Construction of a Fuel Cell from Proton-conducting Silica Nanofilm

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We constructed a fuel cell using a proton-conducting porous silica film with thickness of 650 nm. This fuel cell delivered an open circuit voltage (OCV) of 540 mV and a maximum power density of 51 μW/cm^2 at room temperature. The silanol group on the pore wall promoted proton conduction, and water molecules adsorbed in the pore suppressed permeation of fuel gas.

In the fast-growing fuel cell research, polymer electrolyte membranes such as Nafion® are generally considered to provide the most appropriate electrolyte. However, Nafion membranes are very expensive, and susceptible to deformation due to adsorption and desorption of water as well as degradation of grafted sulfonic groups at elevated temperatures. Inorganic membranes with proton-conducting nanopores may be considered as promising alternatives, because of their lower manufacturing costs and superior mechanical properties.[1–4] In principle, the use of ultrathin electrolyte membrane in fuel cells minimizes electrical resistance of the electrolyte component and raises output-power density.[5] We have developed a low-cost deposition technique for fabrication of proton-conducting nanofilms via template synthesis and subsequent oxygen plasma treatment.[6] This simple technique produces high-quality thin films with pore size of 3 nm, porosity of 68% (V/V), and thickness of one to several hundred nanometers. This silica nanofilm was rich in silanol groups in the nanopore, and its area specific resistance (ASR), a practical measure of the proton conduction efficiency, was comparable to that of a commercially employed Nafion® membrane. In this communication, we report that it is in fact possible to fabricate a silica nanofilm fuel cell using the plasma-treated silica nanofilm as electrolyte membrane.

The utmost requirement for the electrolyte membrane is exclusive transport of protons so that permeation of fuel components, especially hydrogen gas, across the membrane (crossover effect) is suppressed as much as possible. The nanofilm electrolyte may be considered unfavorable for this purpose. This possibility was tested by constructing a nanofilm fuel cell, as represented in Figure 1.

A porous glass sheet (VYCOR® brand 7930, Corning) was used as the cell support. Prior to film deposition, the substrate was polished with a diamond paste and then cleaned in distilled water and ethanol under sonication. The Pt–Pd (Pd, 3 wt %) cathode catalyst layer was sputtered at an ion current of 20 mA for 2 min onto the substrate surface using a vacuum sputter (E-1030, Hitachi Science Systems). The precursor mixture sol[7] was deposited by spin-coating on the Pt–Pd-deposited glass substrate at 2500 rpm for 1 min under the ambient conditions. Subsequently, a porous silica nanofilm was formed by removing the organic moiety with oxygen plasma treatment with RF power of 30 W for 20 min on a PE 2000 Plasma Etcher (South Bay Technology). This spin-coating and plasma-treatment procedures were repeated for three times. Then, the Pt anode catalytic layer was sputtered for 2 min through a shadow mask with a diameter of 3 mm. Finally, lead wires were soldered onto both catalytic layers using silver paste. The fuel cell was assembled into a glass cell for the measurement of electric output. Hydrogen, oxygen, and nitrogen gases were supplied from a cylinder using a regulator, and their flow rates were controlled by a gas flow meter. Fuel cell performances were measured with a home-made fuel cell measurement system.

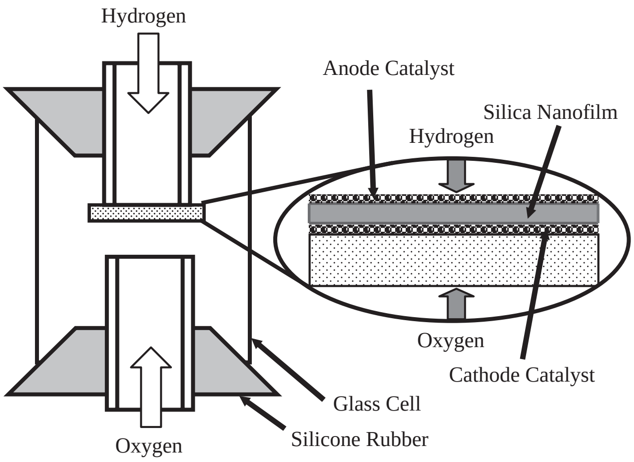

Figure 1. Schematic drawing of silica nanofilm fuel cell.

Figure 2 gives a cross-sectional scanning electron microscope (SEM) image of the assembled three-layer cell, composed of a silica nanofilm electrolyte and anode and cathode catalytic layers above and below the electrolyte film. The cathode and anode layers with thickness of 20 nm are formed by sputtering of Pt–Pd and Pt particles, respectively. The electrolyte layer

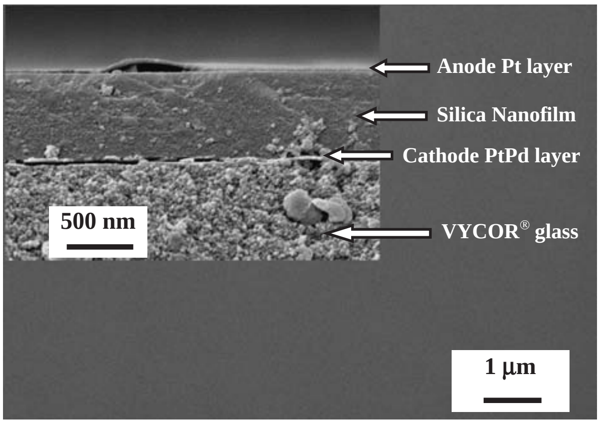

Figure 2. Cross-sectional SEM view (Hitachi S-5200 FE-SEM) of the silica nanofilm fuel cell composed of silica nanofilm electrolyte, anode and cathode catalyst layers on a porous VYCOR® glass substrate.

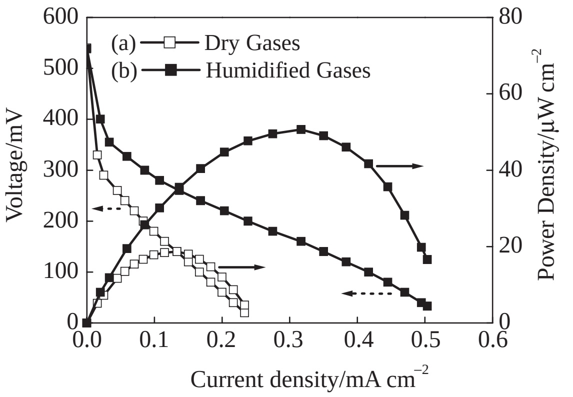

Figure 3. Performance of the silica nanofilm fuel cell at room temperature (20 °C). (a) H_2 at a flow rate of 30 mL/min and N_2 at a flow rate of 30 mL/min are supplied as a fuel gas to the anode, while O_2 at a flow rate of 30 mL/min and N_2 at a flow rate of 30 mL/min are supplied as an oxidant gas to the cathode. (b) Humidified gases passing through a saturated aqueous sodium chloride (75% RH) with the same flow rates as those in (a) were supplied.

(thickness, 650 nm) is uniform and void-free. The combined layers are supported on a porous VYCOR glass plate with pore diameters of 4 to 20 nm. A corresponding top view image of the silica electrolyte film shows that the surface is smooth and crack-free.

Figure 3 shows fuel cell characteristics measured at 20 °C. The open circuit voltages (OCV) of the fuel cell are 538 and 540 mV with and without humidification, respectively. These values are lower than OCV values of 0.8–1.0 V that are typically observed with polymer-based fuel cells. Hydrogen molecule, if permeating across the film, undergoes reaction at the cathode, causing cathode depolarization and decrease in OCV. The almost identical OCV values observed under the dry and humid conditions suggest that the humidity change does not affect permeation of fuel gas in the membrane. Therefore, water molecules adsorbed at room temperature must occupy the narrow microporous channels in the silica film without humidification of fuel gas and block gas permeation at least partially.

The decrease in OCV appears to arise from fuel leakage through tiny cracks within the silica nanofilm electrolyte. Verweij et al.[8] clarified a critical effect of the fabrication conditions on the property of microporous silica membranes for selective gas separation. According to their results, the number of defects caused by air-born particles was estimated to be at least five (diameter of ca. 500 nm) per square centimeter of the film, causing substantial deterioration of separation selectivity, when the clean-room conditions were not employed. Our silica nanofilm was prepared with extreme care under normal laboratory conditions but not in a clean room, and the existence of some tiny cracks that are not detected by the SEM observation is unavoidable. These cracks would cause a distinct crossover effect. The multiple-layer coating could repair cracks and reduce their effect to some extents. This is one of the reasons why we used three-layer fabrication for the porous nanofilm itself. When the fuel cell experiment was conducted at 90 °C, OCV dropped dramatically. This is a sign of extensive crossover. Apparently, the water adsorbed in the pore evaporated at this temperature and lost their blocking effect on gas permeation.

The output powers with dry and humidified gases at 20 °C are 18 and 51 μW/cm^2, respectively. These powers are smaller by three to four orders of magnitude than that for a standard polymer electrolyte fuel cell. This loss is derived from power consumption due to cell interior resistance. The total cell resistance including ohmic contributions of the silica nanofilm electrolyte, the catalytic layers, and their interface can be calculated from a linear variation of overpotential with current density in the ohmic resistance range of *I*–*V* plot. The output powers of 18 and 51 μW/cm^2 correspond to resistances of 1200 (dry gases) and 300 Ω cm^2 (humid gases), respectively. Such much higher resistance values may be associated with the use of the sputtered Pt–Pd and Pt particles with a stack thickness of 20 nm that provide rather poor three-phase contacts and poor electron conduction. For the porous nanofilm, water molecules from ambient moisture can enter the film interior through accessible pore channels and help migration of protons.[9,10] While water molecules that are retained in the film under the dry atmosphere can maintain protonic conduction, the increase in adsorbed water under the humidified atmosphere provides more proton-jumping sites and leads to the enhanced conductivity.[6] The output power of the silica film fuel cell is comparable to the value of ca. 0.1 mW/cm^2 for a glass film fuel cell reported by Nogami et al.[11] The low-temperaute deposition we developed for nanofilm electrolyte is advantageous, in that it could prevent thermal growth of the catalyst particle as well as crack development within nanofilm. The output power of the silica film fuel cell should be improved by creating better three-phase contacts among electrolyte membrane, catalyst layers, and electrodes and by the use of better fuel cell design.

References and Notes

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7 First, 5.2 g (25 mmol) of tetraethoxysiliane (TEOS, Aldrich), 6 g of propanol, and 0.45 g of hydrochloric acid (0.004 mol/L) were mixed and stirred for 1 h at 60 °C. Then, 2 g of hydrochloric acid (0.06 mol/L) was added, and the resulting sol was stirred for additional 1 h at 70 °C. A surfactant solution (1.7 g (2.5 mmol) of $C_{16}EO_{10}$ in 11.4 g of propanol) was slowly added with stirring to the sol solution. After stirring the solution for 1 h at room temperature, a transparent sol was obtained. The final molar composition was 1 TEOS:11.4 propanol:5 H_2O:0.004 hydrochloric acid:0.1 $C_{16}EO_{10}$.
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