and hydrolytic stabilities, etc.

2. Experimental

2.1. Materials

The sulfonated poly (ether ether ketone)s (SPEEKs) containing propenyl groups were prepared by aromatic nucleophilic substitution reaction. Detailed synthesis and characterization of polymers were reported by our previous work [23]. The structure of SPEEK is shown in Scheme 1. 2-Acrylamido-2-

Table 1
Compositions of membranes

Notation	SPEEK (wt.%)	AMPS (wt.%)	Irradiation time (min)	Thickness (μm)
SPEEK	100	0	0	142 ± 5
SPEEK-1	100	0	20	150 ± 3
SPEEK/AMPS 10	90	10	20	124 ± 3
SPEEK/AMPS 15	85	15	20	140 ± 6
SPEEK/AMPS 20	80	20	20	133 ± 2
SPEEK/AMPS 25	75	25	20	124 ± 5
SPEEK/AMPS 30	70	30	20	136 ± 3

methyl-1-propanesulfonic acid (AMPS) was used as received from Aldrich. All the other reagents and solvents were obtained commercially and used without further purification.

2.2. PEM preparation

The crosslinked SPEEK/AMPS blend membranes were prepared by solution casting method. First, the SPEEK and AMPS were dissolved in DMF to form 10–15% solution. Then benzophenone (BP) and triethylamine (TEA) as the photo-initiator system were added to the solution. The resulting mixture was stirred continuously until a transparent solution was obtained. Then the solution was poured into a glass substrate and dried in vacuum at 70 °C for 3 days. After solvent evaporation, the dense and homogeneous membrane was obtained. Followed, the dried membrane was irradiated for 20 min in a 600 W UV light.

The acid form membranes were obtained by immersing the sodium form membranes in 1.0 M HCl solution overnight, afterwards the membranes were rinsed with deionized water to remove any excess acid and were immersed in deionized water for at least 1 month before measurements. The membranes thus prepared were designated as SPEEK/AMPS X, where X is the AMPS content (wt.%) in the membrane. Compositions of the membranes are listed in Table 1.

2.3. Characterization

2.3.1. Structural characterization

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Impact 410 Fourier transform spectrometer using KBr pellets.
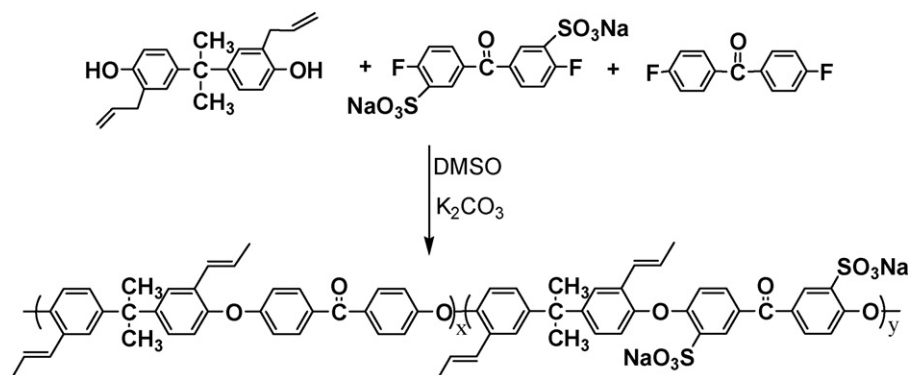
Scheme 1. The structure of SPEEK.

The morphology of the membranes was investigated using a SHIMADZU SSX-550 scanning electron microscope (SEM) at an accelerating voltage of 15 kV. Before preparing the samples used in SEM measurement, all the membranes were soaked in 85 °C deionized water for at least 1 week. The samples were fractured in liquid nitrogen and the fractured surfaces were coated by Au prior to SEM measurements.

2.3.2. Contact angle

The surface hydrophilicity of the membranes was determined by measuring the water contact angle on a JC2000C1 contact angle equipment. All the measurements were carried out using a sessile drop method and at least 10 contact angles were averaged to get a reliable value for each sample.

2.3.3. Water uptake

The water uptake was determined as follows. Before testing, the acid form membranes were vacuum-dried at 100 °C until constant weight (W_{dry}) was obtained. The dried membranes were immersed in deionized water for 24 h at 25 and 80 °C, respectively. Then the membranes were taken out and immediately weighed (W_{wet}) after wiping out the surface water. The water uptake was calculated using the expression:

$$\text{Water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%.$$

2.3.4. Thermal stability

The thermal stability of the membranes was evaluated through the thermogravimetric analysis (TGA) experiment on a Pyris 1TGA (Perkin-Elmer). Before measurement, the samples were preheated to 150 °C and kept at this temperature for 20 min to remove any residual moisture and solvent. Then the samples were cooled to 100 °C and reheated to 650 °C at 10 °C min^{-1} in N_2 flow.

2.3.5. Methanol diffusion coefficient

The methanol diffusion coefficient was measured using a glass diffusion cell [27]. The cell consisted of two compartments that were separated by a vertical membrane. Methanol and water were placed on the two sides of the diffusion cell, respectively. The magnetic stirrer was used in each compartment to ensure uniformity during the measurement. The increases of methanol concentration with time in the water compartment were measured using a SHIMADU GC-8A chromatograph.

The methanol diffusion coefficient was determined as follows:

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

where A (cm^2) and L (cm) are the effective area and the thickness of membrane, respectively. V_B (cm^3) is the volume of permeated compartment. C_A and C_B (mol L^{-1}) are the methanol concentration in feed and in diffusion compartment, respectively. DK is the methanol diffusion coefficient (cm^2 s^{-1}).

2.3.6. Proton conductivity

The proton conductivity in water-equilibrated membranes was measured using the AC impedance technology. The impedance measurement was carried out by SI 1260 + SI 1287 impedance analyzer over the frequency range from 10^2 to 10^6 Hz. Prior to testing, the sample was fully hydrated with distilled deionized water. Then the hydrated sample was sandwiched between two stainless steel electrodes and immersed in distilled deionized water to form a symmetric test cell where the temperatures were controlled.

The proton conductivity (σ) was calculated in equation:

$$\sigma = \frac{d}{Rtw}$$

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

2.3.7. Hydrolytic stability

To confirm the hydrolytic stability of the membranes, the proton conductivity was measured twice with an alternation of 2 weeks in 85 °C deionized water. The hydrolytic stability was estimated from the change of the proton conductivity before and after immersion.

3. Results and discussion

3.1. FTIR study

The structures of the SPEEK and SPEEK/AMPS 30 membranes were characterized by FTIR (Fig. 1). In the FTIR spectrum (a) of SPEEK, the absorption peaks at around 1027 and 1079 cm^{-1} were assigned to the symmetric and asymmetric O=S=O stretching vibration of sulfonic acid groups, respectively. The peak at 1650 cm^{-1} can be clearly observed due to the stretching of carbonyl groups, and the absorption peak at 965 cm^{-1} proved the presence of propenyl groups [23]. However, the FTIR spectrum (b) of SPEEK/AMPS 30
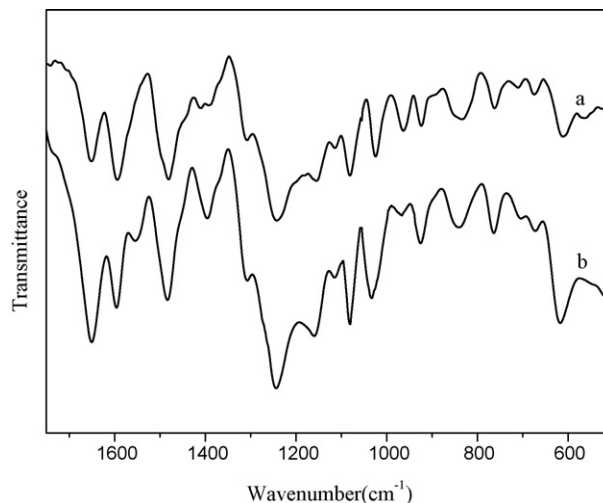

Fig. 1. FTIR spectra of (a) SPEEK and (b) SPEEK/AMPS 30.

showed some differences compared with that of SPEEK. The characteristic peak of carbonyl groups at $1650 \, cm^{-1}$ was overlapped and enhanced by the bending vibration of amide groups ($1650 \, cm^{-1}$) originated from AMPS. The new absorption peak at $1555 \, cm^{-1}$ could be clearly observed owing to the stretching vibration of amide groups of AMPS [28]. In addition, the intensity of the absorption peak at $965 \, cm^{-1}$ assigned to C=C double bonds obviously decreased by UV irradiation, which indicated the occurrence of crosslinking. Therefore, the changes in the FTIR spectrum of SPEEK/AMPS 30 compared with the SPEEK proved distinctly the formation of the crosslinked SPEEK/AMPS blend membrane.

3.2. Scanning electron microscopy (SEM)

The morphologies of membranes were investigated by SEM. Fig. 2 shows the cross-sectional SEM micrographs of the typical SPEEK/AMPS examples. For the two micrographs presented in Fig. 2 (SPEEK/AMPS 10 and SPEEK/AMPS 30), the dark regions correspond to the SPEEK-rich phase, and the bright regions correspond to the AMPS-rich phase. It can be seen from Fig. 2(a) that AMPS dispersed well and did not agglomerate in the membranes. It is also seen that the AMPS phase in Fig. 2(b) was denser than that in Fig. 2(a) and tended to become continuous due to the addition of more AMPS. Thus the more proton domains could interconnect to form the proton-conducting pathways, which will advantage the proton transport [29,30]. In this experiment, we added various contents of AMPS in SPEEK matrix. Before preparing the samples used in SEM measurement, all the membranes were soaked in 85 °C deionized water for at least 1 week. For the samples with AMPS content less than 30%, no visible pores can be observed in SEM micrographs even at magnifications of 40,000×, indicating that AMPS were well interacted with SPEEK and the synthesized membranes were dense. When the content of AMPS was increased to 35%, the micrograph revealed the presence of micropores (not shown in Fig. 2). The formation of micropores may be attributed to that a part of AMPS cannot interact with SPEEK in the case of high AMPS loading and hence dissolve in water during marinating. Through the analysis of SEM micrographs, it can be concluded that AMPS can disperse well and have relatively good stability

Table 2
Contact angle and water uptake of SPEEK, SPEEK-1 and SPEEK/AMPS membranes

Membranes	Contact angle (°)	Water uptake (%)	
		25 °C	80 °C
SPEEK	56.2 ± 1.2	33.6 ± 0.9	69.2 ± 1.3
SPEEK-1	–	14.2 ± 0.7	34.2 ± 1.0
SPEEK/AMPS 10	50.5 ± 1.7	22.5 ± 1.0	49.9 ± 1.6
SPEEK/AMPS 15	40.2 ± 2.0	35.4 ± 1.5	64.7 ± 2.2
SPEEK/AMPS 20	34.7 ± 1.1	45.1 ± 1.2	84.8 ± 0.9
SPEEK/AMPS 25	26.7 ± 1.2	57.3 ± 0.8	108.0 ± 1.8
SPEEK/AMPS 30	20.3 ± 0.8	74.2 ± 1.5	136.3 ± 2.1

in membranes when its content is below 35%. Hence, in this study, we chose 30% as the maximum of AMPS content.

3.3. Contact angle and water uptake behavior

The hydrophilicity of each sample can be easily obtained by water contact angle measurement. The static contact angles of the unmodified and the modified SPEEK membranes are summarized in Table 2. It is observed that the contact angle was especially sensitive, decreasing from 56.2° to 20.3° with increasing AMPS content in the membranes. This decreasing tendency was attributed to the increase of hydrophilicity of membrane surface due to the increment of hydrophilic sulfonic acid groups with the doping of AMPS.

The water uptake is a key consideration for proton exchange membranes. Too low water uptake reduces proton transport, while extreme water uptake causes overmuch swelling and the loss of dimensional stability. The water uptakes of various membranes are shown in Table 2. It can be seen from Table 2 that the water uptake of the non-crosslinked SPEEK membrane was 33.6% at 25 °C, whereas the crosslinked SPEEK-1 membrane exhibited only water uptake of 14.2% under the same conditions. This result clearly shows that crosslinking can induce structural reorientation and hinder chain mobility. Hence, the crosslinked membrane has denser network structure than uncrosslinked one, which leads to the reduction of enough space to retain water around sulfonic acid groups and eventually restricts the water uptake of the SPEEK-1 membrane. Compared with the SPEEK,
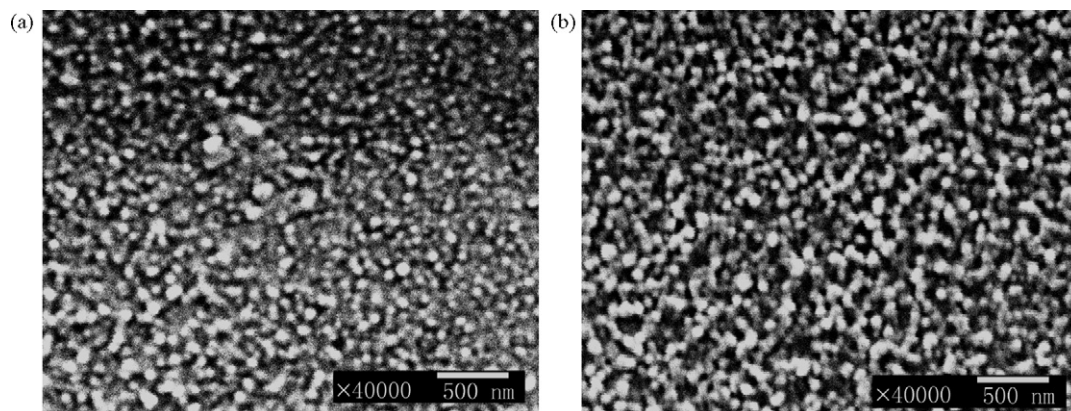

Fig. 2. Cross-sectional SEM micrographs of SPEEK/AMPS membranes: (a) SPEEK/AMPS 10, (b) SPEEK/AMPS 30.

the water uptake of SPEEK/AMPS membranes first decreased, and then gradually increased with the increment of AMPS. The water uptake value of SPEEK/AMPS 10 membrane was lower than that of the SPEEK but higher than that of SPEEK-1. That is, at lower AMPS content, the crosslinking seems to be dominant despite the hydrophilic sulfonic acid groups derived from AMPS increase the water absorption capacity. However, at higher AMPS content (above 10 wt.%), the water uptake of SPEEK/AMPS membranes was found to increase sharply with the rise of AMPS content. The increase can be reasonably attributed to the incorporation of more sulfonic acid groups. As the AMPS content increases, the hydrophilic sulfonic acid groups farther increase and the larger ion clusters could be formed, which leads to more absorption of water. Besides, the higher water uptake may be also caused by the greater flexibility of polymer chains or the microstructure of polymers because doping of plentiful AMPS reduces the density of crosslinking structure, which could allow more water to reside between the polymer chains [28]. These results also indicate that at higher AMPS content, the water uptake is more dependent on the sulfonic acid content than on the crosslinking. Based on the tendency of water uptake, we expected the membranes with higher AMPS content will possess higher proton conductivity. The proton conductivity behavior will be discussed carefully later.

3.4. Thermogravimetric analysis

Fig. 3 illustrates the thermogravimetric analysis spectra of the crosslinked SPEEK/AMPS blend membranes with different contents of AMPS. For all the membranes, two major weight loss stages were observed. The first weight loss was attributed to the splitting-off of the sulfonic acid groups. The second degradation step corresponded to the decomposition of the main chain. The SPEEK/AMPS membranes exhibited lower thermal stability than the pure SPEEK membrane. As shown in Fig. 3, with the increase of AMPS content from 0 to 30%, the 10% weight loss temperature decreased from 335 to 287 °C. In SPEEK/AMPS membranes, two major factors may compete with each other to affect the thermal stability. First, the increase of AMPS content
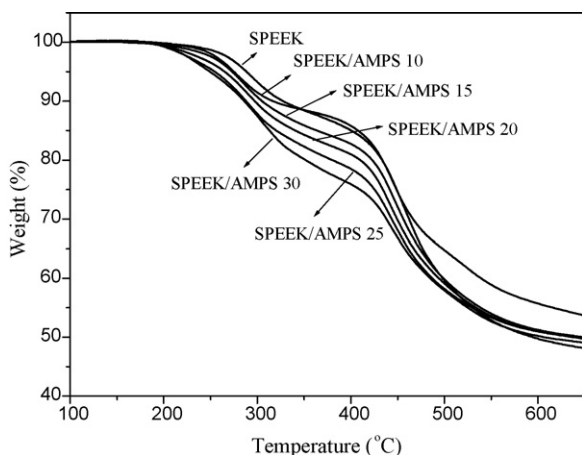

Fig. 3. TGA curves of SPEEK and SPEEK/AMPS membranes.

leads to the incorporation of more sulfonic acid groups and consequently the thermal stability decreases [31,32]. Contrary to this, when the polymer chains are crosslinked, the polymer cohesion and ordering increase, which results in the increase of thermal stability [18,33]. The former factor may be dominant in this study. Although the addition of AMPS causes the membrane to decompose at relatively low temperature, the thermal stability of SPEEK/AMPS membranes is still good enough to serve as the PEMs in DMFCs.

3.5. Methanol diffusion coefficient measurement

The methanol diffusion of PEMs is an important property for DMFCs. In DMFCs, the membranes with low methanol diffusion coefficient are required because methanol diffuses from the anode to the cathode leads to lower cell voltage and decreases fuel efficiency. The methanol diffusion coefficients of the SPEEK membranes with and without crosslinking as well as the SPEEK/AMPS membranes were measured and results are reported in Table 3. For comparison, the methanol diffusion coefficient of Nafion® 117 was also measured under the same experimental conditions. The SPEEK-1 membrane showed the lowest methanol diffusion coefficient (1.02×10^{-7} cm² s⁻¹) due to the effect of crosslinking. Crosslinking results in the formation of more compact network structure in the membrane, which reduces chain mobility and water uptake; hence the channels to pass methanol molecules are restricted. Compared with the SPEEK-1, the methanol diffusion coefficient of SPEEK/AMPS membranes gradually increased from 3.12×10^{-7} to 8.89×10^{-7} cm² s⁻¹ with the increment of AMPS content from 10 to 30%. This tendency was the same as the results of water uptake. The increase in AMPS content leads to incorporation of more hydrophilic sulfonic acid groups as well as formation of more and larger water absorption channels. Hence water and methanol could relatively easily go through the channels and water uptake and methanol diffusion coefficient are enhanced. So, the amount of AMPS should be controlled in order to restrict methanol diffusion. It is noticeable that the methanol diffusion coefficients in our membranes were significantly lower than that in Nafion® 117. Even for the SPEEK/AMPS 30 sample, the methanol diffusion coefficient was only about one third of that of Nafion® 117. This means that the SPEEK/AMPS membranes will be prospective to be used as candidate of Nafion® 117 in DMFCs.

3.6. Proton conductivity

From the point of application, the proton conductivity is clearly one of the most important properties of PEMs. The proton conductivities of the SPEEK, SPEEK-1 and SPEEK/AMPS membranes were measured at 100% relative humidity and are shown as a function of AMPS content and temperature in Table 3 and Fig. 4. For comparison, the proton conductivity of commercially available Nafion® 117 membrane in its fully hydrated state was also measured in our laboratory.

The proton conductivities of these membranes depended on various factors. First, it is found that the crosslinking signif-

Table 3
Methanol diffusion coefficient and proton conductivity of SPEEK, SPEEK-1 and SPEEK/AMPS membranes

Membranes	Methanol diffusion coefficient (10^{-7} cm^2 s^{-1})	Proton conductivity (S cm^{-1})		
		25 °C	85 °C[a]	85 °C[b]
SPEEK	4.18 ± 0.07	0.025 ± 0.001	0.072 ± 0.003	0.066 ± 0.003
SPEEK-1	1.02 ± 0.05	0.013 ± 0.0003	0.046 ± 0.002	0.0458 ± 0.001
SPEEK/AMPS 10	3.12 ± 0.11	0.028 ± 0.001	0.076 ± 0.003	0.073 ± 0.002
SPEEK/AMPS 15	4.08 ± 0.08	0.041 ± 0.001	0.087 ± 0.001	0.083 ± 0.001
SPEEK/AMPS 20	5.32 ± 0.19	0.055 ± 0.002	0.104 ± 0.004	0.098 ± 0.002
SPEEK/AMPS 25	6.51 ± 0.12	0.069 ± 0.003	0.124 ± 0.001	0.115 ± 0.004
SPEEK/AMPS 30	8.89 ± 0.05	0.084 ± 0.001	0.149 ± 0.002	0.135 ± 0.002
Nafion® 117	23.8 ± 0.3	0.05 ± 0.001	0.083 ± 0.003	–

[a] Proton conductivity before 85 °C water test.
[b] Proton conductivity after 85 °C water test.

icantly affects the proton conductivities. By crosslinking, the structure of membranes becomes more compact, which leads to the reduction of the mobility of H$^+$ and space of retaining water around sulfonic acid groups [25]. Hence the proton conductivity is compromised. Typically, the crosslinked SPEEK-1 membrane exhibited the lowest proton conductivity in all the samples. Its proton conductivity was only 0.013 S cm^{-1} at room temperature, which was about half of uncrosslinked SPEEK (0.025 S cm^{-1}) under the same testing conditions.

The structure of proton exchange membranes has been extensively studied by many researchers, and it is well known that protons transfer between ionic clusters consisting of polar groups such as –SO$_3$H. The number of ionic clusters increases with increase of the number of –SO$_3$H groups and water content in the membrane [34]. Be contrary to the crosslinking, the introduction of AMPS in the SPEEK leads to a significant improvement in the proton conductivity. On the one hand, the sulfonic acid groups in the membrane increase and hence more free protonic ions and ionic clusters can be formed due to the addition of AMPS, which elevates proton conductivity. On the other hand, more hydrophilic areas can be formed and the hydrophilicity of membranes increases due to the introducing of more sulfonic acid groups originated from AMPS, which lead to more water absorption and enables protons in the form of hydronium ions to pass through the ionic clusters

more easily, the proton conductivity therefore is enhanced [35]. In conclusion, the introduction of AMPS elevated the proton conductivity of membranes not only by increasing the number of protonic ions (–SO$_3$H) but also through forming more water mediated pathways for protons. It is worth noting that the conductivity of SPEEK/AMPS membranes with higher AMPS content (20–30 wt.%) were higher, over a wide temperature range, than that of Nafion® 117 membrane. Especially, the SPEEK/AMPS 30 membrane achieved the maximum proton conductivity of 0.084 S cm^{-1} at 25 °C with the conductivity of Nafion® 117 was only 0.05 S cm^{-1} under the same measuring conditions.

In addition, the temperature is also one of the essentials that affect proton conductivity. As shown in Fig. 4, all the membrane samples exhibited a positive temperature–conductivity dependency. It is because that elevating temperature can increase structural loose as well as mobility of water and ionic and hence favors proton transport [18]. Compared with Nafion® 117, all the other membranes exhibited more pronounced increase in proton conductivities with temperature, suggesting these membranes have higher activation energy [31].

In summary, to obtain the high proton conductivity level, various factors should be considered seriously during constructing proton exchange membranes. In this paper, the proton conductivities of SPEEK/AMPS membranes with higher AMPS content were sufficiently higher, but methanol diffusion coefficients were much lower compared to Nafion® 117, which made these membranes very promising as PEMs in DMFC applications.

The selectivity, which is defined as the ratio of proton conductivity to methanol diffusion coefficient, is often used to evaluate the potential performance of DMFC membranes. The membranes with higher selectivity are desired for DMFCs [13,36]. Fig. 5 exhibits the selectivity of SPEEK/AMPS and Nafion® 117 membranes at 25 °C. As shown in Fig. 5, all the SPEEK/AMPS membranes displayed higher selectivity in comparison with pure SPEEK and Nafion® 117 membranes and the SPEEK/AMPS 25 membrane possessed the highest selectivity value that was approximately five times greater than Nafion® 117. These results suggest that incorporating AMPS into SPEEK and crosslinking the membranes are favorable for improving PEM performance.
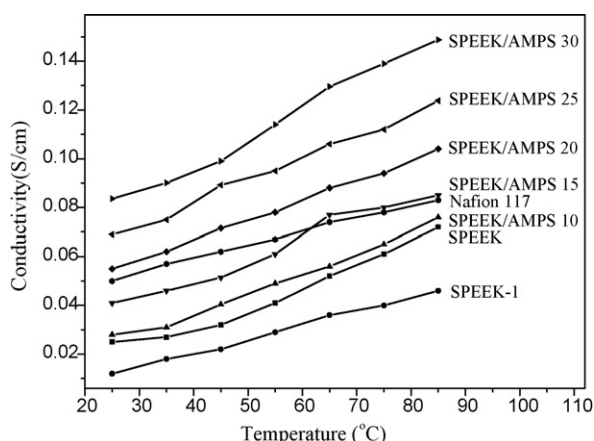

Fig. 4. Proton conductivity of various membranes with different temperatures.
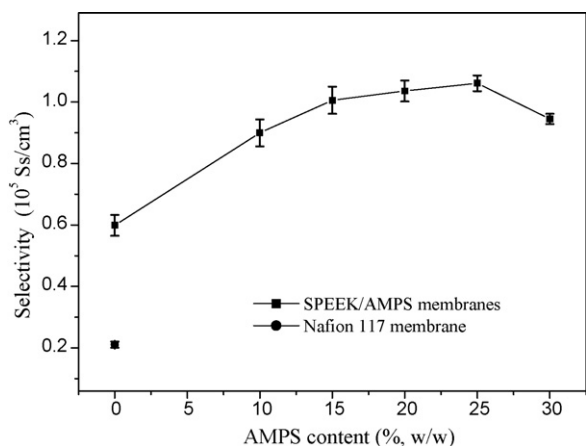
Fig. 5. Selectivity of SPEEK/AMPS and Nafion® 117 membranes at 25 °C.

3.7. Hydrolysis stability

Besides the low methanol diffusion coefficient and high proton conductivity, the membranes applied in DMFCs should also possess good hydrolytic stability. The hydrolysis stability was evaluated in the present study by comparing the proton conductivities before and after soaking the membranes in 85 °C water for 2 weeks. It is thought that little change in proton conductivity corresponds to good hydrolytic stability [37]. As shown in Table 3, the proton conductivity of the non-crosslinked SPEEK membrane was slightly diminished after 85 °C water test, indicating that the sulfonic acid groups were partially decomposed during marinating. However, the crosslinked SPEEK-1 membrane showed the best hydrolytic stability with negligible change in proton conductivity. This is an important result because with crosslinking, the methanol diffusion coefficient can be reduced and the hydrolytic stability can be enhanced, which are advantageous for PEM usage. However, these good properties were achieved with compromise of proton conductivity. Herein, incorporation of AMPS and crosslinking used together offer an effectual route to improve the proton conductivity without sacrificing hydrolytic stability. The results of the study have indeed shown that the crosslinked membranes containing AMPS were relatively stable according as no significant change in proton conductivity. In fact, as shown in Table 3, SPEEK/AMPS 10, SPEEK/AMPS 15 and SPEEK/AMPS 20 membranes showed better hydrolytic stability, without noticeable changes in proton conductivity, appearance, flexibility and toughness after 85 °C water test, than SPEEK membrane. It is because that the crosslinking modification plays an important role in improving the hydrolytic stability. Due to the formation of crosslinked network structure, the sulfonic acid groups were maintained in membranes and did not or less decompose during the test.

However, a further increase in AMPS content leads to relatively low hydrolytic stability of SPEEK/AMPS membranes. It can be understand based on the fact that the water uptake of SPEEK/AMPS membranes elevates with the increasing AMPS content, which induces the decline of compact structure of membranes and hence some sulfonic acid groups leached into the water during marinating. However, it should be mentioned that

all the SPEEK/AMPS membranes developed in this work exhibited better or similar hydrolytic stability in comparison with the pure SPEEK membrane although their water uptake increased with increasing AMPS content. Hence, we can conclude that crosslinking and AMPS used together are particularly effective in obtaining high proton conductive PEMs with negligible sacrifice of hydrolytic stability.

4. Conclusion

The crosslinked SPEEK/AMPS blend membranes with high proton conductivity and low methanol diffusion coefficient have been prepared successfully. The effects of crosslinking and AMPS content on the performance of membranes have been studied and discussed in detail. The crosslinking modification played an important role in improving the membrane performances. Compared with pure SPEEK, the water uptake and methanol diffusion coefficient of the crosslinked SPEEK-1 membrane were reduced considerably and the hydrolysis stability was increased. At a fixed irradiation time, the properties of SPEEK/AMPS membranes markedly depended on AMPS content. Although the water uptake and proton conductivity increased with increasing AMPS content and most SPEEK/AMPS membranes exhibited higher proton conductivity than Nafion® 117, the SPEEK/AMPS membranes shared not only excellent thermal stability but also relatively good hydrolytic stability. Though the methanol diffusion coefficient of SPEEK/AMPS membranes increased with the increase of AMPS content, they were still significantly lower than that of Nafion® 117 under the same testing conditions. In addition, all the SPEEK/AMPS membranes exhibited higher selectivity values in comparison with pure SPEEK and Nafion® 117 membranes. These results indicated that the SPEEK/AMPS membranes possessed good combination of physical and chemical properties were remarkably promising to be used as proton exchange membranes in DMFCs.

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