Polymer Bulletin 58, 673–682 (2007)
DOI 10.1007/s00289-006-0709-x

Polymer Bulletin

Composite Membrane of Sulfonated Poly (phenylene oxide) Doped with Phosphosilicate Gels for Direct Methanol Fuel Cell

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Received: 29 May 2006 / Revised version: 18 November 2006 / Accepted: 19 November 2006

Summary

The newly developed composite membranes of sulfonated poly (phenylene oxide) (SPPO) doped with phosphosilicate gel were prepared for direct methanol fuel cell (DMFC). SPPO with higher ion exchange capacity (IEC) value (IEC=2.83mequiv./g) was chosen as polymer matrix, and the phosphosilicate gel with P/Si equal to 1.5 was employed as dopant. Sulfonation of PPO was confirmed by FT-IR and ^{1}H NMR. And the morphology characterization of sol particles with different stirring time was done by TEM. Moreover, the surface morphology of composite membranes was characterized by SEM. As for methanol permeability (P_M) and proton conductivity (σ), it was demonstrated that all composite membranes were displaying lower methanol permeability than Nafion®112 and comparable conductivity to Nafion®112 at room temperature under hydration state. When it comes to selectivity parameter ($\Phi=\sigma/P_M$), composite membranes show higher Φ values than Nafion®112, and the highest value is 4.70, 5.6 times higher than 0.845 of Nafion®112. It is implied that the composite membranes will be the promising membrane material used in DMFC.

Keywords

SPPO, Phosphosilicate gel, Methanol permeability, Proton conductivity

Introduction

Proton exchange membrane fuel cell (PEMFC) is an efficient and environment-friendly new energy application. Many attentions have been focused on the development of PEMFC. Compared to PEMFC, direct methanol fuel cell (DMFC) possess the superior advantages, such as much simple and convenient fuel processing course, lower temperature operation and so on [1]. It exhibits enormous prospect for portable resource.

Commercial perfluorinated proton exchange membranes, such as DuPont's Nafion®, are most widely used membrane materials for PEMFC at present due to their excellent chemical and thermal stability as well as high proton conductivity. However, their deadly drawback of high methanol permeability restricts their wide application, especially in DMFC [2]. So, large research efforts have been devoted to improve Nafion® in order to obtain excellent properties in DMFC. Choi et al. [3] modified Nafion® using plasma etching. Hobson et al. [4] introduced a thin barrier of PBI at Nafion®117 surface by screen printing. Cho et al. [5] prepared PVDF copolymer/Nafion® blend membrane. Sauk et al. grafted Nafion® by styrene using supercritical CO_2 impregnation [6] and developed Nafion®/PPO-PMA composite membrane [7]. Kim et al. [8] incorporated self-assembled clay-nanocomposite multilayers onto Nafion®. Park et al. [9] proposed Nafion®/polypyrrole blend membrane. These methods reduce the methanol permeability and maintain the higher conductivity of membranes indeed, but the inherent high cost of Nafion® is still the key obstacle for its commercialization.

Sulfonated aromatic hydrocarbon polymers have been investigated extensively as alternative non-fluorinated membrane materials for DMFC. Examples include PBI/SPSf [10], SPEEK [11-12], polystyrene-block-poly (ethylene-ran-butylene) -block-polystyrene (sSEBS) [13-14], sulfonated poly (styrene-isobutylene-styrene) (SSIBS) [15], SPI [16], SPEK/ZP/ZrO_2 [17], SPS-g-PP [18] by plasma-induced polymerization, PSSA/PVDF [19], SPS / SPPO [20-21], PEG/PSf [22], and so forth. It is highly desirable to find new membranes with low methanol permeability, high conductivity and inexpensive cost.

The composite membrane developed for DMFC in the study reported here was prepared by employing SPPO with higher ion exchange capacity (IEC) value as polymer matrix, and doping with phosphosilicate gels (P/Si=1.5). SPPO was characterized by FT-IR and ^{1}H NMR, phosphosilicate sol was investigated by TEM, and the surface morphology, methanol permeability and conductivity of composite membranes were also studied.

Experimental

Sulfonation of PPO

Sulfonation of PPO ([η] equal to 0.4dl/g in chloroform at 25°C, purchased from General Electric Co.) was carried out in chloroform solvent by action of chlorosulfonic acid at 20°C according to the procedure as follows[23]. PPO was dissolved in chloroform solvent to form a 5% solution The calculated chlorosulfonic acid in chloroform (5% solution) previously kept in ice bath was slowly dropwised into the PPO chloroform solution with vigorous stirring at 20°C. After the chlorosulfonic acid in chloroform solution was added, the sulfonation reaction was carried out continually for another 4h. The product with lower sulfonation degree will be precipitated in deionized water, while the higher ones will be precipitated directly in reaction solution. The precipitated product was washed repeatedly in deionized water until neutral pH was reached. Eventually, the washed product was dried first in a convection oven at 50°C, then in a vacuum oven at 60°C.The IEC of SPPO defined as the concentration of sulfonic groups in milli-equivalents per total mass was determined by acid-base back titration seen elsewhere [24]. In this study, SPPO with higher IEC value (2.83mequiv./g) was chosen as polymer matrix.

Preparation of phosphosilicate sol

The preparation process of phosphosilicate (H_3PO_4/SiO_2) sols was similar to the references [25-26]. Tetraethoxysilane (TEOS) was diluted with 2-propanol and hydrolyzed in H_2O under stirring at room temperature for 10 min, with the HCl as catalyze. A known amount of H_3PO_4 was added into the hydrolyzed solution and then stirring for 3h at room temperature. The mole ratio of TEOS/2-propanol/H_2O/HCl/ H_3PO_4 was fixed at 1/8/4/0.01/1.5.

Preparation of composite membrane

A mixed solution consisted of 10wt% SPPO in N-methyl-2-pyrrolidone (NMP) with a calculated amount of phosphosilicate sols was prepared, filtered and ultrasonicated for 30min to guarantee complete mixing. The membrane was prepared by pouring the mixed solution onto a flat glass plate using a casting knife, then the solvent was evaporated as following: the membrane was dried firstly at room temperature for 1day, then at 60°C for 1day in air oven, at last at 80°C for another day in vacuum oven. That is, the composite membrane is prepared by casting technology, the solvent was out of the membrane via evaporation, and there was no further treatment. The resulting membranes were transparent, with thickness about 28±2μm. Based on the IEC value of SPPO, P/Si ratio of phosphosilicate sols and SiO_2 weight content percent (wt%) in composite membranes, the nomenclatures used for composite membranes in this paper are designated such as SPPO-2.83-1.5-7.5, where 2.83 denotes the IEC value, 1.5 represents P/Si ratio and 7.5 stands for weight content percent (doping amount).

Characterization

Fourier transforms infrared (FT-IR)

The thin films of PPO and SPPO membranes were prepared on KBr crystal for FT-IR. And the FT-IR spectra were recorded on a FT-IR spectrometer (Spectrum One, Perkin-Elmer, U.S.A.).

^{1}H nuclear magnetic resonace (^{1}H NMR)

^{1}H NMR spectra of PPO and SPPO were acquired with an spectrometer (NMR-600, OXFORD, England) at 25°C. For samples, the deuterated chloroform was chosen as NMR solvent f or PPO, and deuterated acetone for SPPO, with the tetramethylsilane (TMS) as internal standard.

Transmission electron microscopy (TEM)

Phosphosilicate sol was diluted by 2-propanol, and the morphology of sol was characterized by a transmission election microscopy (JEM-100SX, JEOL, Tokyo, Japan).

Scanning electron microscopy (SEM)

Surface morphology of the membranes was investigated using a SEM (JSM-5910LV, JEOL, Tokyo, Japan). The membranes were mounted on the sample studs by means of double-sided adhesive tapes.

Methanol permeability

Methanol permeability of the membrane was determined using a two-compartment cell shown in Figure 1 at room temperature [27-28].

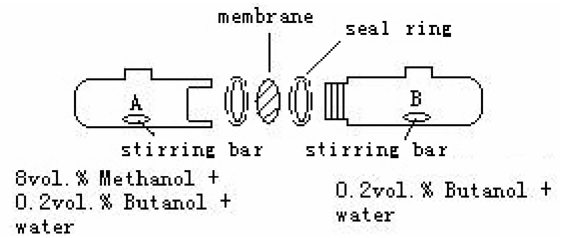


Figure 1. Experimental setup of measurement for methanol permeability.

Compartment A was filled with 8vol.% methanol and 0.2vol.% butanol solution (20ml) while compartment B initially contained 0.2vol.% butanol solution (20ml). The membrane with the diffusion area of 3.14cm^2 sandwiched by O-ring shape Teflon was clamped between the two compartments. Prior to testing, the membrane was equilibrated in deionized water for 24h. The solution samples (2μl) in compartment B were taken at interval and were detected by gas chromatography (GC-16A, Shimadzu, Japan) together with a flame ionization detector (FID). Methanol permeability, P_M was calculated by following Eq.:

$$C_B = \frac{P_M \times C_A \times A}{V_B \times L} \times t \tag{1}$$

where C_B is the methanol concentration in compartment B, C_A is the methanol concentration in compartment A, A is the diffusion area of membrane, V_B is the solution volume of compartment B, L is the thickness of membrane, and t is the permeability time.

Proton Conductivity

Conductivity of fully hydrated membranes (equilibrated in double distilled water for 24h before tested) was measured through complex impedance technology at room temperature, using Solartron SI 1260 Impedance/Gain-Phase Analyzer (England) coupled with Solartron SI 1296 Dielectric Interface with the frequency range from 10Hz to 10MHz and 100mV amplitude of the AC signal. The conductivity of membrane was calculated as following Eq.:

$$\sigma = \frac{L}{RS} \tag{2}$$

where L, is the distance between two Pt plate electrodes; S, is the resistance of membranes; and R is the cross-sectional area of membranes, respectively.

Results and discussion

FT-IR

FT-IR was used to analyze characteristic bands corresponding to the pendant sulfonic groups on the PPO chains. Figure 2 presents the FT-IR spectra of unsulfonated PPO and SPPO. In the SPPO spectrum, new peaks appear at around 1070cm^{-1} and 635cm^{-1}, which can be assigned to the symmetric stretching vibrations of sulfonic groups and C-S bonds, respectively.

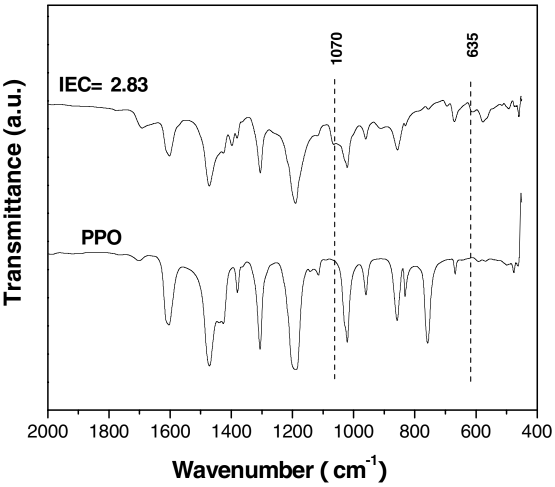
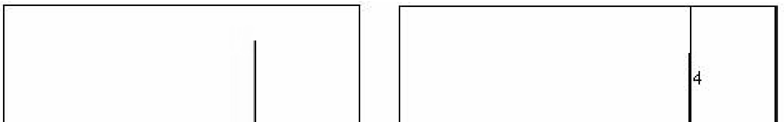


Figure 2. FTIR spectra of PPO and SPPO (IEC=2.83).

^{1}H NMR

^{1}H NMR spectra of PPO and SPPO are shown in Figure 3. For PPO, the characteristic chemical shifts are located at about 2.2ppm and 6.5ppm, which are assigned to methyl group proton and aromatic proton, respectively. For SPPO, the presence of $-SO_3H$ in PPO repeat unit results in the moving of chemical shifts to downfield due to the strong inducement effect of $-SO_3H$. As shown in Figure 3 (b), peak1 was the shift of signal from aromatic proton in *meta* position to $-SO_3H$, and peak 3 was the shift of signal from methyl proton in *ortho* position to $-SO_3H$. From FT-IR and ^{1}H NMR, it is concluded that the introduction of sulfonic groups on PPO chains is successful.

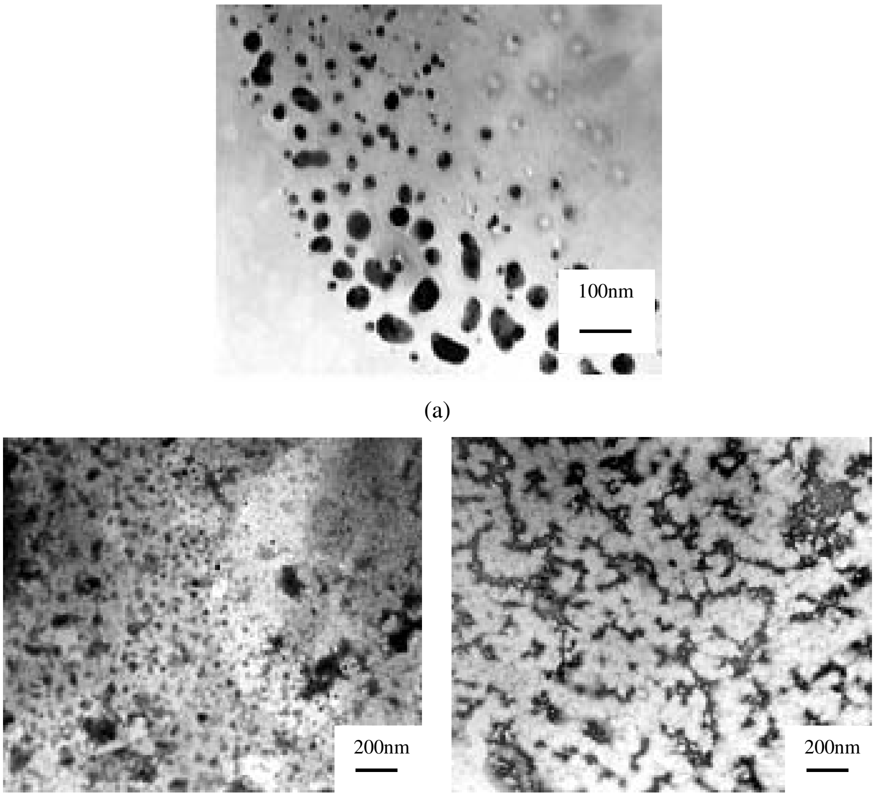


(a) (b)

Figure 3. ^{1}H NMR spectra of (a) PPO and (b) SPPO (IEC=2.83).

TEM

TEM micrographs of H_3PO_4/SiO_2 sol stirring for different time are revealed in Figure 4. When the sol was stirred for 3h at room temperature (seen in Figure 4 (a)), the nano-particles of sol is clearly observed. But the stirring time was extended to 4h (seen in Figure 4 (b)), the sol nano-particles began to aggregate. It was shown in Figure 4 (c) that the network was formed after stirring 72h. In order to guarantee the finely mixing with SPPO solution, 3h was selected as stirring time for H_3PO_4/SiO_2 sol preparation.

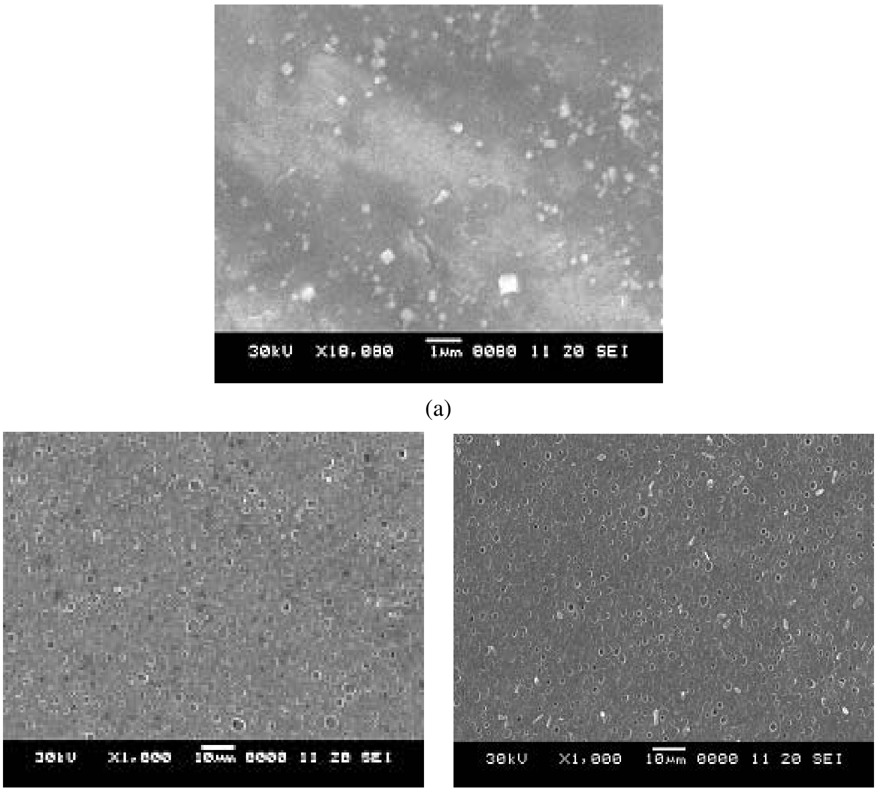


(b) (c)

Figure 4. TEM micrographs of H_3PO_4/SiO_2 sol with different stirring time (a) 3h, (b) 4h, (c) 72h.

SEM

The surface morphology of SPPO-2.83 membrane and composite membranes scanned by SEM are shown in Figure 5. Compared to SPPO membrane (seen in Figure 5 (a)), the composite membranes (seen in Figure 5 (b) and (c)) doped with phosphosilicate gels exhibit different surface morphology owing to the existence of minute particles. During the course of drying of composite membranes, the sols doped into SPPO solution will be changed into gels powder, and finely and uniformly dispersed in SPPO matrix. When the doping amount of sol increased from 5.0wt% to 10.0wt%, the more continuous dispersion of gel powder will be formed, which is considered to be facilitating to proton transportation.



(a)

(b) (c)

Figure 5. SEM micrographs (a) SPPO-2.83, (b) SPPO-2.83-1.5-5.0, (c) SPPO-2.83-1.5-10.0.

Methanol Permeability and Proton Conductivity

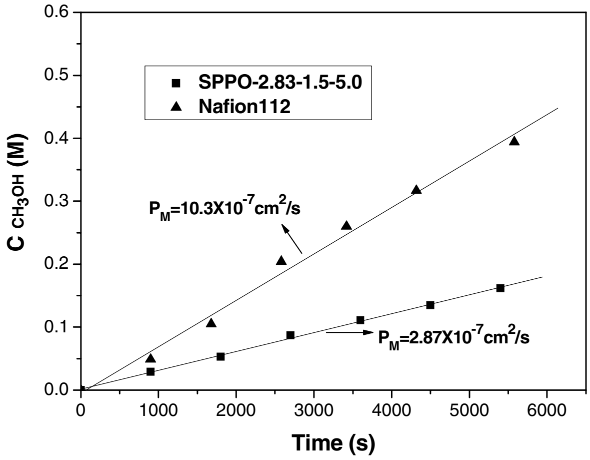


Figure 6. Methanol permeability measured for Nafion®112 and the composite membranes *versus* permeation time.

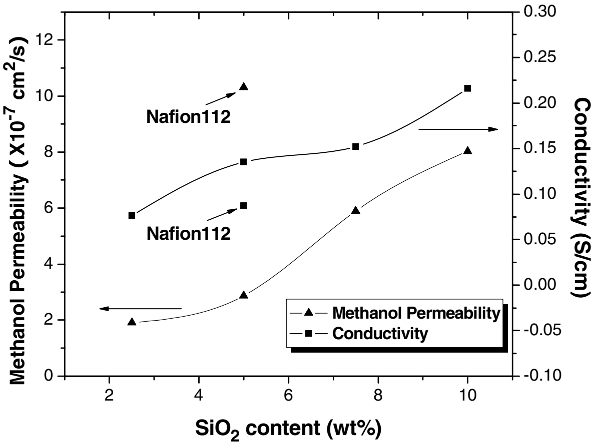


Figure 7. Methanol permeability and conductivity of Nafion®112 and composite membranes *versus* the doping amounts under hydrated state at room temperature.

Methanol concentration in compartment B shown in Figure1 was determined using a GC-FID, by comparing the integrated peak areas of methanol *versus* the butanol reference. As illustrated in Figure 6, methanol concentration of Nafion®112 and composite membrane with 5.0wt% doping amount increase linearly with permeation time. The P_M calculated by Eq. (1) through slope of line of composite membrane with 5.0wt% doping amount is 2.87×10^{-7}cm^2/s, lower than 10.3×10^{-7}cm^2/s of Nafion®112, which is comparable to reference [28].

Figure 7 exhibited methanol permeability and conductivity of composite membranes versus the doping amounts under hydrated state at room temperature. The methanol permeability of all composite membranes is lower than Nafion®112, and increases with increasing SiO_2 doping amount. The conductivity of the composite membranes increases with the doping amount. Compared with Nafion®112, though the thinner thickness of the composite membrane may give rise to a relative high conductivity, the

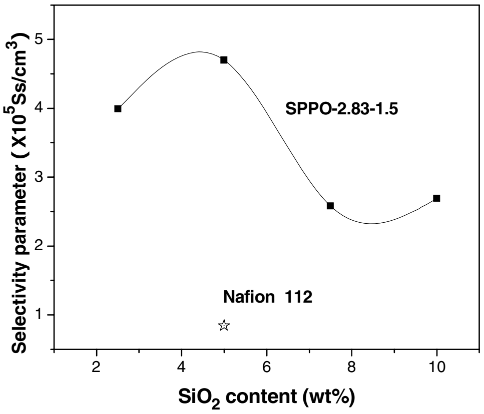


Figure 8. Selectivity parameter of composite membranes and Nafion®112 *versus* the doping amounts.

much higher conductivity value of the composite membrane with a doping amount over 5wt% than Nafion®112 (0.0871S/cm^{-1} of Nafion®112 we measured is comparable to the reference [29]) still demonstrated their advantages.

Performance comparison of membrane can be quantified further by introducing the selectivity parameter (Φ), which is defined as the ratio of conductivity to methanol permeability. As showed in Figure 8 is the selectivity parameter of composite membranes. The values of selectivity parameter of composite membranes are higher than Nafion®112 , and the highest value is 4.70×10^{5}Ss·cm^{-3}, 5.6 times higher than 0.845 of Nafion®112. It is demonstrated that composite membranes are more suitable to use in DMFC than Nafion® 112.

Conclusion

Composite membranes of SPPO with higher IEC value, doped with phosphosilicate gels (P/Si=1.5) for DMFC were prepared. The successful sulfonation of PPO was confirmed by FT-IR and ^{1}H NMR. And the appropriate stirring time for phosphosilicate sol preparation was ascertained at 3h through morphology characterization of sol particles by TEM. SEM for surface morphology of composite membranes showed more finely and uniformly dispersion of phosphosilicate gel powder in SPPO matrix when gel doping amount increased from 5.0wt% to 10.0wt%. Methanol permeability and conductivity of composite membranes increased with increasing gel doping amount. Compared to Nafion®112, composite membranes possessed lower methanol permeability and comparable or higher conductivity under hydrated state at room temperature. Furthermore, the higher selectivity parameter of composite membranes than Nafion®112 suggested that the composite membranes are potential alternative for Nafion®112 used in DMFC.

Acknowledgements. The authors acknowledge the financial support by Polymer Materials Key Laboratory Opening Foundation (020-092245) and International Collaboration Grant (020-093901) from Department of Education of Hubei Province, China.

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