

Preparation of Composite Membrane with Three-Dimensionally Ordered Polyimide Matrix and Proton Conductive Gel Polymer

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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[®]) have been studied due to high proton conductivity, high chemical stability, and so on. However, they are easily expanded by an immersion into water or methanol, which should result in methanol permeation through the membrane.^[1] 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.^[2] On the other hand, a mechanical suppression of polymer expansion is studied as another approach. Some new classes of composite membranes such as pore-filling structure have been proposed.^[3] Recently, we developed the composite membrane consisting of gel 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. In this study, ordered macroporous membrane of polyimide, which might work as proton conductor by itself, was fabricated and evaluated as a matrix of composite electrolyte for fuel cell.

Experimental

Ordered silica membrane was used as template to prepare macroporous polyimide membrane. A suspension containing mono-dispersed silica particles was arranged on a polycarbonate membrane filter with pore size of 0.1 μm by filtration under reduced pressure of 5×10^3 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 $^{\circ}\text{C}$ for 10 min at a heating rate 5 $^{\circ}\text{C min}^{-1}$. A dimethylacetamide solution containing 8 wt% polyamic acid (JFE Chemical Co.) was injected in vacant space of the ordered silica particles and thermally cured at 300 $^{\circ}\text{C}$. Then, the silica template was removed by etching with an aqueous HF solution. The surface and cross-sectional morphologies were observed with scanning electron microscope (SEM).

A composite membrane electrode was prepared by an injection of proton conductive gel polymer into porous polyimide membrane. As the gel polymer electrolyte, 2-acrylamido-2-methylpropane-1-sulfonic acid (AMPS) polymer was used. A conductivity of the prepared composite membrane was measured with an impedance analyzer in frequency range from 100 Hz to 1 MHz.

Result and Discussion

Figure 1 shows typical SEM images of polyimide membrane prepared by using template 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 (Figure 1a). A slight difference between pore size and used silica particles would be due to shrinkage in the course of SEM observation. As shown in Figure 1b, the ordered structure of polyimide membrane was formed three-dimensionally. Figure 2 shows the temperature dependence of proton conductivity of composite membrane between three-dimensionally ordered porous polyimide membrane and AMPS gel polymer. With an increase in temperature, the proton conductivity of composite membrane increased to 0.036 S/cm at 60 $^{\circ}\text{C}$ and 90 % relative humidity. Further optimizations of preparing conditions are now underway. The electrochemical performances of fuel cells with this membrane will be also reported and discussed.

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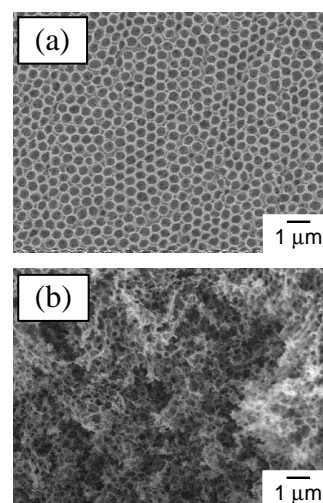


Figure 1. SEM micrographs of polyimide membrane formed by using templates of 550 nm silica particles: (a) typical surface and (b) cross section. Scale bars = 1 μm .

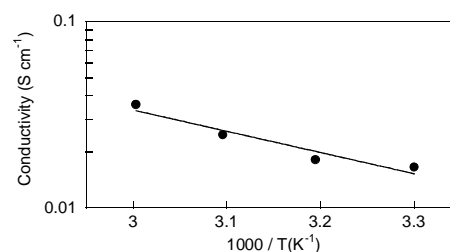


Figure 2. Proton conductivity of composite membrane between three-dimensionally ordered porous polyimide membrane and AMPS gel polymer.