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PWA/silica/PFSA composite membrane for direct methanol fuel cells

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Abstract A novel composite membrane was prepared by incorporation of silica-included phosphotungstic acid (PWA) additive into perfluorosulfonic acid (PFSA) followed by solution casting. Physico-chemical properties of the composite membranes were studied by Fourier transform infrared (FT-IR) spectroscopy, thermogravimetry analysis (TGA), water uptake and swelling ratio. The results of FT-IR and TGA illustrated the stability of the PWA-silica additive in the PFSA matrix. Lower PWA-silica additive loading (2.5 and 5 wt%) in the composite membranes helped to inhibit methanol crossover and enhance the proton conductivity. However, higher additive content shows decrease in both methanol resistance and proton conductivity.

Introduction

With the increasing concern for environmental protection and the depleting of fossil fuel, there is a pressing need to find cleaner and greener energy sources [1]. Over the last two decades, there has been a significant increase in research and development in fuel cell due to its ability to convert chemical energy of fuel into electricity without causing much pollution [1]. The direct methanol fuel cell (DMFC), which utilizes methanol as its fuel, is attractive due to its high efficiency, portable and environment-friendly characteristics [2]. Currently, perfluorosulfonic acid (PFSA) membrane such as Nafion® made by DuPont is the major membrane used in polymer exchange membrane fuel cell (PEMFC). But the commercial PFSA membrane, Nafion® for instance, is a poor barrier to methanol crossover [3]. Methanol crossover to the cathode not only reduces fuel efficiency, but also forms a mixed potential at the cathode, thus resulting in a lower cell performance [3–5]. Therefore, it is beneficial to modify PFSA membranes with high proton conductivity and low methanol permeability.

Heteropoly acids (HPAs) with Keggin type, which are typical strong Brönsted acids like sulfuric acids, possess high proton conductivity at room temperature (0.02–0.1 S/cm) [1]. Some inorganic–organic composite membranes based on HPAs additives in polymer matrix have been prepared for PEMFC and DMFC applications [4, 6]. However, the HPAs are water-soluble materials [7, 8]. Electrochemically produced water may dissolve the HPAs and the acids may leak out through the gas outlet holes, which would result in declining cell performance. In addition, the HPAs tend to migrate to the cathode catalyst layers in the presence of water and current, where they have a detrimental effect on the surfaces of carbon and platinum, thus resulting in increasing overpotential and lowering cell performance [4].

To overcome this problem, HPAs should be incorporated in a host material such as silica [5–10]. Xu et al. [9] prepared Nafion/silica/PWA composite membranes by sol–gel reaction. Proton conductivity of the composite membrane was measured to be 23 mS/cm, and the methanol permeability reached 2.8×10^{-7} cm^2/s, which was lower than that of Nafion® (5.4×10^{-7} cm^2/s). Kim and Chang [5] impregnated silica-supported HPAs using in situ micro-

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emulsion reaction. The resulting membranes showed 50–80% lower methanol cross-over than that of Nafion® membrane, and DMFCs with them showed 10% higher fuel efficiency than that with Nafion® membrane. Hybrid Nafion–silica membrane doped with phosphotungstic acid was also prepared by Shao et al. [8] via mixing PWA powder and nano-sized silica gel with 5 wt% Nafion® solution. In PEMFC testing, at potential of 0.4 V, the cell with the resulting Nafion/SiO_2/PWA membrane delivered current density of 540 mA/cm^2 at 110 °C, 70% relative humidity, compared with Nafion® delivered 95 mA/cm^2 in the same condition. Staiti et al. [10] manufactured HPA/silica/Nafion membrane with PWA and silica powder and commercial Nafion® solution, and got a maximum power density of 400 mW/cm^2 at 145 °C in the presence of oxygen feed, whereas the maximum power density in the presence of air feed was approaching 250 mW/cm^2 in DMFC.

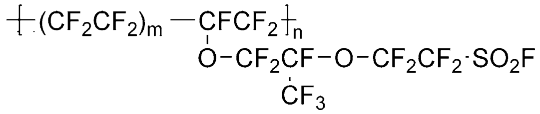
Izumi et al. [11] prepared silica-included HPA catalyst with sol–gel technique, and utilized this kind of catalyst in esterification, hydration, and alkylation. This catalyst was proved to have high acid strength and stability by Izumi and his co-workers. However, to the best of our knowledge, there have no any reports about the composite membrane based on silica-included PWA and perfluorosulfonic acid (PFSA) prepared by solution casting for fuel cell applications.

For the reason of improving methanol resistance, proton conductivity, and stability of additive, a new kind of PWA/silica/PFSA composite membrane was prepared in this study. The silica particles doped with PWA was prepared by following the method reported by Izumi et al. [11]. The composite membrane was prepared by mixing the resulting particles with PFSA/water-DMF solution, followed by vaporize solvent. The composite membrane showed an increase in methanol resistance and proton conductivity as well as thermal stability than pristine PFSA membrane.

Experimental

Perfluorosulfonic acid solution preparation

The PFSA precursor shown in Scheme 1 was supplied by Shandong Dongyue Polymer Materials Co. Ltd. (Zibo, China). The preparation of PFSA solution was followed by the method reported by Luan et al. [12]. The precursor with functional group of –SO_2F was separated, rinsed, and dried. Then the precursor was added to 29 wt% aqueous sodium hydroxide solution and refluxed at 100 °C for 48 h to chemically convert the –SO_2F groups to –SO_3Na groups, followed by immersion into 1 M H_2SO_4 solution and refluxed at 80 °C for 6 h, and the process of immersion in 1 M H_2SO_4 solution was repeated five times, in order to convert the –SO_3Na groups to –SO_3H groups. After that, the PFSA was washed with deionized water and dried under vacuum at 80 °C for 12 h. PFSA was dissolved in DMF/deionized water (1:1) utilizing autoclave at 230 °C for 4 h to obtain 5 wt% solution. The ion exchange capacity (IEC) of the resulting PFSA was 0.914 meq/g, which was measured by titration.



$$\left[(CF_2CF_2)_m-\underset{\displaystyle O-CF_2\underset{\displaystyle CF_3}{CF}-O-CF_2CF_2\cdot SO_2F}{CFCF_2}\right]_n$$

Scheme 1 Molecular formula of PFSA precursor, *m* is about 5–7

PWA/silica/PFSA composite membrane preparation

Silica-included PWA was prepared by the method reported by Izumi et al. [11]. A mixture of water (2.0 mol), 1-butanol (0.2 mol), and $H_3PW_{12}O_{40} \cdot 6.7H_2O$ (5.0×10^{-4} mol) was added to tetraethyl orthosilicate (0.2 mol), and stirred at 80 °C for 3 h. The hydrogel obtained was dehydrated slowly at 80 °C for 12 h in a vacuum oven to give 13.5 g of silica-included PWA ($H_3PW_{12}O_{40}$ 11.1 wt% estimated by ICP analysis). The silica-included PWA was crushed in an agate–mortar to obtain a fine powder.

The silica-included PWA fine powder was added into the resulting PFSA/DMF-water solution and refluxed at 80 °C for 6 h to obtain casting solution. The casting solution was cast in a glass mold and heated at 80 °C for 1 h, followed by rising the heating temperature at 160 °C for 3 h. Then the composite membrane was peeled from the glass mold by adding deionized water. Finally, the composite membrane was treated by boiling in 3 wt% H_2O_2 solution, deionized water, 1 M H_2SO_4 solution, and deionized water at 80 °C, respectively. The after-treated composite membrane was immersed in deionized water. The thickness of the resulting membranes is 100 ± 5 μm.

Fourier transform infrared spectra

Fourier transform infrared (FT-IR) spectra were studied with Fourier Transform Infrared spectroscopy (Parogon 1000, Perkin Elmer Inc., USA).

Thermogravimetry analysis

Thermogravimetry analysis (TGA) of the composite membrane was performed on Thermogravimetric Analyzer (Pyris 1, Perkin Elmer Inc., USA). The temperature was first raised to 120 °C and kept for 10 min, and then raised to 800 °C at the heating rate of 20 °C/min in a N_2 atmosphere.

Water uptake and swelling ratio

Water content uptake (W_{H_2O}) of the composite membrane was determined by desiccating the after-treated wet membrane in vacuum oven at 80 °C and 1 mbar for 24 h, then the water uptake was calculated by Eq. 1, and the weight of both wet and dry membrane were measured by microbalance

$$W_{H_2O} = \frac{M_w - M_d}{M_d} \times 100\% \tag{1}$$

where M_w and M_d are the weights of wet membrane and dry membrane, respectively.

Swelling ratio (S_s) of the composite membrane was calculated by the following Eq. 2:

$$S_s = \frac{S_w - S_d}{S_d} \times 100\% \tag{2}$$

where S_w and S_d are the volumes of dry and wet membrane, respectively.

Proton conductivity

Proton conductivity of the membrane in normal direction was measured at 20 °C and 100% relative humidity using AC impedance method with Autolab PGSTA302 electrochemical test system (Eco Chemie, Netherland). The membrane samples were sandwiched between two stainless steel electrodes, which were gilded and kept clean to avoid any contact resistance, and placed in an insulating PTFE home-made cell containing deionized water to keep the relative humility of 100%. The proton conductivity σ was calculated from the following Eq. 3:

$$\sigma = \frac{d}{RS} \tag{3}$$

where d and R denote the thickness and resistance of the membrane, respectively, and S is the area of the membrane contact to the electrodes.

Methanol permeability

The methanol permeability of membranes was determined in a home-made two-compartment stainless steel diffusion cell. Compartment A of the cell was filled with 2 M methanol solution while compartment B was filled with deionized water. Both of the compartments were magnetically stirred during the permeation experiment at 20 °C. Samples of the solution (0.6 μL per sample) of compartment B were taken out every 15 min and measured by a gas chromatography with a thermal conductivity detector (Fuli, model GC9790-Ⅱ). Equation 4 shows the relationship between the methanol concentration in compartment B and the permeation time.

$$V_B \times \frac{dC_{B(t)}}{dt} = P \times (C_A - C_{B(t)}) \times \frac{A}{L} \tag{4}$$

The methanol permeability (P) was calculated by Eq. 5

$$P = \frac{C_{B(t)}}{t} \times \frac{V_B \times L}{C_A \times A} \tag{5}$$

where $\frac{C_{B(t)}}{t}$ is the slope of the straight-line plot of methanol concentration versus permeation time, V_B the volume of compartment B, L the thickness of the membrane. C_A the concentration of methanol in compartment A, A the exposed area of the membrane.

Results and discussion

FT-IR spectra of pristine PFSA, PWA-silica additive, and PWA/silica/PFSA composite membrane with additive content of 10 wt% were shown in Fig. 1. The major vibrational structures associated with the PWA and silica are found in the composite membranes. The C–F stretching vibration of the PTFE backbones can be observed at 1144 cm^{-1}; and the peaks observed at 1052 cm^{-1} and 980 cm^{-1} can be attributed to the stretching vibrations of $SO_3^-$and C–O–C [8]. The Si–O–Si absorbent peak can be seen at 1080 cm^{-1}. For PWA powders with Keggin structure, there are four characteristic peaks: the P–O stretching band at 1079 cm^{-1}, the terminal oxygen band at 984 cm^{-1}, the bridging oxygen bands at 889 cm^{-1} and 806 cm^{-1}, respectively [11, 13]. In the FT-IR spectrum of PWA-silica additives, the P–O stretching band at 1079 cm^{-1} and one

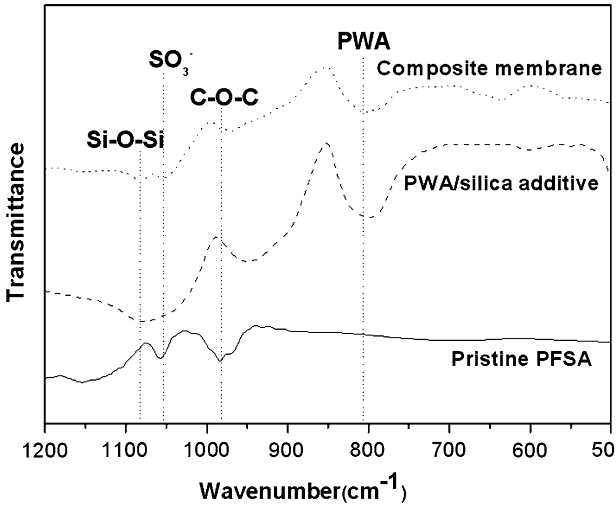


Fig. 1 FT-IR spectra of pristine PFSA, PWA-silica additive and PWA/silica/PFSA composite membrane

bridging oxygen band at 806 cm^{-1} could obviously be seen, and another oxygen band at 889 cm^{-1} showed a shoulder. The terminal oxygen band at 984 cm^{-1} moved to 950 cm^{-1}, which may be attributed to the interaction between the terminal oxygen of PWA and hydroxyl on silica. In the FT-IR spectrum of PWA/silica/PFSA membrane, only one bridging oxygen band at 806 cm^{-1} is observed. The reason is the amount of PWA in the composite membranes was lower compared to that of silica and PFSA and the transmittance of bridging oxygen band at 806 cm^{-1} is relatively stronger compared with other characteristic peaks of PWA [14]. All the above results suggest the PWA-silica additive were existed into PFSA matrix.

Thermal analysis was used to determine the degradation temperature of the membrane as well as the weight ratio of PWA-silica additive. In order to measure the weight ratio of PWA-silica additive on the dry membrane, the composite membrane was initially kept at 120 °C, at which the water in the membrane was easy to volatilize and no degradation of the membrane had occurred, for 10 min to thoroughly remove the trace amount of water content in the composite membrane. As shown in Fig. 2, the first significant mass loss for pristine PFSA membrane occurred at 346 °C. With increasing the content of PWA-silica additive, the mass loss temperature monotonically shifted to higher temperatures. Jiang et al. [15] and Deng et al. [16] have also observed the same phenomenon in Nafion/silica composite membrane. Shao et al. [8] reported that compared with pristine PFSA membrane, the initial degradation temperature of the Nafion/SiO_2/PWA composite membrane is higher. From these experimental facts, it could be concluded that the introduction of PWA-silica increased the thermal stability of PFSA membrane. At 800 °C, the residual weight percentage of pristine PFSA membrane is 0 wt%. At the same temperature, the theoretical PWA-silica content of 5 and 7.5 wt% had residual weight percentage of 4.33 and 6.27 wt%, indicating more than 80% of PWA-silica additive was incorporated into the PFSA membrane matrix. To be consistent, the nominal PWA-silica weight percentage of 2.5, 5, 7.5, 10 wt% were used in all figures and discussions.

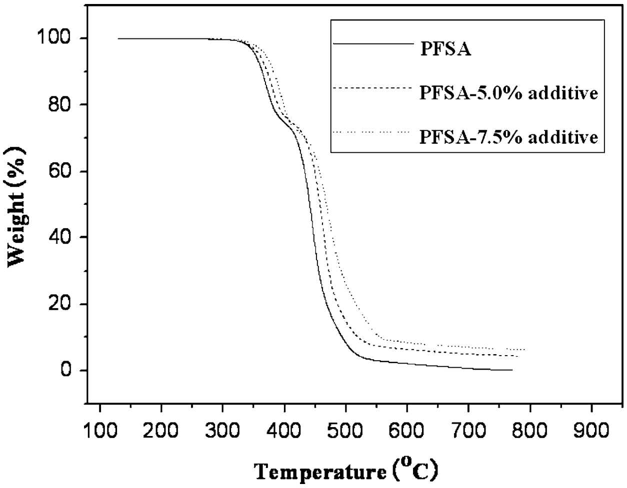


Fig. 2 Thermogravimetry analysis of pristine PFSA and PWA/silica/PFSA composite membranes with various content of additive

Water uptake is closely related to the basic membrane properties and plays an essential role in the membrane behavior [15]. Both proton conductivity and methanol permeability of the membrane depend to a large extent on the amount and behavior of water absorbed by the membrane [15]. The water uptakes of the composite membrane as well as recast PFSA membrane were listed in Table 1. An increase in content of PWA-silica in the membranes showed an increase in water uptake. The hydrophilic sulfonic acid group and the introduced inorganic PWA-silica additive tend to associate with water molecules, so the water uptake increase with additive content linearly. As to the swelling ratio, the results showed an increase with the increase content of PWA-silica additive from 0 to 7.5 wt%. When the content was higher than 7.5 wt%, however, there was a slight decrease in swelling ratio. The enhancement in swelling ratio may due to the increase in water content. Both PWA and silica as the additive into the composite membranes could associate with water molecules, and then the water molecules tend to take more room. However, when the amount of the PWA-silica additive reaches to a higher value, silica in the additive tends to form crosslink network, thus limits the swelling volume of membrane. It is possible that in this experiment, when the composite membrane contains 10% PWA-silica additive, network structure formed, resulting in slight shrinkage in volume.

The proton conductivity of PFSA and PWA/silica/PFSA composite membranes are shown in Fig. 3. The conductivity of Nafion® 115 was 12.0 mS/cm in our experiments. The proton conductivity increases with the increase of PWA-silica content in the composite membranes from 0 to 5 wt%. When the amount of PWA-silica additive is higher than 5 wt%, there is a little decrease in proton conductivity. The proton conductivity of composite membranes is higher

Table 1 Water uptake and swelling ratio of pristine PFSA and PWA/silica/PFSA composite membranes

Additive content (wt%)	Water uptake (%)	Swelling ratio (%)
0	25.6	25.9
1	37.1	33.8
2.5	48.6	40.9
5	55.2	53.9
7.5	57.7	55.0
10	60.1	52.1

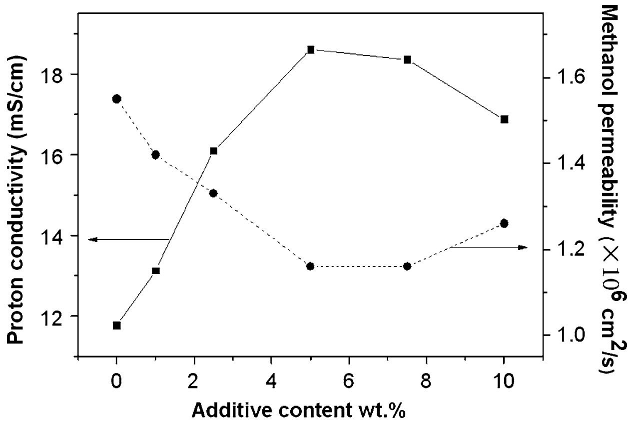


Fig. 3 Proton conductivity and methanol permeability of pristine PFSA and PWA/silica/PFSA composite membranes at 20 °C

than that of Nafion® 115 membrane. With the PWA-silica additive content of 5 wt%, the proton conductivity could reach as high as 18.61 mS/cm. Figure 3 also shows the methanol permeability of the PWA/silica/PFSA composite membranes. The methanol permeability of Nafion® 115 was 1.25 × 10^{-6} cm^2/s in our experiments. With the PWA-silica additive content increasing from 0 to 5 wt%, the methanol permeability decrease from 1.55 to 1.16 × 10^{-6} cm^2/s. However, there is a slightly increase in the methanol permeability when the additive content was higher than 5 wt%. This phenomenon is similar with the reports by Xu et al. [9] and Jiang et al. [15].

For Nafion-based membranes, methanol and proton transport mainly occurs through the ion-cluster pores and the connecting ion channels; and it is possible the methanol permeate through the hydrophobic polymer backbone [15, 17]. When the content of PWA-silica is low, the silica cross-linked network in the PFSA matrix is not so perfect. With increasing the amount of PWA-silica additive, PWA in the additive plays an important role in the membrane matrix, resulting in enhancing the conductivity of the composite membrane. The hydrophilic PWA-silica additives may mainly exist near the hydrophilic ion-clusters and the ion channels, thus changed the microstructure of PFSA matrix, and tend to hold up methanol [9]. When the amount of inorganic additive became more (>7.5 wt%), the PWA-silica additive tends to aggregate unhomogeneously into the polymer matrix, which would result in decreasing proton conductivity and increasing methanol permeability.

From the results for proton conductivity and methanol permeability, we calculated the following selectivity parameter (ϕ) as Eq. 6 to compare the applicability of the different membranes as DMFCs [18, 19].

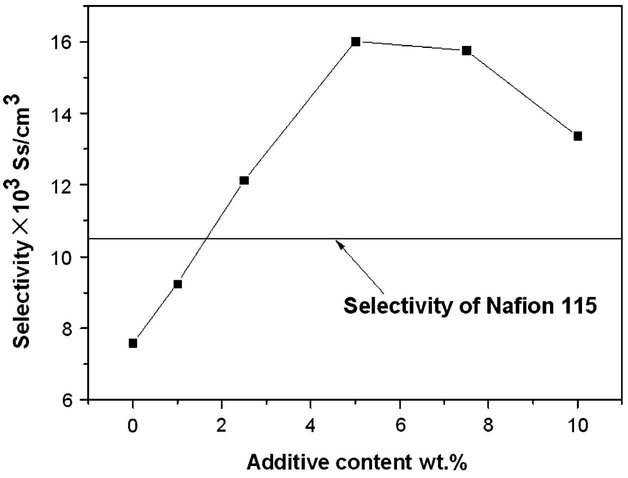


Fig. 4 Selectivity values of pristine PFSA and PWA/silica/PFSA composite membranes

$$\phi = \frac{\sigma}{P} \tag{6}$$

The selectivity values of Nafion® 115, pristine PFSA and PWA/silica/PFSA composite membranes are illustrated in Fig. 4. The value of selectivity increased after adding PWA-silica additive, and the maximum value is about 16.01 Ss cm^{-3} with the PWA-silica additive content of 5 wt%, which is higher than that of Nafion® 115.

The stability of PWA-silica in composite membranes was studied by comparing the conductivity of deionized water and proton conductivity of the composite membranes before and after the membranes boiling in water for 12 h at 80 °C. The conductivity of deionized water used in the experiment is 0.055 μS/cm. After boiling, the conductivity of the water is also 0.055 μS/cm, and the proton conductivity of the composite membranes equals to the value before boiling. This suggests that the PWA-silica additive can be stable in the composite membranes.

Conclusion

The PWA/silica/PFSA composite membranes with different amount of PWA-silica additive were prepared by adding silica-included PWA, which was manufactured by sol–gel reaction, to PFSA solution with DMF/deionized water (1:1) as solvent. FT-IR spectra proved incorporation of PWA-silica additive in the composite membrane. The stability of PWA and silica additive in the composite membranes are proved by Thermogravimetry analysis (TGA) and stability test. The incorporation of PWA and silica has resulted in higher proton conductivity, methanol resistance, selectivity and thermal stability, simultaneity, has not changed swelling stability obviously. Some of the composite membranes showed better performance in proton conductivity, methanol permeability and selectivity than Nafion® 115. Therefore, the composite membranes seem to be candidate electrolytes for DMFCs.

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