FABRICATION AND CHARACTERIZATION OF SOFC CELLS
WITH ScSZ ELECTROLYTE AND LaNi$_{1-x}$Fe$_x$O$_3$ CATHODE
FOR REDUCED TEMPERATURE OPERATION

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ABSTRACT

For lower-temperature operation of SOFC, scandium stabilized zirconia (ScSZ) and LaNi$_{1-x}$Fe$_x$O$_3$ (LNF; $x = 0.4$) are promising materials for the electrolyte and cathode, respectively. We prepared anode-supporting half-cells by co-firing ScSZ electrolyte and Ni/YSZ cermet. Cathodes were fabricated onto the structures by LNF slurry coating. We confirmed that even thin electrolyte layers between 10 and 30 μm thick were sufficiently dense and gas-tight. We varied cell preparation conditions to investigate the power generation performance at operating temperatures between 900 and 750 °C. The cells fabricated under the optimized conditions showed no significant degradation in the power density characteristics with decreasing operating temperature. The maximum power densities were 0.65 and 0.50 W/cm$^2$ at 900 and 800 °C, respectively.

INTRODUCTION

Low-temperature operation of solid oxide fuel cells (SOFCs) will lead to several benefits. One will be a wider choice of component materials for cell stacking, which will reduce the cost of SOFCs. In addition, improved power generation efficiency is expected by coupling low-temperature SOFCs with conventional ones. In order to reduce the operating temperature, a thin and dense electrolyte with high ionic conductivity is required. Scandia stabilized zirconia (ScSZ) (1) is a well-known electrolyte material with high ionic conductivity. We fabricated a thin ScSZ electrolyte layer, 10—30 μm thick, on a Ni-YSZ anode substrate by co-firing ScSZ and NiO-YSZ green sheets. In addition to an electrolyte with high ionic conductivity, cathode materials having low over-potential at reduced temperature are also required. We have already reported that LaNi$_{1-x}$Fe$_x$O$_3$ (LNF) has high electronic conductivity and low over-potential at 800 °C (2,3). In this work, the capability of reduced-temperature operation is discussed for the anode-supporting cells with a LNF cathode on the bases of investigations of the cells’ structural properties and electrochemical characteristics.

EXPERIMENTAL

The anode-supporting cell was fabricated as follows. Electrolyte and anode sheets were prepared by the doctor blade method from a slurry of 10 mol% Sc$_2$O$_3$ stabilized
ZrO$_2$, and a mixture of 40 wt% YSZ and 60 wt% NiO, respectively. Anode green sheets were laminated until the total thickness reached about 1.4 mm, and finally, an electrolyte sheet 15~30 μm thick was laminated. The laminated green bodies were then cut into 35-mm diameter disks. The disks were fired at temperatures between 1300 °C and 1450 °C for 2 hr after a binder burn-out process. After the co-firing, a LaNi$_{0.6}$Fe$_{0.4}$O$_3$ (LNF) cathode with a 10-mm-diameter circular shape was slurry coated on the anode-supporting structure, which was followed by 800 °C sintering for 24 hr. For comparison, a Pt cathode was also prepared by sintering Pt paste at 1000 °C for 1 hr. A photograph of a typical cell and a schematic drawing of the configuration of the co-fired half-cell are shown in Figs. 1(a) and (b), respectively.

(a)

![ScSZ on Ni-YSZ and LNF](image)

(b)

![Anode 1.4~1.2mm](image)

Fig. 1 Photograph of a typical cell and a schematic illustration of cell shape.

The structural properties and electrochemical performances were investigated mainly by scanning electron microscopy (SEM) and DC polarization measurements at operating temperatures between 900 and 750 °C. The setup for the electrochemical measurements is schematically shown in Fig. 2. 50 ml/min of dry H$_2$ and 100 ml/min of dry air were supplied to the anode and cathode, respectively.

![Experimental setup for the electrochemical measurements](image)

Fig. 2 Experimental setup for the electrochemical measurements.
RESULTS AND DISCUSSION

To fabricate the co-fired anode-supported half-cells, we have to choose a sintering temperature at which the shrinkage difference between anode and electrolyte is minimized. Otherwise, the electrolyte will crack or peel from the anode. We investigated co-firing temperatures ranging from 1300 °C to 1450 °C. Figure 3 shows the relationship between the shrinkage ratio of the sheets as a function of the firing temperature. We prepared approximately 3 cm x 3 cm (= $L_0$) square green sheets and measured the length $L$ for each sheet after firing. The shrinkage is represented by the ratio of $L$ to $L_0$. With increasing temperature, both sheets shrink monotonically. The anode sheet tends to shrink much more than the electrolyte so that shrinkage difference was minimized at around 1400 °C. For all samples co-fired at temperatures higher than 1400 °C, the electrolyte peeled off. However, almost all samples fired at temperatures lower than 1400 °C were successfully fabricated, in spite of the shrinkage mismatch.

![Fig. 3 Relationship between the shrinkage of the sheets and firing temperature](image)

(a) co-fired at 1300 °C  
(b) co-fired at 1400 °C

![Fig. 4 Cross-sectional SEM images of the half-cell samples co-fired at (a) 1300 and (b) 1400 °C](image)
In order to investigate the cell fabrication condition more closely, a cross section of a co-fired cell was observed by SEM. Figure 4 shows the cross-sectional SEM images of half-cell samples co-fired at (a) 1300 and (b) 1400 °C. No remarkable difference was observed between them. The SEM images indicate that the electrolyte layer prepared even at 1300 °C is a continuous, well-sintered structure. Here, it should be noted that the surface of the sample fabricated at 1400 °C seems to be smoother.

Gas-tightness is another important requirement for the electrolyte. Gas-tightness was evaluated by measuring the open circuit voltage (OCV) of half-cells sintered at 1300, 1350, and 1400 °C. Figure 5 shows the OCV dependence on the sintering temperature. OCV was measured at operating temperatures of 850 °C, 800 °C, and 750 °C. These data imply that the electrolyte becomes denser and well-sintered with increasing co-firing temperature. This tendency can be explained by the fact that shrinkage mismatch between the electrolyte and anode sheets becomes smaller as the firing temperature approaches 1400 °C.

We also examined the power generation characteristics for the samples co-fired at 1300 °C, 1350 °C, and 1400 °C as shown in Fig. 6. Although the best OCV was obtained for the sample prepared at 1400 °C, overall the power generation characteristics became worse as the firing temperature increased. The reason for this is not clear at this stage, although it might be that the adhesion between the electrolyte and LNF cathode becomes weak, or that the three-phase-boundary length decreases, since the electrolyte surface becomes smoother as the firing temperature increases. Therefore, the co-firing temperature of the half-cells used for the I-V characteristics measurement was fixed at 1300 °C, although the open circuit voltage was slightly lower than the theoretical value due to a small amount of gas leakage through electrolyte.

![Fig. 5 OCV dependence on the firing temperature measured at operating temperatures of 850, 800, and 750 °C.](image1)

![Fig. 6 Relationship between current density and over-potential for co-fired cells prepared at 1300, 1350, and 1400 °C. Over-potential was measured at 800 °C by the current interruption method.](image2)
The I-V characteristics of a co-fired cell with about 10-μm-thick electrolyte are shown in Fig. 7. For comparison, the results for the cell with the Pt cathode measured at 1000 °C are also plotted (the dotted lines). The cells with the LNF cathode showed no significant degradation in the power density characteristics with decreasing operating temperature. The maximum power densities were 0.65 and 0.50 W/cm² at 900 and 800 °C, respectively. This indicates that the performance of the cell at low operating temperature was comparable to that of the cell with Pt cathode measured at 1000 °C. Even at an operating temperature as low as 750 °C, the maximum power density was still about 0.37 W/cm².

Fig. 7  Relationships between current density and cell voltage (a), and between current density and power density measured at 900, 800, and 750 °C. The thickness of the electrolyte was about 10 μm.

For comparison, the results of the cell with the Pt cathode measured at 1000 °C are also shown (dotted lines).

CONCLUSIONS

Lower-temperature-operation characteristics of anode-supported SOFCs using Sc₂O₃-ZrO₂ (ScSZ) electrolyte and a LaNi₁₋ₓFeₓO₃ (LNF; x = 0.4) cathode were investigated. ScSZ electrolyte and Ni/YSZ cermet were co-fired to make anode-supported half-cells with 10 — 30-μm-thick compact electrolyte. The SOFC showed maximum power densities of 0.65 and 0.50 W/cm² at 900 °C and 800 °C, respectively. These results suggest that SOFCs using LNF and ScSZ are promising for low-temperature operation.

REFERENCES

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