PREPARATION OF COMPOSITE MEMBRANE WITH THREE-DIMENSIONALLY ORDERED POLYIMIDE MATRIX AND PROTON CONDUCTIVE GEL POLYMER

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ABSTRACT

A new proton conductive membrane was prepared by using three-dimensionally ordered macroporous polyimide and proton conductive gel polymer electrolyte. The polyimide matrix was synthesized by the colloidal template method with mono-dispersed silica beads. The macroporous polyimide membrane with an adequate mechanical strength, flexibility, and porosity was successfully obtained. A gel polymer of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) was injected into pores to prepare a proton conductive composite membrane consisting of macroporous polyimide and gel polymer. The composite membrane exhibited high proton conductivity of $1.2 \times 10^{-1}$ $\text{S cm}^{-1}$ at 60°C under 90% relative humidity, whose value was comparable with that of Nafion\textsuperscript{®} 117 membrane. This result indicates that the composite membrane with polyimide matrix can be applied to fuel cells as a new type of proton conductive membrane.

INTRODUCTION

Direct methanol fuel cells (DMFCs) using polymer electrolyte membranes have attracted considerable attention as promising power sources for mobile and stationary applications. Perfluorosulfonated polymer membranes (e.g., Nafion\textsuperscript{®}) have been studied due to high proton conductivity, high chemical stability, and so on. However, Nafion\textsuperscript{®} is one of perfluorinated polymers, so that it is very expensive.\textsuperscript{[1]} In addition, they are easily expanded by an immersion into water or methanol, which should result in methanol permeation through the membrane.\textsuperscript{[2]} Methanol cross-over to the oxygen cathode leads to lowering of cell voltage and fuel utilization. Therefore, alternative polymer materials have been investigated by many research groups. Among them, polyimide type polymers have been especially studied and expected as new proton conductive electrolyte membrane because of their good mechanical and chemical properties.\textsuperscript{[3-4]} On the other hand, composite membranes have attracted much attention in a sense of controllable chemical and physical properties produced by combining different properties of
components. Some new classes of composite membranes such as pore-filling structures have been proposed.\textsuperscript{[5]} Recently, we developed the composite membrane consisting of gel polymer electrolyte and three-dimensionally ordered silica matrix, which exhibited both high proton conduction and a low methanol cross-over due to the suppression of polymer expansion by the silica matrix.\textsuperscript{[6]} In this case, a colloidal template method was employed to prepare the three-dimensionally ordered silica matrix. As a template, a uniformly ordered array of mono-dispersed polystyrene beads was used.

In this study, we fabricated ordered macroporous membrane of polyimide by using mono-dispersed silica particles as a template, and evaluated it as a new matrix of composite electrolyte for fuel cell.

**EXPERIMENTAL**

Silica membrane consisting of uniformly ordered silica particles was used as template to prepare macroporous polyimide membrane. A suspension containing mono-dispersed silica particles was accumulated on a polycarbonate membrane filter with pore size of 0.1 μm by filtration under reduced pressure of $5 \times 10^{3}$ Pa. After the filtration, the deposited silica particles were carefully dried under air atmosphere at room temperature for 48 hours. This membrane was removed from the membrane filter and sintered at 1000 °C for 10 min at a heating rate 5 °C min$^{-1}$. A dimethyldioctamidilactone solution containing 8 wt% polyamic acid (JFE Chemical Co.) was injected in vacant space of the ordered silica particles and thermally cured at 200 °C for 30 min, and then at 300 °C for 1 hour. By this thermal treatment, polyamic acid was converted to polyimide as shown in Scheme 1. Then, the silica template was removed by etching with an aqueous HF solution. The surface and cross-sectional morphologies of the obtained polyimide membrane were observed with scanning electron microscope (SEM).

A composite electrode was prepared by an injection of proton conductive gel polymer in three-dimensionally ordered macroporous polyimide membrane. As the gel polymer electrolyte, 2-acrylamido-2-methylpropane-1-sulfonic acid (AMPS) polymer was used in this study. This gel electrolyte exhibited a proton conductivity of 0.37 S cm$^{-1}$ at 60 °C under 90 % humidity, which is higher than that of Nafion$^{\text{®117}}$ membrane (0.15 S cm$^{-1}$ at 60 °C).\textsuperscript{[7]} In order to prepare the cross linked gel polymer, $\text{N, N'}$-methylenebisacrylamide was used as bridging agent. Ammonium persulfate was used as initiator of polymerization. After the injection of these agents, they were heated at 60 °C for 1 hour. A polymerization easily took place to form the composite membrane between three-dimensionally ordered macroporous polyimide membrane and proton conductive gel polymer.

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

The macroporous polyimide membrane was successfully obtained with an extraordinary large size of about 3 cm x 3 cm and a thickness of 200 μm, as shown in Figure 1. Its size and thickness were able to be easily controlled by the silica template. The obtained membrane had high mechanical and chemical stabilities, which were ideal for the matrix of composite membrane. The silica matrix has been previously reported by our group, had also similar properties, however it was fragile. The polyimide membrane had a high flexibility, so that it was easy to be handled.

Figures 2 (a) shows a typical scanning electron microscopic (SEM) image of the surface of macroporous polyimide membrane prepared by using a template membrane of 550 nm silica particles. A continuous ordered structure of polyimide membrane having uniform pore size, which was an inversed structure of silica template, was obtained. A slight difference between pore size and used silica particles is due to shrinkage in the course of SEM observation. The smaller pores observed in holes, were connective windows between large macropores. A presence of these connecting windows means a formation of highly ordered pores in a hexagonal array. In fact, the ordered structure of polyimide membrane was formed three-dimensionally, as shown in Figure 2 (b).

The composite membrane was prepared by an injection of AMPS gel polymer into pores of polyimide matrix. Figure 3 shows the SEM image of the cross-sectional view of the composite membrane. In this SEM image, pores were not observed and only shrinking gel polymer was observed. From a comparison of this image with that in Figure 2 (a) or (b), it can be said that pores of the porous polyimide membrane are perfectly occupied with gel polymer. The AMPS gel injected into the polyimide matrix did not exhibit an expansion by water and methanol, though AMPS gel polymer was easily expanded by swelling of membrane with water or methanol which leads to a low mechanical strength. This behavior is due to a suppression of expansion for gel polymer injected into porous polyimide membrane.

Figure 4 shows the Arrhenius plots for proton conductivities of the composite membrane and the AMPS gel polymer membrane with the monomer concentration of 4.8 mol kg⁻¹. With an increase in temperature, the proton conductivity of composite membrane increased up to 1.2 x 10⁻¹ S cm⁻¹ at 60 °C under 90 % relative humidity. This value was comparable with that of Nafion®117 membrane, which reported to be 1.5 x 10⁻¹ S cm⁻¹. On the other hand, that of the AMPS gel electrolyte was 3.7 x 10⁻¹ S cm⁻¹. Therefore, the conductivity of the composite membrane was smaller than that expected from porosity of the porous polyimide matrix (70 %), namely the obtained value was only 30 % of the AMPS gel polymer electrolyte. 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 -SO₃H. The proton transfer in the composite membrane would also obey such a manner. However, there is a significant difference between proton conductive passes in the composite membrane and that in AMPS gel membrane, because protons in the composite membrane must be transferred through the connective window between pores. The low proton conductivity of the composite membrane would be caused by some of isolated pores without the connective windows. Probably, more uniform porous structure of polyimide membrane provides a higher proton conductivity of the composite membrane.
CONCLUSION

We demonstrated the possibility of colloidal template method to fabricate the macroporous polyimide membrane. The extraordinary large size membrane was successfully fabricated and three-dimensionally ordered macroporous structure of polyimide was obtained. The proton conductive composite membrane consisting of macroporous polyimide and AMPS gel polymer was prepared and it exhibited relatively high proton conductivity of \(1.2 \times 10^{-1}\) S cm\(^{-1}\) at 60 °C under 90 % relative humidity. The obtained value was comparable with that of Nafion\(^{®}\)117 membrane. This result indicates that the composite membrane using polyimide matrix can be applied to fuel cells as a new type of proton conductive membrane. In addition, if sulfonated polyimide is used to prepare the matrix of composite membrane, it will be possible to improve the proton conductivity of composite membrane. Further optimizations of materials for matrix and electrolyte, and preparing conditions are now underway.

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Scheme 1. Formation of polyimide through condensation reaction.

Figure 1. A photograph of three-dimensionally ordered macroporous polyimide membrane prepared by using 550 nm silica particles as a template.
Figure 2. Scanning electron micrographs of the macroporous polyimide membrane formed by using 550 nm silica template: (a) surface view and (b) cross-sectional view. Scale bars = 1 µm.
Figure 3. Scanning electron micrographs of the composite membrane consisting of macroporous polyimide matrix and AMPS gel polymer. Scale bars = 1 μm.

Figure 4. Arrhenius plots for proton conductivities of •: AMPS gel polymer and ■: composite membrane consisting of macroporous polyimide matrix and AMPS gel polymer.