High proton-conducting Nafion®/–SO3H functionalized mesoporous silica composite membranes

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Abstract

A novel organic–inorganic mesoporous silica (L64 copolymer-templated mesoporous SiO_2), functionalized with perfluoroalkylsulfonic acid groups analogous to that of Nafion®, was prepared. A condensation reaction between the surface silanol groups of the mesoporous silicas and 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid Beta-sultone was conducted. High proton-conducting Nafion®/functionalized mesoporous silica composite membranes were prepared via homogeneous dispersive mixing and the solvent casting method. In this investigation, the proton conductivity (σ) of the composite membrane is increased from 0.10 to 0.12 ($S\,cm^{-1}$) as the modified mesoporous silica content is increased from 0 to 3 wt%. The methanol permeability of the composite membrane declined as the sulfonic mesoporous silica content increased. The methanol permeability of the composite membrane that contained 3 wt% $M–SiO_2–SO_3H$ was $4.5 \times 10^{-6}\,cm^2\,S^{-1}$—30% lower than that of pristine Nafion®. Results of this study demonstrate a significant improvement in the performance of DMFCs.
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Keywords: Nafion®; Mesoporous silica; Composite membrane; Proton conductivity; Fuel cell

1. Introduction

Fuel cells are highly efficient and emit low levels of pollutants. They have therefore attracted substantial interests as portable or stationary power sources. Vehicles and portable applications have greatly motivated research in the field of proton-conducting polymers over the past few decades. Currently, the commercial membrane materials used for both PEMFC and DMFC are perfluorinated materials such as Nafion® from DuPont Co. However, challenges remaining, such as the slow kinetics of methanol oxidation and the high methanol crossover of Nafion®. Methanol crossover substantially reduces the fuel cell efficiency and performance, impeding the commercial development of DMFCs [1,2].

Numerous attempts have been made to reduce the methanol permeability through polymer electrolyte membranes. They include (i) modifying the surface of the Nafion® membranes to block the methanol transport [3–5]; (ii) developing new electrolyte polymers [6]; and (iii) introducing a winding pathway for a methanol molecule by preparing a composite with inorganic materials [7–17]. Most composite membranes have been prepared by adding a nonconductive ceramic oxide, such as silica [7,8], zirconia [9], titania [10], organo-montmorillonite [11] and such proton-conductive materials as sulfonated montmorillonite [12–14] and sulfonated phenethyl-silica [15] into the Nafion® membrane. When applied to DMFCs, these composite membranes reduce methanol crossover, but this effect does not always provide the desired improvement in the performance of the membrane–electrode assembly (MEA), mainly because the proton conductivity of the composite membranes that are fabricated with these less proton-conductive oxides was much lower than that of the pristine Nafion® membrane.

García and co-workers [16] reported the preparation of Nafion-functionalized mesoporous MCM-41 silica by condensation between surface silanol groups of the mesoporous silica and 1,2,2-trifluoro-2-hydroxyl-1-trifluoromethyl-ethane sulfonic acid beta-sultone. However, they did not conduct the application of sulfonic mesoporous silica in the proton-conducting
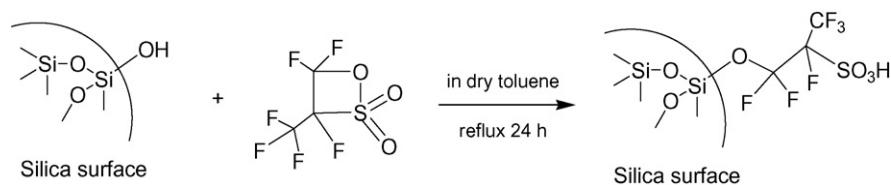
Scheme 1. Idealized representation of the process for preparing the functionalized mesoporous silica (M–SiO$_2$–SO$_3$H).

membrane of a fuel cell. Furthermore, mesoporous silica possesses extremely high surface area and larger and more tunable pore diameters than has conventional zeolites. Accordingly, this work presents the synthesis of functionalized mesoporous silica (M–SiO$_2$–SO$_3$H). Nafion® polymer was modified using various inorganic additives to increase the proton conductivity caused while reducing the methanol permeability. Optimizing the proton conductivity (C) in relation to the methanol permeability (P), as in the C/P ratio (Δ), is still challenging, since hydrated protons and methanol are transported similarly through the membrane.

Mesoporous silica materials have attracted considerable attention since the discovery of MCM-41 in 1992 [17,18]. Recently, several studies of mesoporous SiO$_2$ have been devoted to a range of subjects [19], including the development of various mesostructured materials, the modification of mesoporous silica with heteroatoms or functional groups, the characterization of its spectroscopic and structural properties, the use of this material as a template for fabricating other materials, and the effects of the reactions on catalytic activity in a confined space.

In this investigation, composite membranes with various sulfonic mesoporous SiO$_2$ (M–SiO$_2$–SO$_3$H) contents are prepared. The modified mesoporous SiO$_2$ was analyzed by Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). The effects of M–SiO$_2$–SO$_3$H in Nafion® composite membranes on the methanol permeability and proton conductivity were examined. The performance of these composite membranes in DMFC has been evaluated and the results are discussed.

2. Experimental

2.1. Materials and chemicals

In the typical preparation of the mesoporous silica used in this study, 1.4 g of Pluronic L64 block copolymer (EO$_{13}$PO$_{30}$EO$_{13}$, Pan Asia Co., Taiwan) was dissolved in 50.0 g water to form a clear solution. The L64 copolymer solution was poured into a sodium silicate aqueous solution at 40 °C, which was prepared by mixing 5.5 g of sodium silicate (SiO$_2$ > 27 wt%, Aldrich Co. USA) into 300.0 g water and then adding a proper quantity of 0.5 M H$_2$SO$_4$ aqueous solution to reach a pH value of 5.0. A white surfactant-silica was formed only in a few minutes. After filtration, washing and drying at 60 °C, L64-silica composite was recovered. To obtain the surfactant-free mesoporous silica, the L64-silica composite was calcined in air at 500 °C for 6 h. The calcined mesoporous silica was then soaked in 100 ml NaOH aqueous solution at pH 10.0 for 1 h, followed by filtration and

drying. The silica samples obtained were used in the DMFC studies. Perfluorosulfonylfluoride copolymer resin (Nafion® R-1100 resin) used in this study was supplied by DuPont Co. USA.

2.2. Modification of mesoporous silica

The L64-templated mesoporous SiO$_2$ (2.0 g) was evacuated at 120 °C for 8 h, cooled to room temperature, and a solution of reactant (1,2,2-trifluoro-2-hydroxyl-1-trifluoromethyl-ethane sulfonic acid beta-sultone, 1.0 g) was then added to 50 ml dry toluene. The mixture was refluxed for 24 h. The solid was filtered and washed thoroughly with toluene and finally dried at 100 °C overnight. The reaction route is shown in Scheme 1 [16].
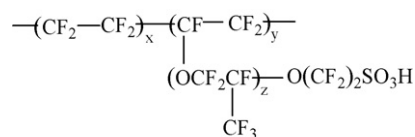
2.3. Fabrication of composite membrane

To prepare a composite membrane, a desired amount of prepared sulfonated mesoporous silica (M–SiO$_2$–SO$_3$H) was added to a 5 wt% Nafion® solution (DuPont Co., USA), and then stirred mechanically and degassed by ultrasonication. Nafion® is with an equivalent weight (EW) of 1100, where $x = 6$–10, $y = z = 1$ as shown in Scheme 2. The contents of functionalized mesoporous silica in the mixture were varied in 1–6 wt% based on Nafion®. The prepared mixture was slowly poured into a glass dish in a quantity that would provide a thickness of ca. 120 μm of the formed composite membrane. The filled glass dish was placed on the leveled plate of a vacuum-dry oven, and then was dried by slowly increasing the temperature from 300 to 333 K to prevent crevice of composite membrane. Finally, the residual solvent in the composite membrane was removed completely by evacuation at 393 K for 12 h.

3. Characterization and property measurements

3.1. Instrumental characterization

Thermogravimetric analysis (TGA) was conducted utilizing a DuPont-TGA951 by heating the samples from ambient tem-

where x = 6-10, y = 1, z = 1 for Nafion® 115
with an equivalent weight (EW) of 1100

Scheme 2. Structure of Nafion®.

perature to 800 °C with a heating rate of 10 °C min^{-1} in N$_2$. The structure of the funtionalized mesoporous silica was characterized with infrared spectroscopy using a Nicolet Avatar 320 FT-IR instrument (WI, USA) in the range of 4000–400 cm^{-1}. The morphology of the composite polymer membranes was investigated using a scanning electron microscope operated at 10–20 kV (JEOL-6300F).

3.2. Water uptake and swelling

Polymer membranes were dried in a vacuum oven at 80 °C for 2 h and weighted. Then the sample was immersed in distilled water and isothermal oscillating at 60 °C for 2 h. The water uptake was calculated using the following equation:

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

where W_{wet} is the weight of wet membranes, W_{dry} is the weight of dry membranes.

3.3. Ion-exchange capacity (IEC)

The ion-exchange capacity (mmol of sulfonic acid g^{-1} of M–SiO$_2$–SO$_3$H) of each sample was determined by the back-titration method. 0.5 g of the sample was soaked overnight in 50 ml of distilled water containing 5 ml of 0.1 N NaOH to exchange the sodium ions with the protons in the inorganic. Back-titration was accomplished by titrating the remaining NaOH in solution with 0.1 N HCl solutions. The IEC values were obtained by subtracting the added volume of 0.1 N HCl from the initial 0.1 N NaOH volume.

3.4. Methanol permeability and proton conductivity

Methanol permeability was determined and calculated by using two connected compartment cells as described in our previous paper [11]. At the beginning, one compartment was filled with 2 M methanol solution in deionized solution, and the other compartment was filled with deionized water. Each compartment was kept stirring during experiment to ensure the uniformity of the cell concentration. The density and weight fraction of methanol were recorded with time and were converted to the methanol concentration. Methanol permeability was obtained by analyzing the methanol concentration with time. Proton conductivities of full hydration membranes were measured at room temperature by AC impedance method using a Solartron Interface 1260 gain phase analyzer, Hampshire, UK over the frequency range of 1–10 Hz. The sample was place sandwiched between two circular platinum electrodes of 1.0 mm diameter in an open cell. A spring linked to one of the electrodes kept the membrane under a constant pressure, thereby providing a good contact between the electrodes and the membrane. The conductivity was calculated from the following equation: $\sigma = L/RA$, where L is the membrane thickness, A is the surface area of the electrodes and R is the resistance.

3.5. DMFC single-cell test

The membranes were immersed in 2 M sulfuric acid for 1 day and then washed with distilled water to remove the remaining sulfuric acid in order to assure of the hydrogen form of the composite membranes. Fuel cell experiments were carried out in a 4 cm^2 self designed single cell as described in our previous publication [11]. The single cell was tested with 1 M methanol solution and air breathing after equilibrium at 40 °C for 4 h. The catalyst employed for the cathode and anode side was 4 mg cm^{-2} loading HP Pt-black Nafion$^{®}$ binder 0.6–0.8 mg cm^{-2} and 3 mg cm^{-2} 60% HP E-Tek Pt/Ru alloy (1:1 a/o) on carbon, respectively.

4. Results and discussion

4.1. Characterization of L64 copolymer-templated mesoporous SiO$_2$

Fig. 1 shows the N2 adsorption–desorption isotherms of the L64-templated mesoporous silica. The representative hysteresis at $P/P_0 = 0.35$–0.6 indicates the mesoporosity of the resulting silica. The BET area, average pore size, and total pore volume are 568 m^2 g^{-1}, 4.8 nm, and 0.45 cm^3 g^{-1}. The TEM image of Fig. 2 reveals that the mesostructure of the L64-templated silica is disordered [19].
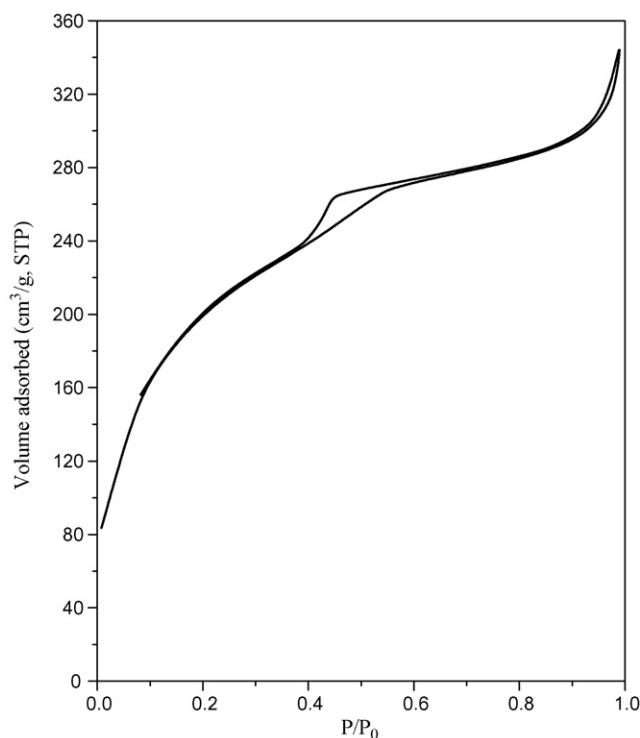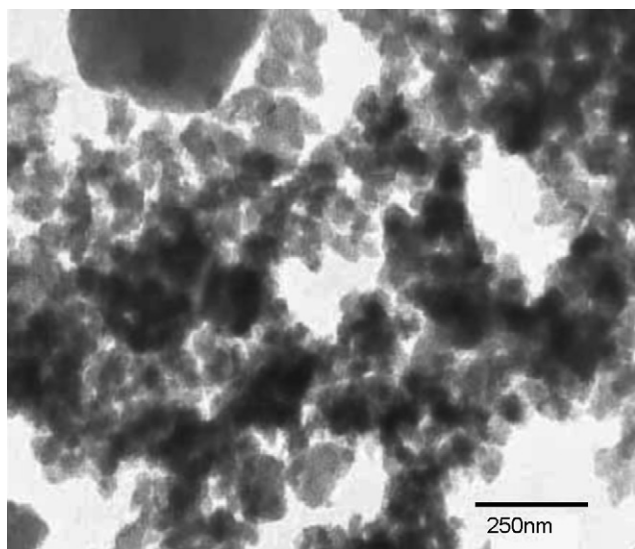

Fig. 1. N$_2$ adsorption–desorption isotherms of the calcined L64 copolymer-templated mesoporous silica, with a BET surface area of 568 m^2 g^{-1}, an average pore size of 4.8 nm calculated by BJH method, and a total pore volume of 0.45 cm^3 g^{-1}.

Fig. 2. TEM image of the mesoporous SiO_2.

4.2. Characterization of functionalized mesoporous SiO_2

Scheme 1 illustrates the synthesis of mesoporous silica bearing sulfonic acid side group by a ring-opening reaction between surface silanol groups of the mesoporous silicas and 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethane sulfonic acid beta-sultone. Curve (a) of Fig. 3 shows the infrared spectrum of M–SiO_2 casting onto the surface of KBr pellet. After modifying M–SiO_2, the new absorption frequencies resulting from the M–SiO_2–SO_3H appear at 613, 734, 1049, 1187, 1365, 1416, and 1650 cm^{-1} as shown in curve (b) of Fig. 3. Table 1 displays the infrared absorptions of M–SiO_2–SO_3H. The new IR bands are summarized that C–S (613 cm^{-1}), species containing CF–CF_3 (734 cm^{-1}), –CF_3 (1365 cm^{-1}) and Si–O–C (1049, 1187 cm^{-1}) are generated. The band at 1416 cm^{-1} is characteristic of ν(S=O) stretching vibrations of undissociated –SO_3H groups as reported previously for Nafion® films and triflic acid [20,21]. Other band observed at 1650 cm^{-1} was assigned to the
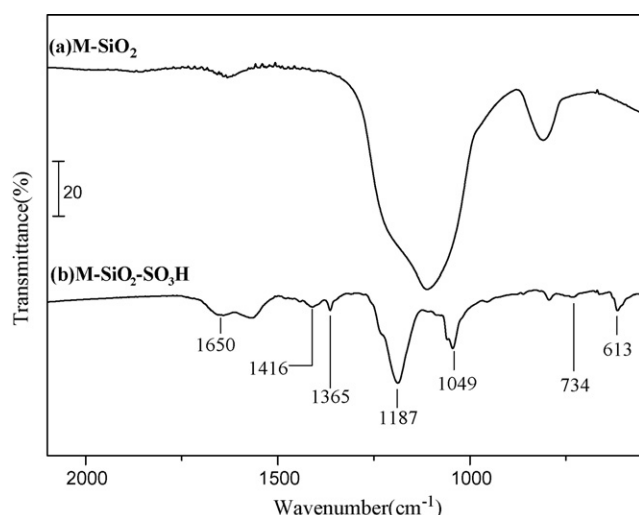
Table 1
The infrared frequencies (cm^{-1}) of M–SiO_2–SO_3H[a]

M–SiO_2–SO_3H (this work)	Assignment [RefS. 20–22]
613	ν (C–S)
734	ν (CF–CF_3)
1049, 1187	ν (Si–O–C)
1365	ν (–CF_3)
1416	ν (–SO_3H)
1650	ν (absorbed water molecules)

[a] ν, stretching.

vibrations of adsorbed water molecules, as reported by Buzzonu et al. [20] and Zecchina et al. [21] in IR studies on Nafion®. FT-IR was used to characterize the progress of the reaction, and confirm that the M–SiO_2–SO_3H had been synthesized successfully.

The thermal stability of M–SiO_2–SO_3H was studied by thermogravimetric analysis (TGA), as displayed in Fig. 4. The weight loss of M–SiO_2–SO_3H in the temperature range 100–150 °C was approximately 2.5 wt%, and was probably caused by water on the surface of the inorganic material. As presented in Fig. 4b, two-step degradation of M–SiO_2–SO_3H was observed. The initial thermal degradation temperature of M–SiO_2–SO_3H around 220 °C was reported as the temperature of thermal decomposition by desulfonation. The second degradation temperature of M–SiO_2–SO_3H, around 410 °C, was that of the thermal degradation of the organic chains. The modified mesoporous silica was analyzed by thermogravimetric analysis (TGA); the results revealed that the 30% of the organic was grafted, as shown in Table 2. The results indicate that the amount of sufonic acid groups, M–SiO_2–SO_3 (1.49×10^{-3} mol g^{-1}), exceeded that of pristine Nafion® (9.09×10^{-4} mol g^{-1}). The ion-exchange capacity (IEC, mmol of sulfonic acid g^{-1} of M–SiO_2–SO_3H) is important in determining the proton conductivity. Thus, the IEC of each sample was determined by back-titration method and the results are summarized in Table 2. The IEC values were obtained by subtracting the volume of 0.1 M HCl that was added from the initially added volume
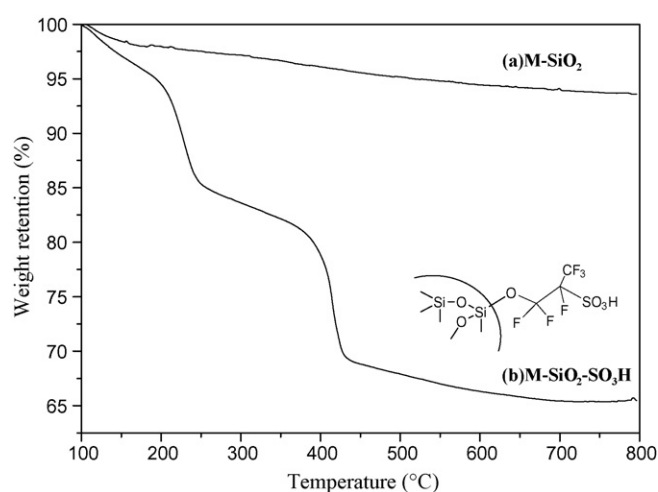

Fig. 3. FT-IR curves of (a) mesoporous silica (M–SiO_2); (b) M–SiO_2–SO_3H.

Fig. 4. Thermogravimetric analysis (TGA) curves of (a) M-SiO_2; (b) M–SiO_2–SO_3H.

Table 2
Physical properties of the functionalized mesoporous silica

Sample	IEC (mmol g^{-1})[a]	BET area (m^2 g^{-1})	Pore size (cm^3 g^{-1})	Wt. fraction (w/w, %)[b]
M–SiO$_2$	0	568	0.45	0/100
M–SiO$_2$–SO$_3$H	1.52	304	0.24	30/70

[a] A back-titration measures the equivalents of sulfonic acid in the inorganics, and the measurement was used to calculate the acid capacity or equivalent weight of the materials.

[b] Weight fraction: organic composition/mesoporous silica (measured by TGA).

of NaOH solution. A high IEC value of 1.52 mmol g^{-1} was obtained by grafting an organic sulfonic acid group on the surface (M–SiO$_2$–SO$_3$H). This value was consistent with the TGA data, as shown in Fig. 4.

4.3. Water uptake and swelling

The water uptake and swelling are critical to DMFC because they are closely related to the proton conductivity and the mechanical strength of the proton-conducting membrane. Nafion® was hybridized with various amounts of functionalized mesoporous silica, which has a relatively hydrophilic sulfonic acid group. Table 3 presents the water uptake and swelling of the membranes. The slight decrease in water uptake and swelling be caused by two competitive factors: (1) the introduced inorganic filler may reduce water uptake and swelling; (2) M–SiO$_2$–SO$_3$H has a very hydrophilic hydrophilic sulfonic acid group. The terminal functional group (–SO$_3$H) of M–SiO$_2$–SO$_3$H was hydrophilic, and was associated with the hydrated species.

4.4. Morphology of composite membranes

The microstructures of pristine Nafion® and Nafion®/M–SiO$_2$–SO$_3$H composite membranes were observed using a scanning electron microscope (SEM). Fig. 5 displays representative surface images of the samples. The SEM microphotograph (a) in Fig. 5 demonstrates that neat Nafion® membrane has a homogenous structure. Fig. 5(b) shows membranes with 3 wt% M–SiO$_2$–SO$_3$H particles in the ionomer matrix. These images clearly show that the (particulate sizes are 1 μm or less, and the distribution of the silica particles is relatively uniform.

4.5. Proton conductivity and methanol permeability

Fig. 6 compares the effect of the unmodified and modified mesoporous silica on the proton conductivity of the Nafion® composite membranes. The foremost basic property of the membrane is the proton conductivity, since it directly affects membrane–electrode assembly (MEA) performance. In this work, the proton conductivity (σ) of composite membrane was increased from 0.10 to 0.12 (S cm^{-1}) as the M–SiO$_2$–SO$_3$H content increased from 0 to 3 wt%, as presented in Fig. 6. Adding M–SiO$_2$ tends to reduce the proton conductivity of the membranes. The increasing amount of M–SiO$_2$–SO$_3$H causes the proton exchange membrane to have a higher IEC value than that of pristine Nafion®. This result can be related to the proton conductivity, as in Table 3. The proton conductivity decreased from 3 wt% M–SiO$_2$–SO$_3$H loading, mainly because of the phase-separated microstructure in the membrane. As mentioned above, numerous attempts have been made to improve the cell performance of DMFCs through the incorporation of inorganic moieties into a Nafion® membrane. However, no significant improvement has been made. Various inorganic particles suffer from low proton conductivity, reducing the ion conductivity of the composite membrane to an unacceptable level. In the system in this investigation, Nafion®/M–SiO$_2$–SO$_3$H provides promising results because of the proton conductivity of M–SiO$_2$–SO$_3$H is higher than that obtained using other inorganic fillers. The increase in proton conductivity may be caused by the M–SiO$_2$–SO$_3$H, which contains more hydrophilic sulfonic acid groups.

Fig. 7 plots the methanol permeability of membranes fabricated with different amounts of pristine M–SiO$_2$ or modified M–SiO$_2$ in Nafion®. The membrane thickness

Table 3
The composition and the properties of the composite membranes

Component[a] Nafion®/wt% M–SiO$_2$–SO$_3$H[a]	M–SiO$_2$–SO$_3$H/Nafion®[b]	–SO$_3$H (mol)[c]	Proton conductivity (S cm^{-1})	Water uptake[d] (%)	Swelling[d] (%)
0	0.000/3.640	3.64×10^{-4}	0.100 ± 0.001	81.20	50.6
1	0.061/3.600	3.66×10^{-4}	0.108 ± 0.001	79.82	48.3
2	0.122/3.564	3.69×10^{-4}	0.115 ± 0.001	77.65	46.2
3	0.182/3.527	3.71×10^{-4}	0.122 ± 0.001	75.76	44.1
4	0.243/3.491	3.73×10^{-4}	0.117 ± 0.001	73.25	42.0
5	0.304/3.455	3.76×10^{-4}	0.113 ± 0.001	71.21	40.5
6	0.365/3.418	3.78×10^{-4}	0.108 ± 0.001	70.50	39.1

[a] The composite membranes fabricated with different amounts of M–SiO$_2$–SO$_3$H.

[b] The ratio of –SO$_3$H from M–SiO$_2$–SO$_3$H to that within the Nafion.

[c] The total amounts of the –SO$_3$H in the composite membranes.

[d] The sample was immersed in distilled water at 60 °C for 1 h.
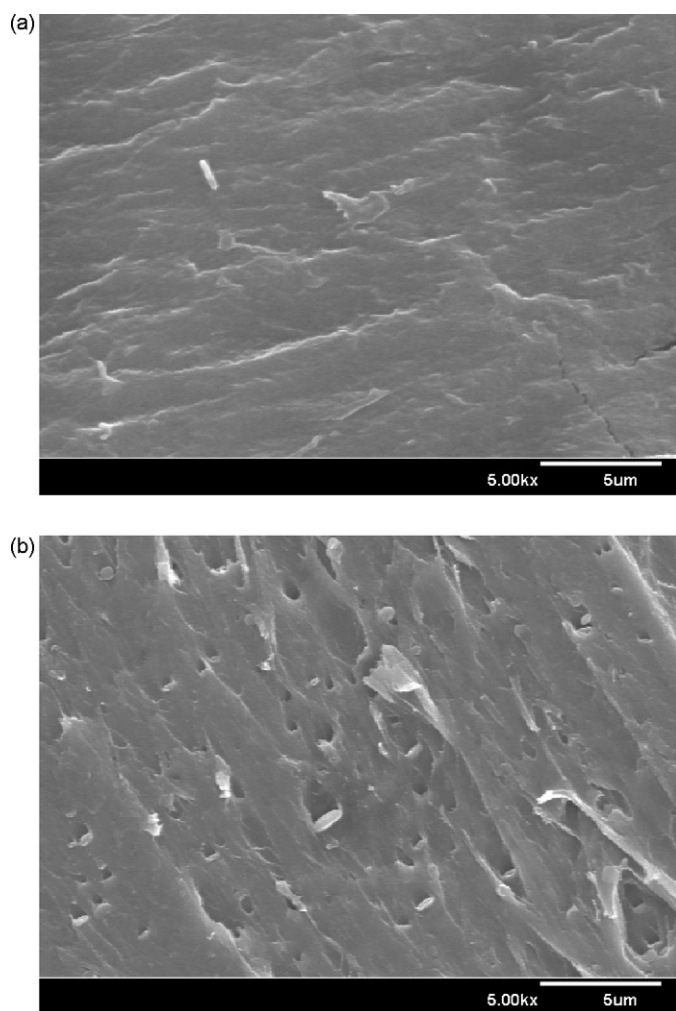
(a)

5.00kx   5um

(b)

5.00kx   5um

Fig. 5. SEM images of the surface of (a) pristine Nafion®; (b) Nafion®/M–SiO₂–SO₃H (3%) composite membranes (bar scale represents 5 μm).
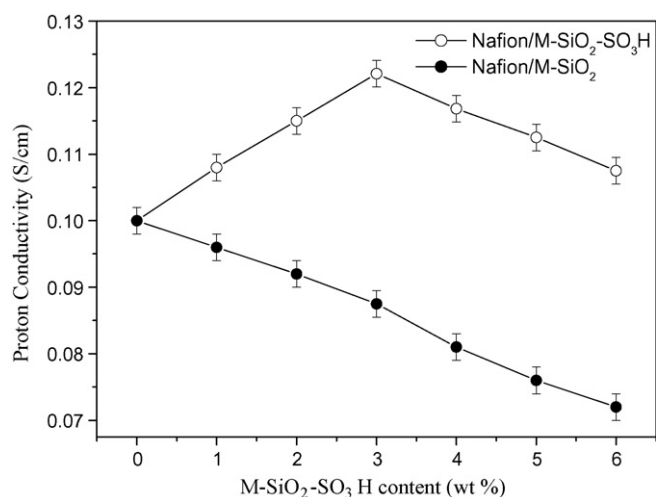

Fig. 7. The methanol permeability on the content of native and modified M–SiO₂ in Nafion® membrane.

Fig. 6. Proton conductivity of native and modified M–SiO₂ in Nafion® membranes.

was maintained at 120 μm using the same total amount of Nafion® and the inorganic filler. The methanol permeability declined rapidly with as the M–SiO₂ or M–SiO₂–SO₃H content that was added to Nafion® increased, as presented in Fig. 7. The methanol permeability of Nafion®/M–SiO₂–SO₃H exceeded that of the Nafion®/M–SiO₂ composite membrane. The methanol molecules transfer easily together with solvated protons as the hydrophilicity of the sulfonate groups of Nafion®/M–SiO₂–SO₃H exceeds that of the Nafion®/M–SiO₂ composite membrane. The methanol permeability of the composite membrane that contained 3 wt% M–SiO₂–SO₃H was $4.5 \times 10^6 \, cm^2 \, S^{-1}$, which was 30% lower than that of pristine Nafion®. Methanol is typically transported in clusters and ion-channels [23]. The M–SiO₂–SO₃H was embedded in the hydrophilic cluster and ion-channels increasing the length of the path of methanol transportation through membrane. Tentatively, therefore 3 wt% M–SiO₂–SO₃H may be the optimum proportion of inorganic filler in the composite electrolyte membrane for DMFCs.

The ratio of −SO₃H content in M–SiO₂–SO₃H to that within the Nafion® was also calculated. Table 3 presents the proton conductivity and the composition of composite membranes. The total amount of −SO₃H of PEM was definitely higher. Therefore, the proton conductivity of PEM increased with the M–SiO₂–SO₃H content, perhaps because different mechanisms of proton transportation applied. Two mechanisms of proton transportation in the composite membrane are proposed: (i) the fact that M–SiO₂–SO₃H had more sulfonic acid groups than pristine Nafion® promoted the hopping mechanism, and (ii) the vehicle mechanism was accelerated on the surface of the introduced silica oxide network [24]. The formation of H_3O^+ was more strongly facilitated by the cluster in the membrane than that by the pristine Nafion®, as displayed in Scheme 3. Consequently, introducing M–SiO₂–SO₃H enhanced the proton conductivity of the composite membrane.

The effect of M–SiO₂–SO₃H in Nafion® composite membranes on proton conductivity is considerable. M–SiO₂–SO₃H in Nafion® composite membranes also improved methanol per-
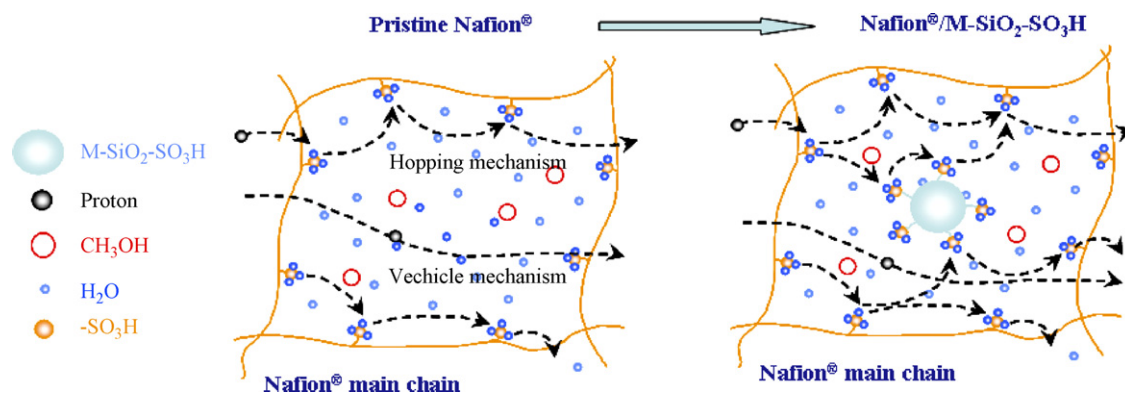
Scheme 3. Schematic illustration of proton transfer mechanism of Nafion®/M–SiO$_2$–SO$_3$H composite membrane.

meability. The performance of these composite membranes in DMFC was evaluated. The ratio of ion conductivity to methanol permeability (*C*/*P* ratio) is increased by adding 3 wt% of M–SiO$_2$–SO$_3$H. However, a higher M–SiO$_2$–SO$_3$H loading of over 3 wt% has less effect, as plotted in Fig. 8. Furthermore, reducing the methanol crossover far below that of pristine Nafion® membrane substantial increased the proton conductivity, and markedly improved the composite membranes tested in DMFC.

4.6. Fuel cell performances

The performance of composite membranes was tested in a single cell DMFC. Fig. 9 plots cell potential as a function of current density for the DMFC membrane–electrode assembly (MEA) with M–SiO$_2$–SO$_3$H and pristine Nafion® composite membranes. Indeed, the suppression of methanol crossover increases OCV at low current densities [25]. In this study, however, the improvement at lower current densities is lower than in the cited investigation, perhaps because of the concentration of the methanol fuel in the DMFCs test. Some groups have established that the OCV change at low current densities with a low concentration of methanol fuel was too small to be distin-
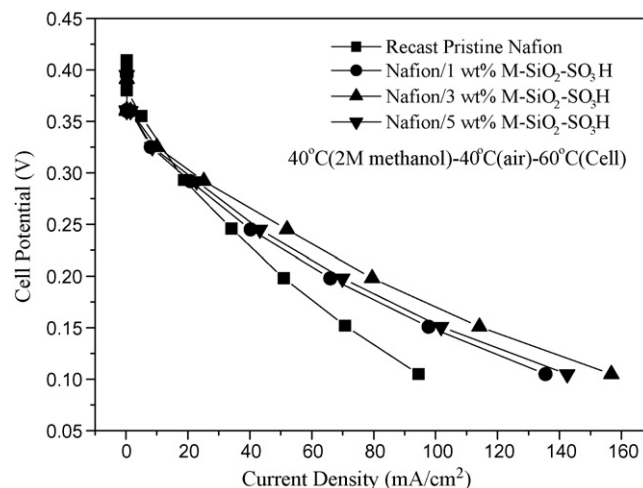

Fig. 9. Polarization curves for the MEA made with pristine Nafion® membrane and composite membranes operated at 313 K.

guished [24,26–28]. In this work, a single cell was tested at low methanol concentration (2 M). Accordingly, the phenomenon exhibited by DMFCs herein may be reasonable. The composite membrane that contains 3 wt% M–SiO$_2$–SO$_3$H outperformed that of pristine Nafion®. The current densities measured with composite membranes with 0, 1, 3 and 5 wt% M–SiO$_2$–SO$_3$H, were 51 and 66, 80 and 70 mA cm^{-2}, respectively, at a potential of 0.2 V. Moreover, all of the composite membranes that contained M–SiO$_2$–SO$_3$H performed better at higher current densities than did pristine Nafion®. However, the membrane with 5 wt% inorganic loading does not show better cell performance than that with 3 wt% loading, perhaps because proton conductivity is lower at 5 wt% inorganic loading, as presented in Fig. 6. The Nafion®/M–SiO$_2$–SO$_3$H system yields promising results for two reasons: (i) the functionalized mesoporous silica has more hydrophilic regions than pristine Nafion®, in the form of sulfonic acid groups; and (ii) the mesoporous silica effectively blocks the passage of methanol.

5. Conclusions

An organic sulfonic acid (–SO$_3$H) was grafted on the surface of mesoporous silica to improve proton conductivity. The perfor-
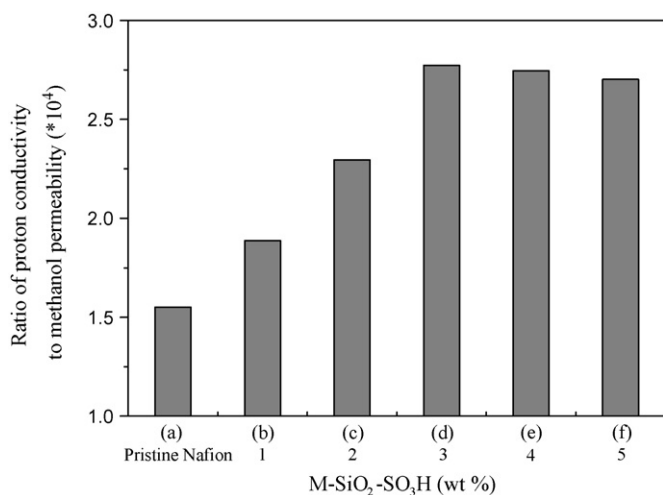

Fig. 8. Ratio of the proton conductivity to the methanol permeability for Nafion® composite membranes filled with various contents of Nafion®.

mance of these Nafion®/M–SiO$_2$–SO$_3$ composite membranes was evaluated for DMFCs in terms of methanol permeability, proton conductivity and cell performance. The proton conductivity of the composite membrane increased from 0.10 to 0.12 (S cm^{-1}) with M–SiO$_2$–SO$_3$H content from 0 to 3 wt%. The increase in proton conductivity may be associated with the M–SiO$_2$–SO$_3$H, which contains more hydrophilic regions, in the form of sulfonic acid groups, than that of pristine Nafion®. The methanol permeability of the composite membrane declined dramatically as the M–SiO$_2$–SO$_3$ content in the composite membrane increased. The methanol permeability of the composite membranes that contained 3 wt% M–SiO$_2$–SO$_3$H was 4.5×10^{-6} cm^2 S^{-1}, which was 30% lower than that of pristine Nafion®. The Nafion®/3 wt% M–SiO$_2$–SO$_3$H membrane had a higher selectivity (*C/P* ratio = 27,737) than recast Nafion® (*C/P* ratio = 15,523). The high selectivity indicates that the composite membrane is suitable for DMFC applications. This effect may significantly improve the performance of a DMFC with Nafion®/M–SiO$_2$–SO$_3$H composite membrane.

Acknowledgements

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