ELECTROCHEMICAL CHARACTERISTICS OF YSZ ELECTROLYTE DEPOSITED ON LSM SUBSTRATE BY ELECTROPHORESIS

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ABSTRACT

Thin-film electrolytes of yttria-stabilized zirconia (YSZ) were deposited on porous La0.8Sr0.2MnO3 (LSM) cathode substrates by electrophoresis for practical application to solid oxide fuel cells. A YSZ film was obtained by electrophoresis combined with reduced pressure (suction) deposition. The gas permeability coefficient (GPC) was 7×10⁻⁶ (cc·cm/g·sec). The maximum power density was 23 mW/cm² at 50 mA/cm² at the operating temperature of 1000°C.

INTRODUCTION

The practical application of solid oxide fuel cells (SOFCs) will depend on the conversion efficiency of the cell as well as the fabrication cost. Thus, cells should be made by simple techniques and their resistance should be reduced to improve the efficiency (1,2). In particular, gas-tight yttria-stabilized zirconia (YSZ) thin-film electrolyte needs to be fabricated by a simple scheme, since the YSZ membranes dominate the cell efficiency at the operating temperature of 1000°C (3). There are several methods of preparing pinhole-free YSZ films, e.g., plasma spraying (4), electrochemical vapor deposition (EVD) (5), and co-firing (6). The thickness of the film obtained by plasma spraying has to be more than 100 μm for sufficient gas tightness (4). In addition, the yield rate of raw materials is low in plasma spraying. EVD requires complicated and expensive systems and the film deposition process takes a long time (5). Co-firing restricts the size and shape of the cell (6).

The electrophoretic method for depositing YSZ on a porous substrate has been studied since it has several advantages: short formation time, simple system, and little restriction on cell shape (7). However, there have been only a few papers on electrophoretic deposition of YSZ onto a strontium-doped lanthanum manganite La0.8Sr0.2MnO3 (LSM) substrate having high porosity and a large average pore diameter (8,9). This may be because it is difficult to sinter a flat, pinhole-free film on high porosity substrates. In this paper, we report that a thin compact YSZ film on an LSM substrate can be made by the combination of electrophoretic deposition with suction deposition to solve the above problems.
EXPERIMENTAL

The experimental setup for electrophoresis combined with reduced pressure deposition is shown in Figure 1. The LSM substrate on which the YSZ was to be deposited acted as a cathode and the anode was Ni. The two electrodes were immersed in a suspension of YSZ (ZrO\textsubscript{2}-8mol\%Y\textsubscript{2}O\textsubscript{3}) dispersed in ethanol. Acetone of 5 vol% was added to optimize the deposition rate (7). The porous LSM substrate was 30 mm$\times$5 mm$^2$ and the Ni anode was 36 cm$^2$. Porous substrates were made from LSM powder by extrusion, cutting into a disk, and firing at 1450°C for 10 h. The porosity and conductivity of the substrate were 30% and 110 S/cm, respectively. The applied voltage was 60 V dc. In order to improve the adhesion of the junction between the LSM substrate and electrophoresis-deposited YSZ and to improve the flatness of the electrolyte membrane, after electrophoretic deposition we reduced the pressure at the back of the electrolyte on the LSM substrate (hereafter called suction deposition) as shown in Figure 1. This resulted in loosely deposited YSZ on porous LSM substrates becoming adherent, and YSZ in the suspension being selectively deposited at the pinholes in the deposited YSZ membrane. We tested YSZ powders having fine (S1) and coarse (S2) particles, which had median particle sizes of 0.18 $\mu$m and 0.48 $\mu$m, respectively. Deposition times were 1 min (2 min) for electrophoretic deposition and 20 sec (15 sec) for deposition with reduced pressure when suspension S1 (S2) was used. The LSM substrates with deposited YSZ were desiccated at 120°C, and the above procedure was repeated several times to obtain a YSZ membrane of the desired thickness, because the membrane was easily cracked when a thick YSZ membrane was deposited in a single step. The resulting LSM substrates with YSZ membranes were sintered at 1350, 1400, or 1450°C for 2 h. These procedures were repeated several times to obtain gas tightness as illustrated in Figure 2.

The YSZ membranes were observed with a scanning electron microscope (SEM). The gas permeability coefficient (GPC) was measured at room temperature using N\textsubscript{2} gas. A lower value represents better gas tightness. Electrochemical characteristics of cells were tested at 1000°C using humidified hydrogen as a fuel and oxygen as an oxidant (Figure 3). The flow rate of both gases was 100 ml/min. The Pt anode (0.785 cm$^2$) was slurry-coated and fired at 1000°C for 1 h in air. $I - V$ characteristics were measured by the DC-polarization method (using a Hokuto HA-501G). The cell impedance was also measured by the AC-impedance method. Voltage was controlled by a potentiostat (Solartron 1287).

RESULTS AND DISCUSSION

In order to optimize the deposition conditions, we investigated the influence of the YSZ particle size and the sintering temperature on the sintering characteristics. The relationship between film thickness and total process time as a function of YSZ particle size is shown in Figure 4, when the electrophoresis-suction processes followed by desiccation at 120 °C were repeated several times. The rates for suction deposition were independent of particle size, while those for electrophoresis deposition depended on the size. Here we estimated the film thickness from microscope
images and also by measuring the weight of deposited YSZ. Currents between two electrodes were approximately 100 and 30 μA/cm² for S1 and S2, respectively. This may be due to their having different total surface areas. The total surface area of S1 was estimated to be three times that of S2, and the total charge should be proportional to the total surface area, assuming that the electron charge per unit area is the same for different particle sizes and that the mobility of the particle is independent of the particle size and shape(10).

GPCs were measured for different particle sizes for optimum deposition conditions and a sintering temperature of 1400°C. GPCs of S1 normalized by the initial GPC of S1 decreased with increasing the number of deposition-sintering cycles, while those of S2 were almost constant, as shown in Figure 5. This may be due to the difficulty of sintering arising from the YSZ particle size. Figure 6 shows SEM images of the cross section area of the cells fabricated from S1 and S2. The thickness of the electrolyte was estimated to be 25 μm for S1 and 30 μm for S2. The density of the YSZ membrane for S1 is seen to be higher than that for S2. These results indicate that S1 is suitable for electrolyte deposition in our method.

Figure 7 illustrates the relationship between GPC and the number of deposition-sintering cycles using S1 for two different sintering temperatures. LSM substrates without deposition were sintered at the same sintering temperatures and their GPCs were measured as references. For practical usage the GPC must be less than 10⁻⁵(cc-cm/g-sec). From the result shown in Figure 7, we used the sample sintered at 1450°C using S1 for testing the cell’s electrochemical characteristics.

Figure 8 illustrates terminal voltage and power density as a function of current density. The electrolyte was fabricated with two deposition-sintering cycles. The open circuit voltage of the cell was 1.0 V. This suggests that the pinholes in the film were almost completely removed by the electrophoresis-suction deposition method. The maximum power density was 23 mW/cm² at 50 mA/cm².

In order to explain the $I-V$ curves of the cells, we measured the AC impedance (Figure 9). The sweep range of the frequency was from 100 kHz to 0.1 Hz. The spectra for the cell had two or three semi-circles. In general, the semi-circle in the high-frequency range suggests that the resistance was related to the interfacial reactions (11). However, comparing those spectra with the ones for plasma-sprayed cell, which was fired at 1300°C for 2 h, we think that the semi-circles in the highest frequency range may originate from the pyrochlore thin layer produced by the reaction between LSM and electrolyte. The bulk resistance of the electrophoresis cell was approximately 0.6 Ω-cm², which was 30 times larger than that of the bulk resistance of YSZ. However, this resistance may be reduced by optimizing the sintering duration.

**CONCLUSIONS**

The influence of the YSZ particle size and sintering temperature on the electrophoretic deposition onto a porous La(Sr)MnO₃ (LSM) cathode substrate was
investigated. We derived the optimum conditions to be a particle size of 0.18 \( \mu m \) and sintering temperature of 1450°C. The gas permeability coefficient of the film with a thickness of 30 \( \mu m \) was 7\times10^{-6} \text{ cc-cm/g-sec}. The cell with YSZ membrane made by the electrophoresis-suction method showed the open circuit voltage of 1.0 V. The maximum power density was 23 mW/cm² at 50 mA/cm² for an operating temperature of 1000°C. Therefore, the electrophoresis-deposition combined with suction-deposition for YSZ fabrication on a porous substrate is promising for SOFC application.

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Figure 1. Experimental setup for electrophoresis and suction with a vacuum pump.

Figure 2. Flowchart for preparation of YSZ film.
Figure 3. Experimental setup for measuring cell performance.

Figure 4. Thickness as a function of accumulated process time for suspensions of YSZ with a median size of 0.18 μm (circles) and 0.48 μm (squares). (E) and (S) indicate electrophoresis and suction methods, respectively.
Figure 5. Gas permeability as a function of the number of cycles of deposition-sintering at 1400°C for various YSZ particle sizes.

Figure 6. SEM images of the cross section of the cells by (a) S1 and by (b) S2.
Figure 7. Gas permeability as a function of the number of cycles of deposition-sintering using Sl:YSZ particle having a median particle size of 0.18 μm for various sintering temperatures.

Figure 8. Terminal voltage and power density as a function of current density.
Figure 9. Cell impedance spectra for the electrophoresis cell and the plasma sprayed cell.