Development of Novel Honeycomb SOFCs for Intermediate Temperature Operation

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We have studied the design and fabrication of an innovative cathode-supported honeycomb SOFCs, which can generate high volumetric power density. Among various cell designs, cathode-supported honeycomb SOFCs are suitable for compact SOFC modules operated at intermediate temperature since they have large effective electrode area per unit volume. In this report, we summarized the material system for the honeycomb SOFC, and we selected (LaSr)MnO3 (LSM), Sc2O3-doped zirconia and NiO-Ce0.9Gd0.1O2 (GDC) as cathode, electrolyte and anode materials, respectively. The LSM-supported SOFC with a LSM-GDC activation layer can generate maximum power densities of 47, 79 and 163 mW cm⁻² at 550, 600 and 650 °C, respectively. The results indicate that the honeycomb SOFC with a volumetric electrode area of 40 cm² cm⁻³, which we have successfully fabricated, could generate a volumetric power density of 2 W cm⁻³ at 600 °C.

Key Words: Honeycomb SOFC, Cathode Monolith, Slurry Coating

1 Introduction

Long-term demonstration of cathode-supported solid oxide fuel cell (SOFC) with a tubular design was successfully conducted over 30,000 h by Siemens Westinghouse Power. Durability and reliability of the cell were very high; however, there are only a few reports on reduction of the operation temperature for the cathode-supported SOFCs. Reduction of the SOFC operation temperature can lead to decrease in material degradation and extension of the SOFC lifetime. The use of alternative high performance electrolyte and electrode materials can enhance the cell performance. Additionally, miniaturization of the cell size and integrating a large number of these small-scale cells is considered one of the effective approaches to reduce the SOFC operation temperature. Micro tubular design has been shown to be ideal with regard to several advantages, such as substantial increase in the net electrode area per unit volume and improvement of the thermomechanical properties. And, it is possible to increase the volumetric power density of SOFCs at lower operation temperatures by gaining the large electrode area per volume, even though the power density of the cell tends to decrease at the lower temperature range.

Among the tubular-cells integration designs, honeycomb-supported SOFC is considered to be one of the most suitable designs for simultaneous achievement of miniaturized cell size and integration of the miniaturized cells, because of structural advantages, such as the cumulative capacity of multiple cells and the ease with which the cell size and configuration can be controlled. Thus, our final target is to develop innovative and low-cost fabrication technologies for reliable and high performance cathode-supported SOFCs to be operated at lower temperatures. This report summarizes the characterization and performance of cathode-supported SOFC, which is developed for the application to the cathode-honeycomb-supported SOFCs.

2 Experimental

(La0.9Sr0.1)MnO3 (LSM), Sc2O3-doped ZrO2 (ScSZ) and NiO-Ce0.9Gd0.1O2 (GDC) was selected as a cathode, an electrolyte and an anode, respectively. In order to improve the electrochemical performances at lower temperatures, a LSM-GDC composite was used as an activation layer for the cathode reaction. A mixture of LSM powder, cellulose binder and distilled water was uniaxially extruded through a die with 2 mm outside diameter and 1 mm inside diameter to form a tubular cathode support. The green LSM tube of 25 mm length was dip-coated with the LSM-GDC slurry, and then calcined at 1000°C for 2 h in air. For comparison, LSM tube without the LSM-GDC activation layer was also calcined at 1000°C for 2 h in air. The calcined cathode tubes were coated with ScSZ slurry, and then co-sintered at 1300°C for 2 h in air to form the ScSZ electrolyte film on the tubular support surface. Next, the ScSZ-coated tubes were further dip-coated with a NiO-GDC anode slurry. The coated tubes were then heated again at 1300°C for 2 h in air to obtain complete tubular SOFCs. The slurries were prepared by ball-milling the powders, dispersant, PVB binder and ethanol-based solvent. The cells with and without the LSM-GDC activation layer are denoted as cell A and cell B, respectively.
The microstructures of the cells were observed using FE-SEM (JSM6330F, JEOL). Current-voltage and AC impedance measurements were conducted at 550, 600 and 650 °C using humidified H₂ (3% H₂O) as fuel and O₂ as an oxidant, and were measured using a Solatron 1260 frequency response analyzer with 1296 interface. Ag wires fixed with Ag paste were used for current collection from both the anode and cathode sides. Current collection from the cathode was conducted by winding the Ag wire around the edge of the cathode tube.

3 Results and Discussion

Figure 1 shows a microstructure of the fabricated honeycomb SOFC supported by an extruded LSM monolith. All of channels can be used as single cells, which are connected in parallel through the LSM monolith body, by preparing electrolyte and anode bilayer on the surface of all channels. In this case, fuel and oxidant are supplied through the honeycomb channels and porous monolith body (open porosity: approximately 30 vol%), respectively. Currently, the effective electrode area per unit volume (1 cm³) above 40 cm² cm⁻³ can be achieved by successful preparation of a honeycomb SOFC with a wall thickness of 0.16 mm and a channel diameter of 0.6 mm.¹⁰ By considering the effective electrode area value (40 cm² cm⁻³), the maximum power density of 50 mW cm⁻² is needed to achieve our targeted volumetric power density of 2 W cm⁻³. Thus we aim to investigate material systems for small-scale cathode-supported SOFCs, which can generate a power density above 50 mW cm⁻² at approximately 600 °C.

Figure 2 shows microstructures of the prepared tubular LSM-supported SOFCs with (a) and without (b) the LSM-GDC activation layer. ScSZ electrolyte layer with a film thickness of approximately 20 μm was prepared on the porous tubular supports; LSM-GDC (10 μm)/LSM (400 μm) for cell A and LSM (400 μm) for cell B. Cells A and B have an anode coating layer with a film thickness of approximately 5 μm. The interfaces between each layer were well adhered.

Figure 3 shows the performances of cells A and B at 550, 600 and 650 °C. Compared to Fig. 3(a), the i-V curves of cell B dropped rapidly at low current densities, mainly due to the lack of polarization activity of the LSM cathode and the three phase boundary at the cathode side. On the other hand, application of the LSM-GDC activation layer (cell A) significantly improves the performances, such the rapid potential drop at low current densities, as shown in Fig. 5(a). Figure 4 shows the electrode polarization of cells A and B, which composed of the anode and cathode reaction polarization and the concentration polarization. With increasing current density, the electrode polarization is increased. The electrode polarization of cell A was improved by application of the LSM-GDC activation layer into the interface between LSM/ScSZ compared with that of cell B. At a current density of 0.1 A cm⁻², the electrode polarizations of cells A and B were 0.292 and 0.512 V at 600 °C, and 0.188 and 0.284 V at 650 °C respectively.

The power densities at 0.7 V were 37, 63 and 123 mW cm⁻² for cell A, and 16, 33 and 68 mW cm⁻² for cell B at 550, 600 and 650 °C, respectively, which indicates that cell A can generate approximately twice the power density of cell B. The maximum power densities were 47, 79 and 163 mW cm⁻² for cell A, and 20, 41 and 81 mW cm⁻² for cell B at 550, 600 and 650 °C, respectively. The maximum
power densities from cell A were also approximately twice as high as those from cell B. This improved performance is a direct result from the use of the LSM-GDC activation layer, and these values are promising compared to other reports of cathode supported SOFCs. These values satisfy the targeted power density (50 mW cm\(^{-2}\)) at the targeted operation temperature.

Currently we are trying to apply the LSM-GDC activation layer to the LSM-supported honeycomb SOFCs, and investigating the effects of the composition and microstructure of the activation layer on the performances of small-scale cathode-supported SOFCs.

### 4 Conclusion

In this report, we discussed the electrochemical performances of the small-scale LSM-supported SOFCs in the temperature range from 550 to 650°C. The evaluated cells were prepared by co-sintering technique of tubular LSM support and ScSZ electrolyte film. The cell with the LSM-GDC activation layer between the support and electrolyte can generate peak power densities of 47, 79 and 163 mW cm\(^{-2}\) at 550, 600 and 650°C, respectively. This indicates that the honeycomb SOFC with an effective electrode area of 40 cm\(^2\) cm\(^{-3}\) could generate approximately 2 W cm\(^{-3}\) at 600°C.

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### References