Synthesis and Characterization of a Series of SPEEK/TiO_2 Hybrid Membranes for Direct Methanol Fuel Cell

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ABSTRACT: Through sol-gel reactions, a series of sulfonated poly(ether ether ketone) (SPEEK)/TiO_2 hybrid membranes with various contents of nano-sized TiO_2 particles were prepared and characterized. It was found that with the increasing of the TiO_2 contents in the hybrid membranes, the water uptake and water retention increased. Meanwhile, the introduction of inorganic particles reduced the methanol permeability. The proton conductivity was enhanced by introduction of hydrophilic inorganic particles into the SPEEK membranes, which might be an effective approach to increase the working temperature of PEM. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1057–1062, 2008

Key words: SPEEK; PEM; TiO_2; membranes; composites; nanoparticles

INTRODUCTION

Proton exchange membrane fuel cells (PEMFC) are promising candidates for the applications in the fields of aerospace, energy and traffic, due to their high-energy conversion efficiency and good performance at low temperature.[1–8] Proton exchange membrane (PEM) is the key component of the PEMFC because of its proton conductivity and its role in the separation of the gas and electrodes. The traditionally used membranes are sulfonated perfluoropolymer membranes, such as Nafion®. These sulfonated perfluoropolymer membranes have high proton conductivity, mechanical strength, and chemical stability at 80°C.[9,10] However, there are some major problems for these sulfonated perfluoropolymer membranes.[11,12] First, the synthesis and sulfonation of the perfluoropolymer are very difficult, which makes them expensive The hydrolysis and sulfonation may degenerate the polymer and against the formation of membranes. Second, the temperature and water uptake are crucial to the performance of these membranes. The best working temperature for Nafion is 70–90°C. The water uptake will decrease rapidly when the temperature is higher, which causes the rapid decrease of conductivity.[13] Third, some hydrocarbons with high permeability, such as methanol, hinder the application of sulfonated perfluoropolymers as the proton exchange membranes in the direct methanol fuel cells (DMFCs). For these reasons, new PEMFCs are required more and more.[14,15] The organic–inorganic hybrid PEM is becoming an important approach. The hydrophilic inorganic particles can increase the hydration of the membrane, which could retain the humidity of the membrane at high temperature, and further increase the proton conductivity. For example, many kinds of hydrophilic inorganic particles have been successfully introduced into the Nafion membranes, including heteropolyacid,[16–20] SiO_2,[21–24] and molecular sieves particles.[25,26]

In the present work, we describe the preparation of a series of sulfonated poly(ether ether ketone) (SPEEK)/TiO_2 hybrid membrane with various contents of TiO_2 through sol-gel reaction. The large specific surface area of nano-sized TiO_2 particles could reduce the water vaporization at high temperature, and further increase the conductivity of the membrane.

EXPERIMENTAL

Preparation of SPEEK/TiO_2 hybrid membrane

The sulfonated degree of the SPEEK we used was 1.0, which was reported in our previous work.[27] First, 10% SPEEK solutions were made by adding certain amount of SPEEK into NMP. Then, $Ti[OBu]_4$, HCl, H_2O, and NMP were mixed together in a ratio of 10 : 0.2 : 2 : 10 and stirred thoroughly into a homogeneous sol. A series of hybrid membranes with different TiO_2 contents were prepared by adding various amounts of Ti-containing sols into the SPEEK solutions, followed by vigorous stirring. The mixed solutions were

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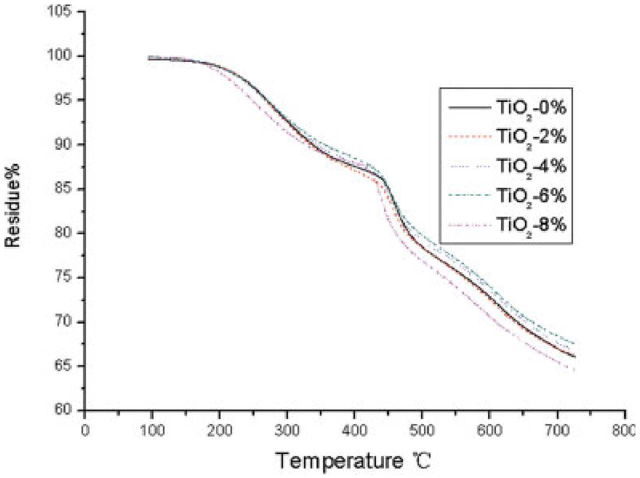


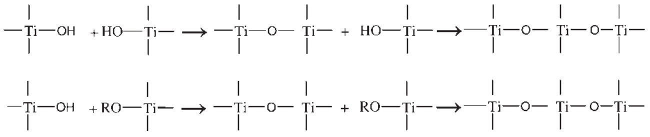
Figure 1 TGA curves of SPEEK and its hybrid membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

cast onto glass plates and dried at 70°C for 24 h. The membranes were further heated at 110°C for 5 h, in order to facilitate the formation of TiO_2 matrix.[28,29] The reactions included are as follows:

Hydrolysis reaction:

$$Ti\,(OR)_4 + x\,H_2O \rightarrow Ti\,(OH)_x\,(OR)_{4-x} + x\,ROH$$

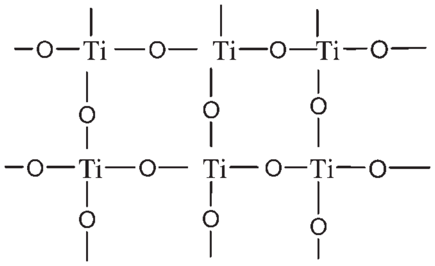
Condensation reaction:



$$-Ti-OH + HO-Ti- \longrightarrow -Ti-O-Ti- + HO-Ti- \longrightarrow -Ti-O-Ti-O-Ti-$$

$$-Ti-OH + RO-Ti- \longrightarrow -Ti-O-Ti- + RO-Ti- \longrightarrow -Ti-O-Ti-O-Ti-$$

where R denotes C_4H_9. At the end of the sol-gel reactions, the TiO_2 matrix was formed:



Characterization of the membranes

Thermal stabilities of the membranes

TGA measurement was performed on Pyris 1TGA (Perkin-Elmer [Shanghai, China]). First, the membranes were heated in N_2 at 100°C for 20 min to remove the remaining water and solvents. Then, the temperature was raised up to 750°C at a heat rate of 10°C/min. The TGA result (Fig. 1) shows that the 10% weight loss temperatures (T_{10}) of all the hybrid membranes are $\sim$ 340–350°C (Table I). From the TGA curves, it is easy to see that there are two main steps during the decomposition of the membranes: one that corresponds to the decomposition of the $—SO_3Na$ groups from the SPEEK, and one that corresponds to the crack of the backbones. The decomposition temperatures of all hybrid membranes are high, and the introduction of TiO_2 particles doesn't decrease the thermal stability of the membranes.

Water uptake and ion exchange capacity of the hybrid membranes

The SPEEK membrane and hybrid membranes with various TiO_2 contents were dried in vacuum oven and weighted as M_{dry}. The membranes were immersed in water for 48 h and then taken out. After the water on the surfaces of them was rapidly wiped off, the weights of the membranes were measured as M_{wet}. The water uptake (WU) was calculated as follows:

$$WU = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100\,\%. \tag{1}$$

The SPEEK membrane and hybrid membranes were immersed in a 1.0 mol/L HCl solution for 24 h. After washing with large amount of deionized water and drying, the membranes were immersed in a 1.0 mol/L NaCl solution to exchange the H^+ with Na^+. The exchanged H^+ ions within the solutions were titrated with a 0.01 mol/L NaOH solution.

Water desorption curves of the membranes

Water desorption analysis was carried out on Pyris 1TGA(Perkin-Elmer). The membranes were heated at

TABLE I
Analytical Parameters of SPEEK and the Hybrid Membranes

Property	TiO_2-0%	TiO_2-2%	TiO_2-4%	TiO_2-6%	TiO_2-8%	Nafion®
T_{10} (°C)	348	340	343	347	345	
Water uptake at 25°C (%)	34.9	42.8	48.3	50.40	61.5	38.6
Water diffusion at 80°C (cm^2/s)	2.51×10^{-9}	1.72×10^{-9}	7.65×10^{-10}	5.31×10^{-10}	2.75×10^{-10}	
Water diffusion at 100°C (cm^2/s)	4.09×10^{-9}	2.23×10^{-9}	1.38×10^{-9}	9.54×10^{-10}	4.12×10^{-10}	
Ion exchange capacity (IEC) (mmol/g)	1.79	1.70	1.72	1.75	1.77	0.91
Methanol permeating coefficient at 25°C (cm^2/s)	4.25×10^{-6}	3.18×10^{-6}	2.02×10^{-6}	1.12×10^{-6}	5.87×10^{-7}	2×10^{-6}
Conductivity at 80°C (S/cm)	0.063	0.071	0.079	0.087	0.096	0.1063
Conductivity at 100°C (S/cm)	0.064	0.080	0.090	0.097	0.107	0.109

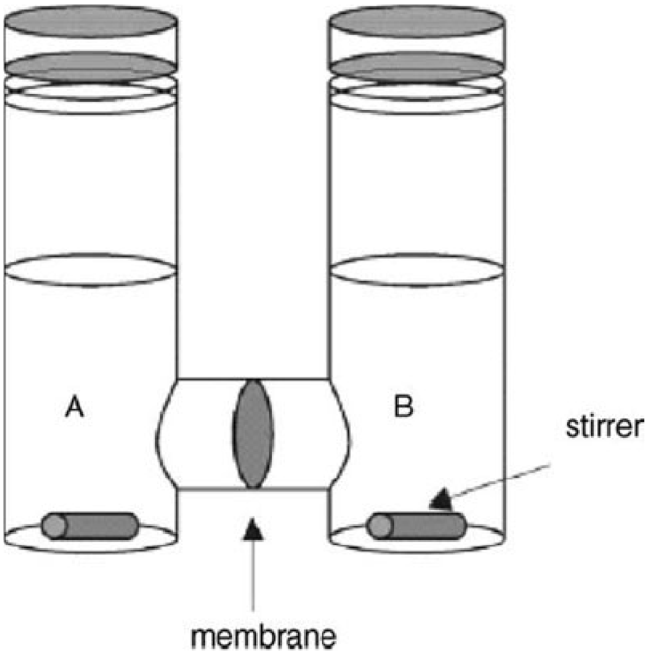


Figure 2 Diffusion cell.

80°C for 1 h. During measurement, the pressure of the test cell was kept consistent. The changes of the contents of water in hybrid membranes with time were recorded.

Methanol permeability

The methanol permeability of the membranes was characterized in the permeation device shown in Figure 2. Deionized water and methanol solution was placed in vessel A and B, respectively, and stirred by magnetic stirrers. The amount of methanol in vessel B was determined by GC (ShimadzuGC-8A). The methanol permeability coefficient was calculated as follows:

$$C_B(t) = \frac{A}{V_B}\,\frac{DK}{L}\,C_A(t - t_0) \tag{2}$$

where C_A and C_B are the concentrations of methanol in vessel A and B, respectively. A and L denote the area and thickness of the membrane, respectively. V_B is the volume of permeated compartment, and DK is the methanol permeation coefficient.

Proton conductivity

The measurements of proton conductivity of the membranes were carried out via the AC impedance spectroscopy using a Princeton Applied Research model 273A potentiostat with a model 5210 Frequency Response Detector (EG&G PARC, Princeton, NJ) from 100 mHz to 100 kHz.[30] The device with the test cell is shown in Figure 3. During testing the humidity was kept at 100%, the proton conductivity was calculated as follows:

$$\sigma = L/RA, \tag{3}$$

where σ denotes the proton conductivity, L denotes membrane thickness, R denotes membrane resistance, and A denotes membrane area.

RESULTS AND DISCUSSIONS

Microstructure of the hybrid membrane

Figure 4 shows the SEM pictures of the hybrid membranes with 2% [Fig. 4(a)], 4% [Fig. 4(b)], and 8% [Fig. 4(c)]. TiO$_2$. It can be seen that the particle diameter increased with the content of the inorganic composition. The particle diameters were about 30 nm when the membrane contained 2% TiO$_2$; the particle diameters were about 60 nm when the membrane contained 4% TiO$_2$; when the content of TiO$_2$ increased to 8%, the particle diameters were about 100 nm, and some aggregations could be found.

Figure 4(d) presents a TEM picture of the hybrid membrane with 4% TiO$_2$. It can be seen that the diameters of the inorganic particles were below 100 nm, which suggested that the inorganic particles dispersed into the membrane were nano-sized.

Water uptake and water desorption

Water is necessary for the conduction of protons in PEM.[31] This is because (1) the existence of water is the prerequisite of the formation of supermolecular matrix; and (2) the H$^+$ ions in the —SO$_3$H groups can form H$_3$O$^+$ with water molecules, which decrease the binding between —SO$_3$H and protons, and further facilitate the movement of protons. This is why a dry membrane is nearly insulated. So, the water uptake of the membrane is an important factor that influences the proton conductivity. The more the water uptake of the membrane, the larger the proton conductivity will be, and vice versa. Table I lists the water uptake of hybrid membranes at room temperature. It can be

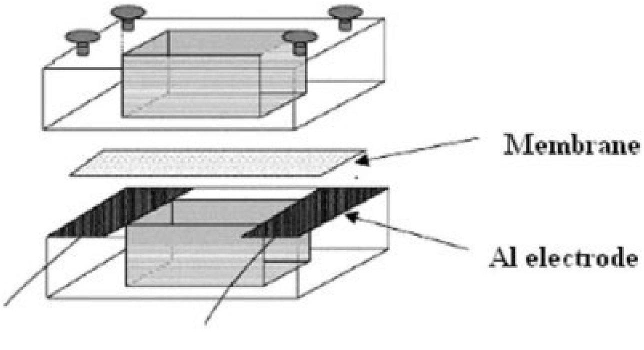


Figure 3 Setup for conductivity measurement.

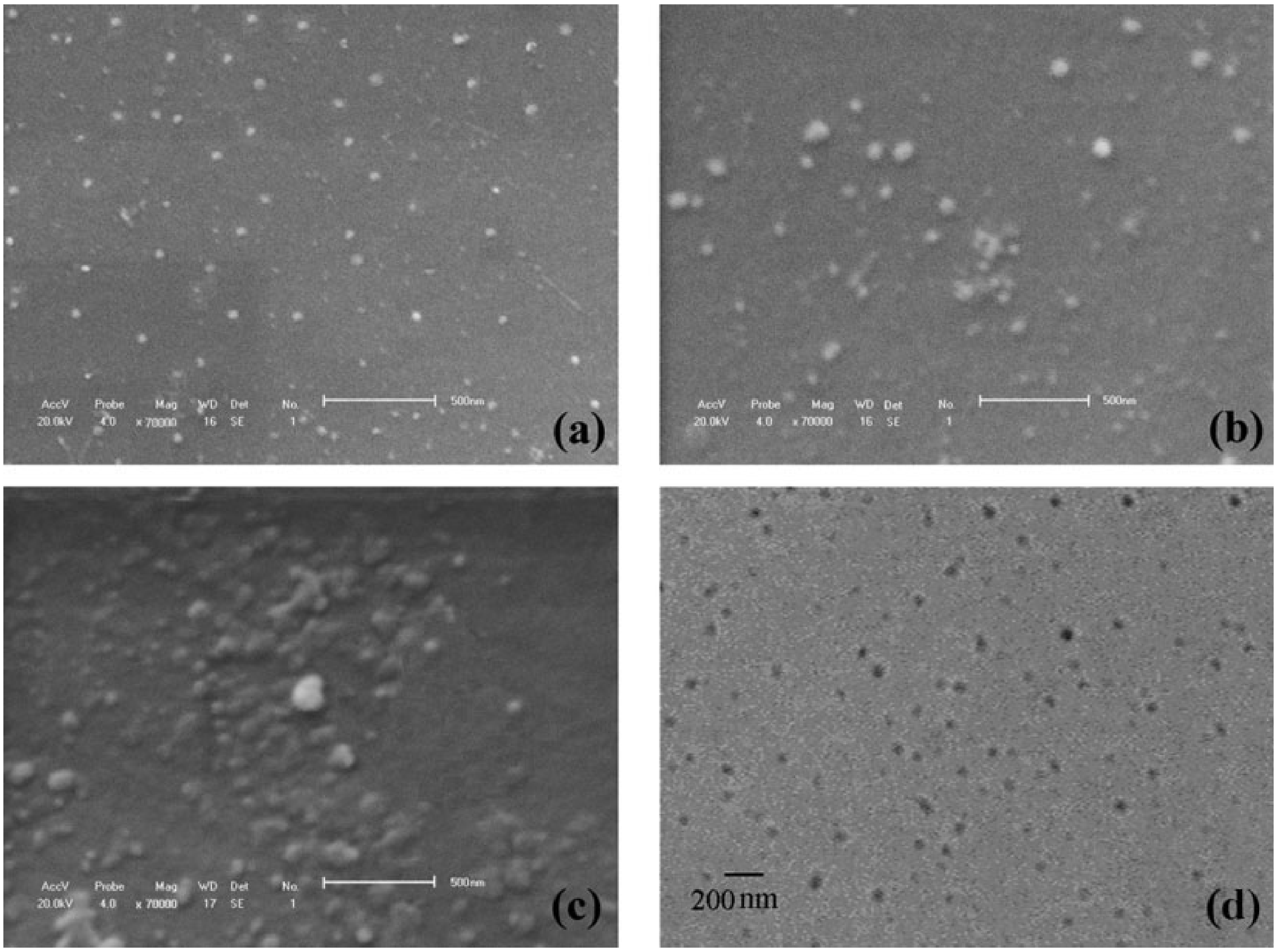


Figure 4 SEM pictures of (a) SPEEK50, 2%; (b) SPEEK50, 4%; (c) SPEEK50, 8%; and (d) the TEM picture of SPEEK50, 4%.

seen that the water uptake increases dramatically with the increase of the contents of TiO_2. This is because that nano-sized TiO_2 particles have large specific surface area, which induce the higher water uptake of hybrid membranes than that of the pure SPEEK membrane.

Similarly, the water retention of PEM also plays an important role on the proton conductivity. The volatility of Nafion at high temperature hinders its application.[32] Figure 5 shows the desorption curves as plots of M_t/M_∞ versus $t^{1/2}$ for different hybrid membranes, which represent the water retention of them. Since the diffusions of water in membranes at the beginning follow the Fickian behavior,[33] the diffusion coefficients could be calculated from the slops of the curves at the beginning:

$$\frac{M_t}{M_\infty} = 4\left(\frac{D_t}{\pi l^2}\right)^{1/2}, \tag{4}$$

where l is the thickness of the membrane, D is the water diffusion coefficient, and M_t/M_∞ denotes the water desorption. The curves in Figure 5 were measured at 100°C, and the thickness of the membranes was about 130 μm. The diffusion coefficients mea-

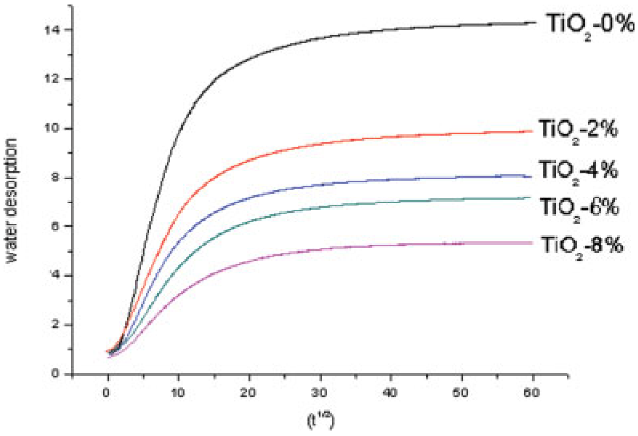


Figure 5 Water desorption isotherm of membranes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

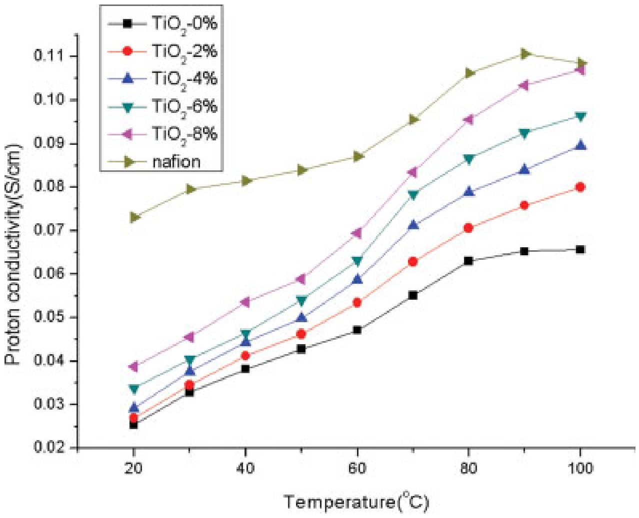


Figure 6 Proton conductivity of membranes with different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sured at 80°C and 100°C are listed in Table I. From these data, it can be seen that the addition of nano-sized TiO$_2$ particles decreases the water diffusion speed and further increases the water retention of the hybrid membranes dramatically.

Proton conductivity and methanol permeability

Figure 6 plots membrane proton conductivity versus temperature. At the same temperature, the introduction of inorganic particles increases the proton conductivity of the membranes. With a temperature of > 80°C, the proton conductivity of SPEEK and Nafion decreases a little bit, while the proton conductivity of hybrid membranes keeps growing. The proton conductivity values of the hybrid membranes with various contents of TiO$_2$ measured at 80°C and 100°C are listed in Table I. From these data, it can be seen that the proton conductivity values of the membranes with 8% TiO$_2$ at 80°C and 100°C are up to 0.096 S/cm and 0.107 S/cm, respectively, which are close to the proton conductivity of Nafion. Ion exchange capacity (IEC) and water uptake play important roles on the proton conductivity of PEMs. From the IEC results listed in Table I, it could be seen that the water uptake of the membranes will be the key factor influencing the proton conductivity, since the IEC values of hybrid membranes are close to that of pure SPEEK. Because there are lots of hydrophilic Ti-OH groups on their surfaces, the introduction of nano-sized TiO$_2$ could increase the water uptake, which could be seen from Table I. Meanwhile, instead of in the form of single particles, TiO$_2$ existed in the form of intersecting matrix, which could greatly enhance the water retention of the membranes at high temperature. From Figure 5, it could be seen that higher water retention of hybrid membranes induced higher IEC compared with pure polymer membrane.[34]

Table I lists the methanol permeability of the SPEEK and the hybrid membranes. It is easy to find that the methanol permeability decreases with the increasing of the content of TiO$_2$ in the membrane. Thus, the methanol permeability of the SPEEK/TiO$_2$ hybrid membranes was effectively reduced compared with pure SPEEK membrane.

CONCLUSIONS

A series of SPEEK/TiO$_2$ hybrid membranes with various contents of TiO$_2$ were prepared through sol-gel reactions, and characterized by various methods. Because of the larger specific surface area and size effect of nano-sized particles, the introduction of TiO$_2$ into the membranes increased the water uptake and water retention, which caused the high proton conductivity of membranes at high temperature. Meanwhile, the introduction of inorganic particles reduced the methanol permeability. The characterization results showed that the introduction of hydrophilic inorganic particles into the SPEEK membranes can effectively increase their working temperature.

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