

Study on Composite Membrane of Three Dimensionally Ordered Macroporous Ceramic and H⁺ Conductive Polymer for Direct Methanol Fuel Cell

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In this study, an inorganic-organic composite membrane consisting of porous silica matrix and polymer electrolyte was successfully prepared. The porous silica matrix was prepared from a composite membrane between three-dimensionally ordered polystyrene beads and colloidal silica by filtration followed by a heat treatment. A polymer electrolyte was prepared inside pores of the membrane to form a composite membrane with a high H⁺ conductivity.

Direct methanol fuel cell (DMFC) has been developed as power sources of electric vehicles. In order to reduce poisoning of Pt catalyst surface, DMFC is operated at high temperature, such as 120 ~ 150 °C. However, most of polymer electrolytes lose mechanical strength at such a high temperature. Moreover, methanol goes through expanded polymer electrolyte from anode to cathode. Cross over of methanol causes voltage drop and low fuel utilization. Therefore, a new polymer electrolyte membrane with low methanol cross-over is needed to realize DMFC. In this study inorganic-organic composite membrane was prepared to reduce methanol cross over. Inorganic-organic composite electrolyte consists of inorganic porous matrix and polymer electrolyte. Inorganic porous matrix can prevent expansion of polymer electrolyte through absorption of methanol. In order to reduce a concentration of mechanical stress, homogenous open pores are desired to improve sufficient percolation of pores. In this study three-dimensionally ordered macroporous ceramic membrane was prepared for this purpose.

Monodispersed polystyrene beads ($\phi=474$ nm) and colloidal silica ($\phi=70\sim 100$ nm) was mixed and diluted by pure water. The mixed suspension was filtrated by membrane filter under pressure difference. A deposit was dried in atmosphere to form a composite membrane consisting of colloidal silica and polystyrene beads. The composite membrane was heated at 450°C for 1 hour to burn out polystyrene beads. Then it was heated at 900°C for 1 hour to sinter colloidal silica. A polymer electrolyte was prepared by polymerization of 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and *N,N'*-methylenebisacrylamide (MBA) monomers. These monomers and ammonium peroxydisulfate were dissolved in water. The obtained silica membrane was immersed in the solution under vacuum. A polymerization of these monomers was conducted at 60°C. Impedance of this composite membrane and an AMPS film were measured at various temperatures under relative humidity of 80 %.

In this study silica membrane with 4 cm diameter and 100 μm thickness, as shown in Fig. 1 was prepared. The form of this membrane was not changed by heating process. A mechanical strength of this membrane was increased after heating at 900°C. The membrane was analyzed by X-ray diffraction. The membrane exhibited an amorphous nature. The membrane was observed by a scanning electron microscopy (SEM). From the SEM photographs it can be seen that polystyrene beads were

ordered and a free space of the polystyrene beads was completely filled by colloidal silica before heat treatment. After heat treatment at 450°C, polystyrene was removed and three-dimensionally ordered macroporous ceramic matrix was formed. After heat treatment at 900°C, colloidal silica was sintered. There were three-dimensionally-ordered macropores on the bottom surface and cross-section. On the other hand, there were few pores on the top surface of the membrane, as shown in Fig. 2. This membrane mostly composed of silica with three-dimensionally ordered pores, however, a thin layer with few pores existed on one side of this membrane. This surface layer was removed by polishing. Fig. 2 show scanning electron micrographs of before and after the polishing of membrane surface.

When silica membrane was immersed in the monomer solution, the membrane became transparent. After polymerization of monomers, it was still transparent. This composite membrane was analyzed by an energy dispersed X-ray (EDX) analysis. The EDX analysis showed presence of sulfur and silicon. These results show that inorganic-organic composite membrane is successfully prepared through above process. The conductivity of the composite membrane exhibited 4.0×10^{-2} S cm^{-1} at 60°C. On the other hand, the AMPS electrolyte film exhibited 5.0×10^{-2} S cm^{-1} at 60°C. A relatively high conductivity of composite membrane may be due to an enhancement of proton conduction by silica matrix.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research on the priority area of DMFC (Grant No. 13134204) from The Ministry of Education, Science, Sports and Culture, Japan.



Fig. 1 Photograph of silica membrane prepared from polystyrene beads and colloidal silica after heating at 900°C 1 h.

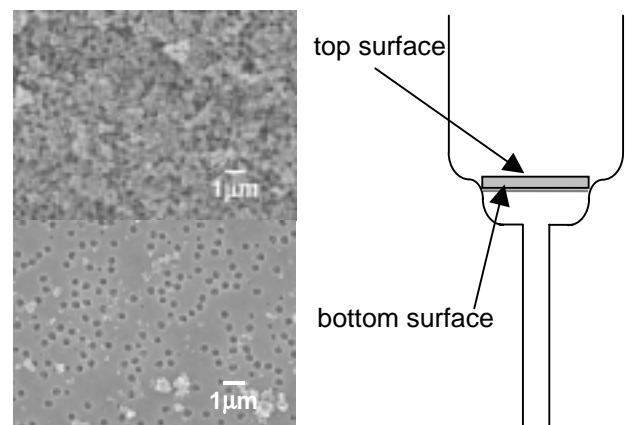


Fig. 2 Scanning electron micrographs of top surface of membrane before and after polishing.