Suppression of methanol cross-over in novel composite membranes for direct methanol fuel cells*

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Abstract: A series of novel composite membranes was prepared by using poly(vinyl alcohol) (PVA) with polyimide (PI) as base material and 8-trimethoxysilylpropyl glycerine ether-1,3,6-pyrenetrisulfonic acid (TSGEPS) as proton conductor for direct methanol fuel cells (DMFCs). The parameters of membranes, including water sorption, hydrolysis stability, dimensional stability, proton conductivity, and methanol permeability were studied. The proton conductivity of the membranes is in the order of 10^{-2} S/cm, and the membranes show better resistance to methanol permeability (1.51×10^{-7} cm^2 s^{-1}) and better selectivity (20.6×10^4 S cm^{-3} s) than those of Nafion115 under the same measurement conditions.

Keywords: composite membranes; direct methanol fuel cells; methanol permeability; polyimide; proton conductivity.

INTRODUCTION

Fuel cells are attracting much attention as promising alternative power sources, owing to many advantages such as high power density and low emission. Of the numerous types, direct methanol fuel cells (DMFCs) are considered as promising power sources in portable applications, because of their high efficiency, high charge density, and simplicity [1,2]. As a key component of DMFCs, proton exchange membranes (PEMs) display several characteristics, including that of permitting the transportation of proton generated at the anode, and acting as a barrier between the fuel and the oxidant. At present, state-of-art membranes such as Nafion, the perfluorosulfonic acid polymer, shows high proton conductivity and chemical stability, but has some drawbacks such as high cost, synthetic difficulties, and especially its high methanol permeability, which leads to reduced efficiency of DMFCs [3]. Accordingly, it is necessary to develop new membranes that reduce methanol permeability and increase proton conductivity.

To date, there have been numerous attempts to reduce methanol permeability of PEMs that mainly focus on modifying the surface of the Nafion membranes and preparing nonfluorinated membranes with low methanol cross-over. Methods to modify Nafion membranes to depress their methanol cross-over include: adding inorganic nanocomposites such as silica and layer clay that introduce a winding pathway for methanol molecules [4,5], and blending polymers that could block the methanol transport such as polyaniline and poly(vinyl alcohol) (PVA) [6,7]. However, their proton conductivity is much lower than that of pristine Nafion membranes. As the nonfluorinated membranes, sulfonated aromatic polymers such as poly(ether ether ketone)s [8–10], poly(ether sulfone)s [11,12], and polyimides (PIs)

[13–15] have been widely investigated as candidate PEM materials, owing to their low methanol permeability. But these membranes require the addition of large amounts of sulfonic acid conductors to increase conductivity, which makes them excessively water-swollen or soluble in water. Therefore, they fail to meet the requirement of durability under DMFCs operating conditions. To overcome these drawbacks, preparation of composite membranes is a promising approach since it has the potential to combine the attractive features of each component [16–18].

In this paper, we describe the preparation of a series of composite membranes by using PVA with PI as base material and 8-trimethoxysilylpropyl glycerine ether-1,3,6-pyrenetrisulfonic acid (TSGEPS) as proton conductor. In this system, sieving out organic proton conductor to blend with polymer, in order to avoid the sulfonic acid group to directly link with the main chain of the polymer leading to the polymer degradation. The properties, such as proton conductivity, water uptake, hydrolytic stability, dimensional stability, methanol permeability, and thermal stability are investigated.

EXPERIMENTAL SECTION

Materials

PI (M_w 200 000) was obtained from Prof. Shiyong Yang's Research Team at the Institute of Chemistry, Chinese Academy of Sciences; PVA (M_w 50 000) was obtained from Kuraray Co. Ltd. (Japan), and γ-glycidoxypropy1 trimethoxysilane was obtained from HUNG PAI Chemistry Co. Ltd. (China). 8-Hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt (Aldrich), dimethyl sulfoxide (DMSO, Beijing Chem.), and sodium hydride (Tianjin Beidouxingchem.) were used as received.

Synthesis of proton conductor

The synthesis of TSGEPS is shown in Scheme 1. In a 250-ml three-necked flask equipped with a magnetic stirring bar and nitrogen inlet, 8-hydroxy-1,3,6-pyrenetrisulfonic acid trisodium salt (2.26 g, 5 mmol) and sodium hydride (0.24 g, 10 mmol) were added to DMSO (50 ml). The mixture was stirred at 50 °C for 2 h, then γ-glycidoxypropy1 trimethoxysilane (2.36 g, 10 mmol) was added, and the mixture was heated at 80 °C for 24 h. The solution was evaporated under vacuum to remove solvent and residual γ-glycidoxypropy1 trimethoxysilane. The residual brown solid was dried at 120 °C under vacuum overnight (yield: 87.6 %). Fourier transform-infrared (FT-IR) (KBr): 3428 (–CH_2–OH), 2927 (–CH_2–), 1625 (C_6H_5–SO_3^-), 1231 (C_6H_5–O–CH_2–), 1150 (CH_2–O–CH_2), and 1007 (Si–O).
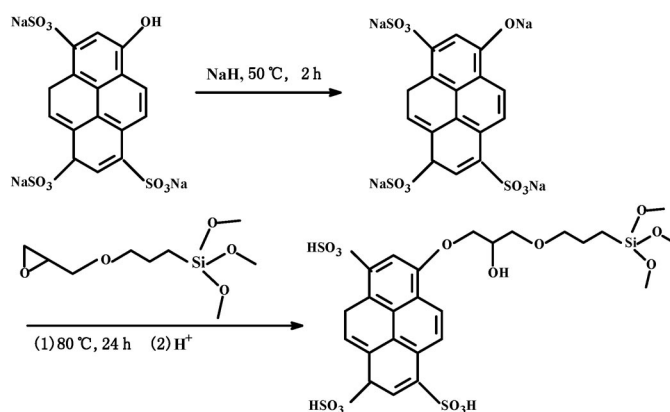
Scheme 1 Synthesis of TSGEPS.

Fabrication of composite membranes

TSGEPS was dissolved in DMSO to form about 8.0 wt % solution. Then it was added to a PI/PVA/DMSO solution (5 wt % PI and 5 wt % PVA). The resultant TSGEPS/PI/PVA/DMSO solution was stirred for 2 h at room temperature for sol-gel reaction, cast onto a flat poly(tetrafluoroethylene) (PTFE) plate, then heated according to a schedule of 60 °C, 6 h; 80 °C, 2 h; 100 °C, 1 h; 120 °C, 1 h; 140 °C, 1 h; and 160 °C, 1 h. The resultant composite membranes were immersed in methanol to remove residues, and then they were acidified with 25 % H_2SO_4 solution for 24 h and washed with deionized water.

Measurement and evaluation of properties

FT-IR spectra were recorded with a Bruker Tensor-27 spectrometer. Scanning electron microscope (SEM) observations of the composite membranes were performed on a Hitachi S-4800 model. The thermal stability of the composite membranes was determined by thermogravimetric analysis (TGA) with a Shimadzu DTG-60. Before the analysis, the membranes were dried at 100 °C under vacuum for 12 h to remove of the absorbed water. The analysis was performed from 30 to 550 °C at heating rate of 10 °C/min in nitrogen.

Water uptake was determined as follows. The composite membranes were vacuum-dried at 100 °C for 12 h and weighed. Then the samples were immersed in distilled water for 2 h, wiped dry, and quickly weighed again. The water uptake of composite membranes was calculated using the following equation:

$$\text{Water uptake (\%)} = (W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100 \tag{1}$$

where W_{dry} and W_{wet} are the weight of dry and corresponding wet membranes, respectively.

Proton conductivity of the samples was measured using HIOKI LCR 3520 HI TESTER at 1 kHz, and the samples were placed in a Teflon spacer ring, compressed between two stainless steel electrodes, and placed in a container containing some distilled deionized water to keep the relative humidity of 100 %. The proton conductivity of the membrane was determined by

$$\sigma = L/(R \times S) \tag{2}$$

where L is the distance between the two reference electrodes, R is the ohmic resistance of the membrane, and S is the cross-section area of membrane.

Methanol permeability was measured using a two-chamber diffusion cell. One 70-ml chamber (A) contained aqueous 5 M methanol; another 70-ml chamber (B) was filled with deionized water (70 ml). A membrane was placed between the two chambers by a screw clamp. Then the methanol concentration was periodically monitored by a GC-14B gas chromatograph (Shimadzu, Japan). The methanol permeability P was determined according to the following equation:

$$P = (k \times V_B \times L)/(A \times C_A) \tag{3}$$

k is the slope of the straight-line plot of methanol concentration in chamber B vs. permeation time, V_B is the initial volume of deionized water, L is the membrane thickness, A is the membrane area, C_A is the initial methanol concentration.

RESULTS AND DISCUSSION

The structures of base materials are shown in Scheme 2. As the base material of membrane, PI and PVA could decrease the methanol cross-over. Besides, PI possesses excellent thermal stability and mechanical strength, and PVA has hydrophilic property that could increase proton conductivity of membrane. As a proton conductor, TSGEPS not only provides a large amount of proton, but also forms a cross-link
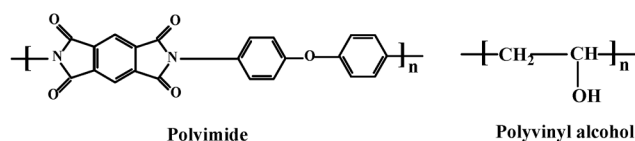
Scheme 2 Structure of base material for the composite membrane.

network with the base material to avoid its weight loss in water. Meanwhile, the organic–inorganic composite membranes are obtained by the sol-gel reaction. The composite membranes are named after PI-PVA-TSGEPS-*n* (*n* corresponds to the weight percent of TSGEPS in composite membrane).

The water uptake is great major factor in DMFCs because it is closely related to the proton conductivity and mechanical strength. The adequate amount of water uptake contributes to enough rate of proton transportation. On the other hand, the excessive amount of water uptake will reduce the mechanical stability of the membranes. So controlling membranes with appropriate degree of water uptake is very important. The water uptake of the composite membranes with the amount of PVA is shown in Fig. 1. It indicates that the water uptake increases with the content of PVA. When the addition amount of PVA is 50 %, the water uptake of the membrane is close to that of Nafion115 and has enough mechanical strength.
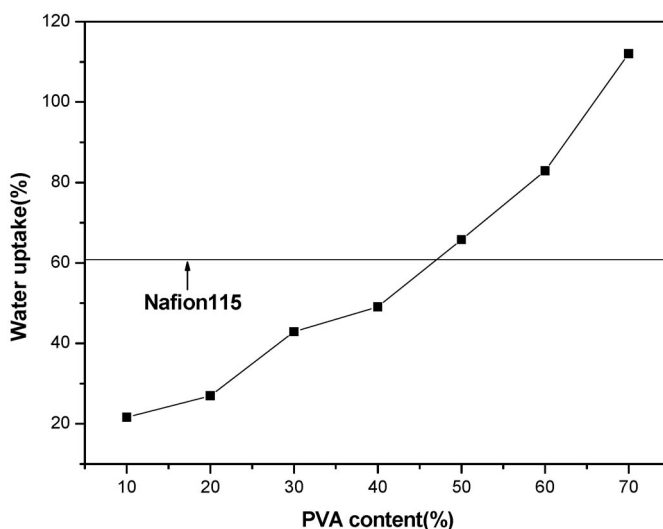

Fig. 1 Water uptake behavior to different content of PVA in composite membranes.

The morphology of composite membranes is analyzed by a scanning electron microscope. From the SEM micrographs of composite membranes (Fig. 2), it can be seen that polymers exhibit fine microstructures indicating homogeneous morphology without separation. In low content of TSGEPS, the homogeneity of disperses of silica in the composite membrane, the particles sizes are 20–100 nm. When the content of TSGEPS equals 30 %, silica aggression occurred in composite membranes.

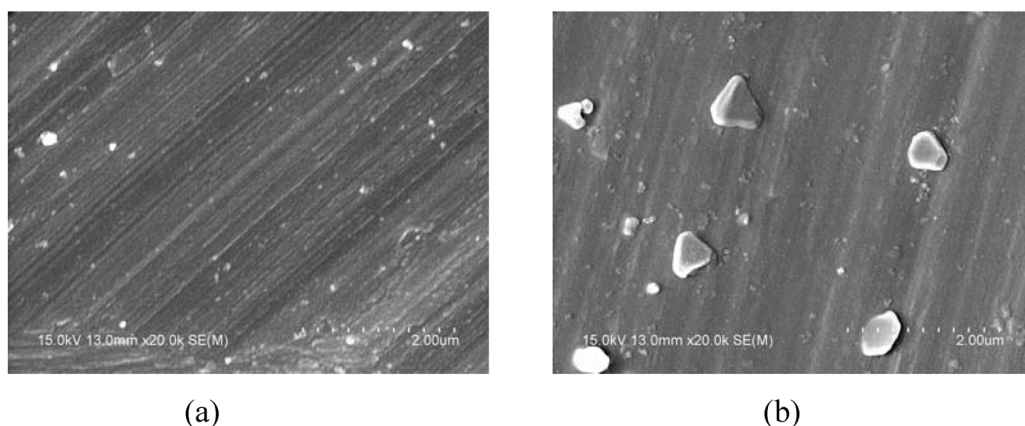(a)   (b)

Fig. 2 Cross-section SEM microphotograph of composite membranes: (a) PI-PVA-TSGEPS-10; (b) PI-PVA-TSGEPS-30.

The proton conductivity is especially important to membranes since it acts as a significant role in the performance of DMFCs. Figure 3 shows the data of the proton conductivity of composite membrane at 100 % related humidity at different temperatures. It obeys the Arrhenius relationship. When the concentration of TSGEPS increases, the proton conductivity of membrane also increases. At 70 °C with 100 % relative humidity (RH), the proton conductivity of PI-PVA-TSGEPS-30 is 0.084 S/cm, close to that of Nafion115 (0.093 S/cm). However, the membrane is fairly fragile when the amount of TSGEPS exceeds 30 %. The mechanical strength of composite membranes might decrease due to the increase of the sulfonic acid group. Thus, the TSGEPS content is a major factor in controlling the proton conduction in membranes.
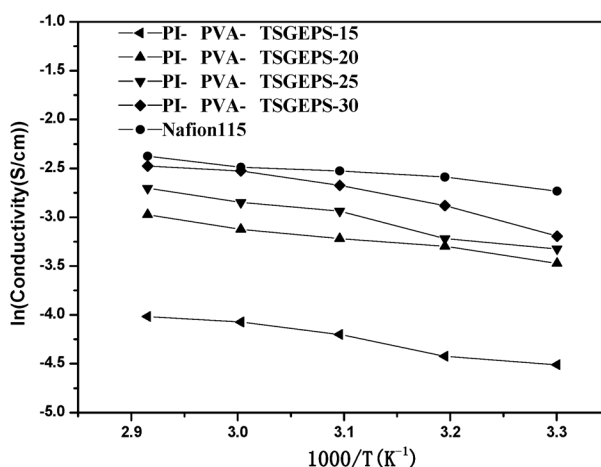

Fig. 3 Relationship between temperature and proton conductivity with different concentration of TSGEPS in composite membranes at 100 % RH.

Methanol permeability of Nafion115 and the composite membranes is shown in Fig. 4. The membrane thickness was maintained at nearly 90 μm, which is much lower than that of Nafion115 (120 μm). The methanol permeability of composite membrane is nearly one order of magnitude lower than that of
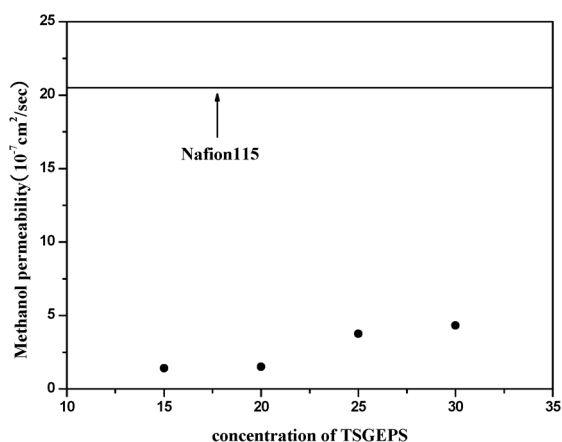
Fig. 4 Methanol permeability for composite membranes.

Nafion115 (2.05×10^{-6} cm^2 s^{-1}) under the same testing conditions. This phenomenon could be mainly attributed to two reasons: (1) PI and PVA have great resistance to methanol cross-over, and (2) the silica by a sol-gel reaction exists in the ion-channel to increase the length of the path along which methanol permeates through the membrane.

Selectivity is a characteristic factor that can be used to evaluate both proton conductivity and methanol permeability. Careful attention should be paid to the use of selectivity because low methanol permeability, and even low proton conductivity gives high selectivity. Accordingly, the selectivity must be employed only in comparison with the same order of magnitude in proton conductivity. So, the selectivity can be used just as a barometer to develop the best proton-conductive membranes with reduced methanol permeability. Table 1 summarizes the selectivity (φ), proton conductivity (σ), and methanol permeability (P_{MeOH}) for Nafion115 and the composite membranes. All of the composite membranes have higher selectivity than Nafion115 due to their high proton conductivity and low methanol permeability. Among these, PI-PVA-TSGEPS-20 membrane has a good comprehensive performance and exhibits the φ value seven times higher than that of Nafion115. Accordingly, this composite membrane appears to be a promising candidate that can avoid severe decreasing of proton conductivity and simultaneously promote the methanol resistance of membrane.

Table 1 Proton conductivity, methanol permeability, and selectivity of composite membranes.

Membrane	Proton conductivity (σ) (S cm^{-1})	Methanol permeability (P_{MeOH}) (cm^2 s^{-1})	Selectivity ($\varphi = \sigma/P$) (S cm^{-3} s)
PI-PVA-TSGEPS-15	1.1×10^{-2}	1.40×10^{-7}	7.8×10^4
PI-PVA-TSGEPS-20	3.1×10^{-2}	1.51×10^{-7}	20.6×10^4
PI-PVA-TSGEPS-25	3.6×10^{-2}	3.76×10^{-7}	9.5×10^4
PI-PVA-TSGEPS-30	4.1×10^{-2}	4.32×10^{-7}	9.5×10^4
Nafion115	6.5×10^{-2}	20.5×10^{-7}	3.1×10^4

The TGA curves of the composite membranes (Fig. 5) show that the weight loss temperature started at about 220 °C, indicating these composite membranes have great thermal stability. The thermal stability slightly decreases with the TSGEPS content due to the increase of the sulfonic acid group.
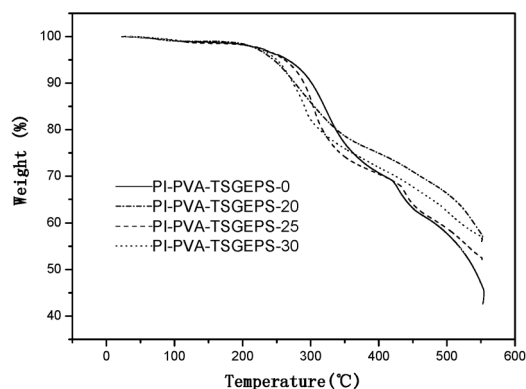
Fig. 5 TGA thermo-diagram of PI-PVA-TSGEPS composite membranes.

The hydrolytic stability test for the composite membranes was performed by immersing them into deionized water at 80 °C, and the stability was characterized by the elapse time when the hydrated membranes lost mechanical properties [19]. The hydrolytic stability of PI-PVA-TSGEPS-20 membrane exceeded 500 h, which was superior to that of SPI reported in ref. [19]. Dimensional changes were measured by immersing the membranes into deionized water at 80 °C, the area changes were calculated from following equation: $\Delta A = (A - A_0)/A_0$. A_0 and A are the area of membrane before and after soaking treatment [20]. The ratio of area change in PI-PVA-TSGEPS-20 membrane is 10.8 %, much lower than that of Nafion115 membrane (25.0 %) under the same measurement conditions. So the composite membranes possess great stability of dimension and hydrolysis.

CONCLUSIONS

In summary, a series of novel composite membranes based on the polymers with PI, PVA, and proton-conductor of TSGEPS have been prepared, and their methanol permeability is one order of magnitude lower than that of Nafion115 membrane and possesses better thermal, hydrolysis, and dimensional stability. The composite membrane with 20 % TSPS exhibits that proton conductivity of about 10^{-2} S/cm, very low methanol permeability (1.51×10^{-7} cm^2 s^{-1}), and φ value seven times higher than that of Nafion115. As a result, these composite membranes have the potential for technological application in DMFCs.

ACKNOWLEDGMENTS

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