

Sulfonated Poly(ether sulfone)/Silica Composite Membranes for Direct Methanol Fuel Cells

Sheng Wen,^{1,2} Chunli Gong,¹ Wen-Chin Tsen,³ Yao-Chi Shu,³ Fang-Chang Tsai²

¹Faculty of Chemistry and Material Science, Xiaogan University, Xiaogan 432100, Hubei, China

²Ministry-of-Education, Key Laboratory for the Green Preparation and Application of Functional Materials, Faculty of Materials Science and Engineering, Hubei University, Ministry of Education, Wuhan 430062, China

³Department of Polymer Materials, Vanung University, Tao-Yuan 32045, Taiwan, Republic of China

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ABSTRACT: A series of sulfonated poly(ether sulfone) (SPES)/silica composite membranes were prepared by sol-gel method using tetraethylorthosilicate (TEOS) hydrolysis. Physico-chemical properties of the composite membranes were characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscope-energy dispersive X-ray (SEM-EDX), and water uptake. Compared to a pure SPES membrane, SiO₂ doping in the membranes led to a higher thermal stability and water uptake. SEM-EDX indicated that SiO₂ particles were uniformly embedded throughout the SPES matrix. Proper silica loadings (below 5 wt %) in the composite membranes helped to inhibit methanol permeation. The permeability coefficient of the composite membrane with 5 wt % SiO₂

was 1.06×10^{-7} cm²/s, which was lower than that of the SPES and just one tenth of that of Nafion[®] 112. Although proton conductivity of the composite membranes decreased with increasing silica content, the selectivity (the ratio of proton conductivity and methanol permeability) of the composite membrane with 5 wt % silica loading was higher than that of the SPES and Nafion[®] 112 membrane. This excellent selectivity of SPES/SiO₂ composite membranes could indicate a potential feasibility as a promising electrolyte for direct methanol fuel cell. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1491–1498, 2010

Key words: sulfonated poly(ether sulfones); composite membrane; methanol permeability; proton conductivity

INTRODUCTION

Fuel cells have been identified as a very feasible energy source with minimal noxious emissions and have been the subject of academic and industrial interest for over a decade.¹ Among the various fuel cells, direct methanol fuel cells (DMFCs) are the most suitable for portable devices (cell phones and laptops) because they have a high charge density, low operating temperature, and simple fuel cell setup (with easy storage of methanol and no need for a reformer).^{2–4} The electrolyte is the most important component in any fuel cell system. One of the main components in DMFCs is the electrolyte membrane. Dupont Nafion[®] or other perfluorinated sulfonic acid membranes are widely acknowledged to be good electrolyte membranes because of their high proton conductivity and chemical stability. However, Nafion[®] membranes have some drawbacks^{5,6}: (i) Nafion[®] is too expensive and difficult to process; (ii) there is a strong dependence on relative humidity in maintaining the proton conductivity of Nafion[®]

membranes. This is the reason why proton conductivity decreases with the dehydration at high temperature; (iii) thermal instability at high temperature. This property causes the membrane to physically shrink during high temperature operation, with subsequent poor contact and proton conductivity between the membrane and the electrodes; (iv) high methanol permeability, which not only wastes fuel but also reduces cell performance for application in DMFCs.

Contemporary electrolyte membrane research involves the development of new polymer electrolytes that are based on hydrocarbon polymers.⁷ The main approach, which is presently of considerable industrial interest and has been adopted by numerous researchers, involves the attachment of sulfonic acid groups onto various aromatic polymers with high thermal, chemical, and oxidative stability, good mechanical properties, and low cost. Examples include sulfonated poly(arylene ether sulfone),^{8–10} sulfonated poly(ether ether ketone),^{11–13} and sulfonated polyimides.^{14–17} However, proton exchange membranes based on these polymers suffer from excessive swelling of aromatic polymers, loss of proton conductivity due to degradation of sulfonic acid groups at high temperature, and overall low proton conductivity.⁶ The addition of inorganic materials

Correspondence to: S. Wen (shengwen@xgu.cn).

into a polymer membrane can alter and improve physical and chemical polymer properties of interest (such as elastic modulus, proton conductivity, solvent permeation rate, tensile strength, hydrophilicity, and glass transition temperature) while retaining its important polymer properties to enable operation in the fuel cells. An effective way to reduce methanol crossover is to mix sulfonated polymers with hygroscopic oxides (e.g. SiO₂, TiO₂, and ZrO₂). The sulfonated polymer/silica organic-inorganic composite membranes that prepared in various ways have been used in fuel cells for different operation conditions. Tsai et al.⁶ prepared the nanocomposite membranes by incorporation of silica into sulfonated 4,4'-dihydroxy- α -methylstilbene (HMS)-based poly(arylene ether sulfone) copolymer. Their membrane showed higher single cell performance in DMFCs at 80°C with compared to the Nafion[®] 117 membrane. Lee et al.¹⁸ prepared a similar type of composite membrane in DMFCs and investigated the influence of SiO₂ nanoparticles with different surface properties on the properties of composite membranes. Shen et al.¹⁹ investigated the composite membrane by doping nano-SiO₂ into PVDF-*g*-PSSA, and the results showed the SiO₂ in the membrane can slow the methanol permeation.

Although there have been several researches on sulfonated aromatic polymer/SiO₂ composite membranes, very little has yet been done in terms of preparing and characterizing SPES/SiO₂ composite membranes for application in DMFCs. Therefore, in this article, we describe a sulfonated poly(ether sulfone) (SPES)/silica composite membrane via *in situ* sol-gel reaction of tetraethylorthosilicate (TEOS). The morphologies and properties, including the thermal and water uptake, proton conductivities, and methanol permeability, have been varied by the variation of the composition of the composite membrane.

EXPERIMENTAL

Sulfonation of poly(ether sulfone) and membrane preparation

Sulfonation of PES (Ultrason[®] E6020P, $T_g = 225$ °C, $M_w = 51$ kg/mol, $M_w/M_n = 3.5$, BASF corporation) was carried out in a concentrated sulfuric acid (98%) solvent using chlorosulfonic acid as a sulfonating agent following the procedure described by Dai et al.²⁰. The ion exchange capacity (IEC) value of SPES was determined by the acid-base back titration method according to known references.^{13,20} SPES membrane samples were soaked in a 1M NaCl solution for at least 48 h. Thus, the protons of the sulfonic acid groups were exchanged with sodium ions. Then the exchanged protons were titrated with 0.01 M NaOH solution with phenolphthalein as an indicator.

The titrated IEC was determined from formula:

$$\text{IEC} = \frac{C \times V}{M} \times 100 \quad (1)$$

where C is the concentration of NaOH, V the volume of NaOH, and M the weight of the membrane.

The corresponding degree of sulfonation (DS) was calculated as following equation:

$$\text{IEC} = \frac{1000DS}{232 + 81 \times DS} \quad (2)$$

where 232 and 81 are the molecular weights of the PES unit and the sulfonic acid group, respectively. In this article, the IEC of the obtained SPES was 1.34 m eq/g, that is, DS was 35%.

The organic-inorganic hybrids were prepared by sol-gel technology using TEOS (99.9%, Beijing Aufang Technology & Trade Co., China) as precursors for preparation of SiO₂. TEOS was introduced into a beaker with ethanol under stirring condition to make TEOS/ethanol solutions. Deionized water was added to the TEOS/ethanol solution with an H₂O : TEOS ratio of 4 : 1 (mol/mol). In addition, using HCl to obtain pH = 3. Then a desired amount of 10 wt % SPES/*N,N*-dimethylacetamide solution was added into the beaker (containing TEOS, ethanol, water, and HCl) and stirred with a magnetic stirrer for 12 h and degassed by ultrasonication. The content of SiO₂ in the mixture were varied in 3, 5, 10, and 15 wt % based on SPES. To remove any impurities, the casting solutions were filtered through a 0.2 mm pore size Teflon filter before membrane preparation. The prepared mixture was slowly poured into a glass dish in an amount that would give a thickness of ca. 60 μm of the formed composite membrane. The procedure of membrane-drying involved air-drying at 80°C for 4 h, followed by 120°C for 12 h, and then drying under vacuum at 120°C for 24 h. Hereafter, the notations of composite membranes are denoted as SPES/SiO₂ x , where x is the weight percentage of SiO₂ in the SPES matrix.

Thermogravimetric analysis

The thermogravimetric spectra were obtained by using thermogravimetric analysis (TGA, TA SDT-Q600). Initially, the samples were heated under nitrogen to 100°C for 10 min to remove the water absorbed in the samples, cooled down to 50°C and reheated till 800°C at a rate of 10°C/min under a nitrogen atmosphere.

Morphology

The cross-section of the membranes was examined using a scanning electron microscope (SEM) X-650

from HITACHI equipped with an energy dispersive X-ray (EDX) spectrometer. The membranes were fractured by brief immersion in liquid nitrogen. Fresh cross-sectional cryogenic fractures of the membranes were vacuum-sputtered with a thin layer of Pt/Pd before analysis.

X-ray diffraction

X-ray diffraction (XRD) experiments were performed on a Rigaku X-ray Automatic Diffractometer D/max-IIIc (Japan). The dried membranes were mounted on an aluminum sample holder. The scanning angle ranged from 3 to 40° with a scanning rate 3°/min and with a step size of 2θ equal to 0.05°.

Water uptake

The composite membranes were dried in a vacuum oven at 100°C for 24 h, weighed (W_{dry}), and immersed in deionized water at different temperature for 48 h. Then, the wet membranes were blotted to remove surface water droplets and quickly weighed (W_{wet}). The water uptake of membranes was calculated as follows:

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (3)$$

Proton conductivity

Proton conductivities of blend membranes were measured using the AC impedance method. In a chamber, the tested membranes were put into the clamp, connected by two platinum electrodes to a complex impedance analyzer (Solatron 1260 Impedance Analyzer) with a frequency range of 0.1 Hz–10 MHz and an AC voltage amplitude of 10 mV. Before the proton conductivity was measured, all membranes were hydrated by immersion in deionized water for 24 h at room temperature. A sample of prehydrated membrane (3 × 3 cm) was clamped between the two electrodes. The proton conductivity was calculated as follows:^{21,22}

$$\sigma = l/Rdw \quad (4)$$

where l is the distance between the electrodes; d and w are the thickness and width of the films, respectively, and R is the resistance value measured.

Methanol permeability

Methanol permeability of the membrane was carried out using a two-compartment cell shown in Figure 1 at room temperature.

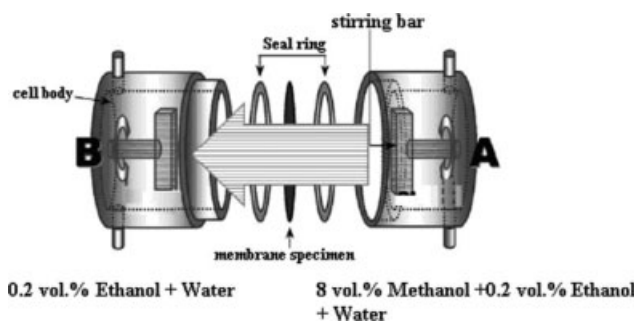


Figure 1 Experimental setup of measurement for methanol permeability.

Initially one compartment B of the cell ($V_B = 20$ mL) was filled with 0.2 vol % ethanol solution in deionized water. The other compartment A ($V_A = 20$ mL) was filled with 8 vol % methanol and 0.2 vol % ethanol and deionized water. The membrane with the diffusion area of 3.14 cm² sandwiched by O-ring shape Teflon was clamped between the two compartments. The membrane samples were equilibrated in deionized water for 24 h before testing. The diffusion cell was kept stirring slowly during experiment. The solution samples (about 2μL) in compartment B were taken at interval and were analyzed by gas chromatography (GC-5890 series//, Hewlett Packard) using HP-20M (CARBOWAX 20M phase) chromatographic column together with a flame ionization detector. Methanol permeability was calculated by following equation²³:

$$C_B = \frac{D \times K \times C_A \times A}{V_B \times L} \times t \quad (5)$$

where C_B is the methanol concentration in compartment B , C_A is the methanol concentration in compartment A , A , L , and V_B are the diffusion area of membrane, the thickness and the solution volume of compartment B . D , K , and t are the methanol diffusivity, the solubility and the permeability time, respectively. The methanol permeability (P_m) is defined as the product of diffusivity and solubility (DK).

RESULTS AND DISCUSSION

Thermal stability

TGA measurement was performed to evaluate the thermal properties of the composite membranes. Figure 2 shows that the TGA and DTG curves of the SPES/SiO₂ composite membranes in nitrogen are very similar to that of the SPES membrane. In each TGA curve one can observe two distinct weight loss steps. The first mass loss event for the SPES

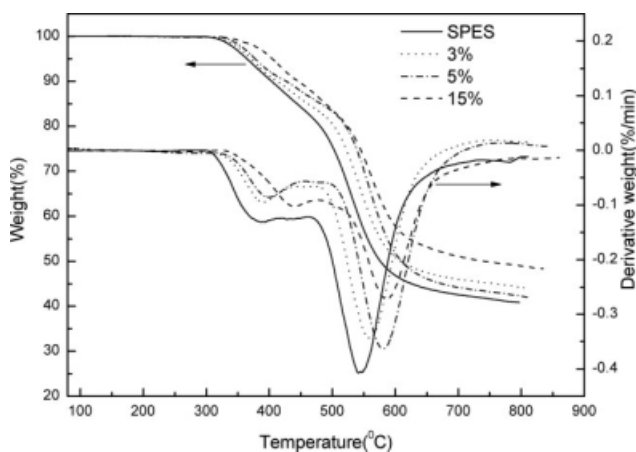


Figure 2 Thermogravimetric and DTG curves for SPES/SiO₂ composite membranes.

membrane, starting from 307°C, is believed to be associated primarily with the loss of the sulfonic groups by evolution of SO and SO₂.²⁰ This degradation temperature monotonically shifted to higher temperatures as the silica loading increased. The temperature increased to 314, 323, and 332°C with 3, 5, and 15% silica loading, respectively. This confirmed the phenomena observed by Tsai et al.⁶ The improvement in thermal stability for high temperature applications is attributed to the inhibition of SO₂ evolution due to immobilization in the polymer by silica cages.

Morphology

The distribution of the silica particles in the SPES matrix has a great influence on their transport properties. The cross-sections of SPES and composite SPES/SiO₂ membranes were analyzed using SEM to observe the morphology and distribution of silica. As shown in Figure 3(a), the SPES membrane shows a very homogeneous and dense cross-section. On the other hand, the images of the SPES/SiO₂ composite membranes prepared by sol-gel technique depict some very interesting features and exhibit a micro-phase separation inside the membrane, as shown in Figure 3(b,e). Figure 3(f) shows the energy dispersive X-ray (EDX) spectrum of the particles in the SPES/SiO₂ 15% membrane cross-section. Silica particles with a domain size of about 0.2–1.2 μm are observed as microspheres shape on SEM micrographs and are uniformly embedded throughout the sulfonated polymer matrix. With the weight ratio of the SiO₂ increasing, the domain size of the inorganic phase increases. When the weight ratio of the SiO₂ is 3%, the SiO₂ domain size is about 0.2 μm. The domain size for SPES/SiO₂ 10% and SPES/SiO₂ 15% is

approximately 1 μm and 1.2 μm, respectively. The interaction between the sulfonic acid groups and silica may facilitate easy dispersion of the SiO₂ particles in the SPES matrix. This phenomenon might lead increase of the thermal stability and reduce the methanol permeability.

X-ray diffraction

The microstructures of the membranes made of SPES and SPES/SiO₂ of various SiO₂ content were studied with XRD. The scattering spectra are very similar and show broad scattering maxima, indicating that all the samples are in the amorphous state (Fig. 4). A summary of the analysis of the XRD patterns of SPES and SPES/SiO₂ composite membranes is listed in Table I. The major peak is located at 2θ around 18°. The value of *d*-spacing does not vary with the SiO₂ content and is close to the value of 4.78 Å reported by Guan²⁴ for SPES. However, compared with the SPES membrane, the pattern of SPES/SiO₂ composite membrane shows a broadened peak with a decrease in peak intensity. The relative degree of amorphous phase can be estimated from the full-width at half maximum (FWHM) from the each peak. The FWHM values of SPES, 3, 5, 10, and 15 wt % SiO₂ membranes are 9.77, 9.98, 10.67, 10.93, and 11.09°, respectively. Apparently, a bigger FWHM value corresponding to a broadened peak indicates stronger hydrogen bonding occur in the SPES/SiO₂ composite membrane, which give rise to the perturbation of long-ranged spacing between the chains. Jung and coworkers^{25,26} investigated the blend membranes with sulfonated polystyrene (SPS) and sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO). They found that the electrostatic cross linking resulting from the ionic groups of sulfonated polymers increase the amorphous region abruptly, which is consistent with what we have observed.

Water uptake

Water uptake is closely related to the basic membrane properties and plays an essential role in the membrane behavior. Proton conductivity and methanol permeation across the membrane depend to a large extent on the amount and behavior of water absorbed by the membrane. Water influences the ionomer microstructure, cluster and channel size, plastisizes, and modifies the mechanical properties. Table I lists the water uptake of the composite membranes at room temperature. It can be seen that an increase in silica in the membranes showed an increase in water uptake. The increase in water uptake can be attributed to the water retention of

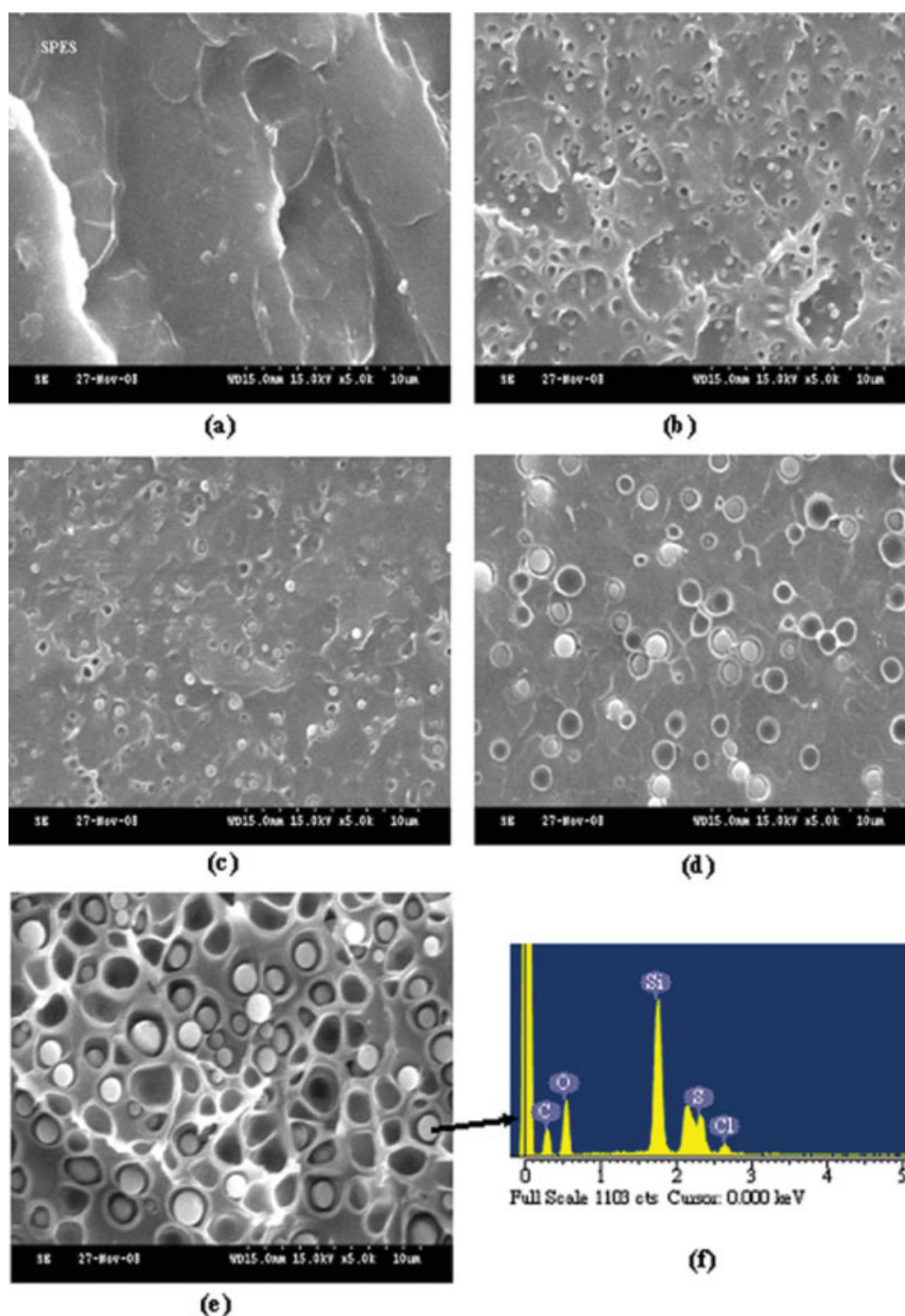


Figure 3 Cross-sectional SEM micrographs of the composite membranes: (a) SPES, (b) SPES/SiO₂ 3%, (c) SPES/SiO₂ 5%, (d) SPES/SiO₂ 10%, (e) SPES/SiO₂ 15%, (f) EDXA of the particles in the (e) cross-section. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the incorporated silica due to the hydrogen bonding of H₂O molecules with the SiOH groups.

Proton conductivity

The proton conductivity is a decisive property for fuel cell membranes as the efficiency of the fuel cell depends on the proton conductivity. Generally proton conductivity directly depends on the water

uptake and IEC of the sulfonated polymer.²⁷ Figure 5 compares proton conductivity of Nafion[®] 112 and SPES/SiO₂ membranes with various silica loadings at different temperatures. It can be seen that the conductivity of all the membranes increased with increasing temperatures and the relationship of $\log[\sigma(\text{S}\cdot\text{cm}^{-1})]$ and the parameter $1000/T$ satisfied an Arrhenius equation [$\sigma = \sigma_0 \exp(-E_a/RT)$]. This indicates that the proton conduction in the

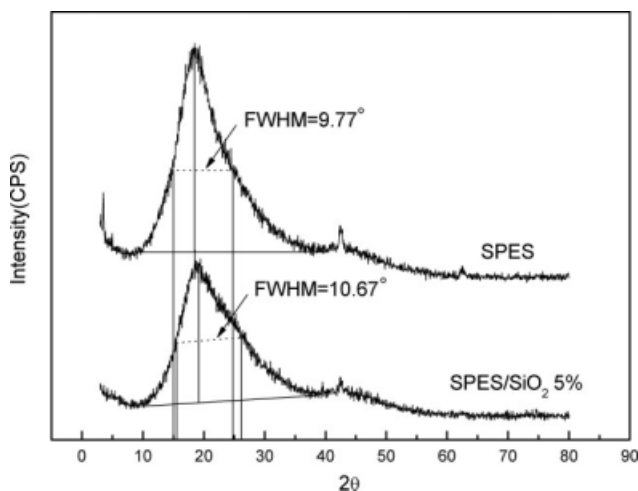


Figure 4 X-ray diffraction spectra of the SPES and SPES/SiO₂ membranes.

membranes is governed by hopping like mechanism.²⁸ Compared with the slope in Figure 5, the conductive active energy (E_a) of the SPES and SPES/SiO₂ membranes are higher than that of Nafion[®] 112 membrane. This can be explained as follows: the $-SO_3H$ pendant groups in Nafion[®] 112 shows strong acidity because of the strong induction of fluorine. Thus the sulfonic acid groups are in complete dissociation status and therefore the effect of temperature on proton conductivity is little. However, the lower acidity of SPES compared with perfluorosulfonic acid results in the dissociation degree of $-SO_3H$ groups increasing with temperature. Therefore, the degree of proton conductivity increasing with temperature is more obvious than that of Nafion[®] 112 membrane.

As shown in Figure 5, we can also notice that the composite SPES/silica membranes exhibited lower proton conductivity than that of the SPES membranes at room temperature and up to 80°C, and the conductivity decreased with increasing silica loadings. Jiang et al.²⁹ reported similar phenomenon with their sol-gel-derived-silica-containing Nafion 115 membranes. According to the discussion of them, excess water molecules are likely to be involved in hydrating the incorporated silica. Thus,

TABLE I
The X-Ray Diffraction Data and Water Uptake of SPES/SiO₂ Membranes

Sample	Peak position (2θ°)	FWHM (°)	d-Space (Å)	Water uptake (%)
SPES	18.55	9.77	4.78	20.05
SPES/SiO ₂ 3%	18.82	9.98	4.71	24.67
SPES/SiO ₂ 5%	18.98	10.67	4.68	27.75
SPES/SiO ₂ 10%	18.82	10.93	4.71	34.56
SPES/SiO ₂ 15%	18.85	11.09	4.71	40.23

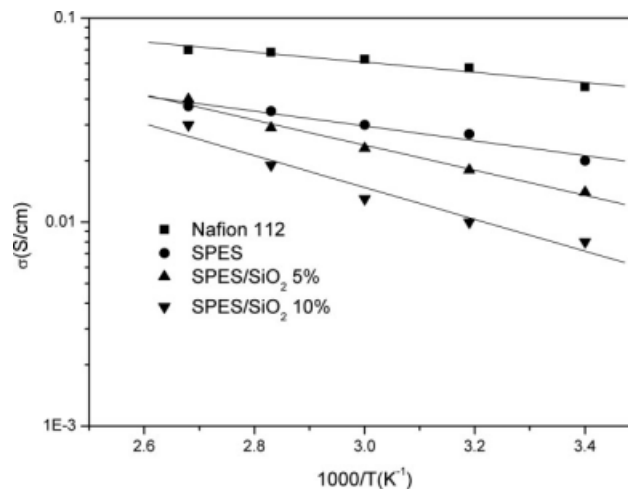


Figure 5 The relationship of the proton conductivity in Nafion[®] 112 and SPES/SiO₂ composite membranes with temperature.

water available for hopping mechanism may be lower. This could lead to the interruption of hopping mechanism and thus decreases the conductivity. But when at high temperature, i.e., above 80°C, the composite SPES/SiO₂ membranes showed similar proton conductivity, and even more than the SPES membrane. For example, the proton conductivities of SPES and SPES/SiO₂ 5% at 100°C are 0.037 S/cm and 0.04 S/cm, respectively. This phenomenon may be due to the increased mobility of water and structural reorientation as well as increased molecular mobility.

Methanol permeability

Methanol permeability plays a very important role in DMFC. The permeability of methanol (P_m) was determined by the concentration change of C_B with time obtained by a linear slope as shown in Figure 6. The value of methanol permeability for Nafion[®] 112 membrane was 1.05×10^{-6} cm²/s, which is the close value as Jang measured.³⁰ The SPES/SiO₂ 5% composite membrane had a lower slope, indicating a lower methanol permeability (1.06×10^{-7} cm²/s), compared with that of Nafion[®] 112 membrane. Figure 7 compares the methanol permeability values of composite membranes with different silica loadings. With increasing silica loading from 0 to 5 wt %, the methanol permeability decreased from 5.43×10^{-7} to 1.06×10^{-7} cm²/s. However, a further increase in silica loading to 10 and 15 wt % did not contribute to any additional decrease in methanol permeability. Assuming that the methanol mostly passes through a channel where ion cluster forms, there is a reasonable explanation for methanol permeability of composite membranes. At low silica loadings, the hydrophilic silica particles formed by the sol-gel

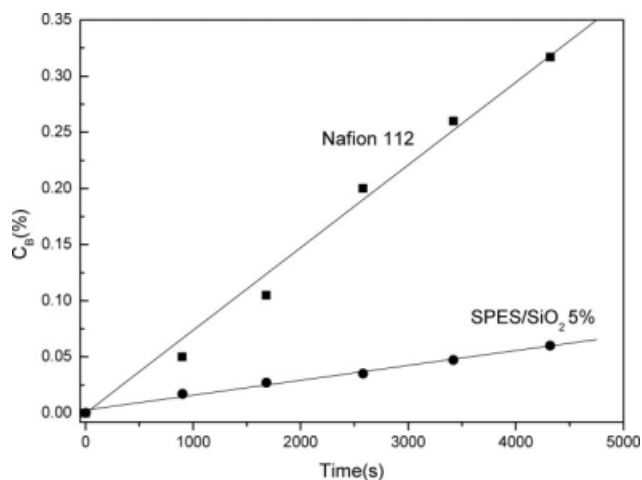


Figure 6 Concentration change of methanol with time for Nafion[®] 112 and the composite membrane.

technique may mainly exist around the hydrophilic ion cluster and the ion channels and change the microstructure of SPES, increasing the tortuosity of the methanol transport channels. As reported by Jiang et al.,²⁹ silica may exist among the structure of the polymer backbones by solution casting, especially for the higher silica loadings. At higher silica loadings, the hydrophilic silica may increase the contribution of the hydrophobic polymer backbones for methanol permeation.

As one crucial part of the direct methanol fuel cell, the electrolyte membranes must have both excellent proton conductivity and low methanol permeation. However, sometimes these mutually incompatible. To compare the comprehensive character of the membranes, a new parameter, selectivity (S), the ratio of proton conductivity and methanol permeability, was defined. The higher S value, the better the membrane performance.²⁸ The S values of

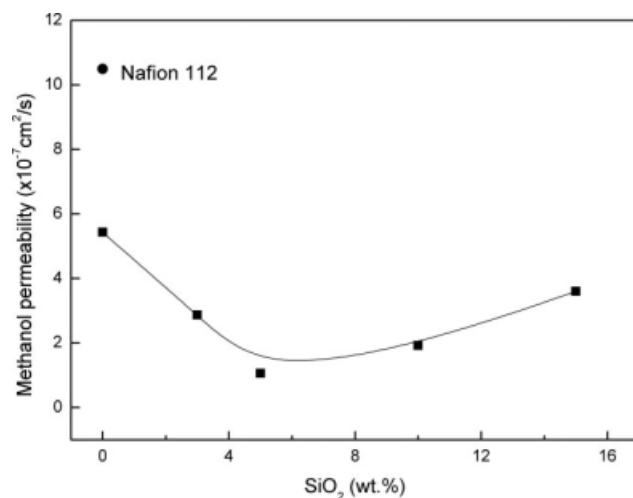


Figure 7 Methanol permeability of membranes vs. silica loading.

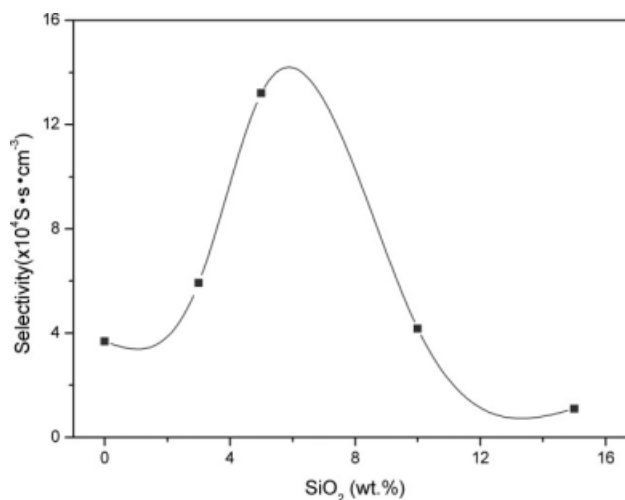


Figure 8 The selectivity of composite membranes with different amount of SiO₂.

membranes investigated in this work are compared in Figure 8. When the silica loading is below 5 wt % in the composite membranes, the selectivity increased with increasing silica content. The SPES/SiO₂ 5% membrane has the highest selectivity in our experiments, $1.32 \times 10^{-5} \text{ s cm}^{-3}$, which is almost four times than that of Nafion[®] 112 membrane. The SPES/SiO₂ composite membranes can therefore be a viable substitute for Nafion[®] in DMFC.

CONCLUSIONS

The SPES/SiO₂ composite membranes with various silica loadings were prepared. The effect of silica on the properties of composite membranes was evaluated by thermal stability, water uptake, morphology, proton conductivity, and methanol permeability. The composite membranes showed higher thermal stability than the SPES membrane. Water uptake of the membranes was enhanced by incorporation of silica into SPES matrix. Methanol permeability was suppressed in the membranes with lower silica loadings (below 5 wt %); higher silica loading presented no further decrease in methanol permeability. The excellent comprehensive property, especially the selectivity (the ratio of proton conductivity and methanol permeability), of the composite membrane with 5 wt % silica loading suggests its suitability as electrolyte in DMFC applications.

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