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Preparation of Composite Membrane between a Uniform Porous Silica Matrix and Injected Proton Conductive Gel Polymer

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A new proton-conducting membrane was prepared consisting of uniformly macroporous silica and a proton-conducting gel polymer electrolyte. Three-dimensionally uniformly ordered macroporous silica was synthesized by use of a colloidal template method with monodisperse polystyrene beads. A macroporous silica membrane with adequate mechanical strength and porosity was successfully obtained. A gel polymer, 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), was injected into all of the pores to prepare a proton-conducting membrane that is a composite of macroporous silica and the gel polymer. The prepared membrane exhibited high proton conductivity and low methanol permeation. A H_2-O_2 fuel cell was constructed in order to test the composite membrane. The electrochemical performance obtained for the fuel cell with the composite membrane was similar to that for a fuel cell with a Nafion 117 membrane. From this result, it can be concluded that the composite membrane consisting of ceramic and polymer can be applied to fuel cells working at low temperature.

Introduction

The polymer electrolyte membrane fuel cell (PEMFC) has been extensively investigated as a power source for electric vehicles and portable electronic devices because of its promising energy conversion efficiency, energy density, and power density.[1,2] In this fuel cell system, polymer electrolytes such as Nafion have been utilized in the membrane-electrode assembly, which is the most important part of the fuel cell. Nafion is a very good ion exchange membrane, having high proton conductivity, high chemical stability, and so on.[3,4] However, Nafion is a perfluorinated polymer, so it is very expensive.[2] In addition, the proton conductivity in Nafion depends on its water content.[5−7] Therefore, it cannot be used at higher temperatures, such as 120 °C. Moreover, Nafion expands or shrinks depending on the atmosphere, and also its mechanical strength changes with temperature and humidity.[8,9] Thus far, a number of different types of polymer electrolyte membranes have been developed with the use of different types of polymers. For example, polyimide polymer has been sulfonated to add proton conduction.[10,11] This is a very mechanically hard, chemically stable polymer. Of course, other hydrocarbon polymers have also been extensively investigated to develop stable, low-cost polymer electrolyte membranes.[12] Composite polymers that include carbon and silicon in the main chain of the polymer have been synthesized as a new category of proton-conducting polymers.[13] Most of the new polymer electrolyte membranes are soft. For large-size fuel cell applications, these kinds of membranes have been placed into the fuel cell stack with the use of thick separators. When designing micro-fuel cells, this soft nature may not be suitable. If hard materials, such as ceramics and metals, can be applied in micro-fuel cells, separators are not necessary. It is likely that thinner fuel cell units may be constructed by use of hard-type electrolyte membranes. In this study, a composite electrolyte membrane was prepared with a three-dimensionally uniform porous silica membrane and a proton-conducting gel polymer electrolyte. In this composite membrane, shape changes of the polymer electrolyte can be suppressed by the porous silica matrix. This membrane is self-standing, leading to easier construction of micro-fuel cells.

Various types of fuels have been utilized in fuel cells.[1] In the cases of polymer electrolyte fuel cells, hydrocarbons cannot be utilized directly because of their low-temperature operation. Thus, a reformer is usually needed.[14] This additional equipment decreases the energy density of the PEMFC. Therefore, hydrogen may be more suitable as a fuel

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for PEMFCs. However, gaseous fuels have storage problems. Metal hydrides and hydrogen cylinders have been used to store hydrogen gas compactly.[15] Methanol is also a promising fuel and is a liquid.[1,16] If methanol is used as a fuel for PEMFCs, high-energy densities are possible. Thus far, many researchers have studied the direct methanol fuel cell (DMFC). In the case of the DMFC, there are two problems. One is the low electrochemical activity of the Pt catalyst, which can be solved by using either a Pt−Ru alloy catalyst or a higher operation temperature.[17,18] As a portable power source, higher operation temperatures cannot be used, so the usage of Pt−Ru catalysts may be appropriate for micro-fuel cells. Another problem is methanol permeation through the ion exchange membrane. When Nafion is used as a polymer electrolyte membrane for the DMFC, methanol permeates through the membrane and reaches the cathode to react with oxygen.[19,20] This is a type of self-discharge reaction for the DMFC, leading to lowering of both the cell voltage and the fuel utilization. To develop the DMFC further, new electrolyte membranes must be synthesized. Methanol permeation is usually enhanced by an expansion of the polymer due to absorption of methanol by the polymer itself.[21,22] One of the possible solutions is to try to suppress the polymer expansion by methanol absorption. In general, hard, cross-linked polymers have been used in DMFCs.[12] On the other hand, composite polymer electrolyte membranes have also been investigated in order to lower the methanol permeability by means of the mechanical suppression of polymer expansion.[23] In the present study, the methanol permeability through a prepared composite membrane was also examined.

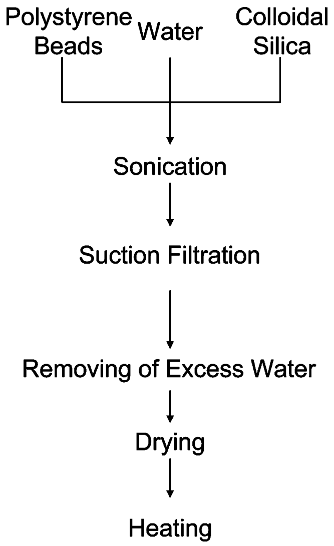

Figure 1. Schematic diagram of the preparation process for three-dimensionally ordered, uniformly macroporous silica membrane.

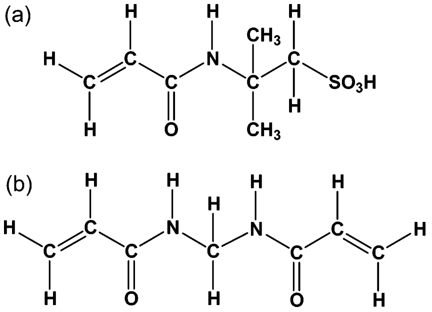

Figure 2. Schematic illustrations of monomers for the AMPS gel polymer electrolyte membrane used in this study: (a) 2-Acrylamido-2-methyl-1-propanesulfonic acid and (b) *N*,*N*′-methylenebisacrylamide.

Experimental Section

Figure 1 shows a schematic diagram for the preparation process for the composite electrolyte membrane, which consists of uniform macroporous silica and gel polymer electrolyte. An outline of the preparation process can be seen from this illustration. First, colloidal silica particles ($\phi = 70-100$ nm, Snowtex ZL, Nissan Chemical Co.) and monodisperse polystyrene beads ($\phi = 474$ nm, OptiBind, Seradyn Inc.) were mixed to prepare a stable suspension. The concentrations of the polystyrene beads and colloidal silica beads were 0.5−2.0 and 0.125−0.5 vol %, respectively. The ratio of polystyrene beads to colloidal silica beads was 4:1 by volume. This ratio was estimated from the volume of the close-packed polystyrene beads and the void volume associated with this layer. Specifically, the volume percentages of polystyrene beads and voids were 74% and 26%, respectively. This suspension was filtered on a nitrocellulose membrane filter with a pore size of 0.1 μm. The amount of filtered suspension needed in order to obtain a 150-μm thickness of macroporous silica layer was determined and the shape of the silica layer was regulated by a silicon rubber template on the membrane filter. The size and thickness of the porous silica membrane are able to be easily controlled by changing the silicon rubber template and the volume of suspension, respectively. After the filtration, the deposited composite layer, consisting of polystyrene beads and colloidal silica particles, was removed from the membrane filter. This membrane was placed on a flat ceramic plate and heated at 450 °C for 1 h and then 890 °C for 1 h at a heating rate of 2 °C min^{-1}. During this heat treatment process, the polystyrene beads were burned away, and the colloidal silica particles were sintered slightly. In these procedures, some of the membranes broke into several pieces. This is due to residual mechanical stresses in the polystyrene−silica composite membrane. Therefore, it is very important to dry the deposited composite membrane uniformly. A slow drying process was very effective in the preparation of intact porous silica membranes with no cracks. Further heat treatment at 890 °C for 1 h and then at 980 °C for 10 min at a heating rate of 20 °C min^{-1} was conducted to sinter the colloidal silica particles. A flat ceramic plate was put on the silica membrane in this heat treatment to keep the flatness of the silica membrane. The second sintering is necessary in order to maximize the mechanical strength of the porous silica membrane.

A proton-conducting polymer gel electrolyte was used in this study. The gel electrolyte was prepared by polymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and *N*,*N*′-methylenebisacrylamide (MBA). Ammonium persulfate (APS) was used as the initiator of polymerization. Figure 2 shows the chemical structures of these compounds. An aqueous solution consisting of AMPS, MBA, and APS with optimized concentrations of 4.82, 6.49

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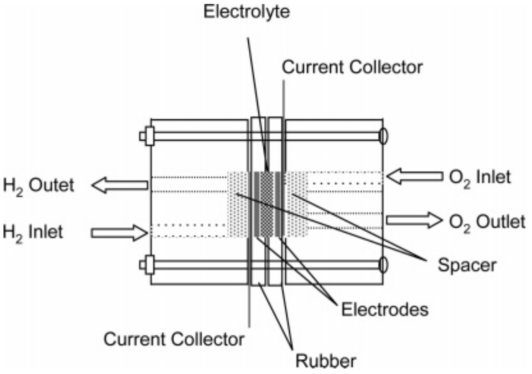

Figure 3. Schematic illustration of the in-house-constructed H_2-O_2 fuel cell.

$\times 10^{-2}$, and 4.38×10^{-2} mol kg^{-1}, respectively, was applied to prepare the AMPS gel electrolyte membrane. The equivalent weight in terms of sulfonic acid groups was 4.8 mmol g^{-1}. This aqueous solution was injected into the pores in the porous silica membrane and then heated at 60 °C for 1 h.

The conductivity of the prepared composite membrane was measured with an impedance analyzer (YHP 4192A) in the frequency range from 100 Hz to 1 MHz under controlled temperature and humidity conditions. From the Cole−Cole plot, the resistance of the composite membrane was estimated, and then the conductivity of the composite membrane was calculated using the apparent thickness and electrode area. Au electrodes were used for this measurement.

A catalyst layer for the hydrogen−oxygen fuel cell was prepared with the composite membrane. An ink consisting of platinized fine carbon powder, Nafion solution, glycerin, and water was prepared and painted on the carbon paper. After drying of the painted ink at 100 °C for 1 h, a hot press process was conducted to form the catalyst layer on the carbon paper. The ink consisted of 38 wt % Pt-carbon (0.15 g), glycerol (1.0 g), H_2O (0.75 g), and 5 wt % Nafion solution (1.0 g). The amount of Pt catalyst loaded on the carbon paper was 0.3 mg cm^{-2}. The prepared carbon paper with catalyst layer was attached to the composite electrolyte or AMPS gel polymer electrolyte to construct the MEA. The thicknesses of the composite and the AMPS gel polymer membranes were 150 and 500 μm, respectively. This means that the resistance of the composite membrane was comparable to that of the AMPS gel polymer, as shown below. Figure 3 shows the hydrogen−oxygen fuel cell, constructed in-house, which was used in this study. Both gases were supplied through porous plastic plates. The electrode area was 1.77 cm^2. Au mesh was used as the current collector. Fully humidified hydrogen and oxygen were flowed into the fuel cell. The cells were operated at 30 °C under 90% relative humidity. Flow rates for hydrogen and oxygen were 20 mL min^{-1}. The polarization measurements were conducted by use of a Solartron (SI 1287) under galvanostatic conditions at 30 °C.

Methanol permeation through the composite membrane was measured by means of an electrochemical method. In this case, a Pt−Ru catalyst layer was used for the cathode side. Nitrogen gas was flowed into the anode compartment, and 1.0 mol dm^{-3} methanol aqueous solution was placed into the cathode compartment. A voltage of 0.85 V was applied to this cell. When methanol goes through the composite membrane, current for methanol oxidation is observed. According to Faraday's law, the permeation rate of methanol was estimated.

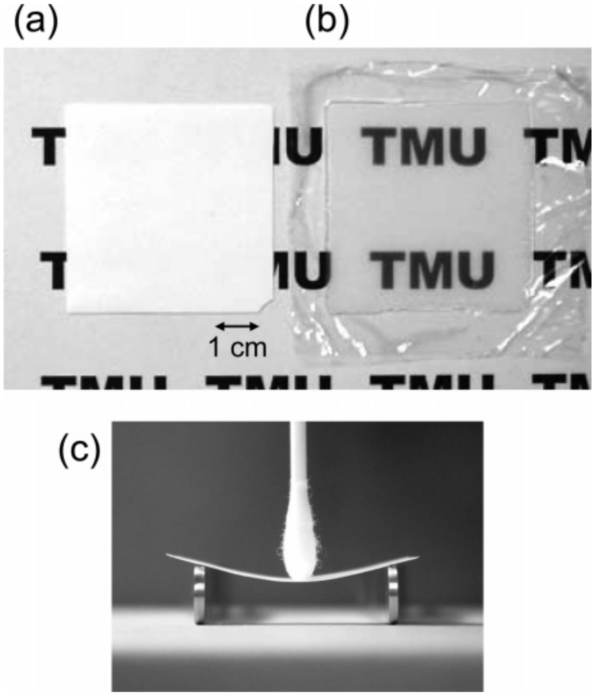

Figure 4. Photographs of (a, c) as-prepared three-dimensionally ordered uniform macroporous silica membrane and (b) composite silica membrane after filling with AMPS gel polymer.

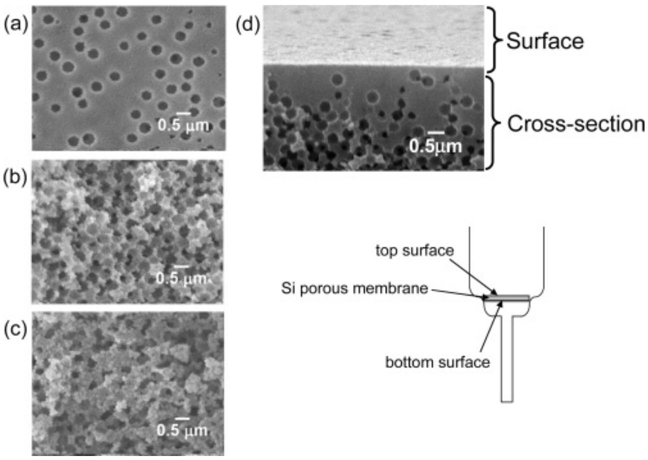

Figure 5. Scanning electron micrographs of an as-prepared macroporous silica membrane: (a) top surface, (b) cross section, (c) bottom surface, and (d) cross section near the top surface.

Results and Discussion

Figure 4a shows a photograph of the macroporous silica membrane, which was about 4 cm × 4 cm. If there are mechanical stresses remaining in the membrane, the membrane breaks into several small pieces in the course of the preparation. To avoid crack formation, the drying process was carefully performed. In particular, the removal of water from both sides of the membrane should be controlled. Draining excess water on the surface of the deposited composite layer with filter paper is an effective method, which provides uniform water distribution in the composite layer. This careful preparation process provided intact porous silica membranes with adequate mechanical strength as shown in Figure 4c. The as-prepared membrane was white, but after injection of gel polymer, it became transparent, as shown in Figure 4b. This change indicates that all of the pores in the composite membrane were completely filled with gel polymer.

Figures 5a−d show scanning electron micrographs of the macroporous silica membrane. One of the two surfaces was

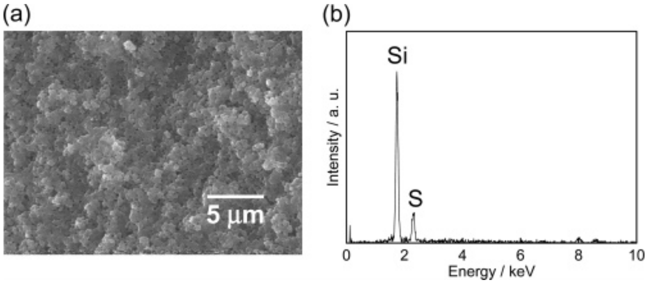

Figure 6. (a) Scanning electron micrograph of composite membrane consisting of three-dimensionally ordered uniform macroporous silica membrane and AMPS gel polymer and (b) EDX spectrum for this composite membrane.

very porous, but the other was not porous. From the cross-sectional view of the macroporous silica membrane, the tightly closed layer was 2 μm in thickness. Except for this surface layer, other parts were porous. The pore size was about 400 nm and was very uniform, which well reflects the fact that polystyrene beads were used as the template. The tightly closed layer produced a high resistance for proton conduction through the composite membrane, due to the low proton conductivity of silica. Therefore, this layer should be removed before the injection of the gel polymer. In this study, mechanical polishing with emery paper or diamond paste was utilized to remove the tightly closed surface layer. However, it may be possible to omit the polishing process by optimization of the suspension and filtration process. The composite membranes shown in Figure 4 were for a membrane without the tightly closed surface layer.

Figure 6a shows a scanning electron micrograph (cross-sectional view) of the composite membrane consisting of macroporous silica membrane and AMPS gel polymer. In this micrograph, pores were not observed, and only gel polymer that had undergone slight shrinkage due to the vacuum environment was observed. From a comparison of this micrograph with that in Figures 5c or 5d, it can be concluded that the pores of the porous silica membrane were perfectly occupied with gel polymer. Figure 6b shows an energy-dispersive X-ray (EDX) spectrum for the composite membrane consisting of porous silica and AMPS gel. A strong peak corresponding to silicon was clearly observed in this spectrum. A peak attributed to sulfur was observed only for the composite membrane. The distribution of sulfur was uniform, indicating that all of the pores were uniformly filled with gel polymer.

The apparent density of the porous silica membrane was measured with a pycnometer. The estimated porosity was greater than approximately 70%. The ideal (calculated) value of the porosity was 74%, so the value obtained was slightly smaller than the ideal value. This suggests that some of the pores were not ideally connected with each other. Three-dimensionally ordered macroporous silica has been studied by a number of researchers, and it is known that all of the pores are interconnected by six small holes. In the present case, the prepared porous silica membrane was very porous, but some of the pores may be isolated. The number of such isolated pores should be diminished.

Figure 7 shows the proton conductivity of the AMPS gel membrane and the composite membrane. In the case of the conductivity measurement for the composite membrane, thin gel polymer membranes were attached to both sides of it, to eliminate the effect of a contact problem between the Au electrode and the composite membrane. This is caused by the hard nature of the composite membrane. The proton conductivity of the attached thin layers was much smaller than that of the composite membrane, so the proton conductivity of the composite membrane could be estimated simply from the overall value obtained. The proton conductivity of the AMPS gel membrane depended only slightly on the monomer concentration; however, that of the composite membrane was strongly affected by the monomer concentration of the AMPS gel electrolyte. With a monomer concentration of 4.8 mol kg^{-1}, the proton conductivity of the composite membrane had a peak value of 0.04 S cm^{-1} at 30 °C. This behavior is likely to be induced by a matrix effect of the porous silica membrane. The structure of ionomeric membranes has been extensively studied by many researchers, and it is well-known that protons transfer between ionic clusters consisting of polar groups such as $-SO_3H$.[24-26] The number of these ionic clusters increases with an increase of water content and the number of $-SO_3H$ groups in the membrane. For example, as is widely known, the proton conductivity of ionomeric membranes is sensitive to humidity. In fact, as shown in Figure 7a, a good correlation was observed between the proton conductivity of the AMPS gel membrane and its monomer concentration, i.e., water content in the AMPS gel. The proton transfer in the composite membrane would also tend to obey such a rule. However, there is a significant difference in the proton-conducting pathways, comparing the composite membrane and the AMPS gel membrane, because protons in the composite membrane must be transferred through the very small connecting windows between pores. Therefore, the proton conductivity of the composite membrane may exhibit behavior different from that of the AMPS gel membrane.

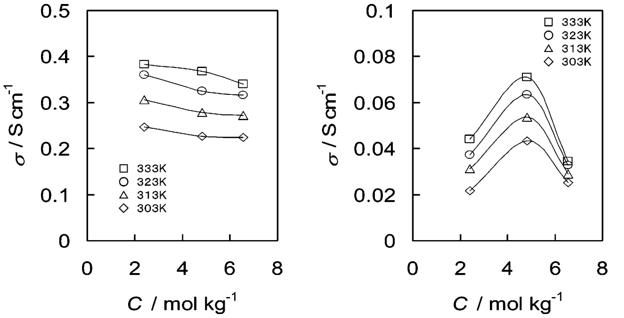

Figure 7. Dependence of the proton conductivity on the concentration of AMPS monomer at various temperatures and 90% humidity: (a) AMPS gel polymer electrolyte membrane and (b) composite membrane composed of macroporous silica and AMPS gel polymer. Macroprous silica was prepared from 474-nm polystyrene beads and 70−100 nm silica beads.

A schematic diagram of proton transfer in the composite membrane is shown in Figure 8. With a small monomer concentration, some parts of the gel network may be isolated

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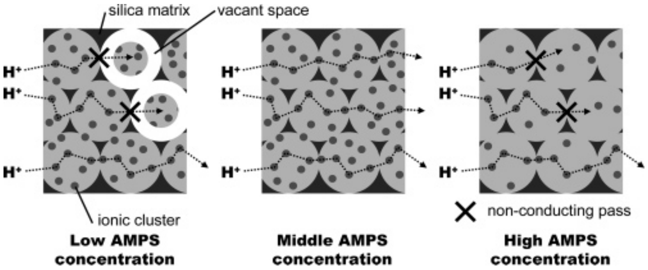

Figure 8. Schematic illustration of proton transfer in the composite membrane.

in the silica matrix, as shown in Figure 8a, because an AMPS gel electrolyte with low monomer concentration easily loses its water and shrinks, depending on the atmosphere. The isolated pockets of gel cannot take part in proton transfer, which results in a severe loss of proton-conducting paths. The small proton conductivity of the composite membrane observed at the monomer concentration of 2.4 mol kg^{-1} would be caused by such gel isolation. On the other hand, low conductivity was also observed at high monomer concentration. As mentioned above, the number of ionic clusters in the AMPS gel changes according to the monomer concentration. Therefore, the value obtained would result mainly from the fact that these clusters become scattered at high monomer concentration. However, this drop in the proton conductivity of the composite membrane was drastic compared to that of the AMPS gel membrane. This result implies that proton transfer in the composite membrane requires more narrowly defined conditions for the gel electrolyte than those for the AMPS gel membrane due to the connective windows between pores, as shown in Figure 8c. If so, the threshold of proton transfer in the gel electrolyte may be evaluated from the dependence of the proton conductivity in the composite membrane on the monomer concentration. Such information combined with other measurements could be very helpful in discussing the physical states of gel electrolytes, especially concerning the number of ionic clusters, their size, and their dispersibility.

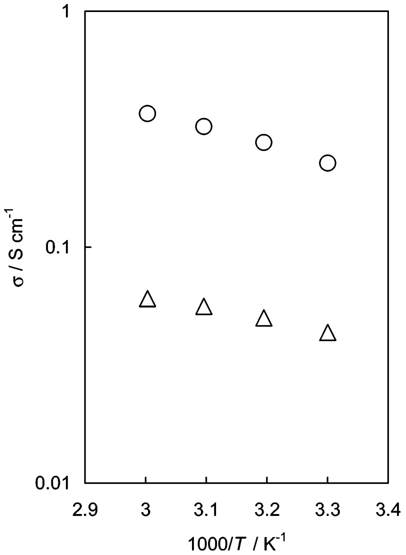

Figure 9. Arrhenius plots for proton conductivity of AMPS gel polymer (○) and composite membrane composed of three-dimensionally ordered uniform macroporous silica membrane and AMPS gel polymer (△).

Figure 9 shows Arrhenius plots for the conductivity of the composite membrane and of the AMPS gel polymer membrane with a monomer concentration of 4.8 mol kg^{-1}. The conductivity of the composite membrane was 30% of that of the AMPS gel polymer electrolyte. This value was smaller than that expected from the porosity of the porous silica matrix (70%). This may be due to an imperfect porous structure of the porous silica membrane. The proton conductivity of the composite membrane at 60 °C under 90% humidity was estimated to be 6.1×10^{-2} S cm^{-1}. On the other hand, that of the AMPS gel electrolyte was 3.6×10^{-1} S cm^{-1}. The proton conductivity of Nafion 117 was reported to be 1.5×10^{-1} S cm^{-1}.[27] The composite membrane exhibited a smaller ionic conductivity than that of Nafion 117. However, the AMPS gel polymer electrolyte had a higher ionic conductivity than Nafion 117. It is likely that a more highly uniform porous structure of the silica membrane could provide a higher proton conductivity of the composite membrane. The activation energy for the proton conduction in the composite membrane was estimated to be 0.17 eV, which was larger than that observed for the AMPS gel electrolyte. Proton conduction in acid solutions and compounds containing a quasi-liquid state of protonic species has been explained by the Grotthus mechanism. In these cases, the activation energy should range from 0.1 to 0.4 eV.[28] The activation energies for both the composite and AMPS membranes were well within this range, so the proton conduction in the composite membrane can still be explained via the Grotthus mechanism. The difference between the two membranes may be due to the physical state of the water molecules in the AMPS gel polymer and in the AMPS gel polymer constrained by the porous silica matrix. The former state may provide highly free motion for the water molecules.

With use of the prepared composite membrane, hydrogen−oxygen fuel cells were constructed to examine the performance of the composite membrane. Curves (a) and (b) in Figure 10 are the current−voltage curves for two fuel cells with different types of catalyst layers. One was prepared by use of a standard hot pressing of the catalyst layer on the composite membrane, and the other was prepared by a hot pressing of the catalyst layer on carbon paper. To compare the current−voltage curves with membrane electrode assemblies (MEAs) prepared with AMPS gel electrolyte membrane and Nafion 117, additional curves are shown in (c) and (d), respectively, of Figure 10. All fuel cells were operated at 30 °C, and both hydrogen and oxygen gases were fully humidified, as stated in the Experimental Section. The fuel cell with membrane−electrode assembly prepared by hot pressing of the catalyst layer on the composite membrane exhibited a very low electrochemical performance. This is due to a contact problem between the catalyst layer and the composite membrane. The surface of the composite membrane was rough compared with the polymer electrolyte membrane, due to the hard silica matrix. The contact between the catalyst layer and the AMPS gel polymer or silica was not good, so most of the catalyst was not operational. In

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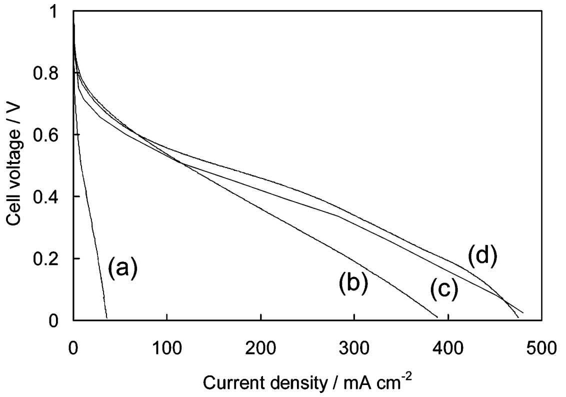

Figure 10. Current−voltage curves for fuel cells with (a) and (b) composite membrane composed of three-dimensionally ordered uniform macroporous silica membrane and AMPS gel polymer; (c) AMPS gel polymer; and (d) Nafion 117, under the following operating conditions: humidity, 90%; flow rate of fully humidified H_2 and O_2, 20 mL min^{-1}; and temperature, 30 °C. For (a) and (d), the fuel cell with MEA was prepared by hot pressing the catalyst layer on the composite membrane, and for (b) and (c), the fuel cell with MEA was prepared by hot pressing the catalyst layer on carbon paper.

Table 1. Summary of Thicknesses, Methanol Oxidation Current Densities, and Methanol Permeabilities of Membranes

	thickness (cm)	current density (mA cm^{-2})	permeability (mol cm^{-1} s^{-1})
Nafion 117		42.0	1.67×10^{-9}
composite membrane	0.020	5.48	1.9×10^{-10}
AMPS gel membrane	0.12	5.11	1.1×10^{-9}

other words, the hot press technique is not suitable for the preparation of membrane−electrode assemblies involving the composite membrane. On the other hand, the fuel cell prepared by hot pressing the catalyst layer on carbon paper exhibited performance comparable with that for the fuel cell with the AMPS gel polymer electrolyte membrane, indicating that the attachment of the catalyst layer was very good. This difference in the two catalyst layers is due to the hardness of the porous silica matrix and the rough surface nature of the composite membrane. Thus, in the future, the interface between the composite membrane and the catalyst layer should be controlled by use of a new MEA preparation process. In our previous paper, we reported a new fabrication method of MEA onto Nafion 117 membrane by using the electrophoretic deposition (EPD) process.[29] This process has been applied to a formation of various kinds of materials. In particular, various ceramics have been formed by this process to develop various ceramics devices, such as filters, solid oxides electrolyte layers, and dielectric layers.[30,31] It is possible to form well-attached layers by the EPD regardless of the hardness of the substrate. Therefore, the EPD process may be one of the appreciated methods to fabricate the catalyst layer on the composite membrane.

Table 1 shows a summary of methanol permeation through three kinds of membranes. The methanol permeation of the gel electrolyte was smaller than that of the Nafion 117 membrane. This may be due to the cross-linked structure of the gel polymer electrolyte used in this study. The methanol permeation for the composite membrane was one-fifth of that for the gel electrolyte. This is due to the suppression of expansion of the gel polymer injected into the porous silica membrane. To compare the composite membrane with the Nafion 117 membrane, the inverse of the methanol permeability was plotted versus the proton conductivity, as shown in Figure 11. This figure shows that the methanol permeability for the composite electrolyte is half of that for the Nafion 117 membrane, when the proton conductivities of the two membranes are the same. This means that the composite membrane has an advantage; however, this should have been greater. In the future, the proton conductivity of the composite membrane should be improved through changes in the type of injected polymer or modifications of the macroporous silica structure.

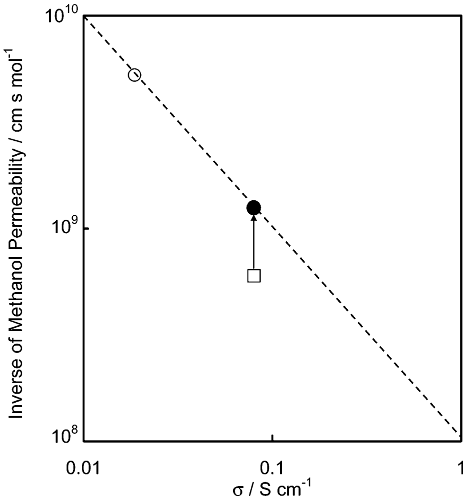

Figure 11. Relationship between proton conductivity and the inverse of methanol permeability for the composite membrane composed of three-dimensionally ordered uniform macroporous silica membrane and AMPS gel polymer (○); Nafion 117 membrane (□); and the inverse of the methanol permeability of the composite membrane when it has the same proton conductivity as that for Nafion 117 (●).

When the gel polymer electrolyte was immersed in 1 mol dm^{-3} methanol solution, its thickness increased greatly. On the other hand, the composite electrolyte membrane did not change dimensions after immersion into methanol solution. This means that the expansion of the gel polymer is completely suppressed by the porous silica matrix. There are various kinds of porous silica membranes. However, for most of these, the membrane structure breaks as a result of expansion of the polymer injected into the pores. Our porous silica membrane is similar to three-dimensionally ordered macroporous silica. The mechanical stresses due to polymer expansion are generated uniformly inside the porous silica membrane. On the other hand, ordinary porous silica matrixes are somewhat nonuniform in structure, so the mechanical stresses are also nonuniform, which can lead to crack formation. The ideally three-dimensionally ordered macroporous membrane is the most suitable for the preparation of composite membranes composed of porous silica and a polymer electrolyte.

Conclusions

A proton-conducting composite membrane composed of macroporous silica and gel polymer was successfully pre-

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pared in this study. The composite membrane exhibited relatively high proton conductivity and low methanol permeation. A hydrogen−oxygen fuel cell was constructed with the composite membrane in order to confirm the potential of the composite membrane for fuel cell application. The electrochemical performance obtained was comparable with that of a fuel cell incorporating a Nafion 117 membrane. This result indicates that the composite membrane can be applied to fuel cells as a rigid proton-conducting membrane. In addition, its conductivity can most likely be improved by appropriate selection of the proton-conducting polymer injected into the macroporous silica, e.g., sulfonated poly(ether ether sulfone).

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