

Preparation and Characterization of Composite Membrane for Low Temperature Direct Methanol Fuel Cells

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Abstract: A series of H₃PO₄-doped composite membranes based on poly(vinyl alcohol)(PVA) and silica have been prepared by sol-gel process. The proton conductivity, as well as properties of swelling, methanol permeation, was measured in this study. The proton conductivity increased with the molar ratio of H₃PO₄ to silica. With the silica content increasing, swelling degree decreased and methanol permeability showed a slight increase. It suggested that the former was mainly determined by hydrophilicity of the membrane, while the latter was dominated by the interconnectivity of matrix. According to the value of σ/P , the optimal conformations of these composite membranes were 60,70,80 wt.% of PS-*x* in membranes, where *x* were 1.5,1.0, and 0.5, respectively. These composite membranes were thermal stability up to 200°C.

Keywords: Proton conductivity, Composite material, Sol-gel, DMFC

1. Introduction

Direct methanol fuel cells (DMFCs) are attractive as mobile and portable power sources because methanol is cheap and can be carried conveniently and efficiently in comparison with pure hydrogen. Most of the attentions have been focused on DMFCs with solid state electrolyte due to its advantages such as simpler system, lower weight and smaller size of fuel cells.¹⁻²⁾

A successful membrane for DMFC must be not only good proton conductor, but also good fuel barrier during cell operation. The commercial available polymer electrolyte membrane, like Nafion[®] has a high conductivity at room temperature and high chemical and mechanical stability. However, large-scale applications of these membranes are limited due to high cost and poor barrier to methanol crossover. The crossover not only leads to fuel loss, but also decrease cell performance.³⁾ Considerable efforts have been made to reduce methanol crossover,

as well as to reach high proton conductivity using organic-inorganic composite membranes, such as Nafion/silica,⁴⁾ in which silica served as physical barrier to methanol crossover. Since 1985, when a solid proton conductor was invented by mixing poly(vinyl alcohol)(PVA) and phosphoric acid⁵⁾, great efforts have been devoted to the PVA-base solid polymer electrolytes.⁶⁻⁸⁾ PVA has been widely used as membrane materials due to the good film-forming property, high chemical resistance, and high hydrophilicity, especially due to a good barrier for methanol crossover⁹⁾, but not appropriate at high temperature. Moreover, for the acid-doped PVA membranes, the doping contents were limited to lower level due to the mechanical and thermal stability problems. In our research work, the thermal stability and mechanical stability of these composite membranes are expected to be enhanced by the addition of the silica¹⁰⁾ with higher phosphoric acid content. In this study, we mainly focused on characterization of proton conductivity and methanol crossover.

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2. Experimental Procedure

2.1 Preparation of the composite membrane

PVA(85 hydrolyzed with a molecular weight of 88,000g/mol) was dissolved in deionized water at 90°C and diluted to be 10wt.%. Tetraethoxysilane (TEOS) and 3-glycidoxypropyltrimethoxysilane (GPTMS) were diluted in deionized water and hydrolyzed by HCl solution (pH=0.26). After stirring for 1h, an appropriate amount of H₃PO₄ (85%, aqueous) followed by PVA solution was added drop by drop under stirring. The molar ratio of TEOS/GPTMS/H₃PO₄=0.66/0.34/*x*, *x* was varied from 0.5, 1.0, to 1.5. The sol was denoted as PS-*x*. (*x*=0.5, 1.0, and 1.5). The amount of PVA, with respect to the weight of (PVA+PS-*x*), was varied from 10 to 60 wt.%. After stirring at room temperature for another 5h, the sol was cast onto the Teflon petri dish. The resultant membrane was dried at 60°C for 24 h after gelation at ambient temperature.

2.2 Characterization

Thermal stability was determined by DTA-TG at a heating rate of 10/min in air (TG 8110, Rigaku). The AC conductivity was determined from Cole-Cole plot obtained with an impedance analyzer (HP4192A, Hewlett Packard) in a frequency range of 10Hz~10MHz. Silver coated membranes with a thickness about 0.2 mm were sandwiched between two similar brass electrodes of a spring-loading sample holder. All the impedance data were recorded after the resistance became constant for at least 2 h in a temperature-and humidity-controlled chamber at 25°C, 60% relative humidity. Water uptake was measured by soaking the membranes in distilled water for more than 24h, and then they were wiped with a filter paper and weighed immediately. The membranes were then dried under vacuum until a constant weight was obtained. Swelling degree was calculated by using the following equation: SW(%)=100×(W_s-W₀)/W₀, where W_s and W₀ were weight of fully swollen membrane and dry membrane, respectively.

Methanol permeability of composite membrane

was determined using a diffusion cell. This diffusion cell consists of two reservoirs. One reservoir (V_A) of the cell was filled with methanol solution with a concentration of *c*_A (*c*_A=1 mol/L, 30°C). The other (V_B) was filled with deionized water. The membrane was vertically fixed between these two reservoirs. Before the measurement, the membranes were hydrated in deionized water for at least 24 h in order to remove the soluble parts of the films. A flux of methanol (*c*_B) in the pure water reservoir was measured with time using differential refractometry. It is supposed that *c*_A ≫ *c*_B during the experiments. The methanol concentration in the receiving reservoir as a function of time is given by¹¹⁾

$$c_B(t) = \frac{A}{V_B L} DK c_A (t - t_0) \quad (1)$$

where *A* is the membrane area, *L* the membrane thickness, *D* and *K* are the methanol diffusivity and partition coefficient, respectively. The product *DK* is the methanol permeability (*P*). *t*₀, which termed time lag, is related to the diffusivity, *t*₀=*L*²/6*D*.

3. Results and Discussion

The swelling of the composite membranes of PS-*x*/PVA were tested and the results are shown in Fig. 1. Curves show the relationship between the PS-*x* weight fraction and the swelling degree (SW) of the composites where the molar ratio between H₃PO₄ and SiO₂ are varied from 0.5 to 1.5. As can be seen that SW decreases rapidly with the PS-*x* increases from 40% to 90%. The reason for the decrease in water uptake with increasing PS-*x* content is that higher rigid SiO₂ network structure suppresses the water uptake due to a reduce in chain mobility and channel.⁹⁾ Another reason may be the interaction of PVA with the Si-OH or P-OH, which alters hydrophilic-hydrophobic balance inside the membranes. The hydrophilic OH groups were changed into hydrophobic -Si-O-CH= and less hydrophilic =CH-O-P-groups in the process of dehydration during heat-treatment.¹²⁻¹³⁾ And these interactions may

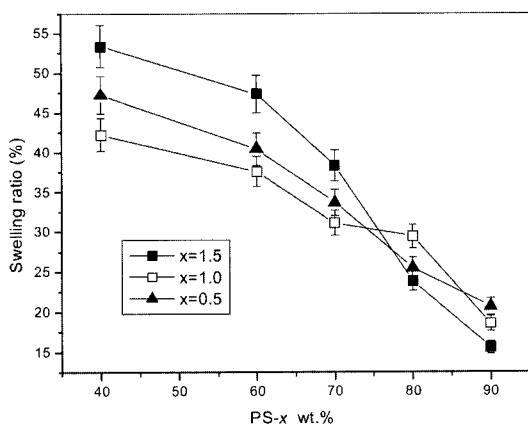


Fig. 1. Swelling ratios of membranes at different PS-x contents in weight. (■:x=1.5; □:x=1.0; ▲:x=0.5).

increase with PS-x content increasing. The resultant hydrophobic network will repel the water molecules from entering the membrane network structure. The difference of SW with different H₃PO₄ ratio may be attributed to the change in SiO₂ network or the interaction of PVA with acid during the process at various H₃PO₄ ratios.

As the PVA/SiO₂ matrix has neither electric nor ionic conduction, the proton conductivity of the membranes doped with H₃PO₄ depends on the proton transport in the membranes. Fig. 2 shows the changes in proton conductivity of composite mem-

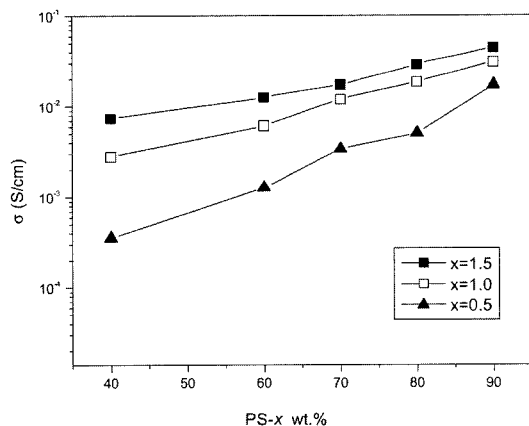


Fig. 2. Proton conductivity of membranes at different PS-x contents in weight. (■:x=1.5; □:x=1.0; ▲:x=0.5).

branes as a function of the PS-x content in membranes at 25°C under 60% R.H. It can be seen that the conductivity increases with PS-x content increasing. For instance, the conductivity increases from 7.44×10^{-3} to 4.47×10^{-2} S/cm when the PS-1.5 content increases from 40 wt.% to 90 wt.%. However, with a content of PS-x higher than 90 wt.%, the membranes become brittle. Since the proton is dissociated from H₃PO₄ molecule, the proton concentration in the membrane increases with molar ratio of H₃PO₄/Si, resulting in an increase of proton conductivity of the composite membrane.

Fig. 3. shows the relationship between the PS-x content and the methanol permeability, P(cm²/s), of the composite membrane. It can be seen that at higher PS-x content than 70wt.%, an increase in methanol permeability was observed. For example, when the PS-1.0 weight fraction is 40wt.%, P is 9.9×10^{-8} cm²/s, while, for PS-1.0 is 90 wt.%, P increases up to 7.0×10^{-7} cm²/s. It is known that, methanol permeability is correlated with the water and methanol uptakes. Methanol permeation consists of methanol sorption and methanol diffusion. As the uptakes of the methanol-water increases, methanol diffusion was more facile. As the results shown in Fig. 1, the permeability should have a curve with a similar tendency in comparison with swelling data.

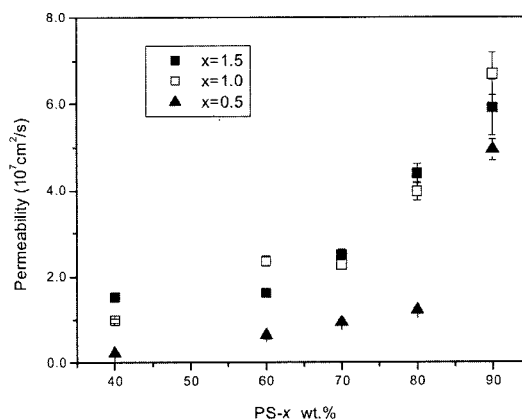


Fig. 3. Methanol permeability at different PS-x content. (■:x=1.5; □:x=1.0; ▲:x=0.5)

According to the study of A. Lewandowski *et al.*,¹⁴⁾ we suppose that the increase of methanol permeability is probably due to an increase in connectivity of the membrane with PS- x increasing. Water uptake was dominated by the hydrophilicity of composite membranes; on the other hand, methanol permeation was determined by the interconnectivity and the compatibility of SiO₂ with polymer matrix. It is well known that SiO₂ network structure derived by sol-gel process is microporous, so the interconnectivity will be understandably increased with the content of the SiO₂.

As a membrane for direct methanol fuel cell, its proton conductivity, σ , should be as high as possible and the diffusion coefficient of methanol, P , should be as low as possible. That is to say, the higher the value of σ/P , the better the membrane is. So the value of σ/P was adopted to determine the optimal conformation of the composite membranes. Fig. 4 shows the result of the σ/P for membranes at different PS- x content, which derived from sol-gel with different H₃PO₄/Si molar ratios. From the highest point of the curve, one can see the optimal conformations of the composite membranes are 60, 70, and 80 wt.% for membranes with H₃PO₄/Si ratios are 1.0, and 0.5, respectively. With H₃PO₄/Si ratio is 1.5, the optimal conformations of the composite membrane are 60 to

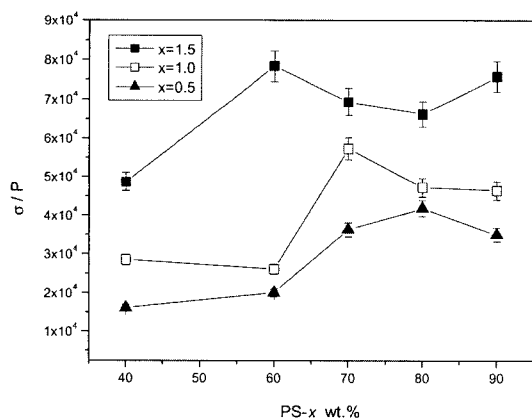


Fig. 4. Ratio of conductivity to methanol permeability for membrane at different PS- x content. (■: $x=1.5$; □: $x=1.0$; ▲: $x=0.5$)

90wt.% for membrane. However, we count out the 90wt.% for membrane because the value of permeability is too high. Therefore, the optimal values of P are in the range from 4.18×10^4 to 7.83×10^4 , which is higher than that of Nafion117, 2.43×10^3 ,¹⁵⁾ indicate potential for the present composite membranes in DMFC applications.

Fig. 5. shows the thermal stability of membrane with a 40 wt.% of PS-1.5 in the membrane. In the DTA and TG curves, a large and broad endothermic peak at about 100°C with a weight loss is attributed to the evaporation of the physically absorbed water in the micropore in the composite membrane. And relative small endothermic peak at about 200°C is probably ascribed to the evaporation of strongly adsorbed water or dehydration of phosphoric acid. On the other hand, a sharp exothermic peak with a weight loss is seen at around 258°C, which should be caused by the combustion and/or carbonization of the organic moiety of GPTMS. These results suggest that the composite membrane has water molecules with a good affinity in the composite matrix and has an excellent thermal stability even at around 200°C, which can be a candidate for low temperature DMFCs.

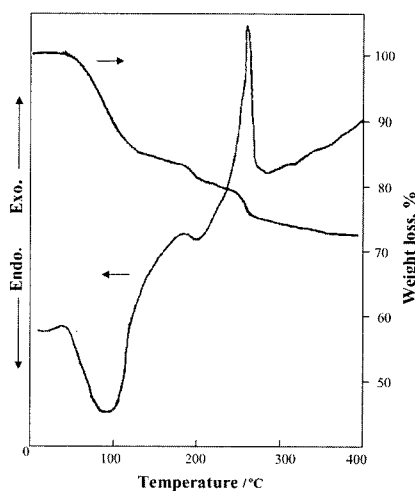


Fig. 5. DTA-TG curve for membrane with 60wt.% of PS-1.5 at a heating rate of 10°C/min in air.

4. Conclusion

A series of H₃PO₄-doped composite membranes based on poly(vinyl alcohol)(PVA) and silica have been prepared by sol-gel process in this study. The proton conductivity increased with the molar ratio of H₃PO₄ to silica. With the silica content increasing, swelling degree decreased and methanol permeability showed a slight increase. It suggested that the former was mainly determined by hydrophilicity of the membrane, while the latter was dominated by the interconnectivity of matrix. According to the value of P, the optimal conformations of these composite membranes were 60,70,80 wt.% of PS-*x* in membranes, where *x* were 1.5, 1.0, and 0.5, respectively. These composite membranes with a high value of P and thermal stability up to 200°C indicate potential application for low temperature DMFCs membrane.

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