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Editor's Choice

Surface-modified Tubular Glass Electrolyte for Portable Direct Methanol Fuel Cell

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A fast-proton-conducting porous tubular glass electrolyte was prepared by surface modification of glass, and the direct methanol fuel cell performance of the glass electrolyte was measured. The glass electrolyte showed very low methanol permeability of $2.1 \times 10^{-7}\,\mathrm{cm^2\,s^{-1}}$ compared with the polymer electrolyte Nafion® ($2.3 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$). An open-circuit voltage of approximately 0.7 V was obtained at room temperature, which corresponds to 15 V when the tubes are stacked in a $6.5\,\mathrm{cm^3}$ portable cell.

Direct methanol fuel cells (DMFCs) using oxygen gas and methanol as fuels have attracted considerable attention owing to their very high energy density per unit volume and portability. Methanol is a liquid at room temperatures and can be carried easily using a cartridge compared with hydrogen gas. Consequently, DMFCs have been considered as a portable power source for cellular phones, laptop computers, and digital cameras.[1–4] The open-circuit voltage (OCV) of DMFCs has been calculated theoretically to be 1.21 V. However, in general, proton-conducting polymer electrolytes such as Nafion® become swollen in methanol, and unreacted methanol at the anode permeates through to the cathode, which is called *methanol crossover*. This results in a serious drop in voltage from 1.21 V to approximately 0.4 V. Consequently, there is considerable interest in development of a new electrolyte with low methanol permeability, high proton conductivity, and good mechanical strength.

Proton-conducting porous glass electrolytes have also been reported.[5–7] We have previously studied the proton conductivity of sodium borosilicate (Na_2O–B_2O_3–SiO_2)-based nanoporous glasses.[8,9] These glasses show spinodal-type phase separation to Na_2O–B_2O_3-rich and SiO_2-rich phases when they are heated above the glass-transition temperature.[10,11] Because the Na_2O–B_2O_3-rich phase dissolves almost completely in acid solution, continuous pores of a few nanometers can be easily obtained. The nanoporous glasses modified with (3-sulfanylpropyl)trimethoxysilane [$(OCH_3)_3SiC_3H_6SH$] and subsequent oxidation of thiol ($-C_3H_6SH$) to sulfonic acid ($-C_3H_6SO_3H$) groups were found to show a high proton conductivity of approximately $1 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ at 90% relative humidity. First principles calculation showed that the oxidation reactivity from thiol to sulfonic acid groups was predominantly determined by the alkyl chain length.[8] Compared with Nafion®, the porous glass electrolyte is chemically and thermally stable and does not swell in solutions of methanol or water.

A crucial aspect of mobile fuel cells is their volume power density.[12] Compared with traditional plane electrolytes (membranes), tubular electrolytes can be stacked more effectively in a unit volume. The formability of glasses for tubular electrolyte is a distinctive advantage for practical application of the DMFC. In this letter, the methanol permeability and DMFC performance of a surface-modified tubular glass electrolyte is reported for the first time.

Tubular glass with a composition of $7.4Na_2O\cdot24.8B_2O_3\cdot65.9SiO_2\cdot1.9Al_2O_3$ (mol %) was prepared by conventional melting at 1550 °C.[8,10] Inner and outer diameters of tubular glass were 4.9 and 6.1 mm, respectively. The length was about 1.7 cm. The obtained porous glass was treated with a mixture of toluene and (3-sulfanylpropyl)trimethoxysilane (mass fraction 3%), and surface modification was carried out under reflux for 24 h. The sample was then washed with pure toluene to remove unreacted chemicals. The resultant samples were treated with a 34.5% aqueous hydrogen peroxide (H_2O_2) solution for 24 h to convert the thiol groups (–SH) to sulfo groups ($-SO_3H$).

Pore structures of the tubular glass were measured by nitrogen gas adsorption–desorption. The specific surface area of the glass was $269\,\mathrm{m^2\,g^{-1}}$. The average pore diameter was calculated to be 3.2 nm by the Dollimore–Heal method[13,14] using desorption branch data.

The concentrations of methanol that permeated through the surface-modified glass were measured at 25 °C. The methanol permeability of Nafion® was estimated to be $1.5 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$. Similar values have been reported in the literature: 2.3×10^{-6} and $1.98 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$.[15,16] Note that methanol permeability through the porous glass ($2.1 \times 10^{-7}\,\mathrm{cm^2\,s^{-1}}$) is more than one order of magnitude lower than that of Nafion®. It is clear that nonswelling tubular glass well blocks the methanol permeation.

In the case of plane electrolytes, generally, anode and cathode electrodes are hot-pressed to reduce the contact resistance between electrolyte and electrode interfaces. However, the hot-press process cannot be applied to the inner surface of tubular glass, and in this study a layer-by-layer (LBL) technique was used to prepare the electrolyte/electrode assembly. The LBL technique offers an easy and inexpensive solution process. LBL assembly is mainly conducted through electrostatic interaction, where oppositely charged materials such as polyelectrolytes are alternately deposited on a charged substrate.[17] Because the PtRu/C electrode (Tanaka Kikinzoku Kogyo, Japan) for methanol oxidation is negatively charged in aqueous solutions, the strong polycation poly(diallyldimethylammonium) chloride (PDDA) was used as the binder as shown in Figure 1. A PDDA solution containing $0.5\,\mathrm{mol\,L^{-1}}$ NaCl ($1\,\mathrm{mg\,mL^{-1}}$) and an ethanol solution of PtRu/C (ethanol volume fraction 40%, PtRu/C $25\,\mathrm{mg\,mL^{-1}}$) were used for the LBL.

The mass of deposited PtRu/C catalyst was measured by using a quartz crystal microbalance as follows:

$$\Delta F = -[2F_0^{\,2}/A\cdot(\rho\mu)^{0.5}]\cdot\Delta w \qquad (1)$$

where A is the surface area ($\mathrm{cm^2}$), ρ and μ are the density ($2.648\,\mathrm{g\,cm^{-3}}$ at 298 K) and elastic modulus ($2.947 \times 10^{11}\,\mathrm{g\,cm^{-1}\,s^{-2}}$) of quartz, respectively, F_0 is the basis frequency (9.0 MHz), and ΔF and Δw are the frequency and mass changes

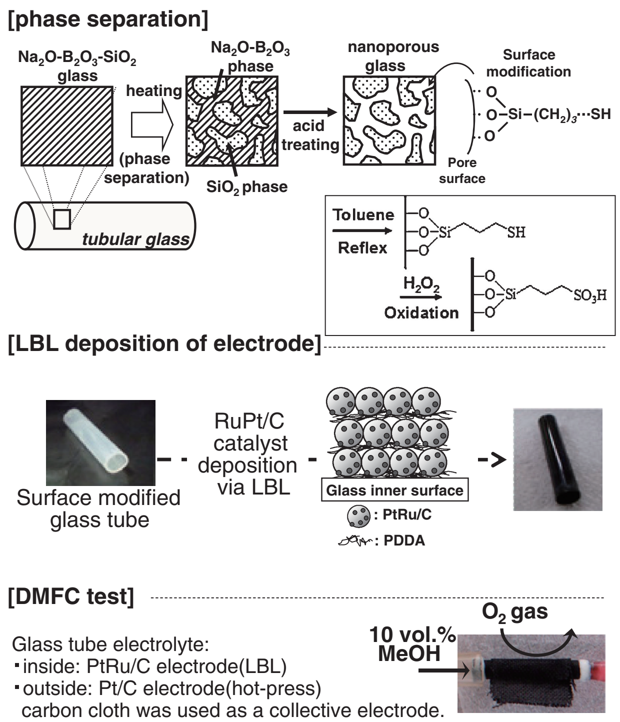

Figure 1. Preparation procedures of the tubular glass DMFC electrolyte.

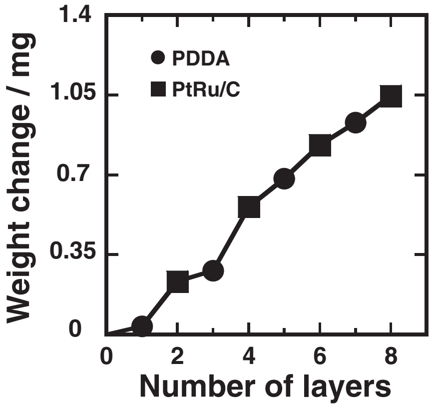

Figure 2. Changes in the amount of deposited PDDA and PtRu/C catalyst calculated from the QCM frequency decrease (ΔF) with the number of layers.

before and after deposition, respectively. The eq 1 shows that a change of 1 Hz would correspond to a mass of 7 ng.

Figure 2 shows the relationship between the number of layers and calculated mass change for alternately deposited PDDA and PtRu/C. Note that the mass of deposited PtRu/C increased almost linearly as the number of layers increased. This is because multiple PDDA and PtRu/C bilayers were deposited regularly and homogeneously. The mass per unit area of PtRu/C on the glass surface was estimated to be 0.74 mg cm^{-2} from eq 1.

DMFC performance of the surface-modified tubular glass was measured at room temperature using a 10 vol % methanol solution and pure oxygen gas as the fuel (Figure 1). The cathode electrode paste was prepared by mixing Nafion® solution (mass fraction 5%, Sigma-Aldrich, St Louis MO), Pt/C with a 50% mass fraction of deposited Pt (Tanaka Kikinzoku Kogyo, Japan), a 40% (volume fraction) aqueous ethanol solution, and 10% (mass fraction) poly(tetrafluoroethylene) (PTFE) (Sigma-Aldrich, St Louis, MO) solution. These solutions were mixed in a weight ratio of 10:1:20:2. A carbon cloth was used as the electron collector, and the cathode electrode paste was hot-pressed onto the tubular glass at 120 °C for 2 min with care to avoid a break. As described above, the anode was prepared by the LBL method, and the cathode was prepared by hot-pressing using Pt/C catalyst paste. Figure 3 shows the voltage (OCV) and power density of the cell as a function of the current density. Note that the OCV obtained (0.67 V) was much higher than that typically observed in Nafion®-based DMFC (approximately 0.4 V). As shown in Table 1, the tubular glass shows much lower methanol permeability than Nafion®.

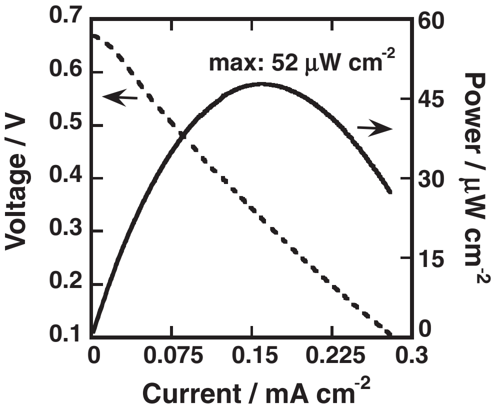

Figure 3. Direct methanol fuel cell performance of surface-modified tubular glass electrolyte measured at room temperature.

Table 1. Properties of Nafion® and tubular glass measured at 25 °C

	Tubular glass[a]	Nafion®[b]
Methanol permeability /cm^2 s^{-1}	2.1×10^{-7}	1.5×10^{-6}
OCV/V	0.67	0.40[18,19]
Maximum power density/mW cm^{-2}	0.052	2.0[18,19]

[a] The amount of deposited PtRu/C catalyst: 0.78 mg cm^{-2}.
[b] The amount of deposited PtRu/C catalyst: 4 mg cm^{-2}.

This would make the methanol crossover of the glass lower than that of Nafion, which would contribute to the larger cell voltage (0.67 V). The maximum power density was 52 µW cm^{-2}, which is low at present because of the high resistance per square of the LBL electrode (1500 Ω). Conseqently, a suitable active electrode for the glass electrolyte is required to improve the power density. In this study, practical potentials can be demonstrated for the application of the tubular glass DMFC operated at around room temperature.

The advantage of tubular DMFC is the very large surface-to-volume ratio of the electrode. For instance, the voltage obtained here was approximately 0.7 V. When using tubular glass with a

2-mm diameter, an OCV of approximately 15 V can be obtained by stacking 24 tubular glass electrolytes. The cell volume of this was calculated to be 6.5 cm^3, which is roughly equal to the volume of a cellular phone lithium ion battery. This stacking can only be achieved with the tubular electrolyte. Considering the chemical/thermal stabilities and formability, the tubular glass electrolyte could also be applied in biofuel cells such as cardiac pacemakers, and further investigations into these applications are in progress.

In summary, this is the first report of the preparation and DMFC performance of a surface-modified tubular-glass electrolyte. The cell had approximately one order of magnitude lower methanol permeability than the polymer electrolyte Nafion®, which leads to a much higher open-circuit voltage for the tubular glass electrolyte.

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