

Short communication

Proton conduction in Nafion composite membranes filled with mesoporous silica

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Abstract

Studies of proton-conductive polymer membranes are vital for the future development of high-performance polymer electrolyte membrane fuel cells (PEM-FC). In particular, a method for inhibiting the volatility of water in the polymer matrix at high temperatures is a crucial issue, directly related to the operation of PEM-FC system. In this study, we focus on polymer composite membranes, which consist of commercial Nafion and mesoporous silica (MPSi) as novel inorganic additives, and investigate an improvement in the total proton conductivities and the good electrochemical stability at high temperatures. MPSi, which can be synthesized with pore sizes from 1 to 10 nm, has a wide range of potential applications because of its extraordinary properties, such as extremely large surface area, flawless surface condition and well-regulated porous structure. We found that the Nafion composites filled with MPSi have approximately 1.5 times higher proton conductivities (more than 0.1 S cm^{-1} at 80°C and 95%RH) than pure Nafion and can display good temperature performance relative to pure Nafion and the particle SiO_2 composite. Moreover, the conductivity of Nafion/sulfonated MPSi was the highest (0.094 S cm^{-1}) at 40°C and 95%RH. These are probably due to the large surface area of MPSi, which can increase the water adsorption in Nafion matrix.

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1. Introduction

Development of fuel cell system is noteworthy as a new electrical power source, and the fuel cell is expected to be used in a future hydrogen society with a clean environment. In particular, the polymer electrolyte membrane fuel cells (PEM-FC) have attracted much interest as a novel power source for electronic devices and vehicles, because it has high-energy efficiency and low heat emission compared with internal combustion systems using fossil fuel. As a polymer membrane for PEM-FC, Nafion has been used because of its good chemical, physical and thermal stabilities with relatively high proton conductivity. Although Nafion has excellent performance at moderate temperature, it needs to work in high humidity conditions with pure hydrogen as fuel. Operation is difficult at high temperatures above 80°C , because the conductivity decreases drastically with decreasing water from the Nafion matrix. This makes it unsuit-

able for practical use to achieve high-energy efficiency in the PEM-FC. Moreover, during the operation of the PEM-FC system at low temperature, CO-poisoning causes a decrease in the activity of the Pt at the anode side [1]. As a result, the performance degrades, and higher temperature operation system for the PEM-FC is highly desirable. Many scientists have reported that the properties of Nafion can be improved by the addition of: (I) hydrophilic inorganic materials, such as SiO_2 , clay and zeolite [2–5], which maintain high water content and prevent the Nafion dehydration at high temperatures; (II) solid acids, such as sulfonated ZrO_2 [6,7] which increase the concentration of acid sites to promote local migration; (III) heteropolyacids, such as phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) [8], which are widely used to improve proton conductivity at relatively high temperatures.

We have investigated hexagonally ordered mesoporous silica (MPSi) as an inorganic additive for polymers [9–12]. Since MPSi was discovered by Kuroda and co-workers (namely FSM-16) [13] and Mobil Corporation (namely M41S) [14], there have been many studies of the associated novel synthesis method [15,16], hybridization with organic compounds [17] and alignment of mesopores as thin-films [18] for the development of

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MPSi in materials science. A wide range of applications, including catalyst, sensor, ion-exchanger and selective separation has been considered by various researchers. MPSi is a unique inorganic material, because it possesses periodic mesoporous structure with controllable pore size and functionalization using organic groups, such as amine, thiol, benzyl and imidazole. Recently, MPSi containing sulfonic acid groups was synthesized by simple surface treatment or by *in situ* methods, which can be applied in the catalytic applications [19–22]. Ozin and co-workers have reported a novel MPSi containing sulfonic acid template molecules (*meso*-SiO₂-C₁₂EO₁₀OH-CF₃SO₃H) as the proton-conducting solid electrolyte [23]. In spite of the extraordinary properties of MPSi, there are no reports of polymer composite membranes filled with MPSi for proton-conductive electrolyte membranes. We therefore expected that the MPSi composite membranes could improve the retention of water and the conductivity at high temperatures compared with the neat polymer or other composites.

Here, we report on Nafion composites, including MPSi, which was modified on the surface by sulfonic acid groups as a novel type of additive. We expect the periodic porous structure of MPSi to be suitable for the migration of protons in the polymer matrix at relatively high temperatures. In this paper, detailed characterizations of neat and sulfonated MPSi/Nafion composites are deduced from the impedance measurements and SEM observations.

2. Experimental

2.1. Synthesis of Ne-MPSi and Su-MPSi

Neat MPSi (Ne-MPSi) was synthesized by the sol-gel method using a nonionic surfactant, EO₂₀PO₇₀EO₂₀ (EO and PO denote the ethyleneoxide and propyleneoxide unit, average $M_w = 5800$, Aldrich Co.) [15]. Tetraethyl orthosilicate was added to the surfactant aqueous solution in which the pH was adjusted to 1.0 using 36% HCl. The mixture was stirred at 35 °C for 24 h, and was then kept in a convection oven at 80 °C for 24 h. The reactant was filtered, and the precipitate was calcined at 400 °C in a muffle chamber. Sulfonated MPSi (Su-MPSi) was synthesized by the surface treatment of Ne-MPSi using 3-(trihydroxysilyl)-1-propane-sulfonic acid (30–35% in water, melting point -62 °C, specific gravity 1.12, Gelest Co.). The original filler was dispersed in ethanol, and the silane coupling agent (10 wt.% to the filler) was dropped in at room temperature. The mixture was then stirred at 60 °C for 24 h, and the precipitate was rinsed three times with 50 ml ethanol.

2.2. Preparation of inorganic filler/Nafion composites

Inorganic filler/Nafion composite films were prepared by the casting method. Nafion solution (20 wt.% in ethanol/water) was purchased from Aldrich Co. The original solution was evaporated at 60 °C *in vacuo* to obtain the Nafion resin. The resin was then dissolved in dimethyl formamide (DMF), which is well suited to the preparation of composite membranes [24]. Ne-MPSi, Su-MPSi and commercial particle silica (p-SiO₂) were

used for the composites as inorganic additives. The p-SiO₂ was purchased from Kanto Chemical Co. (NanoTek[®], average particle size 18.5–83.6 nm). These were dispersed into the DMF solution and the resulting slurry was stirred at room temperature for 24 h. The slurry was cast onto a Petri dish and was left to dry in an oven at 50 °C for 24 h. After this, the resulting self-standing film was completely dried at 120 °C *in vacuo*. Finally, each film obtained was immersed in 2 M H₂SO₄ solution for 24 h, and was then kept in purified water.

2.3. Measurements

Transmission electron microscope (TEM) measurement was carried out using JEM-200CX system (JEOL Co.). Small-angle X-ray scattering (SAXS) measurements were made using a RU-200 system (Rigaku Co.) with Cu K α radiating conditions of 40 kV and 180 mA. The Brunauer–Emmett–Teller (BET) surface area of Ne- and Su-MPSi was determined using a Coulter SA3100 system (Beckman Coulter Co.). The ion-exchange capacity of all fillers was determined by the titration method. The filler (0.05 g) was added to the 2 M NaCl solution and was stirred adequately. The solution was titrated by adding 0.01 M NaOH, and the potentiometric ratio was measured using a pH meter [20]. The morphology of the inorganic filler/Nafion composite membranes was determined using a scanning electron microscope (SEM, Shimadzu SS-550). The cross-section of the membranes was etched by an ion coater (Eiko IB-3) at 2 mA for 10 min, and was coated by Au using a sputter (Hitachi E-1020) at 15 mA for 120 s. Water uptakes of pure Nafion and the composite (5 wt.% filler content) membranes were calculated from $(W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \times 100$ (%), where W_{wet} and W_{dry} are the weights of samples after swollen in purified water and after dried at room temperature for 2 h *in vacuo*. Proton conductivity was measured by a complex AC impedance method using an impedance analyzer (Solartron 1280) in the frequency range 0.01 Hz to 20 kHz. A four-probe cell was used consisting of Teflon[®] blocks with blackened Pt electrodes (two plates for current application and two wires for voltage measurement). Sample (5 mm \times 40 mm) was placed between two plates (under sample at the both ends) and two wires (on the center of sample), and these were sandwiched by two Teflon[®] blocks [25,26]. The conductivity was measured using a constant current mode (10 μ A); the entire process was carried out in a humidity-controllable chamber (Espec SH-221). In this study, the relative humidity (RH) for all measurements was fixed at 95%. The cell was set into the chamber at 40 °C and 95%RH for at least 3 h before the measurement, and was maintained for at least 90 min at each temperature measured.

3. Results and discussion

Fig. 1 shows TEM photograph and schematic image of Su-MPSi domain structure. This indicated that the MPSi has well-ordered arrays of mesopores, and the distance between mesopores is estimated to be approximately 10 nm. Fig. 2 shows SAXS diffraction patterns of Ne- and Su-MPSi. These spectra revealed that the Ne- and Su-MPSi possess well-ordered meso-

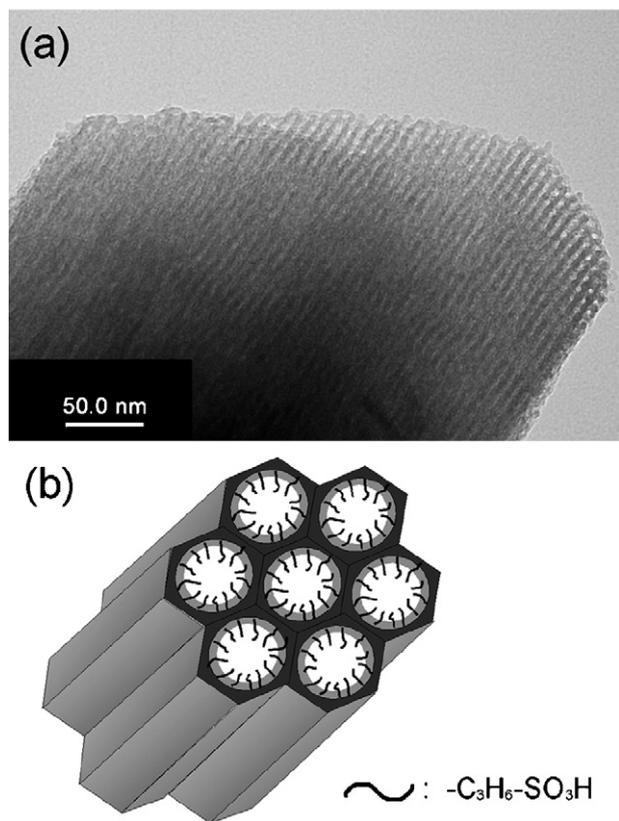


Fig. 1. (a) TEM photograph and (b) structural image of Su-MPSi.

porous structures. From the SAXS diffraction patterns, it was confirmed that each MPSi shows three peaks, indicated as (1 0 0), (1 1 0) and (2 0 0), at approximately 0.9° , 1.5° and 1.7° for the hexagonal structure. A peak-top value at 0.9° for Ne-MPSi was shifted to slightly lower angles. This may be due to the surface treatment using the organic groups, which can change the apparent long-range structure of the MPSi. The periodic structure can be estimated from the one-dimensional correlation function (γ) of the SAXS data (Fig. 2b) [9]. The physicochemical properties of Ne-MPSi, Su-MPSi and p-SiO₂ are summarized in Table 1. A long period and a pore diameter of Ne- and Su-MPSi were determined; these values differ slightly from each other. The BET surface area can also be estimated from the N₂ adsorption–desorption isothermal measurement. The value of Su-MPSi was much larger than that of p-SiO₂ and was smaller than that of Ne-MPSi. This suggests that the difference in the

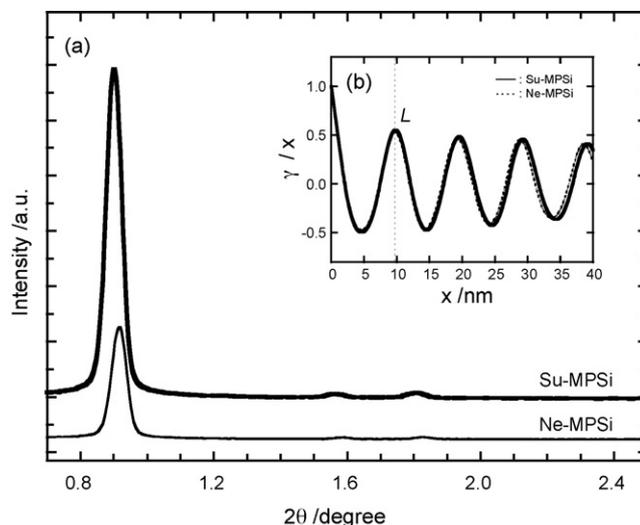


Fig. 2. (a) SAXS diffraction patterns and (b) one-dimensional correlation functions of Ne- and Su-MPSi.

surface area between Ne- and Su-MPSi is caused by the surface treatment. To confirm the surface condition of the inorganic fillers, the ion-exchange capacity was measured by the titration method. The acidity of Su-MPSi was found to be 1.2 times that of Ne-MPSi.

Fig. 3 shows the relation between proton conductivity and filler content at 40°C and 95%RH. All composites display greatest conductivity at 5 wt.% of filler content; the maximum value can be seen in the Nafion/Su-MPSi composite. The value was estimated to be 0.094 S cm^{-1} , and was approximately 1.4 times higher than that of pure Nafion. According to a previous report, the typical Nafion/SiO₂ composite has good cell performance and some useful properties, such as inhibition of methanol crossover [27,28]. However, it is sometimes difficult to achieve higher proton conductivity than with the pure Nafion. The MPSi can increase water content in the composite as a solid acid [29], so that proton conduction may easily take place into pores and at the interface between Nafion and MPSi. The Su-MPSi might be suitable for migration via the strong acid site mainly on the internal surface, and the composite can have higher conductivity. From Table 1, the acidity of Su-MPSi is certainly higher than the others, and we believe that this high performance was achieved by the extraordinary properties of MPSi, such as high surface area and acidity. On the other hand, the conductivities of all composites are less at filler content exceeding

Table 1
Physicochemical properties of inorganic fillers

Sample	Long period ^a L (Å)	Pore diameter ^a d (Å)	Surface area ^b ($\text{m}^2\text{ g}^{-1}$)	Acidity ^c H^+ (mmol g^{-1})	Water uptake ^d (%)
Su-MPSi	98.0	67.1	717	0.46	22.3
Ne-MPSi	97.0	67.4	837	0.38	15.7
p-SiO ₂	–	–	89 ^e	0.06	10.6

^a These were estimated from the one-dimensional correlation function (γ) of each SAXS diffraction pattern.

^b BET surface area was determined from the Barrett–Joyner–Halenda (BJH) equation.

^c Ion-exchange capacity was estimated from titration in 2 M NaCl_{aq}.

^d The value of pure Nafion membrane was 11.0%.

^e Data quoted from our previous report [9].

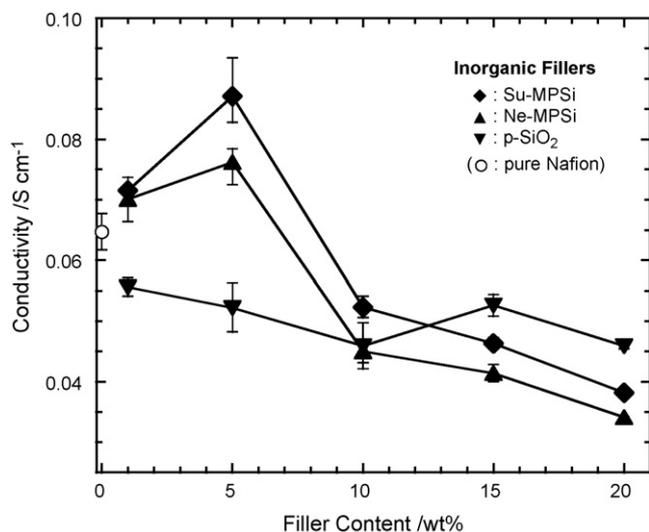


Fig. 3. Relation between proton conductivity of Nafion composites and filler content at 40 °C and 95%RH.

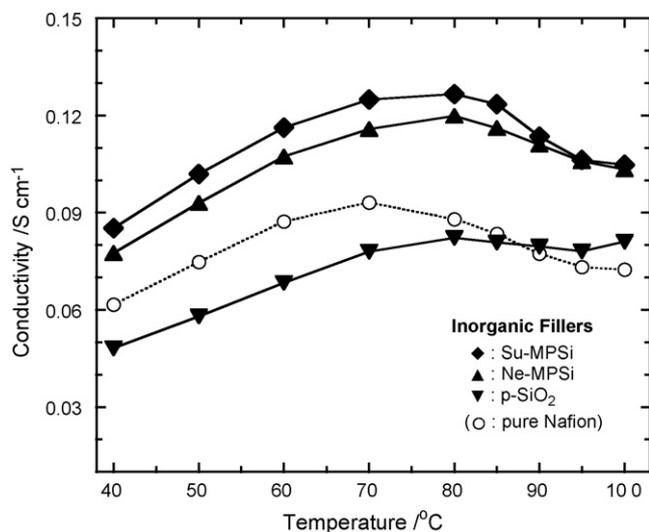


Fig. 4. Temperature dependence of proton conductivity for Nafion composites (5 wt.% each) at 95%RH.

10 wt.%. This decline may be caused by increase in the insulative phase, which consists of the agglomerates of MPSi domains, where ionic transport is prevented in the conductive Nafion matrix.

Fig. 4 shows the temperature dependence of the proton conductivity for the Nafion composites at 95%RH. The filler contents were all fixed at 5 wt.% in this case. Pure Nafion changes conductivity with temperature, having highest conductivity at 70 °C. At lower temperatures, the proton conduction behavior may be related to the water diffusion coefficient obtained from the Nernst–Einstein equation. However, the conductivity decreases with increasing temperature above 70 °C because of dehydration from the matrix. Dehydration is one of the most important problems for the PEM-FC system [30]. On the other hand, the Ne- and Su-MPSi/Nafion composites exhibited higher conductivity than the pure Nafion over the entire measurement temperature range, and these values were highest at 80 °C. The weight uptakes of inorganic fillers show that the Ne- and Su-MPSi can maintain good water content in the composite membranes, and these also possess surface area useful for the migration of protons (Table 1). These properties of MPSi seem to make dehydration from the matrix difficult at relatively high temperatures. In particular, the Su-MPSi/Nafion composite showed the highest proton conductivity in other composites, because it possesses sulfonic acid groups on the surface, which can enhance the migration of protons in the composites. In our results, the Su-MPSi is a useful additive because of its high water content and acidity in the polymer matrix. In the case of the p-SiO₂ composite, the lowest conductivity was shown in the lower temperature range, but the value at higher temperatures remains almost the same, at approximately 0.07 S cm⁻¹. This agrees with the previous report that the particle SiO₂ composite can attain good performances at higher temperatures [27,28]. Higher conductivities at low temperatures are rarely achieved by simple composites, such as Nafion/p-SiO₂, and our functional MPSi is strongly expected to act as a high-performance PEM-FC system.

Finally, we tried to observe the dispersion state of added fillers into the Nafion matrix. Fig. 5 shows SEM images of the cross-section of dried Nafion composite membranes. In the Ne- and Su-MPSi composites, micron-order oval domains are clearly observed. The Su-MPSi composite shows some aggregates of the filler domains (Fig. 5b), whereas the Ne-MPSi can disperse homogeneously in the Nafion matrix (Fig. 5a). This probably means that the strong interactions between MPSi are influenced by the surface treatment using silane-coupling agent, which may promote the filler aggregations. This result is consistent with the difference in the BET surface area of Ne- and

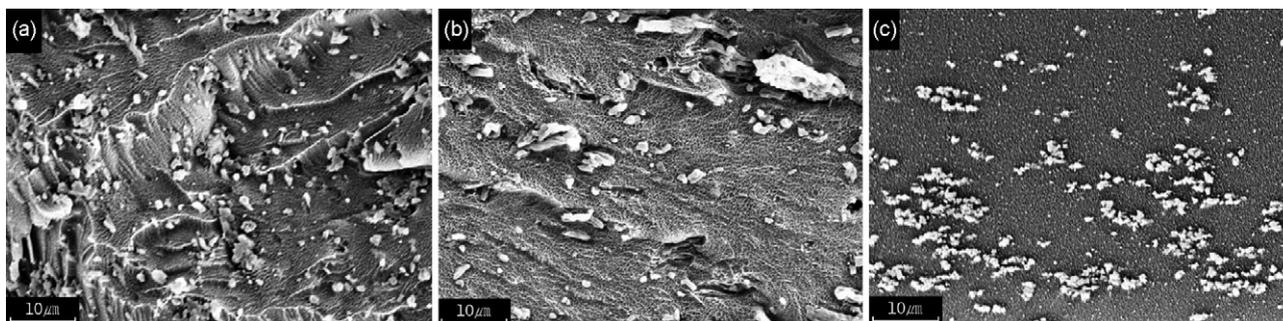


Fig. 5. SEM images of Nafion composites with 5 wt.% of (a) Ne-MPSi, (b) Su-MPSi and (c) p-SiO₂.

Su-MPSi, as seen in Table 1. On the other hand, the p-SiO₂ composite obviously shows micron-order SiO₂ agglomerates on the surface (Fig. 5c). These SEM data indicate that homogeneous dispersion of fillers in the Nafion matrix is not always necessary for the increase in conductivity. However, the SEM observations in this study were carried out on dried membranes, and the dispersion state may be completely different under wet conditions. In future work, *in situ* morphological measurement using an environmental SEM should be performed with swollen Nafion membranes.

4. Conclusion

We prepared high-performance Nafion membranes filled with mesoporous silica (MPSi), and studied the effect of MPSi addition on the proton conductivity. The addition of neat MPSi (Ne-MPSi) and sulfonated MPSi (Su-MPSi) increased the proton conductivity in the Nafion matrix, and Nafion/Su-MPSi (5 wt.%) exhibited the highest conductivity of all composites at 40 °C and 95%RH. Moreover, these MPSi composites displayed good temperature performance relative to pure Nafion and the p-SiO₂ composite. This is probably due to the difference in the surface area between MPSi and p-SiO₂, which can increase the water adsorption. In particular, the Su-MPSi composite had the highest proton conductivity, because of the treatment using sulfonic acid groups on the surface. We expect that efficient proton conduction in polymer can be achieved by the addition of functional MPSi.

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