HIGH PERFORMANCE CELL DEVELOPMENT USING SCANDIA DOPED ZIRCONIA ELECTROLYTE FOR LOW TEMPERATURE OPERATING SOFCs

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ABSTRACT

The Sc$_2$O$_3$-ZrO$_2$ system, which has higher electrical conductivity compared to the Y$_2$O$_3$-ZrO$_2$ system, was examined for electrolyte component of the planar type SOFC. For low temperature operation, the effect of cathode material and Sc$_2$O$_3$ dopant concentration in electrolyte were investigated; maximum power density of 0.6 W/cm$^2$ was obtained for electrolyte-supported cells using humidified H$_2$ as fuel and air as oxidant at 800°C. Furthermore, the maximum power density of 2.4 W/cm$^2$ was obtained for anode-supported cells in humidified H$_2$ as fuel and O$_2$ as oxidant at 800°C.

INTRODUCTION

Toho Gas has investigated scandia-stabilized zirconia (ScSZ) system for the electrolyte and electrode in planar SOFCs. The conductivity of ScSZ is higher than that of conventionally used yttria-stabilized zirconia (YSZ), therefore ScSZ system is expected to improve the power density and reduce the operating temperature (1-6). We have previously reported that tetragonal ScSZ with a lower Sc$_2$O$_3$ dopant concentration has better electrical and mechanical properties than the tetragonal YSZ (7,8); it has exhibited improved electrolytic performance and mechanical reliability when used in SOFCs.

From the viewpoint of cost reduction and long term durability, the operation of SOFCs at a lower temperature is very attractive. To operate at a lower temperature, SOFC should have the following properties; [1] an electrode material with higher activity compared to conventional material, [2] an electrolyte with high electrical conductivity, and [3] thin electrolyte with high mechanical reliability. In order to examine these subjects, [1] we changed the cathode composition from La$_{0.8}$Sr$_{0.2}$MnO$_3$ (LSM) to La$_{0.8}$Sr$_{0.2}$Co$_{0.2}$Fe$_{0.8}$O$_3$. 

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(LSCF) (9); [2] increased the amount of Sc$_2$O$_3$ dopant from 4 mol% to 6 mol% (7,8); and [3] changed the cell structure from electrolyte-supported to anode-supported (2,9-12).

EXPERIMENTAL

The ScSZ powder for electrolyte material was obtained by a co-precipitation process of Daiichi Kigenso Kagaku Kogyo Co., Ltd. (DKKK). Anode materials were NiO (Nacalai-Tesque Inc.) - ScSZ (DKKK) cermets. NiO and ScSZ were mixed with ethanol for 24 hours using ball milling process and then dried to obtain the predetermined mass ratio (Ni : YSZ = 4 : 6). Cathode materials were composites of LSM (Seimi Chemical Co.) or LSCF (Seimi Chemical Co.) and YSZ (Tohos Co.) or SDC (DKKK). These materials were mixed with polymer binder to obtain the predetermined mass ratio (LSM or LSCF : YSZ or SDC = 8 : 2).

Electrolyte Supported Cells

A schematic diagram of an electrolyte-supported cell tested in this report is shown in Fig. 1 (A). The ScSZ electrolytes were obtained by tape casting method. The thickness of the electrolyte was 100~140 µm. The electrode materials were screen-printed using polymer binder on electrolyte plates, and then fired at 1350°C for anodes and 1150°C for LSM (or 850°C for LSCF) cathodes. The electrode surface area for the test cell was 16 cm$^2$. Fig. 2 shows the schematic diagram of the cell test set-up. In this test, an Al$_2$O$_3$ gas manifold and current collector of Pt-mesh were used to measure the mean cell performance. The cell test was conducted at 800 (~950) °C; 3 % humidified hydrogen gas and air were supplied to anode and cathode compartments, respectively. The flow rates in both compartments were set at 1 L/min.

Figure 1. Schematic diagram of electrolyte-supported cell and anode-supported cell used for this experiment.
Anode Supported Cells

A schematic diagram of anode-supported cell tested in this experiment is shown in Fig. 1 (B). The green sheets for anode substrate, and also the film used for electrolyte, were obtained by tape casting method. The thickness of the anode and electrolyte were approximately 300 and 20 μm, respectively. The anode substrate and electrolyte film were pasted in a cold press, and then co-sintered at 1300°C. The cathode materials were screen printed on electrolyte using polymer binder and then fired at 1150°C for LSM, or 850°C for LSCF cathodes. The cathode surface area for the tested cell was 0.2 cm². The cell test was conducted at 800°C, and 3% humidified hydrogen gas and oxygen were supplied to anode and cathode compartments, respectively. The flow rates in both compartments were set at 0.1 L/min.

RESULTS AND DISCUSSION

The Effect of Cathode Material on Cell Performance

Fig. 3 shows the characteristics of current density $i$ versus voltage $V$, and $i$ versus power density $P$ for electrolyte-supported cells developed for high temperature operation(13), which use 140 μm 4ScSZ electrolyte and LSM cathode. At 950°C, maximum power density approaches approximately 1.0 W/cm², which implies good power generation characteristics. However, when the temperature is reduced to 800°C, the maximum power density decreases to 0.4 W/cm², because [1] the activity of LSM cathode decreases, and [2] the electrolyte resistance increases rapidly.

First, we changed the cathode from LSM to LSCF for operation at 800°C, as shown in Fig. 4. When the cell used LSCF cathode, power density was approximately 0.6 W/cm² at 0.6 V. The value of area specific resistance (ASR) calculated by $i$-V curve, was 0.49 Ωcm² and 0.63 Ωcm² for LSCF and LSM cells, respectively. To confirm the effect of the cathode material change on cell performance, cathode overvoltage for each cell was
measured by AC impedance method. The value of overvoltage for the LSCF cathode is lower than that for LSM cathode, meaning the application of LSCF cathode to 4ScSZ electrolyte cell is effective for low temperature operation, as reported also for the YSZ electrolyte system.

The Effect of SciQi Dopant Concentration on Cell Performance

Second, we changed the Sc$_2$O$_3$ dopant concentration. Fig. 5 shows X-ray diffraction pattern for the tetragonal ScSZ with Sc$_2$O$_3$ dopant concentration of 4-7 mol% (7). All crystals had a tetragonal or cubic phase, and showed no monoclinic phase. The bending strength measured by the three-point bending at room temperature using rectangular bar

Figure 3. \(i-V\) and \(i-P\) characteristics of the experimental cell with changing operating temperatures.

Figure 4. Effect of cathode on \(i-V\) and \(i-P\) characteristics of test cell.
specimens of 3 mm x 4 mm x 40 mm (in compliance with JIS R1601) as well as the electrical conductivity measured at 1000°C is shown in Fig. 6 (7,8). 3-4ScSZ shows the highest bending strength, because it had almost 100% tetragonal phase. With increasing Sc$_2$O$_3$ dopant concentration, the bending strength decreased. On the other hand, the electrical conductivity increases with increasing Sc$_2$O$_3$ dopant concentration. These results suggest that the cubic phase increases together with the Sc$_2$O$_3$ dopant concentration. To reduce the operating temperature, the conductivity needs to be higher than that of 4ScSZ, whereas to maintain reliability of the cell, the high value of bending strength is required. In considering the above result, a Sc$_2$O$_3$ dopant concentration at 6 mol% seems to be appropriate in this system. Fig. 7 shows electrical conductivity for 4ScSZ and 6ScSZ as a function of temperature. The 6ScSZ had the conductivity twice as high as the 4ScSZ, it was also flexible enough to be bent by hand: we expect it to deliver high electrolyte performance at lower operating temperatures.

Figure 5. X-ray pattern of tetragonal ScSZ with different Sc$_2$O$_3$ dopant concentration.

Figure 6. Change of electrical conductivity and bending strength against Sc$_2$O$_3$ concentration.
Figure 7. Temperature dependence of Electrical conductivity for 4ScSZ and 6ScSZ.

Fig. 8 shows $i-V$ and $i-P$ characteristics for 4ScSZ and 6ScSZ at 800°C, using thick 140 μm electrolytes and LSM cathode, respectively. For the cell using 6ScSZ electrolyte, power density is approximately 0.6 W/cm$^2$ at 0.6 V. The value of area specific resistance calculated by $i-V$ curve, is 0.48 Ωcm$^2$ which is 75% lower than in 4ScSZ. In this study, the application of LSCF cathode to 6ScSZ electrolyte was examined, but the cell performance was less than that for the cell using LSM cathode. This result does not agree with the results for 4ScSZ electrolyte. We assume this results from a reaction between LSCF and cubic zirconia (contained in 6ScSZ electrolyte). Furthermore, higher performance is expected for 6ScSZ if the cathode materials are improved.

Figure 8. Effect of ScSZ dopant concentration on $i-V$ and $i-P$ characteristics of the experimental cell.
The Cell Performance for Anode Supported Cells

Fig. 9 shows $i-V$ and $i-P$ characteristics for anode supported cells at 800 °C, using LSM LSCF cathodes. For the cell with LSM, the maximum power density is approximately 1.5 W/cm$^2$ (4 times as high as that for the 4ScSZ / LSM electrolyte supported cell). Because the IR drop is decreased since the electrolyte is 11ScSZ (with 3 times conductivity as high as that for 4ScSZ, and 1/7 as thick as in conventional electrolyte supported cells). On the other hand, the power density approaches 2.4 W/cm$^2$ for the cell using LSCF (since cathode activation is increased). However, LSCF affects cubic zirconia negatively, so the LSCF cell is unstable in the long term operation. This result is compatible with the result of 6ScSZ electrolyte. Inserting an interlayer between ScSZ electrolyte and LSCF cathode is necessary to maintain high performance in the long term operation.

![Figure 9. Effect of cathode on $i-V$ and $i-P$ characteristics of anode-supported cell.](image)

CONCLUSIONS

Development of SOFC using ScSZ for low temperature operation can be summarized as follows:

1. The LSCF cathode is more active than the LSM cathode at 800°C for 4ScSZ electrolyte. The maximum power density obtained is 0.6 W/cm$^2$.

2. Changing Sc$_2$O$_3$ dopant concentration from 4 mol% to 6 mol% allows the conductivity to increase twice, and the power density obtained is 0.6 W/cm$^2$ at 800°C for the cell using LSM cathode.

3. For anode supported cell using LSCF cathode, we achieved 2.4 W/cm$^2$ at 800 °C.
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