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Solution blown sulfonated poly(ether ether ketone) nanofiber–Nafion composite membranes for proton exchange membrane fuel cells

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In this study, a new type of modified Nafion membrane containing sulfonated poly(ether ether ketone) (SPEEK) nanofibers was fabricated for proton exchange membrane fuel cells. The solution blowing method was used for fabrication of SPEEK nanofibers, which were impregnated into Nafion solution to form pore-filled composite membranes with different contents of SPEEK nanofibers. The performance of the composite membranes as proton exchange membranes was investigated and compared with Nafion 117. The results showed that the introduction of SPEEK nanofibers into the Nafion matrix significantly improved its thermal stability, proton conductivity, swelling rate and selectivity. The maximum value of the proton conductivity of 0.09 S cm^{-1} was obtained when the nanofiber content was 10 wt% at 20 °C and 100% RH, higher than that for Nafion 117 (0.083 S cm^{-1}). It is indicated that solution blown nanofibers are a kind of promising filler material for enhancing the performance of Nafion membranes, and the composite membrane containing SPEEK nanofibers can be considered as a novel proton exchange membrane for fuel cell applications.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) convert chemical energy directly into electrical energy and they are attractive, energy efficient and environmentally friendly power sources for many applications including portable and automotive applications. The proton exchange membrane (PEM) is the core component of PEMFCs.^{1,2} The important roles of the PEM include transporting proton and separating the reactant fuels. Perfluorosulfonic acid membranes, such as Nafion, have been extensively used in PEM because of their good chemical and physical stabilities as well as high proton conductivity under high humidity conditions.³ However, the drawbacks of perfluorosulfonated membranes, including high production cost, the low thermal stability, relatively low operation temperature and high permeation rate of methanol, have limited its applications in PEMFCs, especially in direct methanol fuel cells (DMFCs).⁴

To overcome these problems, many efforts have been made to modify the Nafion membrane. A variety of inorganic and organic fillers are used for the preparation of the Nafion-based composite proton exchange membranes. The inorganic composite membranes mainly include Nafion/inorganic oxides (SiO_2 , TiO_2 , ZrO_2) membrane, Nafion/natural ore (montmorillonite and zeolites) membrane and Nafion/phosphotungstic

acid membrane, *etc.* Miyake *et al.*⁵ prepared the Nafion/silica hybrid membranes by sol-gel process, and found that the methanol permeation rate of the hybrid membrane had a significant decrease due to the addition of silica. Ramani *et al.*⁶ prepared the Nafion-based composite membranes with different inorganic heteropolyacid (HPA) additives such as phosphotungstic acid, silicotungstic acid, phosphomolybdic acid and silicomolybdic acid. Those membranes were investigated at high temperature (120 °C) and low relative humidity environment, and the proton conductivity of the membranes measured at 120 °C and 35% relative humidity condition reached 0.015 S cm^{-1} . The organic composite membranes mainly include Nafion/conductive polymers (polyaniline) membrane and Nafion/PTFE membrane, *etc.* Yang *et al.*⁷ fabricated a Nafion and polyaniline composite membrane using an *in situ* chemical polymerization method, and the composite membrane showed a proton conductivity that was superior to that obtained with Nafion 112 at low humidities.

Recently, researchers have focused on studying the properties of the nano-sized membrane material which can be used for improving the functionality of the membrane. Nanofibers possess some unique properties including large specific surface area and superior mechanical properties. Molla *et al.*⁸ incorporated polyvinyl alcohol (PVA) nanofibers into Nafion matrix and the methanol crossover of the obtained composite membranes for PEMFC was reduced. Yao *et al.*⁹ prepared the composite membranes of sulfonated polystyrene fibers and Nafion with better proton conductivity. These show that the

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nanofibers were considered as promising materials for application in fuel cells.

Solution blowing has been reported as a new nanofiber preparation process in recent years. In this process, a polymer solution is blown and attenuated to the nanofibers by high velocity airflow.¹⁰ Compared with electrospinning, solution blowing process has significant advantages such as high productivity due to its high solution feed rate, easy accessibility and low energy consumption due to not using high-voltage equipment.¹¹ Moreover, the solution blown nanofibers are different from the electrospun nanofibers and they are commonly curled in three dimensions.¹⁰

In this work, the sulfonated poly(ether ether ketone) (SPEEK) nanofibers was prepared using the solution blowing process firstly. SPEEK has been widely studied as PEMs materials due to its appropriate proton conductivity, acceptable cost and superior chemical and thermal stabilities. Then, SPEEK nanofiber mats were impregnated into Nafion solution to form pore-filled nanofiber composite membranes. The structure and properties of the nanofiber composite membranes were examined as proton exchange membrane.

2. Experimental

2.1 Materials

Victrix PEEK (450p) was purchased from ICI and was sulfonated using sulphuric acid (98%). Nafion 5 wt% solution, was obtained from DuPont Co. *N,N*-Dimethylformamide (DMF) was analytical reagent and used as received.

2.2 Preparation of SPEEK

PEEK (18 g) after dried in an oven at 100 °C for 12 h was added to 200 mL sulfuric acid (98 wt%) and the solution was stirred vigorously for 4 h at 55 °C. After the reaction, the solution was slowly dropped into ice-cool deionized water. Then the precipitated polymer was collected by filtration and washed thoroughly with deionized water until the wash water reached a pH of 7. Finally, the sulfonated PEEK was dried under vacuum at 60 °C for 24 h. The degree of sulfonation of the SPEEK obtained was 0.62, which was determined by ¹H-NMR spectrum, as described by Nolte *et al.*¹²

2.3 Preparation of SPEEK nanofiber mat

The SPEEK nanofiber mats were fabricated using a solution blowing process with a multi-orifice die. The setup is similar to our previous work,¹⁰ and a schematic is shown in Fig. 1. The polymer solutions were obtained by dissolving SPEEK in DMF at 45 °C to form a 18 wt% solution. The spinning processes were briefly as follows: the spinning solution was feed to the orifices by the syringe pump, and the compressed air was delivered to the slots with controlling the pressure regulator. As soon as solution stream was pressed out of the orifices, it was subsequently attenuated to fibers by the high-velocity airflow. Then, the solvent evaporated and the nanofibers were deposited on a porous collector to form a fibrous mat. The main spinning parameters was shown below: air-blowing pressure (0.06 MPa),

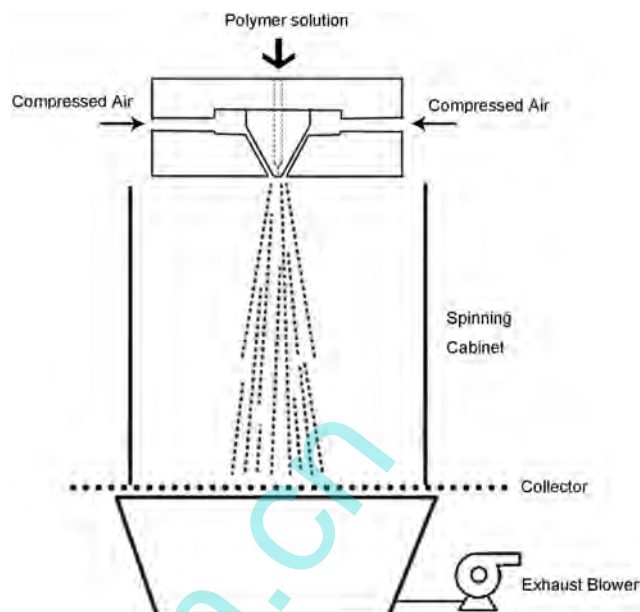


Fig. 1 Schematic of the solution blowing setup.

solution feeding rate per orifice (16 mL h^{-1}), orifice diameter (0.38 mm), width of the air slot (0.5 mm) and collecting distance (60 cm).

2.4 Preparation of SPEEK nanofibers/Nafion composite membrane

The fabricated nanofiber mats were dried under vacuum oven at 100 °C for 12 h to remove the residual solvent. After dry, the nanofiber mats were mechanically compressed between two metal plates at room temperature at 6 MPa for 3 minutes. Then, SPEEK nanofiber mats with different thickness were impregnated into Nafion solution to form pore-filled and fully dense nanofiber network composite membrane. Membranes containing 5, 10, 15, and 20 wt% of nanofibers were prepared and the samples have been designated as SPEEK/Nafion-5, SPEEK/Nafion-10, SPEEK/Nafion-15 and SPEEK/Nafion-20, respectively. In addition, pure Nafion and SPEEK membrane was prepared by solvent-casting method for a comparison. Thickness of the membranes was in the range of 190–220 μm .

2.5 Characterization

The morphologies of the surfaces of SPEEK nanofibers and composite membranes, as well as their cross sections, were studied by Atomic Force Microscope (AFM) using CSPM5500 and field emission scanning electron microscope (FESEM) using Hitachi S-4800. The membrane cross sections were obtained by immersing samples in liquid nitrogen.

X-ray diffraction (XRD) were performed on XRD spectroscopy (D8 Discover with GADDS, 40 kV, 40 mA) from 10° to 60° with a $\text{CuK}\alpha$ radiation ($\lambda = 1.541 \text{ \AA}$).

The thermal stability of the membranes was determined by thermogravimetric analysis (TGA) (STA409PC, Netzsch co,

Germany) with a heating rate at $10\text{ }^{\circ}\text{C min}^{-1}$ from $25\text{ }^{\circ}\text{C}$ to $800\text{ }^{\circ}\text{C}$ in nitrogen atmosphere.

Water uptake (WU) was measured by weighting the dry and wet membranes. The dry weight (W_d) was measured after the membranes were dried in vacuum oven at $60\text{ }^{\circ}\text{C}$ for 12 h. Then, the membranes were immersed in distilled water for 24 h at temperatures ranging from $20\text{ }^{\circ}\text{C}$ to $80\text{ }^{\circ}\text{C}$. The wet membranes were wiped dry with filter paper rapidly and weighed again as wet weight (W_w). The WU of membranes was calculated by the following formula:

$$\text{WU}(\%) = \frac{W_w - W_d}{W_d} \times 100$$

Swelling ratio was measured by the same method. The dry area (A_d), dry thickness (T_d), wet area (A_w) and wet thickness (T_w) of the membranes were obtained using the above method. The swelling ratio in-plane (ΔA) and through-plane (ΔT) of membranes was calculated by the following equations:

$$\Delta A(\%) = \frac{A_w - A_d}{A_d} \times 100$$

$$\Delta T(\%) = \frac{T_w - T_d}{T_d} \times 100$$

The proton conductivity of membranes was measured using four electrodes.¹³ The proton conductivity was calculated from the impedance data using the following equation:

$$\sigma = \frac{l}{lwR}$$

where, σ [S cm^{-1}] is proton conductivity, l [cm] is the distance between the electrodes, t [cm] and w [cm] are the thickness and width of the membrane, respectively. R [Ω] was derived from the low intercept of the high-frequency semicircle on a complex impedance plane with the real axis. The proton conductivity of the membranes are measured at different temperatures and humidities, and temperature and humidity are controlled by a constant temperature and humidity box (GP/GPS-D, shanghai Guangpin Equipment Co. Ltd).

The methanol diffusion coefficient through the membrane was measured using a diffusing equipment having two glass compartments, which were separated by the test membrane. One compartment contains distilled water and the other contains a 10 mol L^{-1} methanol solution with the same volume. Magnetic stirrers were used on the two compartments to ensure uniformity. Taking the specimen with the distilled water side every five minutes, and three specimens from a membrane. The methanol concentration of all specimens is determined using gas chromatography method. The methanol diffusion coefficient of the membrane was calculated by first Fick's law, using the following equation:

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

where, DK [$\text{cm}^2 \text{s}^{-1}$] is methanol diffusion coefficient, $C_{B(t)}$ is the methanol concentration of the water compartment, A [cm^2] is surface area of the membrane, L [cm] is membrane thickness, V_B [L] is the diffusion volume, C_A is the methanol concentration of the methanol compartment.

Tensile strength of the composite membranes was measured using an Instron universal testing machine (3369, USA) at room temperature. The specimen dimensions were 10 mm (W) \times 40 mm (L). At least 3 specimens of each membrane were tested and the values were averaged.

3. Results and discussion

3.1 Morphology and properties of SPEEK nanofibers/Nafion composite membranes

Solution blowing process is a new nanofiber spinning method with high productivity, and SPEEK was found easy to form fibers using the method. Fig. 2 shows the SEM micrographs of the solution blown SPEEK nanofibers and the corresponding diameter distribution map. The SPEEK nanofibers with diameters ranged between 80 nm – 210 nm had smooth surfaces and were arranged disorderly.

After the mats were impregnated into Nafion solution, the pores were filled up with Nafion solution and the pore-filled composite membrane formed. The membranes are compact and smooth, and Fig. 3 shows a typical surface and cross section morphology. Fig. 3(a) and (b) show 2D and 3D AFM micrographs of the surface morphology of the SPEEK/Nafion-20 membrane. The S_a (roughness average) value was 28.8 nm , which indicated the surface of the membrane was relatively smooth. Fig. 3(c) and (d) show the SEM images of the cross section of SPEEK/Nafion-20 membrane at different magnifications. No significant crack was observed and the nanofibers were totally immersed into a Nafion phase, which indicated good compatibility between nanofibers and the Nafion phase.

The XRD curves of SPEEK, Nafion, and the composite films are shown in Fig. 4. The peaks for SPEEK and Nafion were broad

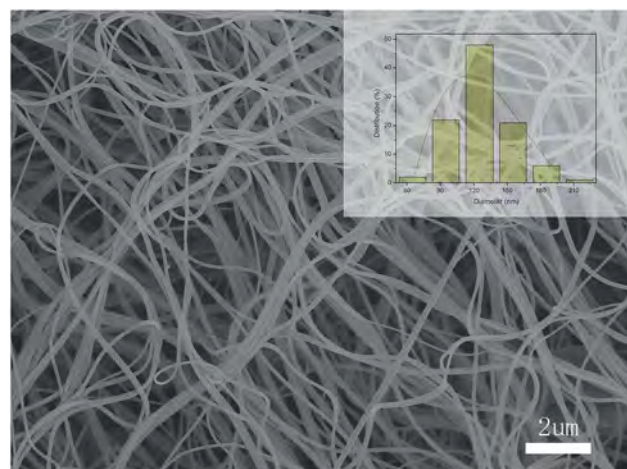


Fig. 2 SEM images of SPEEK nanofibers and the corresponding diameter distribution map.

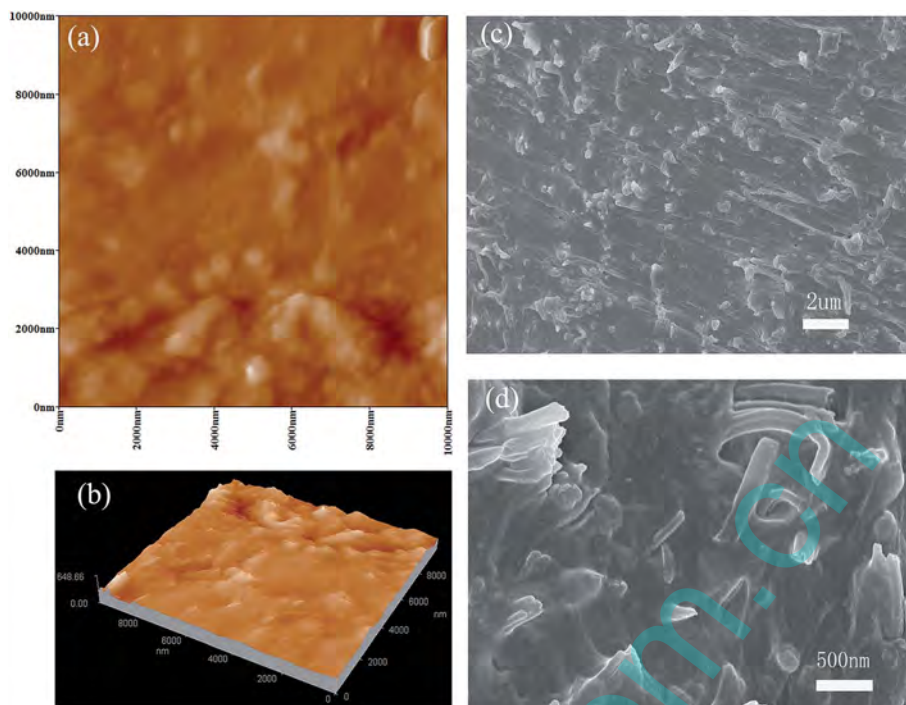


Fig. 3 Micrographs of SPEEK/Nafion-20 membrane, (a and b) 2D and 3D AFM images of surface, (c and d) SEM images of cross-section at different magnifications.

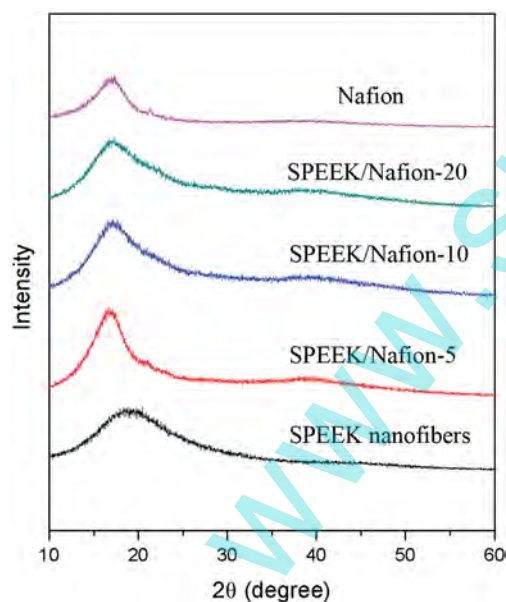


Fig. 4 XRD patterns of SPEEK, Nafion, and the composite membranes.

and occurred at 2θ of 20° and 17° , respectively. It was observed that the peak for the composite membranes occurred a shift along the direction of 2θ , and a new broad peak appeared at about 39° . This result was caused by the SPEEK nanofiber redistribution in the Nafion and revealed the good compatibility of the materials.

The thermal properties of all the membranes were analyzed using TGA, as shown in Fig. 5. The first step weight loss at 100–

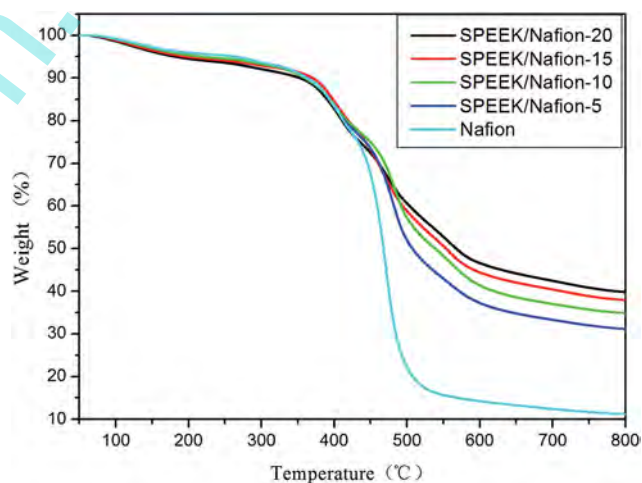


Fig. 5 TGA of SPEEK, Nafion, and the composite membranes.

200 °C for all samples was the evaporation of residual solvent and water. The second step weight loss of the composite membranes occurred at about 350 °C, representing the degradation sulfonic acid groups. The third step weight loss of the composite membranes occurred at about 500 °C, representing the main chain degradation of polymers.¹⁴ Nafion membrane possessed the most inferior thermal stability, and its weight loss was nearly 90% at 500 °C. The composite membranes showed highly thermal stability than Nafion membrane, which mainly owing to the addition of SPEEK nanofibers. SPEEK with superior thermal stability is the key to improve the thermal stability of the composite membranes.

3.2 Performance of the composite membranes as proton exchange membrane

3.2.1 Water uptake and swelling ratio. Water uptake is a quite important characteristics of any PEM. One of the proton conduction mechanisms in proton exchange membrane is Vehicular mechanism. In this mechanism, the water connected protons ($H^+(H_2O)_x$) gets through the membrane under the electroosmotic drag and the protons are transferred with them.¹⁵ Therefore, the existence of water can enhance the proton conductivity of the membrane to some extent. The WU of different membranes is shown in Fig. 6. As can be seen, all the composite membranes had higher WU than Nafion 117, and the WU values of the composite membranes increased with the increase of nanofibers in composite membranes. The pure SPEEK membrane possessed the highest WU. Higher WU by the introduction of SPEEK nanofibers into the Nafion matrix could be contributed to the strong interaction between the nanofibers and Nafion matrix,¹⁶ which could bound more water molecules.

The in-plane swelling ratio of all studied membranes is shown in Fig. 7(a). It was obviously observed that the SR values

of the composite membranes were lower than Nafion 117 and decreased with the increase of nanofibers in composite membranes. In general, the high water uptake also leads to high swelling of the membrane, however, the composite membrane containing nanofibers possessed both high water uptake and low swelling ratio, and a similar phenomenon was reported by Hung *et al.*¹⁷ The nanofibers with a crimp state in the composite membrane intertwined together, and formed a three-dimensional network structure which had a good dimensional stability. Combined with the good compatibility between nanofibers and the Nafion phase, the nanofibers mat acted as a skeleton in the composite membrane and suppressed the in-plane swelling of the membrane.

Fig. 7(b) shows the comparison of in-plane swelling and through-plane swelling at 20 °C of Nafion 117, the SPEEK/Nafion-5 and the SPEEK/Nafion-20 membrane. The through-plane swelling ratio of the composite membranes was slightly decreased with the increase of nanofibers in composite membranes, which also caused by the existence of the nanofibers in the composite membrane. However, the decrease of the in-plane swelling ratio was more pronounced than the through-plane swelling ratio, because the transverse stretching of the nanofibers was difficult than the longitudinal stretching of the nanofibers because of more nanofibers distribution in-plane, that is, the nanofibers skeleton limited the in-plane swelling more sufficiently than that in through-plane of the membranes. What's more, the Nafion matrix at the surface layers was easier to swelling in the thickness direction.

3.2.2 Proton conductivity. Proton conductivity behavior is studied as one of the most important features of a PEM for fuel cell application. Fig. 8(a) shows the measured proton conductivity of all the membranes at temperatures ranging from 20 °C to 80 °C at 100% relative humidity.

Firstly, it could be found that conductivity of all membranes exhibited positive dependency with temperature, which indicates that proton conduction is a thermally activated process. The conductivity values of all the composite membranes containing nanofibers were higher than Nafion 117 over the whole temperature range. Despite the existence of nanofibers played a positive role for the proton conduction, the content of

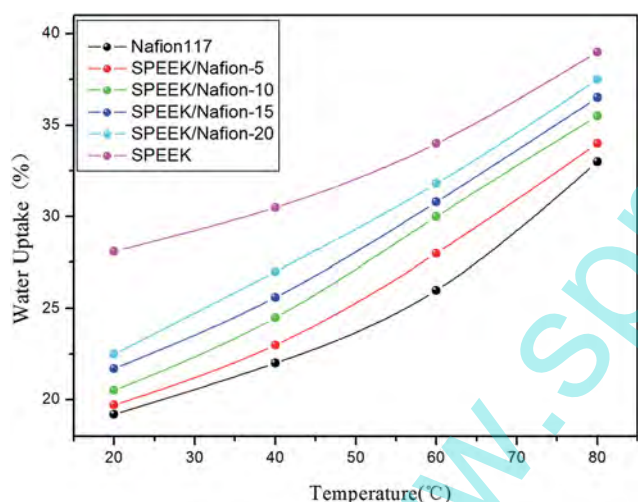


Fig. 6 Water uptake of Nafion 117, SPEEK and the composite membranes.

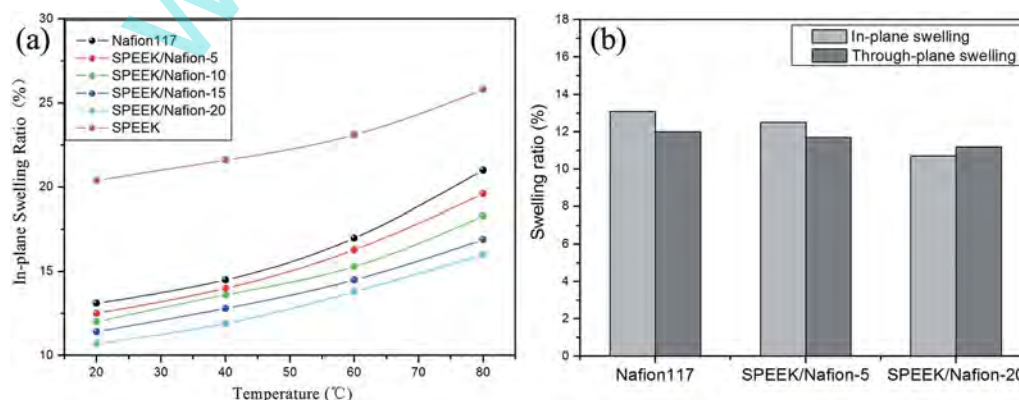


Fig. 7 Swelling ratio of Nafion 117, SPEEK and the composite membranes.

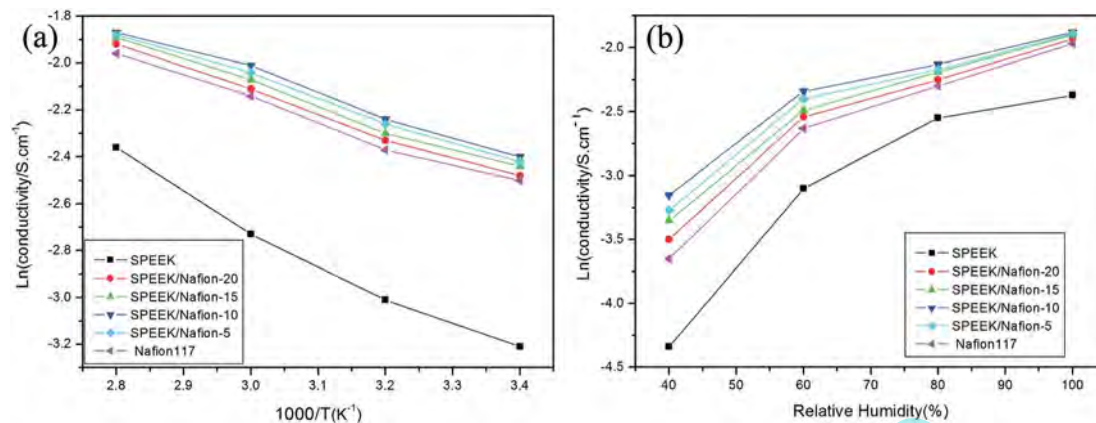


Fig. 8 (a) Temperature and (b) relative humidity dependence of proton conductivity for Nafion 117, SPEEK and the composite membranes.

Table 1 Methanol permeability, selectivity and of Nafion, SPEEK and the composite membranes

Sample	Methanol permeability $\times 10^{-7}$ (cm ² s ⁻¹)	Selectivity (10 ⁴ sscm ⁻³)	Tensile strength (MPa)
Nafion 117	14.1	5.7	27
SPEEK/Nafion-5	10.4	8.5	28
SPEEK/Nafion-10	9.9	9.2	29
SPEEK/Nafion-15	9.5	9.1	31
SPEEK/Nafion-20	9.2	9.0	32
SPEEK	6.1	6.5	42

nanofibers also affected the proton conductivity of the composite membrane. When the nanofiber content is less than 10 wt%, the conductivity of composite membranes increased with an increase in nanofibers. This may be because that nanofibers in composite membrane formed some channels through which the protons were transported rapidly and efficiently. However, the conductivity began to decrease when the nanofiber content was beyond 10 wt%. The decrease in proton conductivity at higher nanofiber content could be caused by the excess addition of SPEEK with lower proton conductivity than Nafion. Fig. 8(b) shows the effect of relative humidity (RH) on the proton conductivity of the membrane at 80 °C. The proton conductivity of all the membranes increased with increasing RH and the composite membranes containing nanofibers had shown higher proton conductivity than Nafion 117 over whole humidity range. This result was due to the higher water absorption of the composite membrane than that of Nafion 117.

3.2.3 Methanol permeability, selectivity and mechanical strength. Methanol crossover is a common problem to the DMFC. High methanol permeability not only causes the waste of methanol fuel but also reduces the efficiency of the cell.¹⁸ This problem is prominent in the Nafion membrane for DMFC, so it is very important to improve the methanol permeability of Nafion. The methanol permeability of all samples were measured at room temperature, as shown in Table 1. Obviously, the methanol permeability values of Nafion 117 was higher than that of all the composite membranes containing nanofibers by an order of magnitude, and the methanol permeability of the

composite membranes increased with the increase of nanofibers in composite membranes. This result revealed that the incorporation of nanofibers had an influence on the methanol crossover. Nanofibers in composite membranes may form a tortuous and anfractuous channel, which prevents the methanol crossover.¹⁹

Selectivity, which is defined as the ratio of proton conductivity to methanol permeability, is usually used as a comprehensive index to evaluate the performance of DMFC membranes.¹⁹ Room temperature selectivity values of all samples are shown in Table 1. The SPEEK/Nafion-10 membrane had the best selectivity, that is 9.2. It was concluded that the incorporation of SPEEK nanofibers into Nafion improved the selectivity of the composite membrane.

The mechanical properties of all the membranes are summarized in Table 1. Compared with the Nafion 117, the tensile strength of the composite membranes increased because of the fiber skeleton. The effect of the introduction of SPEEK nanofibers is obvious and all membranes had acceptable mechanical properties for PEM application.

4. Conclusion

Nanofiber mats based on SPEEK were successfully fabricated through solution blowing method, and the SPEEK nanofibers/Nafion composite membranes were prepared through impregnation method. The results showed that the incorporation of the SPEEK nanofibers into Nafion matrix enhanced the

performance of the composite membrane as proton exchange membrane and solution blown nanofiber was a promising filler in Nafion. The composite membrane containing 10 wt% of nanofibers showed the best proton conductivity and selectivity among all the samples. These results suggest that such modified Nafion membranes can be potentially used in fuel cells.

Acknowledgements

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