Short communication

Modification of sulfonated poly(ether ether ketone) proton exchange membrane for reducing methanol crossover

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ABSTRACT

A drawback of sulfonated aromatic main-chain polymers such as sulfonated poly(ether ether ketone)s (SPEEKs) is their high methanol crossover when the proton conductivity is sufficient for direct methanol fuel cell (DMFC) applications. To overcome this disadvantage, in this paper, the SPEEK substrate was coated with the crosslinked chitosan (CS) barrier layer to form the two-layer composite membranes. Scanning electron microscope (SEM) micrographs showed that the CS layer was tightly adhered on the SPEEK substrate and the thickness of CS layer could be adjusted by varying the concentration of CS solution. It was noticed that with the increment of thickness of CS layer, the methanol diffusion coefficient of the composite membranes significantly dropped from 3.15×10^{-6} to 2.81×10^{-7} cm^2 s^{-1} at 25 °C which was about one order of magnitude lower than those of the pure SPEEK and Nafion® 117 membranes. In addition to the effective methanol barrier, the composite membranes possessed adequate thermal stability (the 5% weight lose temperature exceeded 240 °C) and good proton conductivity. The proton conductivity of all composite membranes was in the order of 10^{-2} S cm^{-1} and increased with the elevation of temperature. Furthermore, the composite membranes exhibited much higher selectivity (conductivity/methanol diffusion coefficient) compared with the pure SPEEK and Nafion® 117 membranes. These results indicated that introducing the crosslinked CS layer onto the SPEEK surface was an effective method for improving the performance of the SPEEK membrane, especially for reducing the methanol crossover.

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1. Introduction

There is a growing interest over the past few years in the development of direct methanol fuel cells (DMFCs) due to their potential applications in portable devices and vehicles [1,2]. The proton exchange membrane (PEM) is a key component of DMFCs and mainly serves as proton carrier and methanol obstructor. Up to now, perfluorinated copolymers such as Nafion® are the most commonly used PEMs owing to their good chemical and physical stability and high proton conductivity, however, the expensive cost, high methanol crossover and difficulty in synthesizing and processing still limit their extensive commercialization [3,4]. Therefore, numerous efforts have been dedicated to develop new PEM materials and a great number of polymers have been proposed [5–10]. Among the potential alternatives, sulfonated poly(aryl ether ketone)s (SPAEKs) have attracted considerable attention because of their advantages of low cost, easy preparation, controllable composition, good mechanical strength and high chemical and thermal stabilities [6,11–13]. However, like other sulfonated aromatic main-chain polymers, the SPAEKs should possess high sulfonation level in order to achieve sufficient proton conductivity. Unfortunately, too high loading of acidic groups induces excessive methanol crossover, which not only wastes fuel but also causes catalyst poisoning and energy efficiency loss [14,15]. In order to reduce the methanol crossover, many approaches such as blending, crosslinking, grafting, developing hybrid and/or composite membranes have been put forward to modify the SPAEKs and the modified membranes were found to have lower methanol crossover than the pure ones [16–19,2].

In addition to these general methods, another alternative and effective way to tackle the methanol crossover issue is to coat a methanol barrier layer onto the surface of proton exchange membranes. For example, Shao et al. [20] proved that the methanol crossover of Nafion® membrane could be reduced by casting a thin film containing the mixture of polyvinyl alcohol and Nafion® on the Nafion® membrane. Hobson et al. [21] introduced a thin layer of polybenzimidazol on the Nafion® 117 surface and the modified membranes showed good result in reducing methanol crossover.

In this paper, our work focused on the modification of sulfonated poly(ether ether ketone) (SPEEK) by coating a crosslinked chitosan (CS) layer on the surface of SPEEK membrane. To our knowledge, this kind of modified SPEEK membrane had not been

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reported. The choice of CS as the barrier layer was inspired by the fact that CS is very cheap and possesses a rare combination of physicochemical properties including good membrane-forming ability, high mechanical strength and excellent chemical/thermal resistance. Besides, large quantities of amino and hydroxyl groups existed in CS can interact with sulfonic acid groups of SPEEK. Hence, the CS layer could have good adhesion to the SPEEK substrate. More importantly, the CS membrane can exhibit excellent methanol barrier and certain conductivity when it is crosslinked by acid [22–24]. Considering the advantages of CS and in order to decrease the methanol crossover and simultaneously to keep the wonderful performance of SPEEK membrane, the two-layer composite membranes consisting of SPEEK substrate and crosslinked CS thin layer were prepared and their possibility as proton exchange membranes in direct methanol fuel cell was investigated by estimating the thermal stability, water uptake, methanol uptake, methanol diffusion coefficient, proton conductivity and selectivity.

2. Experimental

2.1. Materials

The sulfonated poly(ether ether ketone)s (SPEEKs) were prepared by aromatic nucleophilic substitution reactions. The detailed synthesis procedures and characterization of polymers were reported by our previous work [25]. In this paper, for the purpose of obtaining high proton conductivity, only the SPEEK with relatively high ion exchange capacity ($2.12\,\mathrm{mmol\,g^{-1}}$) was prepared. Chitosan (CS) was purchased from Sanland-chem International Inc. (Xiamen, China). All the other reagents and solvents were obtained commercially and used without further purification.

2.2. Membrane preparation

The preparation of modified SPEEK membranes (SPEEK/CS composite membranes) involved a two-step process. In the first step, the pure SPEEK membranes were prepared by pouring the solution of 10–15% SPEEK in DMF onto a glass plate and dried at $70\,^{\circ}\mathrm{C}$ for 3 days. These SPEEK membranes were used as substrates to construct the SPEEK/CS composite membranes. In the second step, CS was dissolved in 2% (v/v) acetic acid aqueous solution to form the CS solution with desired concentration. Then the CS solution was smoothly spread on the surface of SPEEK membrane, dried at $60\,^{\circ}\mathrm{C}$ for 6 h and $120\,^{\circ}\mathrm{C}$ for 1 h. The resultant SPEEK/CS composite membranes then were submersed in acetone solution containing glutaraldehyde and H_2SO_4 for 24 h to crosslink and protonate the CS layer. These membranes were rinsed repeatedly with deionized water to remove the nonreactive monomers and stored in deionized water for further analysis.

2.3. Membrane characterization

2.3.1. Scanning electron microscope

The thickness of CS layer on the SPEEK substrate was determined using a SHIMADZU SSX-550 scanning electron microscope (SEM). The samples were dried, fractured in liquid nitrogen and the fractured surfaces were sputter-coated with Au prior to SEM measurements.

2.3.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of membranes was performed using a Pyris 1TGA (PerkinElmer). Prior to measurement, all samples were preheated to $120\,^{\circ}\mathrm{C}$ and kept at this temperature for 20 min to remove moisture and solvent. After that, the mem-

branes were cooled to $100\,^{\circ}\mathrm{C}$ and then reheated to $600\,^{\circ}\mathrm{C}$ with a heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$ under N_2.

2.3.3. Water uptake and methanol uptake

Before testing water uptake, the membranes were vacuum-dried at $100\,^{\circ}\mathrm{C}$ until constant weight was obtained. The dried samples (W_{dry}) were immersed in deionized water for 24 h at different temperatures. Then the samples were taken out and immediately weighed (W_{wet}) after wiping out the surface water. The water uptake was calculated using the expression:

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

The methanol uptake was determined using the same method as water uptake, except that the samples were soaked in pure methanol. The percentage of the absorbed methanol with respect to original weight was taken as the methanol uptake.

2.3.4. Determination of methanol diffusion coefficient

The methanol diffusion coefficient of membranes was determined using a glass diffusion cell. The cell consisted of two reservoirs which were separated by a vertical membrane. Prior to testing, the membranes were equilibrated in deionized water for 24 h. $1.0\,\mathrm{M}$ methanol–water solution was placed on one reservoir (donor reservoir A) and deionized water was placed on the other reservoir (receptor reservoir B). During the measurement, the solutions in each reservoir were stirred continuously and the temperature of diffusion cell was controlled by a water bath. The increase of methanol concentration with time in the water reservoir was measured using a SHTMADU GC-8A gas chromatograph. The methanol diffusion coefficient was calculated in formula [26]:

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

where A, L and V_B are the effective area, the thickness of membrane and the volume of receptor reservoir, respectively. C_A and C_B are the methanol concentration in the donor and receptor reservoirs, respectively. DK and t_0 are the methanol diffusion coefficient and the time lag, respectively.

2.3.5. Proton conductivity measurements

The proton conductivity in water-equilibrated membranes was measured using the AC impedance technology. The impedance measurement was carried out by SI1260+SI1287 impedance analyzer over the frequency range from 10 to 10^6 Hz. Before 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 was measured at temperatures ranging from 25 to $80\,^{\circ}\mathrm{C}$.

3. Results and discussion

3.1. SEM analysis

The surface modification of SPEEK membrane was achieved by coating a thin CS layer onto the surface of SPEEK substrate and crosslinking the coating layer with glutaraldehyde and H_2SO_4. From the previous work, it had been proven that CS had remarkable affinity for many substances and susceptibility to chemical modifications due to the presence of reactive amino and hydroxyl groups [27,28]. Hence, it is expected that the separation tendency of top layer and supporting layer could be significantly reduced as the
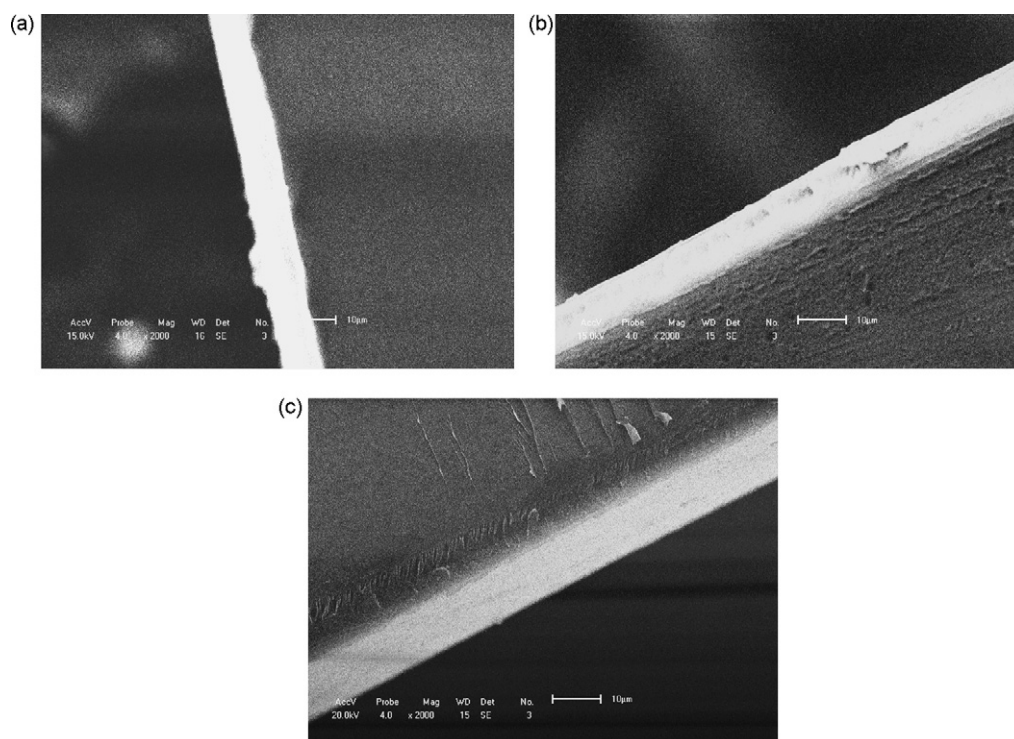
Fig. 1. SEM micrographs of SPEEK/CS composite membranes: (a) SPEEK/CS 1, (b) SPEEK/CS 2, (c) SPEEK/CS 3.

result of the strong affinity between SPEEK and CS. The cross-sections of modified membranes were investigated using SEM and the SEM micrographs are presented in Fig. 1. Before preparing the samples used in SEM measurement, all the membranes were soaked in deionized water for at least 2 months. The micrographs showed clearly the presence of the two-layer structure, which proved that the CS layer had been coated successfully on the SPEEK substrate. From the micrographs, it also could be noted that no visible cracks were found in the interface of the coated CS layer and SPEEK substrate, indicating that CS layer had not been detached from SPEEK substrate even under the long-term immersion. This result revealed that there was a strong affinity between SPEEK substrate and CS layer due to the acid–base interaction between the amino groups of CS and the sulfonic acid groups of SPEEK as well as the formation of hydrogen bonds between the hydroxyl groups of CS and the sulfonic acid groups of SPEEK.

In order to evaluate the effect of the CS barrier layer on the performance of SPEEK membrane, the composite membranes with different CS thicknesses were prepared and the CS thicknesses were determined by SEM (Fig. 1). From the micrographs, it can be observed that the thicknesses of CS layer were approximately 7.9, 9.8 and 11.5 μm, respectively.

Based on the SEM results, it can be concluded that CS could be easily coated onto the surface of SPEEK membrane and the CS layer was with good adhesion to the SPEEK substrate. Furthermore, the thickness of CS layer could be adjusted by varying the concentration of CS solution.

3.2. Thermal stability studies

The thermal stability of membranes was evaluated using the TGA experiments and the results are presented in Fig. 2. The thermal degradation behavior of the pure SPEEK was divided into two stages. The first weight loss step appeared in the temperature range 260–440 °C was attributed to the elimination of sulfonic acid groups and the second thermal degradation occurred at about

440 °C corresponded to the decomposition of polymer backbone. The change tendency of TGA curves of composite membranes was almost the same as that of pure SPEEK. In order to distinguish the variety of thermal degradation behavior of composite membranes more clearly, the 5% weight loss temperatures (T5%) of SPEEK and SPEEK/CS composite membranes are shown in Table 1. The T5% for SPEEK took place at about 271 °C, meanwhile the corresponding values for composite membranes were shifted to 262, 257 and 241 °C, respectively, based on the thickness of CS layer.

In general, it is known that hydrogen bonds can contribute to raising the thermal stability of membrane [29]. As mentioned previously, coating CS onto the SPEEK could form hydrogen bonds between the sulfonic acid groups of SPEEK and the functional groups of CS. Hence, the composite membranes should show a
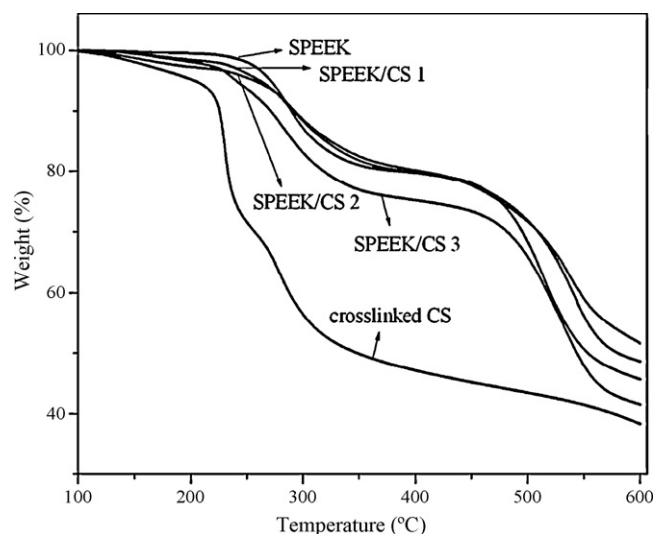
Fig. 2. TGA curves of SPEEK, crosslinked CS and SPEEK/CS composite membranes.

Table 1
Property of modified SPEEK membranes

Notation	CS thickness (μm)	5% weight loss temperature (T5%) (°C)	Methanol uptake (%)			Methanol diffusion coefficient (10^{-7} cm^2 s^{-1})		
			25 °C	40 °C	60 °C	25 °C	40 °C	60 °C
SPEEK	0	271	48.2	63.8	79.7	31.5	58.7	92.1
SPEEK/CS 1	7.9	262	46.1	59.1	74.3	9.79	17.5	25.3
SPEEK/CS 2	9.8	257	45.3	58.2	72.0	4.94	7.79	13.2
SPEEK/CS 3	11.5	241	44.9	57.5	70.6	2.81	4.52	6.77

higher T5% than the SPEEK if only one factor, hydrogen bonds, was taken into account. However, the T5% of composite membranes slightly decreased with the increment of CS thickness. This result may be relative with the thermal stability of crosslinked CS layer. From Fig. 2, one can see that the first weight loss of crosslinked CS was in the temperature range 120–200 °C which might be attributed to the desorption process of water molecules since it was difficult to completely eliminate the water absorbed by crosslinked CS [30]. The variation of T5% of the composite membranes suggested that the effect from residual water in composite membranes was much stronger than that from hydrogen bonds. Hence, the composite membrane with thicker CS layer exhibited lower T5%. Although the introduction of CS slightly decreased the thermal stability of membrane, the composite membranes were still stable enough to serve as the PEMs for fuel cell applications (5% weight lose temperature exceeded 240 °C).

3.3. Water uptake and methanol uptake behaviors of membranes

In this study, CS was coated to the surface of SPEEK membrane to form the thin methanol barrier layer. However, CS is highly hydrophilic because of the presence of the amino and hydroxyl groups [31]. The absorption of large amount of water can cause excessive swelling and lose of mechanical strength, which will lead to the fall in membrane performance. Crosslinking is one of the efficient strategies to improve the membrane resistivity to water and enhance its stability. In order to examine the efficiency of crosslinking, glutaraldehyde and H_2SO_4 were used as the crosslinking agents to first crosslink the pure CS membrane. The result showed that the water uptake of crosslinked CS membrane was reduced sharply to 59.8%. It is because that when CS was crosslinked, the formation of imine linkage between the amino groups of CS and the aldehydic groups of glutaraldehyde as well as the existence of coulombic interaction between the amino groups of CS and the sulfate ions of H_2SO_4 resulted in the information of crosslinked network structure [32,33]. Thus the polymer chains became more rigid and the CS membrane became more compact, which led to the marked decrease in water uptake of CS membrane. In addition, water uptake depends also upon the hydrophilicity. Both of effects mentioned above led to the reduction of the hydrophilic groups (amino groups), which helped to decrease the hydrophilicity of membrane. This is also one of the reasons why the water uptake of crosslinked CS membrane decreased.

Based on the above experiment, it is clearly that crosslinking can effectively inhibit the water absorption of CS membrane. Hence, the thin CS layer was crosslinked by glutaraldehyde and H_2SO_4 after CS was coated onto the surface of SPEEK membrane. The water uptake of pure SPEEK membrane and composite membranes with various CS thicknesses are shown in Fig. 3. It is noticed that compared with the pure SPEEK membrane, the composite membranes showed slightly higher water uptake and the water uptake increased from 44.9 to 46.1% at 25 °C as the CS thickness increased from 7.9 to 11.5 μm. This result could be attributed to the higher water adsorption ability of CS layer. Despite crosslinking, the water uptake (59.8%) of crosslinked CS membrane was still higher than that of SPEEK, which may be responsible for the increase of water

uptake. Hence, the thicker the crosslinked CS layer was, the higher the water uptake of composite membranes was.

Table 1 also shows the methanol uptake of pure SPEEK membrane and composite membranes. From Table 1, one can seen that the addition of CS decreased the methanol uptake of SPEEK membrane and the methanol uptake of composite membranes decreased with the increment of CS thickness. This tendency was opposite to the result of water uptake, indicating that the CS had a higher selective tendency to water than to methanol. Thus, the methanol uptake in composite membranes was restricted and the SPEEK/CS 3 composite membrane with the thickest CS layer exhibited the least methanol uptake of 44.9% at 25 °C.

In addition, it is apparent that water and methanol uptakes of all the membranes had an increasing tendency with the elevation of temperature. It is because that the mobility of polymer chain and the free volume for water and methanol adsorption increased when the temperature elevated, which led to the increment of water and methanol uptakes.

3.4. Effect of CS barrier layer on methanol diffusion

To prevent fuel waste and reduce catalyst poisoning and energy efficiency loss, the proton exchange membranes used in DMFCs should possess low methanol crossover. In order to reduce the methanol crossover of SPEEK with relatively high proton conductivity, the SPEEK substrate was coated using the crosslinked CS barrier layer here. The crosslinked CS membranes had been widely used in the pervaporation technology for separating water from organic compounds like methanol due to the high selectivity of water/organic compounds [34,35]. Hence, we expected that the combination of SPEEK and CS was beneficial for the decrease of methanol crossover.

The methanol diffusion coefficients of the pure SPEEK membrane and SPEEK/CS composite membranes were calculated and
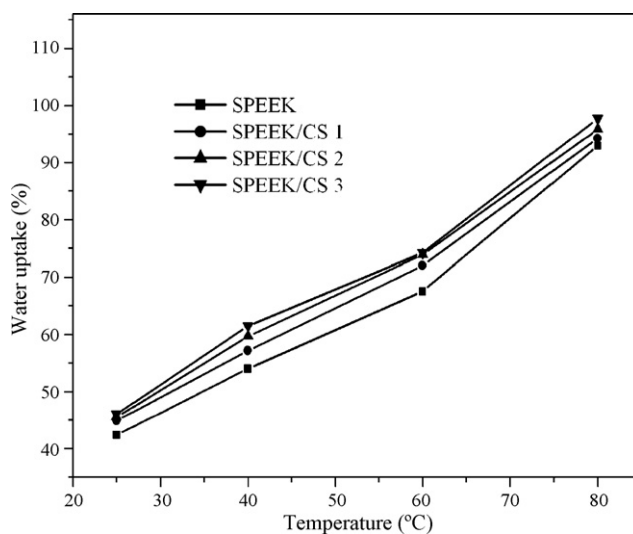
Fig. 3. Water uptake of SPEEK and SPEEK/CS composite membranes at different temperatures.

the results are shown in Table 1. As expected, the composite membranes exhibited better methanol barrier property than the pure SPEEK membrane and the methanol diffusion coefficient decreased with the increment of thickness of CS layer. The notable feature is that the methanol diffusion coefficients of all composite membranes were much lower than that of Nafion® 117 and the lowest value (2.81×10^{-7} cm^2 s^{-1}) was only about one tenth of that of Nafion® 117 (2.38×10^{-6} cm^2 s^{-1}) at 25 °C. This result indicated that the methanol crossover might be reduced significantly if the composite membranes were used in DMFCs.

The reduction of methanol diffusion coefficient in the composite membranes might be attributed to two main factors. One is the effect of intermolecular interaction between SPEEK and CS, and the other is the effect of crosslinked CS layer itself. Coating CS on the surface of SPEEK led to the interaction of SPEEK and CS. That is, the amino and hydroxyl groups of CS could interact with the sulfonic acid groups of SPEEK, forming a dense layer on the interface between SPEEK substrate and CS top layer, which interrupted the diffusion of methanol and hence reduced the methanol diffusion coefficient of composite membranes. In addition, it is very interesting that the methanol diffusion coefficient of composite membranes decreased although the water uptake increased with increasing thickness of CS layer as described in Section 3.3. This is because that in the methanol diffusion experiment, the water molecules having relatively smaller molecular size than methanol molecules could diffuse through the crosslinked CS membrane more easily. That is, the crosslinked CS had a higher selective tendency to water than to methanol [36]. Therefore, the methanol diffusion coefficient of composite membranes decreased with increasing thickness of CS layer due to the preferential transport of small-sized water molecules through the CS barrier layer.

The influence of temperature on the methanol diffusion coefficient for SPEEK and SPEEK/CS composite membranes is also shown in Table 1. It can be seen from Table 1 that an increase in the temperature led to an increase in the methanol diffusion coefficient. For example, when the temperature raised from 25 to 60 °C, the methanol diffusion coefficient through the SPEEK/CS 3 membrane increased from 2.81×10^{-7} to 6.77×10^{-7} cm^2 s^{-1}. This is easily understandable because with the elevation of temperature, the motion of polymer chains and the free volume of membranes increased. Hence, the resistance of membranes for methanol diffusion became smaller and the methanol diffusion coefficient increased.

3.5. Proton conductivity measurements

The proton conductivity is a crucial property for fuel-cell membranes. Fig. 4 represents the conductivity curves of composite membranes with different CS thicknesses. For comparison, the proton conductivity of pure SPEEK and Nafion® 117 membranes measured under the same experimental conditions are also exhibited in Fig. 4. From Fig. 4, it can be noted that the thickness of CS layer had no obvious impact on the proton conductivity of composite membranes. As the thickness of CS layer increased from 7.9 to 11.5 μm, the conductivity of composite membranes only showed a very slight sacrifice from 0.044 to 0.039 S cm^{-1} at 25 °C. This is because that the CS layer was protonated by H$_2$SO$_4$ in order to keep the proton conductivity of composite membranes. However, it should be mentioned that for the present case, the hydrogen bonds were formed between the functional groups of CS and the sulfonic acid groups of SPEEK, which consumed a certain amount of sulfonic acid groups. Although this led to a slight reduction in proton conductivity, the conductivity values of the composite membranes were still preserved at the level of 10^{-2} S cm^{-1}, which were comparable to that of Nafion® 117.
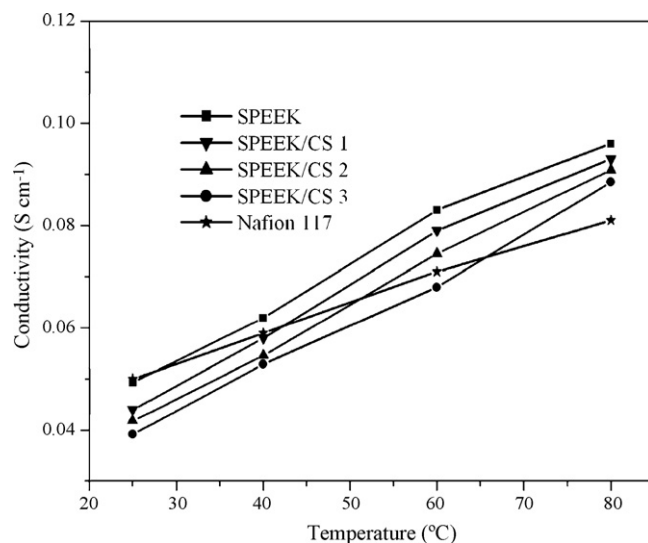

Fig. 4. Proton conductivity of SPEEK, SPEEK/CS and Nafion® 117 membranes at different temperatures.

In addition, it can be observed that temperature played an important role on the proton conductivity and all membranes exhibited the positive temperature-conductivity dependency. For example, as the temperature elevated from 25 to 80 °C, the proton conductivity of SPEEK/CS 1 membrane increased from 0.044 to 0.093 S cm^{-1}. It is because that with the elevation of temperature, the free volume of membranes and the motion of water and proton increased, which facilitated the transport of proton [37]. Besides, the increase of temperature led to the increment of water uptake. More water as the proton transport medium might allow protons to move more easily and hence contributed to the improvement of proton conductivity.

3.6. Comparison of selectivity (proton conductivity/methanol diffusion coefficient)

The PEMs applied in DMFCs should possess simultaneously high proton conductivity and low methanol diffusion coefficient. Hence, the selectivity can be used as a barometer to evaluate the performance of PEMs and the high selectivity is expected for DMFC
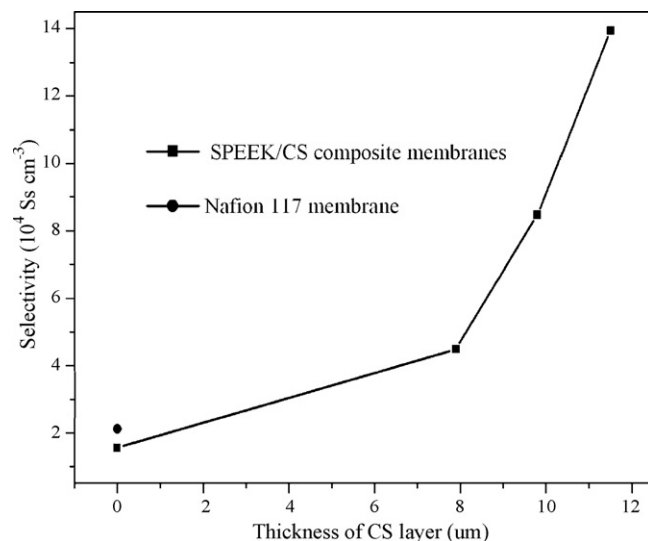

Fig. 5. Selectivity of SPEEK, SPEEK/CS and Nafion® 117 membranes.

applications. The selectivity of pure SPEEK, SPEEK/CS composite membranes and Nafion® 117 membrane at 25 °C are compared in Fig. 5. It can be seen that coating CS onto the SPEEK was helpful for increasing the selectivity of SPEEK membrane and the selectivity of composite membranes improved with the increment of thickness of CS layer. The SPEEK/CS 3 membrane showed the maximum selectivity (1.40×10^5 S s cm^{-3}) which was approximately nine times of that of SPEEK membrane (1.57×10^4 S s cm^{-3}) and seven times of that of Nafion® 117 membrane (2.12×10^4 S s cm^{-3}).

The methanol diffusion coefficients of all composite membranes were significantly lower meanwhile their selectivity were much higher than those of the pure SPEEK and Nafion® 117 membranes, suggesting that coating CS layer to the SPEEK substrate formed advanced membranes and these membranes might be promising as PEMs for DMFC applications.

4. Conclusions

In this paper, in order to decrease the methanol crossover of SPEEK membrane, the SPEEK/CS composite membranes were constructed by coating a thin CS layer onto the surface of SPEEK membrane followed by crosslinking and protonating the CS layer with glutaraldehyde and H_2SO_4. SEM studies demonstrated the presence of thin CS layer on the surface of SPEEK membrane. The properties of composite membranes such as the thermal stability, water uptake, methanol uptake, methanol diffusion coefficient, proton conductivity as well as selectivity were investigated to evaluate their suitability as proton exchange membranes for DMFC applications. The preliminary results displayed that the composite membranes were thermally stable (the 5% weight lose temperatures were above 240 °C) and the thickness of CS layer had no obvious effect on the thermal stability and water uptake. In comparison to the pure SPEEK and Nafion® 117 membranes, the composite membranes showed significantly stronger methanol barrier property. The methanol diffusion coefficient markedly decreased from 3.15×10^{-6} to 2.81×10^{-7} cm^2 s^{-1} at 25 °C as the thickness of CS layer increased from 0 to 11.5 μm, implying that an improvement in fuel utilization efficiency could be realized if these composite membranes were used in DMFCs. Although the addition of CS layer slightly decreased the proton conductivity, the composite membranes still retained good conductivity level of 10^{-2} S cm^{-1}, which was comparable to those of SPEEK and Nafion® 117 membranes. In addition, it was also noted that the selectivity values of all composite membranes were much higher than those of SPEEK and Nafion® 117 membranes. Based on these results, it could be concluded that

the composite membranes appeared to have good potential used as PEMs in DMFCs.

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