

# Properties of composite proton-conducting membranes prepared from three-dimensionally ordered macroporous polyimide matrix and polyelectrolyte

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A new proton-conducting composite membrane has been prepared by use of a three-dimensionally ordered macroporous matrix of polyimide and a proton-conducting gel polymer; the resulting composite membrane exhibited very high conductivity of  $1.7 \times 10^{-1} \text{ S cm}^{-1}$  at 60 °C under 90% relative humidity.

Polymer electrolyte fuel cells (PEFCs) have received considerable attention as alternative power sources in various fields. In particular, direct methanol fuel cell (DMFC) which can feed methanol directly to an anode without a reformer, has many advantages for portable applications.<sup>1</sup> Perfluorosulfonic acid membranes, such as Nafion<sup>®</sup> membrane, have been studied as the polymer electrolytes in PEFCs due to their high proton conductivity and high chemical stability. However, they are easily swollen by methanol absorption, which causes the methanol permeation through the membrane from the anode to the oxygen cathode.<sup>2</sup> This phenomenon, so called “methanol crossover”, lowers the cell voltage and fuel utilization. In addition, there are some other drawbacks such as high environmental load and cost due to the complicated production process. This situation triggered research to develop alternative electrolyte membranes. Poly (ether ether ketone)s, polyphenylenes, polybenzimidazoles, and some other hydrocarbon polymers based on arylene main chain have been synthesized and tried in fuel cells.<sup>3</sup> Composite membranes consisting of these and inorganic materials have also been studied because of the controllable chemical and physical properties produced by combining different properties of components.<sup>4</sup> For example, the addition of inorganic fillers such as hygroscopic metal oxides and zirconium phosphates into Nafion<sup>®</sup> membranes has been reported as an effective way to achieve low humidity and high temperature operation of fuel cells.<sup>5</sup> “Pore-filling” is another concept to prepare composite membranes. This kind of composite membrane is prepared from a porous substrate and a filling material that fills the pores of the substrate and has been widely developed for liquid and gas separations.<sup>6</sup> The application of this concept for fuel cells has been started by Yamaguchi *et al.* using a polytetrafluoroethylene substrate with cylindrical pores.<sup>7</sup> Recently, we developed the composite membrane consisting of a proton-conducting polymer electrolyte and three-dimensionally ordered macroporous (3DOM) silica matrix.<sup>8</sup> This membrane exhibited

both high proton conductivity and low methanol cross-over due to the ordered pores and the suppression of polymer expansion by the silica matrix, respectively. However, the hard nature of the silica matrix is not suitable for some applications. In the present study, we fabricated a 3DOM membrane of polyimide, which is a proven engineering plastic with high mechanical, chemical, thermal, and oxidative stability, as well as flexibility, and evaluated it as a new matrix for the composite membrane.

The 3DOM polyimide matrix was prepared by using a colloidal crystalline membrane of highly mono-dispersed silica particles as a template. A suspension containing 550 nm silica particles was filtered through a mixed cellulose membrane filter with pore size of 0.1  $\mu\text{m}$  (Advantec Toyo Kaisha, Ltd) under the pressure difference of  $5 \times 10^3 \text{ Pa}$ . After the filtration, the deposited silica particles were removed from the filter and sintered at 1100 °C for 4 h at a heating rate of 25 °C  $\text{min}^{-1}$ . The structure of the silica template was observed with a scanning electron microscope (SEM, JEOL JSM-5310). As shown in Fig. 1a, a very flat silica template with 200  $\mu\text{m}$  thickness was obtained. Its thickness is easily controlled by the volume of suspension. When the surface was observed by SEM, it was found to be completely crystalline, built up of mono-dispersed silica particles (Fig. 1b). A dimethylacetamide solution containing 8 wt.% polyamic acid (JFE Chemical Co.) was injected into the vacant space of the ordered silica particles and thermally cured at 200 °C for 1 h, and then at 300 °C for 1 h. By this thermal treatment, polyamic acid was converted to polyimide as shown in Fig. 2. Then, the silica template was removed by etching with

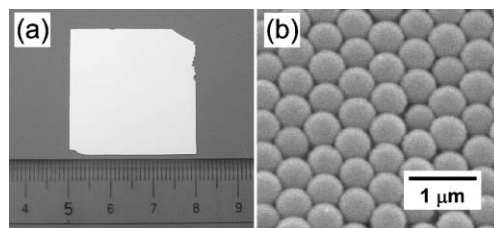


Fig. 1 (a) Photograph and (b) surface SEM image of 550 nm silica template.

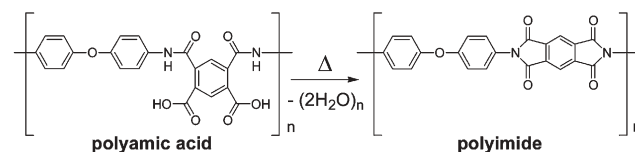


Fig. 2 Formation of polyimide from polyamic acid.

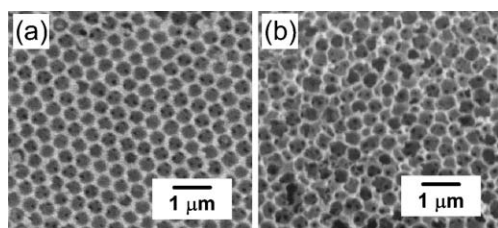
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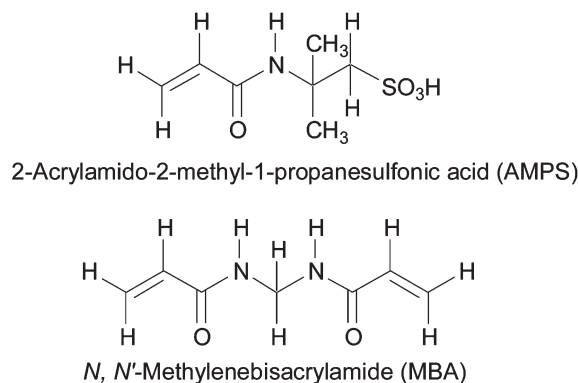
10 wt.% aqueous HF solution and a 3DOM polyimide membrane with thickness of 200  $\mu\text{m}$  and size of about 3 cm  $\times$  3 cm was obtained. The thickness and size of the 3DOM polyimide membrane coincided well with those of the silica template. Therefore, it is possible to prepare the 3DOM polyimide membrane with desired morphology by using the corresponding silica template.

The surface and cross-sectional SEM images of the 3DOM polyimide are shown in Fig. 3. A continuous ordered structure of polyimide with uniform pore size, which was an inversed structure of the silica template, was obtained. The smaller pores observed in holes, were connective windows between large macropores. The presence of these connecting windows means a formation of highly ordered pores in a hexagonal array.<sup>9</sup> Actually, a porosity of the 3DOM polyimide close to 74% was obtained.

A proton-conducting polymer electrolyte prepared by polymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) and *N,N'*-methylenebisacrylamide (MBA) was used in this study. Ammonium persulfate (APS) was used as an initiator of polymerization. Fig. 4 shows the chemical structures of these compounds. An aqueous solution consisting of AMPS, MBA, and APS with optimized concentrations of 4.82 mol kg<sup>-1</sup>, 6.49  $\times$  10<sup>-2</sup> mol kg<sup>-1</sup>, and 4.38  $\times$  10<sup>-2</sup> mol kg<sup>-1</sup>, respectively, was injected into the pores of the 3DOM polyimide membrane, and then heated at 60  $^{\circ}\text{C}$  for 1 h for polymerization to take place.<sup>5</sup> We selected this polymer for its ease of preparation and high proton conductivity at ambient temperature. In particular, the latter factor is very important for low temperature DMFC operation. It is of course possible to use other kinds of proton-conducting polymers according to application. The proton conductivity of the



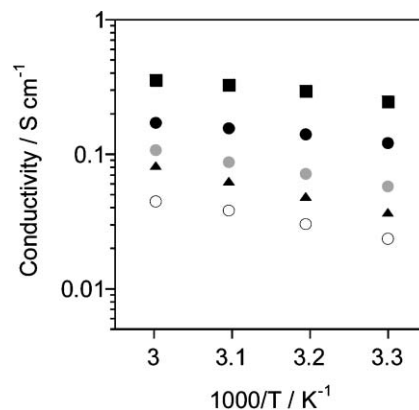
**Fig. 3** Scanning electron micrographs of the 3DOM polyimide membrane prepared by using a 550 nm silica template: (a) surface view and (b) cross-sectional view.



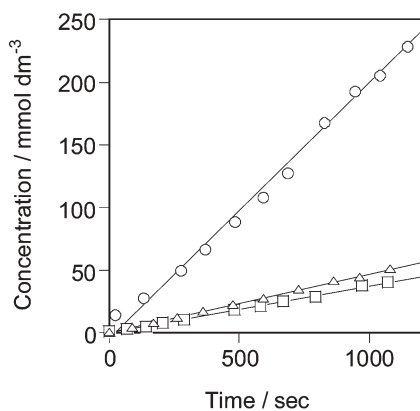
**Fig. 4** Chemical structures of 2-acrylamido-2-methyl-1-propanesulfonic acid and *N,N'*-methylenebisacrylamide.

membranes was measured with an impedance analyzer (YHP 4192A) in the frequency range from 10 Hz to 100 kHz. A sample of the membrane was clamped between two Au electrodes by using a home-made Teflon cell and kept under controlled temperature and humidity conditions. From the Cole–Cole plot, the resistance of the membrane was estimated, and then the conductivity of the membrane was calculated using the apparent thickness and electrode area. Fig. 5 shows the proton conductivity vs. the reciprocal temperature for the 3DOM polyimide composite, AMPS gel, and Nafion<sup>®</sup> 117 membranes. With an increase in temperature and relative humidity (RH), the proton conductivity of the composite increased up to 1.7  $\times$  10<sup>-1</sup> S cm<sup>-1</sup> at 60  $^{\circ}\text{C}$  under 90% RH. This value was considerably higher than that of Nafion<sup>®</sup> 117 membrane. However, it was smaller than the value expected from the porosity of the 3DOM polyimide matrix (2.6  $\times$  10<sup>-1</sup> S cm<sup>-1</sup>). Probably, higher uniformity of the 3DOM polyimide provides higher proton conductivity of the composite membrane. In low-temperature DMFC application, the membrane is exposed to methanol aqueous solutions. Therefore, proton conductivity measurements of the membranes equilibrated with liquid water at 30  $^{\circ}\text{C}$  were also conducted. The membrane was immersed into deionized water at room temperature for 24 h before the measurement. The 3DOM polyimide composite, AMPS gel, and Nafion<sup>®</sup> 117 membranes exhibited 0.87  $\times$  10<sup>-1</sup> S cm<sup>-1</sup>, 1.2  $\times$  10<sup>-1</sup> S cm<sup>-1</sup>, and 0.78  $\times$  10<sup>-1</sup> S cm<sup>-1</sup>, respectively. The decrease in the proton conductivity of the AMPS gel membrane was probably due to the high content of water swelling, which resulted in the decrease of sulfonic acid groups by volume.

Polymer electrolytes with high proton conductivities are generally too soft to be used as membranes by themselves. Furthermore, the shape of those membranes is drastically changed by atmospheric conditions. In fact, the AMPS gel polymer was easily expanded by absorption of water and methanol. On the other hand, the composite membrane did not show such shape changes. In the case of water immersion at 30  $^{\circ}\text{C}$ , the thicknesses of the 3DOM polyimide composite and AMPS gel membranes enlarged 1.1 times (from 200  $\mu\text{m}$  to 220  $\mu\text{m}$ ) and 2 times (from 200  $\mu\text{m}$  to 400  $\mu\text{m}$ ), respectively. Expansion in the same ratio was observed in the plane direction. The water uptake of the



**Fig. 5** Proton conductivity vs. reciprocal temperature of 3DOM polyimide-AMPS gel composite (circle), AMPS gel (square), and Nafion<sup>®</sup>117 (triangle) membranes. Solid, gray, and open symbols represent the conductivity under 90% RH, 80% RH, and 70% RH, respectively.



**Fig. 6** Time dependence of concentration of methanol permeated at 30 °C through AMPS gel (circle), 3DOM polyimide-AMPS gel composite (square), and Nafion<sup>®</sup>117 (triangle) membranes.

membrane was also estimated from the adsorption weight of water. The AMPS gel prepared in this study already had a large amount of water (49.5 wt.%) before water immersion. Thus, an apparent water uptake ( $WU_{app}$ ) of the membranes was calculated from the weight difference between fully hydrated membrane and as-prepared one by using the following equation:

$$\text{Water swelling } (WU_{app}) = \frac{W_{wet} - W_{pre}}{W_{pre}} \times 100\%$$

where  $W_{wet}$  and  $W_{pre}$  are the weights of fully hydrated and as-prepared membranes, respectively. The water swelling of the 3DOM polyimide composite was estimated to 90%, which was about seven times lower than 612% of AMPS gel membrane.

The methanol permeability of the membranes was measured using a two-compartment cell, in which the test membrane was clamped. One side of the cell was filled with 2 mol dm<sup>-3</sup> methanol solution and the other side was filled with deionized water. A methanol flux across the membrane to the water compartment was monitored using a flame ionization gas chromatograph (Shimadzu GC-14B) (Fig. 6). The methanol permeability of the composite membrane calculated from the slope of the straight line, was about six times lower than that of AMPS gel polymer (Table 1). This significant improvement in the cross-over is due to the suppression of expansion of the polymer by the 3DOM matrix. Membrane performances estimated from the ratio of the proton conductivity in water to the methanol permeability were also listed in Table 1. As compared to Nafion<sup>®</sup> membrane, the composite showed better performance. It is expected that the performance will be further increased by an appropriate selection of the filling electrolyte into the 3DOM matrix and the matrix itself.

**Table 1** Proton conductivity ( $\sigma$ ), methanol permeability ( $P_M$ ), membrane performance ( $\phi = \sigma P_M^{-1}$ ), and apparent water uptake ( $WU_{app}$ ) of tested membranes at 30 °C

	$\sigma$ (S cm <sup>-1</sup> ) <sup>a</sup>	$P_M$ (10 <sup>-6</sup> cm <sup>2</sup> s <sup>-1</sup> ) <sup>b</sup>	$\phi$ (10 <sup>4</sup> S cm <sup>-3</sup> s)	$WU_{app}$ (%) <sup>a</sup>
Nafion <sup>®</sup> 117	0.078	2.2	3.5	—
AMPS	0.12	11	1.1	612
3DOM composite	0.087	1.8	4.8	90

<sup>a</sup> In liquid water. <sup>b</sup> Feed solution: 2 mol dm<sup>-3</sup> aqueous methanol solution.

In this study, we have successfully prepared a novel composite membrane composed of 3DOM polyimide and a proton-conducting gel polymer electrolyte. However, it is noted that an imide link in aromatic polyimides is not sufficiently stable at low pH conditions and the degradation kinetics will be amplified due to the high surface area of porous structure. Therefore, we are trying to synthesize hydrolytically stable polyimides based on naphthalene structures for improvement of matrix reliability. It is also possible to use other kinds of polymers to prepare 3DOM matrix. This approach using the 3DOM matrix demonstrated a promising possibility to fabricate the electrolyte membrane with higher performance.

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