Preparation of Dense Thin-Film Solid Electrolyte on Novel Porous Structure with Parallel Pore Channel

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1. Introduction

Ion-conducting electrolyte films can be applied to various fields such as electrochemical cell for exhaust gas purification, gas separation, solid oxide fuel cells, and so on, since the ohmic loss across the electrolyte is lowered as its thickness is reduced. This allows the electrochemical devices to operate at lower temperatures and higher efficiency. In order to prepare the thin-film electrolyte, various thin-film processes have been investigated such as electrochemical vapor deposition, sputtering, physical vapor deposition, electrophoretic deposition, and slurry coating. In this study, we have focused on the colloidal deposition process, such as slurry-coating because it is cost-effective and scalable.

For application mentioned above, the electrolyte thin-film should be supported by the porous electrode substrate. However, it is very difficult to get fully dense ceramics by sintering a colloidal deposit on non-shrinking substrate. Therefore, the co-firing of an electrolyte layer and a substrate considers to be a resonable solution. The porous substrate should work as a good electrode as well as a structural support or a gas transport passage so that the substrate for co-firing should meet many contradictory requirements. Accordingly, the properties of the thin-film electrolyte device strongly depend on the porous substrate. These problems are regarded as one of the challenging issues of "Ceramic Integrations."

The substrate must be processed to yield continuous porosity and high surface area microstructure, without compromising the strength of the bi-layer. However, a small and narrow pore-size distribution is also necessary in order to deposit homogeneous electrolyte layer, at least near the surface where the electrolyte will be deposited. It is assumed that the pore size should be smaller than the thickness of the electrolyte layer. However, reducing the pore size may increase the tortuosity of gas transport passage, which gives rise to increase a concentration polarization. Additionally, lowering the co-firing temperature and/or decreasing the sinterability of the substrate for obtaining sufficient porosity are not recommendable because these may lead to electrolyte films of low density with large number of pinholes.

In order to achieve sufficient amount of open pores after co-firing, mixing of the burnable pore-former such as starch or carbon with electrode powder during substrate forming step has been reported. Although this process has been widely used in thin-film solid oxide fuel cell research due to its simplicity, it has many drawbacks to be solved. The percolation of the pore former is essential in this process, thus fairly large amount of pore-former is required. But, the substrate may collapse during burn-out process if the amount of pore-former is too much. Homogeneous distribution of the pore-former and electrode powder is difficult due to their large differences in density and particle size. Therefore, cracking or wrapping of the substrate frequently occurred after burning out the pore former or co-firing the bi-layer.

Another well-known method to fabricate porous substrates for solid oxide fuel cell researches is the coat-mix process. Instead of using pore former, the majority of open pores of the coat-mix process are formed between the intentionally coagulated agglomerates, which are coated with thermo-setting resin. The production of the green substrate is preformed by warm-pressing of the resin-coated coagulates in a metallic die at about 120°C with a pressure of between 0.8 and 1 MPa. A careful control is required for particle packing in a mold during warm-pressing. Additionally, burning out the thermo-setting resin such as phenolformaldehyde, which is used as a binder, may bring about serious environmental problem.

This study reports an approach to fabricate the bi-layer, thin-film of CGO electrolyte on a porous LSCF–CGO cathode with parallel open pore channel, which is considered to be ideal for constructing electrochemical cells. Recently, a process of preparing porous alumina with macroscopically aligned open pores by freeze-drying has been reported. It was very simple and environmentally friendly process for preparing porous ceramics. The macroscopic pore channel obtained in the report is expected to be very effective for gas transport through the substrates. However,
the size of the pore channel was too large so that the deposition of thin-film electrolyte layer onto the substrate seems to be difficult. During this study, we have found that the microstructure and pore size of the freeze-dried substrate are different along the freezing direction. Using this gradient in pore structure of the substrate, we could easily integrate the thin-film electrolyte layer and macro porous substrate. The thin-film of CGO electrolyte was successfully coated on the macro porous substrate and then co-fired to full density.

2. Experimental

La_{0.6}Sr_{0.1}Co_{0.2}Fe_{0.8}O_{3-δ} (prepared in-house by citric acid method)-Ce_{0.9}Gd_{0.1}O_{1.95} (LSCF–CGO) composite electrode powders (50 mass% of CGO) were mixed with a small amount of dispersant (Alon A-6114, Toa-Gosei Chemicals, Tokyo) and were ball-milled for 20 h. A slurry concentration of 27 vol% was prepared. The slurry was de-aired by stirring under vacuum. It was then poured into a cylindrical container, and the bottom of the container was immersed in a refrigerant in a freezing bath, as shown in Fig. 1.

The bottom of the container was made of metal, which has a high thermal conductivity. On the other hand, the wall of the container was made of Teflon, which has a low thermal conductivity. Ethanol cooled at −80°C was used as refrigerant. After the slurry was completely frozen, the container was put into a drying vessel, and it was dried for about 12 h under vacuum. The sample was carefully removed from the container. The freeze-dried substrate was then heated and held at decomposition temperature of the dispersant, and partially sintered at 900°C for 5 h to the green body strong enough to handle for electrolyte deposition. The substrate was coated with Ce_{0.9}Gd_{0.1}O_{1.95} (CGO, Anam Kasei) slurry, which was prepared by dispersing CGO powder in distilled water with a small amount of dispersant (Alon A-6114). The bi-layer was co-fired at 1350°C for 2 h to fully densify the electrolyte film. The pore-size distributions of the pre-fired and sintered substrates were measured by mercury porosimetry (Model Pore Master GT33/66, Quantachrome, USA). The microstructures of the surfaces and cross sections were observed by scanning electron microscopy (SEM, Model JSM-5600, JEOL, Ltd., Tokyo).

3. Results and discussion

Figure 1 illustrates schematically the integration process of thin-film electrolyte and macroscopically porous substrate applied in the present study. During the freezing of the water-based slurry of LSCF–CGO composite substrate, the growth direction of ice was controlled unidirectionally. When ice is removed by sublimation, the spaces of ice will be converted into the pore channels. There was no or little change in volume during freeze-drying. This enables us to prepare an extremely heterogeneous structure, as is the case in this study, without causing any drying problems.

The green body prepared by freeze-drying showed significantly different microstructure along the growth direction of ice. The large flat shaped macro pores were observed at the surface of the top side (Fig. 2(a)). On the other hand, it was found that the surface of the bottom side consisted of the homogeneously distributed micro pores (Fig. 2(b)).

It is considered that such a unique microstructure resulted from the differences in ice formation rate between the bottom and top side. Initially, the freezing rate at the bottom side is so rapid that the slurry in the vicinity of the bottom side frozen immediately with its dispersion state as it is. However, ice formed on the bottom side then interferes the heat transfer from the slurry to the metal container. As a consequence, the freezing rate of the slurry rapidly decreased. The top side of the container was opened so that the upper side of the slurry was exposed to the room temperature. Thus ice was stimulated to grow macroscopically in the vertical direction. The pores are generated by the sublimation of ice and aligned along its growth directions. The SEM micrographs of the cross section parallel to the growth direction of ice in Fig. 2(c) shows that the thickness of the micro porous layer in the green body is in the range of 30–40 μm.

The porosity of the LSCF–CGO substrate prepared by freeze-drying process are listed in Table 1. The LSCF–CGO substrate showed sufficient porosity even after sintering as high as 1350°C. The porosity calculated from the relative density was almost the same as given by mercury porosimetry. Therefore, it is considered that most of the pores were open pores. Figure 3 shows the pore-size distribution determined by mercury porosimetry. The pre-fired substrate sintered at 900°C showed a bimodal pore-size distribution. Two peaks appeared approximately at 10 μm and 0.1–0.2 μm in the case of the pre-fired substrate at 900°C.

When the substrate was sintered at 1350°C for 2 h, the smaller pores, which appeared at 0.1–0.2 μm disappeared,
while the macroscopic pores still remained. It is likely that the small pores, indicative of the initial stage of sintering, disappear as the sintering is carried out at high temperature.

The SEM micrographs of the substrate after sintering at 1350°C for 2 h are shown in Fig. 4. As shown in Figs. 4(a) and (b), the flat shaped macro pores of the top side were remained after sintering at 1350°C for 2 h. The width of the flat shaped pore is about 10 µm, and this corresponds to the average pore diameter indicated by mercury porosimeter. Figure 4 (c) shows that the micro pores of 2-6 µm remain at the bottom side after sintering. These pores were not clearly detected by mercury porosimeter since the thickness of the layer was fairly thin. The formation of the micro porous layer on the bottom side of the LSCF-CGO substrate appears to be very important and effective, because it is difficult to deposit dense thin-film directly on the macro porous surface with the microstructure as shown in Fig. 4(a). Additionally, the micro porous layer should work as a triple phase boundary where electrochemical reactions would take place. Therefore, the formation of this micro porous layer by controlling the freezing rate of the surface is considered to be the most critical step in the present study.

Figure 5 shows SEM micrographs of the co-fired CGO film after triple dipping cycles (Figs. 5(a) and (b)), and nine dipping cycles (Figs. 5(c) and (d)). Obviously, several cracks and pores are observed in the film which was dipped three times. These cracks and pores almost disappeared after nine repetitions of the dipping and drying cycles, because the influence of constrained sintering lessened with increasing the thickness of the films. However, in the long run, it is necessary to adjust the total shrinkage and the rate of shrinkage of both substrate and thin-films. This is possible by adjusting the pre-firing temperature of the substrate and by tailoring the particle size distribution for both components.

Figure 6, which is the lower magnification photographs of

<table>
<thead>
<tr>
<th>Sintering Temperature (°C)</th>
<th>Relative Density (%)</th>
<th>Open Porosity by Archimedes Method (%)</th>
<th>Porosity by Mercury Porosimetry (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>900°C</td>
<td>30.1</td>
<td>68.2</td>
<td>68.6</td>
</tr>
<tr>
<td>1350°C</td>
<td>56.7</td>
<td>43.1</td>
<td>42.1</td>
</tr>
</tbody>
</table>
the Fig. 5(c), demonstrates the variations of pore size distribution along the growth direction of ice. The incorporation of straight and parallel pores may reduce the effective path length necessary for gas phase diffusion. A thick porous substrate requires gas phase to travel a long tortuous path to reach a triple phase boundary, whereas the parallel pore configuration reduces this path length. On the other hand, the micro porous layer existed in the vicinity of the thin-film electrolyte provides sufficient amount of triple phase boundaries. Therefore, the structure shown in Fig. 6 can be regarded as an ideal structure for the application to the solid oxide fuel cell or membrane reactor.

It is very simple to fabricate porous bodies of various shapes with the unique pore structure by modifying the container design. For example, we have prepared the LSCF–CGO porous tube by freeze-drying process. The con-
The configuration of container structure for the tube-type porous body, and the microstructure of the obtained LSCF-CGO porous tube are shown in Fig. 7. As illustrated in Fig. 7, the container consists of two parts; one is a metal cylinder, and the other is a Teflon bottom and pole. Since ice unidirectionally grows inward from the metal side, one can get the unique microstructure with macropores, which is highly aligned inward. As is similar to the disc-type body, which is described in Fig. 4, the tube-type porous body also have micro porous layer near at the circumference of the tube.

4. Conclusion
Freeze-drying is an attractive technique as a forming process because it is simple, environmentally friendly and easy to scale-up. Using this process the macro porous structure and dense thin-film have been successfully integrated for satisfying the complicated requirements in microstructure for applications such as SOFC, membrane reactor, gas separation membrane, and so on. Porous LSCF-CGO substrate with a unique structure composed of aligned open pores and micro pores on the surface were prepared by freezing a water-based slurry unidirectionally and sublimating ice at a reduced pressure. The formation of micro pores on the surface of the macro porous structure by controlling the freezing rate of the slurry is considered to be the most critical step for integrating the thin-film and the macro.
porous substrate layer.

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References