

Three-dimensionally ordered macroporous polyimide composite membrane with controlled pore size for direct methanol fuel cells

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Abstract

Three-dimensionally ordered macroporous (3DOM) polyimide matrix with different pore size (1.3 μm –200 nm) was fabricated, and its structural effect on some properties of composite membrane was investigated. The composite membrane prepared by impregnation of 2-acrylamido-2-methylpropanesulfonic acid polymer (PAMPS) exhibited swelling ratios as low as 2–3% in water or methanol solutions, compared with about 400% of PAMPS itself. The swelling ratio of composite membrane was constant regardless of the 3DOM pore size. However, methanol permeability strongly depended on the pore size. In particular, it was drastically reduced when connecting windows among macropores became less than 100 nm. On the other hand, proton conductivity changed with 3DOM matrix porosity according to Archie's law. The porosity of 3DOM matrix is basically constant even if the pore size changes. Therefore, we suppressed the methanol crossover without lowering of proton conductivity due to reducing the matrix pore size, and the selectivity (proton conductivity/methanol permeability) of $1.2 \times 10^5 \text{ S cm}^{-3} \text{ s}$, which was one order of magnitude greater than that of Nafion[®], was achieved.

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1. Introduction

Direct methanol fuel cells (DMFCs) have been developed for use especially in portable applications due to their characteristics such as light weight and small size. The energy density of DMFC increases with increasing concentration of methanol solution fed to an anode. However, the feeding of high concentrated methanol solution causes methanol permeation from anode to oxygen cathode through a polymer electrolyte membrane. This permeation results in an occurrence of a chemical short-circuit reaction at the cathode which decreases the cell voltage and fuel utilization. This “crossover” is mainly induced by expansion of electrolyte membranes due to water or methanol absorption [1]. Therefore, a morphological stability of membranes is a key

factor for high performance in DMFC. Perfluorosulfonic acid polymers such as DuPont's Nafion[®] have been generally used for hydrogen–oxygen fuel cells. Although they have high proton conductivity and good chemical stability, the methanol permeability is too high to use in practical. Many researchers have investigated alternative polymers with hydrocarbon structures including polysulfones, poly(ether ether ketone)s, polyimides, and polybenzimidazoles [2,3]. However, they must be sulfonated at certain level to obtain proton conductivity enough for DMFC, so that alternative polymers expand through methanol or water. As a result, the suppression of crossover is practically difficult. Recently, increasing attention has been paid to a combination of polymer electrolyte and other components such as inorganic fillers [4,5]. Chemical and physical properties of composite membranes can be controlled by a kind and content of filling components. However, a distribution of inorganic filler in polymer electrolyte membrane is sometimes not so uniform, which strongly influences on the membrane performance. We previously reported a composite membrane composed of three-dimensionally ordered macroporous (3DOM) silica matrix and a

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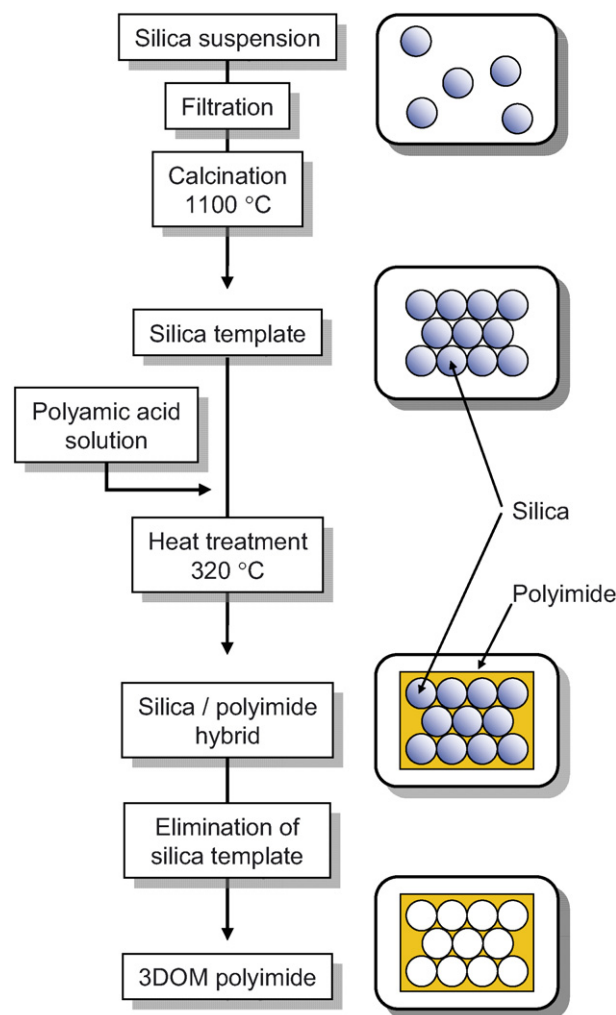
proton conducting polymer, and claimed that the 3DOM matrix was effective to reduce methanol crossover [6,7]. This suppression is due to mechanical repressing of polymer expansion by the matrix. Therefore, high mechanical strength is required for the matrix. Recently, we prepared 3DOM polyimide matrix [8]. Polyimide is one of engineering plastics having high mechanical strength, thermal and chemical stability. Compared with 3DOM silica, the polyimide matrix had more uniform structure, which was preferable to obtain composite membranes with desired properties. An easy pore size control is also one of conspicuous benefits of 3DOM polyimide.

In the present work, we have prepared 3DOM polyimide matrix with different pore size, and investigated its structural effects on the characteristics of composite membrane to develop alternative membranes with high performance for DMFC application. Improvement of membranes has been discussed based on transfer mechanisms of protons and methanol molecules in the composite membrane.

2. Experimental

3DOM polyimide matrix was prepared by colloidal crystal templating method (Scheme 1) [6]. Mono-disperse silica particles with diameter of 1.5 μm , 550 nm, or 280 nm were used as template. Each silica particle was provided as 20.5 wt% aqueous suspension (SEAHOSTAR) from Nippon Shokubai Co., Ltd. A dilute silica suspension prepared by mixing 2 ml of SEAHOSTAR and 30 ml of water (550 nm and 280 nm particles) or ethylene glycol (1.5 μm particles), was filtrated through a mixed cellulose membrane filter (pore diameter = 0.1 μm , Advantec MFS, Inc.) under reduced pressure of 1×10^4 Pa compared with an atmospheric pressure. The silica layer deposited on the membrane filter was peeled off and then calcinated at 1100 $^{\circ}\text{C}$ to obtain a silica template. The sintering process of silica particles was adjusted depending on the particle size. Thus, the duration was changed to 10 h, 2 h, and 20 min for 1.5 μm , 550 nm, and 280 nm silica particles, respectively. In this study, polyamic acid was used as a precursor of polyimide. A dimethyl acetamide solution containing 10 wt% polyamic acid was injected into the vacant space of silica template. Then, it was heated at 320 $^{\circ}\text{C}$ to convert polyamic acid to polyimide. Then, 3DOM polyimide matrix was obtained as a membrane by etching the silica template with 10 wt% hydrofluoric acid solution. We used 2-acrylamido-2-methylpropanesulfonic acid polymer (PAMPS) as a filling electrolyte for the 3DOM polyimide matrix (Scheme 2). An aqueous solution containing 2-acrylamido-2-methylpropanesulfonic acid, *N,N'*-methylenebisacrylamide, and ammonium persulfate with concentrations of 4.83 mol kg⁻¹, 2.60 $\times 10^{-1}$ mol kg⁻¹, and 4.38 $\times 10^{-2}$ mol kg⁻¹ was filled into the 3DOM pores by vacuum impregnation method, and then polymerized at 60 $^{\circ}\text{C}$ for 1 h to obtain the composite membrane. The composite membrane with thickness of 150 μm and size of about 3 cm \times 3 cm was used in all experiments. For comparison, PAMPS (200 μm) and Nafion[®] 117 membranes were also examined.

The structure and surface area of a sample membrane were characterized with a scanning electron microscope (SEM, JSM-

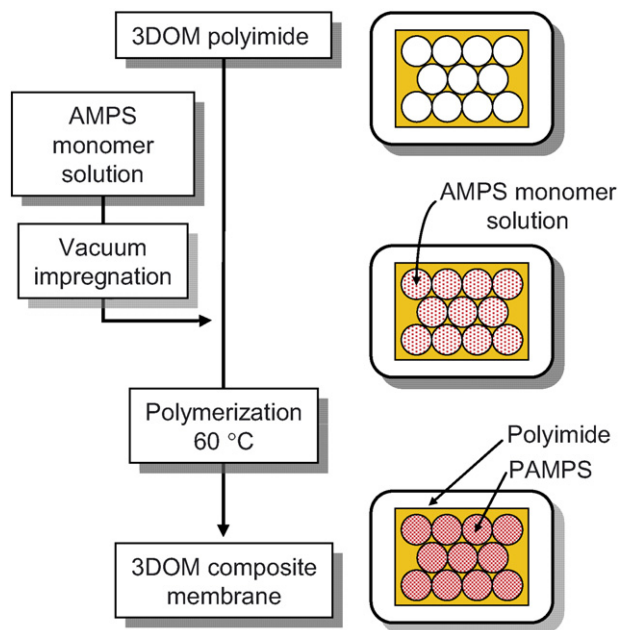


Scheme 1. Procedure for the preparation of 3DOM polyimide matrix.

5310, JEOL) and N_2 adsorption instrument (Belsorp 2, Bel Japan Inc.). The porosity was estimated from the weight difference between the membrane before and after an impregnation of glycerol. The methanol permeability of membranes was determined using a glass cell with two reservoirs [9]. Prior to the measurement, a sample membrane was equilibrated in water at room temperature, and then set at the middle of the cell. One side of the cell (donor compartment) was filled with methanol solution, and the other side (receptor compartment) was filled with deionized water. A methanol flux across the membrane to the water compartment is given by Eq. (1) as a function of time,

$$C_{\text{receptor}}(t) = \left(\frac{A}{V_{\text{receptor}}} \right) \left(D \times \frac{K}{L} \right) C_{\text{donor}}(t - t_0) \quad (1)$$

where C_{donor} and C_{receptor} are methanol concentrations in the donor and receptor compartments, respectively, A and L the cross-sectional area and thickness of the membrane, V_{receptor} is the volume of receptor compartment. D and K are the methanol diffusivity and partition coefficient between the membrane and the adjacent solution, respectively. The product DK is generally estimated as the methanol permeability (P_M). C_{receptor} was



Scheme 2. Procedure for the preparation of 3DOM composite membrane.

measured with a gas chromatograph (GC-14B, Shimadzu Corp.) and the P_M was calculated from a slope of the time-correlated C_{receptor} curve. The proton conductivity (σ) of membranes was measured with an impedance analyzer (4192A, YHP) in frequency range from 100 Hz to 1 MHz. A sample membrane was clamped between two Au electrodes by using a home-made Teflon cell and kept under controlled temperature and humidity. From Cole–Cole plots, resistances of membranes (R) were estimated, and then the proton conductivity was calculated using the following equation:

$$\sigma = \frac{L}{R \times A} \quad (2)$$

where L is the thickness of membrane and A is the electrode area. R of each membrane was measured at least four times to ensure high reproducibility of this measurement.

3. Results and discussion

The silica templates with different colors were obtained by filtration method. These colors, e.g. green in 280 nm particle template, are based on Bragg diffraction of visible light by the three-dimensionally ordered arrays of silica particles, indicating that the prepared silica template had highly uniform arrangement of particles [10,11]. The uniformity of templates was also confirmed from SEM observation. As shown in Fig. 1, a hexagonal close-packed arrangement of silica particles, where each particle touched six others in the same layer and each three on both top upper and lower layers, was observed. As decreasing particle size, it is concerned that the thermal motion of particles in the course of filtration process may influence on the deposited structure. Some disordered parts were actually observed in the smallest 280 nm template. However, from the comparison of sur-

face area and porosity with their ideal values, it was confirmed that the templates had relatively high uniformity (Table 1).

Fig. 2 shows SEM images of the 3DOM polyimide membranes prepared using 1.5 μm , 550 nm, and 280 nm silica templates. The ordered uniform macropores were successfully obtained from each template. However, the pores were a lit-

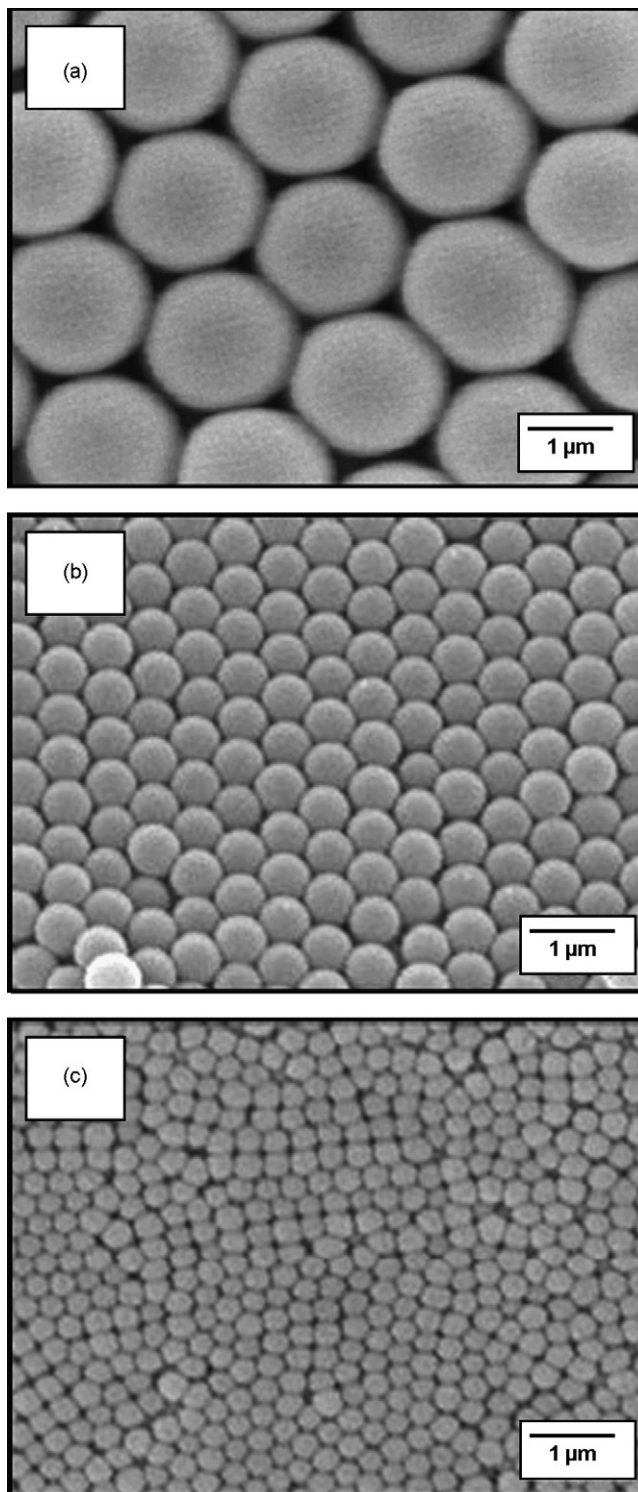


Fig. 1. SEM micrographs of silica templates composed of (a) 1.5 μm , (b) 550 nm, and (c) 280 nm particles.

Table 1
Structural properties of silica template

Silica particle	Porosity (%), experimental/ideal	Surface area ($\text{m}^2 \text{cm}^{-3}$), experimental/ideal
1.5 μm	29/26	2.9/3.0
550 nm	23/26	9.8/8.1
280 nm	22/26	19.3/15.9

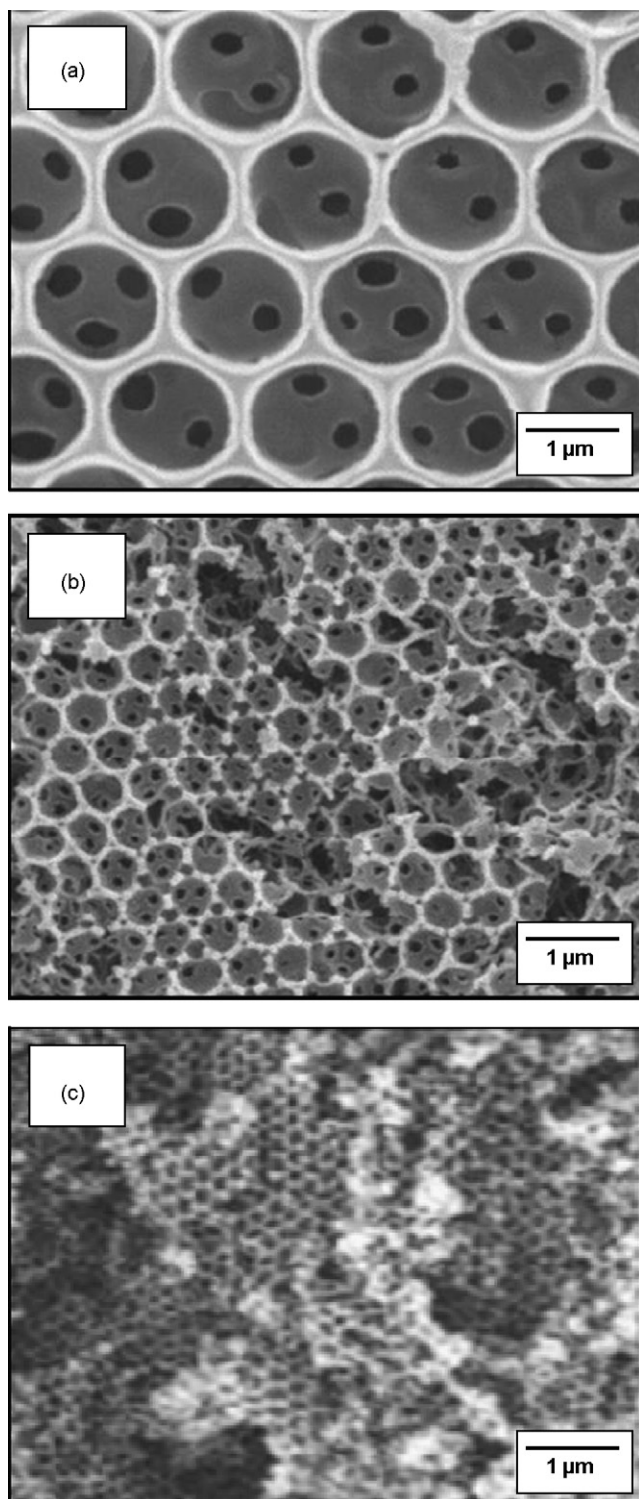


Fig. 2. SEM micrographs of 3DOM polyimide matrices prepared by using (a) 1.5 μm , (b) 550 nm, and (c) 280 nm templates.

tle smaller compared with the silica particles used as template. Polyimide is a hard engineering plastic, but it slightly shrinks or expands. Therefore, the slightly smaller pore size observed with SEM may result from the vacuum environment for SEM observation. By the way, it was also observed that smaller holes were formed in the macropores. These are connecting windows among neighboring macropores. As decreasing macropore size, the connecting windows also became smaller with almost same size ratio of 4:1 (Table 2). The formation of 3DOM structure was also supported by a reasonable porosity in each pore size. However, large deviations were observed in the surface area. For example, the surface area of 3DOM polyimide membrane prepared by 1.5 μm silica template was $9.0 \text{ m}^2 \text{ cm}^{-3}$ although that of the silica template was $2.9 \text{ m}^2 \text{ cm}^{-3}$, suggesting that the surface of 3DOM polyimide membrane could be relatively rough. The conversion of polyamic acid to polyimide provides water as a by-product. This reaction proceeds at a relatively high temperature (above 200°C). Therefore, the water is produced as a vapor, resulting in the larger surface area of 3DOM polyimide.

For preparation of composite membranes, PAMPS was used as proton conductive polymer, due to easy impregnation into the matrix and high proton conductivity. The morphological stability of membranes was estimated according to the swelling ratio: $\Phi_S (\%) = (S_{\text{wet}} - S_{\text{dry}}) / S_{\text{dry}} \times 100$ with the surface areas in both hydrated state (S_{wet}) and dry state (S_{dry}). Even though the swelling ratio of PAMPS was considerably high (460% in water, 330% in 20 mol dm^{-3} methanol solution), the composite membrane hardly swelled both in water (3%) and in methanol solutions (2–3%). This suppression effect was constant regardless of the 3DOM pore size. Thus, the physical and chemical states of PAMPS in the composite membranes do not depend on pore size of 3DOM polyimide membrane. In the course of swelling–drying cycles, cracks appeared on the surface of PAMPS membrane. These cracks grew and caused fragmentation of the membrane. In contrast, the morphology of composite membranes was maintained, indicating that the mechanical stress by expansion and shrinkage of PAMPS in 3DOM polyimide matrix could be dispersed uniformly by the 3DOM matrix.

Fig. 3 shows the methanol permeability through Nafion[®], PAMPS, and composite membranes. Compared with Nafion[®], PAMPS and composite membranes had opposite concentration dependences, i.e. the methanol permeability decreased with increasing methanol concentration. This result shows that mass transfer (methanol) in the composite membrane mainly occurs in the PAMPS phase and not at the interface region between PAMPS and polyimide. This kind of behavior is usually observed in hydrocarbon polymers such as sulfonated

Table 2
Structural properties of 3DOM polyimide matrix

3DOM polyimide (template size)	Mean macropore size (nm)	Mean connecting window size (nm)	Porosity (%), experimental/ideal	Surface area ($\text{m}^2 \text{cm}^{-3}$), experimental/ideal
1.5 μm	1300	350	85/74	9.0/3.0
550 nm	400	100	80/74	16.4/8.1
280 nm	200	50	72/74	22.6/15.9

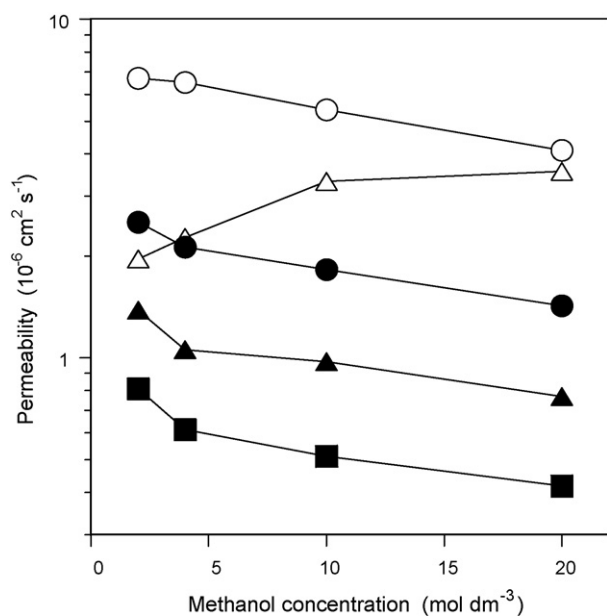


Fig. 3. Methanol permeability of (○) PAMPS, (△) Nafion[®], and composite membranes prepared by using (●) 1.5 μm , (▲) 550 nm, (■) 280 nm templates as a function of methanol concentration at 30 °C.

poly(arylene ether sulfone)s [12,13], and the detail mechanism has been discussed by Kreuer in terms of the microstructures and $\text{p}K_{\text{a}}$ of acidic functional groups [14]. By applying 3DOM matrix, the methanol permeability of PAMPS was successfully reduced. This suppression can be naturally understood because the size and distribution of hydrophilic channels responsible for methanol permeation strongly depend on the swelling state of polymer. However, the pore size dependence of methanol permeability was surprisingly observed despite the same physical and chemical state of PAMPS in the composite membranes as mentioned above. In order to discuss the effect of pore size more clearly, the methanol permeability was plotted to the connecting window size. The connecting windows should work as a bottleneck of mass transfer in the composite membrane. As shown in Fig. 4, a good correlation was obtained in each methanol concentration, where a drastic drop was observed at less than 100 nm window size. In addition to the size dependence, the methanol permeability depended on the methanol concentration. This behavior is due to the characteristics of PAMPS itself, as discussed above. From the results obtained here, a mechanism controlled by connecting window size and intrinsic properties of a filling electrolyte can be proposed for methanol transfer in the composite membrane. $0.42 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ was obtained as the lowest value for the composite membrane with 50 nm windows under feeding 20 mol dm^{-3} methanol solu-

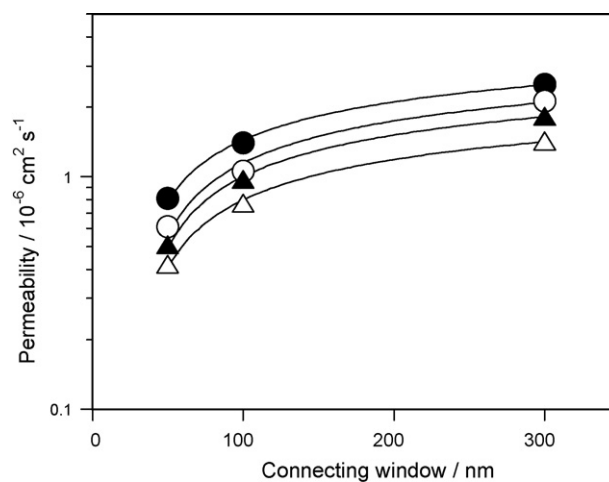


Fig. 4. Relationship between the connecting window size and methanol permeability of the composite membrane measured in (●) 2 mol dm^{-3} , (○) 4 mol dm^{-3} , (▲) 10 mol dm^{-3} , and (△) 20 mol dm^{-3} methanol solution at 30 °C.

tion at 30 °C, which was eighth part of $3.5 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$ in Nafion[®].

Fig. 5 shows the proton conductivity of composite membranes measured in 90% relative humidity. The dependence of proton conductivity on the matrix structure was observed,

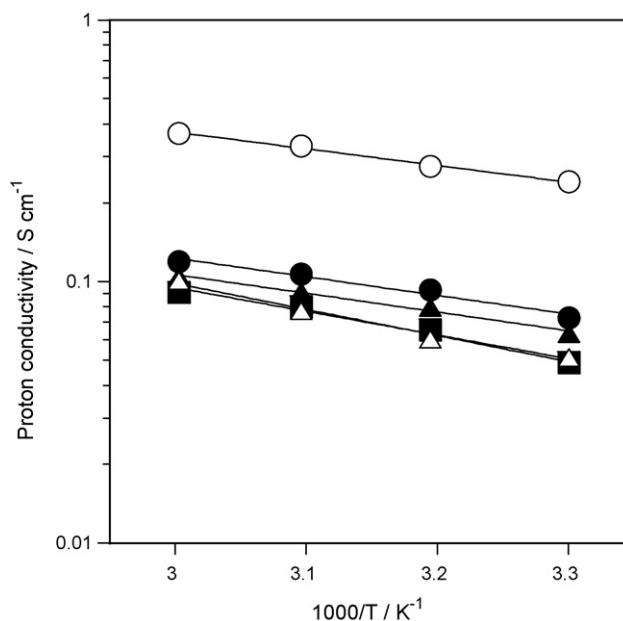


Fig. 5. Proton conductivity of (○) PAMPS, (△) Nafion[®], and composite membranes prepared by using (●) 1.5 μm , (▲) 550 nm, (■) 280 nm templates as a function of temperature. Measurement was conducted in 90% relative humidity.

Table 3
Selectivity (α) of membranes estimated in each methanol concentration at 30 °C

Membrane	α at 2 mol dm ⁻³ ($\times 10^4$ S cm ⁻³ s)	α at 4 mol dm ⁻³ ($\times 10^4$ S cm ⁻³ s)	α at 10 mol dm ⁻³ ($\times 10^4$ S cm ⁻³ s)	α at 20 mol dm ⁻³ ($\times 10^4$ S cm ⁻³ s)
Nafion [®]	2.5	2.2	1.5	1.4
PAMPS	3.6	3.7	4.4	5.9
Composite (1.5 μ m template)	2.9	3.4	4.0	5.0
Composite (550 nm template)	4.4	5.9	6.4	8.0
Composite (280 nm template)	6.1	8.0	9.6	12.0

however it was correlated with the porosity, but not with the pore size. The conductivity of a two-phase material is often explained by Archie's law [15–17]. The polyimide matrix can be considered as an insulator phase in the composite membrane. Thus, the effective conductivity ($\sigma_{\text{composite}}$) is simply denoted as $\sigma_{\text{composite}} = \sigma_{\text{PAMPS}} \times C \times \phi^m$, where σ_{PAMPS} is the conductivity of PAMPS and ϕ is the porosity of 3DOM matrix. C and m are medium dependent constants. Archie's plot between $\log(\sigma_{\text{composite}}/\sigma_{\text{PAMPS}})$ and $\log(\phi)$ for composite membrane is shown in Fig. 6. A good linear relationship, namely the evidence for the dependence of conductivity on porosity was obtained. The m estimated from the slope was 2.3. This value is called "cementation index" and concerns with the connectivity of PAMPS phase. The range from 1.5 to 2.5 applies to sedimentary rocks containing saline aqueous fluids in upper crustal basins [17].

For comparison of structural effects by 3DOM matrix, the selectivity (α) was estimated as a ratio between proton conductivity (σ) and methanol permeability (P_M) at 30 °C. As listed in Table 3, the selectivity was improved as decreasing pore size. According to an affinity of PAMPS to methanol, the selectivity also increased with increasing methanol concentration. These aspects well correspond to those observed in Fig. 4. The porosity of 3DOM matrix responsible for the proton conductivity were similar to each other, independently from the pore

size. Therefore, its effect was hardly observed. As a result, 1.2×10^5 S cm⁻³ s could be obtained as the highest selectivity, which was one order of magnitude greater than that of Nafion[®]. If an ideally perfect 3DOM structure were produced, the selectivity would follow only the methanol permeability. In short, the suppression of methanol crossover without losing proton conductivity can be realized by a decrease in the window size.

4. Conclusions

Pore size controlled (1.3 μ m–200 nm) 3DOM polyimide matrix was successfully fabricated by colloidal crystal templating method. Each matrix provided high morphological stability to PAMPS in the composite membrane, which was directly reflected in the swelling ratio. The methanol permeability decreased as decreasing pore size, and it was found that the connecting window with less than 100 nm diameter was favorable for the crossover suppression. On the other hand, the proton conductivity was governed by the porosity of 3DOM matrix. The porosity of 3DOM matrix was almost constant even if the pore size changed, so that the transfer selectivity of composite membrane between protons and methanol molecules mainly depended on the pore size. Consequently, the selectivity of 1.2×10^5 S cm⁻³ s, which was one order of magnitude greater than that of Nafion[®], was successfully attained.

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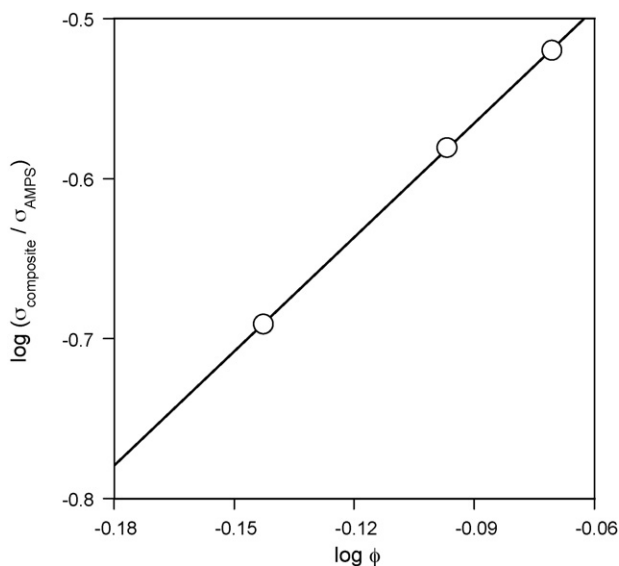


Fig. 6. Archie's plot for the composite membrane as a function of the porosity of 3DOM matrix. Both $\sigma_{\text{composite}}$ and σ_{PAMPS} were collected at 30 °C.

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