INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS WITH DOPED LANTHANUM GALLATE ELECTROLYTE, La(Sr)CoO$_3$ CATHODE, AND Ni-SDC CERMET ANODE

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ABSTRACT

The intermediate temperature SOFC with La$_{0.5}$Sr$_{0.5}$Ga$_{0.8}$Mg$_{0.2}$O$_{3.85}$ electrolyte (thickness: 0.5 mm), La$_{0.5}$Sr$_{0.5}$CoO$_3$ cathode, and Ni-(CeO$_2$)$_{0.8}$(SmO$_2$)$_{0.2}$ cermet anode showed a fairly good initial performance. Spray pyrolysis technique was used to synthesize the electrode materials and the optimization of the sintering temperature gave the lowest polarization of less than 30 mV (300 mA/cm$^2$) for both the anode and the cathode. Moreover, about 50% Ni content in Ni-SDC cermet anode was found to make the anodic polarization the lowest. The high maximum power density of 0.51 W/cm$^2$ at 800°C was better than those for the conventional SOFC with yttria-stabilized zirconia (YSZ) electrolyte, Ni-YSZ cermet anode, and La(Sr)MnO$_3$-YSZ cathode at 1000°C. Long term cell test at 800°C with 300 mA/cm$^2$ showed a cathodic polarization increase with operation time. Calcination of LSCo powder prior to sintering onto the electrolyte was effective to improve the stability of the cell.

INTRODUCTION

Solid oxide fuel cell (SOFC) is one of the most attractive power generation systems, because of its high efficiency, low pollution, and fuel flexibility. A conventional SOFC is usually operated at high temperatures near 1000°C, which causes serious problems concerning materials. To overcome these problems, it is desirable to operate SOFC at temperatures below 800°C. To develop a practical intermediate temperature SOFC, two approaches are under active consideration. One is to use an extremely thin YSZ membrane to make the ohmic loss due to the electrolyte as small as possible. Another is to use a new electrolyte material that shows an excellent oxide ion conductivity at temperatures below 800°C, comparable to that of YSZ at 1000°C. It has been reported recently (1-3) that doped lanthanum gallate, La(Sr)Ga(Mg)O$_4$ (LSGM) possesses oxide ion conductivity high enough to be used as an electrolyte at intermediate temperature over a broad range of oxygen partial pressures. Its conductivity at 800°C is about the same as that of YSZ at 1000°C. Therefore, LSGM is considered to be a strong candidate for the electrolyte of an intermediate temperature SOFC.

Since lowering the operation temperature increases not only the ohmic loss but also the polarization loss at the anode and the cathode, it is necessary to develop highly active...
electrodes that show sufficiently low polarization at intermediate temperatures. Hence, developing highly active electrodes that are compatible with LSGM electrolyte is important. The performances of Ni and yttria-stabilized zirconia (YSZ) cermet anode(4,5), and La(Sr)MnO₃-YSZ composite cathode(6,7) prepared from powders showed the importance of microstructure control for high temperature SOFCs. In both cases, composite electrodes were prepared from particles produced by spray pyrolysis, and control of the microstructure was carried out by the electrode sintering temperature.

In this study, we applied spray pyrolysis technique to obtain highly dispersed composite particles and controlled the electrode microstructures by changing the sintering temperature. Ni-(CeO₂)₀·₈(SmO₁·₅)₀·₂ (SDC) cermet was chosen as the anode material, because the high mixed ionic and electronic conductivity of SDC was expected to enlarge the reaction area to include the entire particle surface beyond the boundary zone of the anode and the electrolyte. The chemical composition of (CeO₂)₀·₈(SmO₁·₅)₀·₂ was chosen in this study, because it displays the highest ionic conductivity among the rare-earth oxide doped ceria compounds(8-10). On the other hand, La(Sr)CoO₃ was used as the cathode material, because it also possesses mixed oxide ionic and electronic conductivity(11-15). The initial cell performance and the long term stability were investigated.

EXPERIMENTAL

Preparation of LSGM Electrolyte

LSGM with the composition of La₀·₈Sr₀·₁Ga₀·₈Mg₀·₂O₃·₈₅ was prepared with the solid state reaction method(16). The starting materials were La₂O₃, SrCO₃, Ga₂O₃, and MgO. The ball-milled powder mixtures of the starting materials were calcined in air at 1150°C for 10 h. The calcined powder, uniaxially pressed into pellets at a pressure of 49 MPa, followed by isostatic pressing at 294 MPa, was sintered in air at 1500°C for 10 h. The densities of the sintered materials were measured using the Archimedes method. The relative density was about 98%. Powder X-ray diffraction was measured with pulverized sintered materials to confirm their perovskite structure.

Preparation of NiO-SDC Composite Powder and LSCo Powder by Spray Pyrolysis

NiO-SDC composite powders with different NiO contents were synthesized by spray pyrolysis technique, which was similar to that used in a previous study(6). Aqueous solutions containing different compositions of corresponding cations were prepared by dissolving Ni(CH₃COO)₂•4H₂O, Ce(NO₃)₃•7·5H₂O, and Sm₂O₃. These solutions were atomized with an ultrasonic vibrator operating at 1·7 MHz. The droplets were transported into a reaction furnace using air as a carrier gas with a fixed flow rate of 3 L/min. The reaction furnace consisted of four independent heating zones, of which temperatures were set at 200, 400, 800, and 1000°C, respectively. The particles were collected using an electrostatic precipitator, and were calcined at 1000°C for 24 h. The compositions of synthesized powders were evaluated by X-ray fluorescence analysis.

Starting powders for the cathode, which had compositions of La₀·₆Sr₀·₄CoO₃ (LSCo) and La₀·₆Sr₀·₄CoO₃ (LSCO10) were also synthesized by spray pyrolysis. An aqueous nitric acid solution containing La₂O₃, SrCO₃, and Co₂O₃, with the concentration of 0·1 mol/L, as the composition of LSCO, was used similar to the case of NiO-SDC composite powder preparation. The compositions of synthesized powders were evaluated by X-ray fluorescence analysis.

Single SOFC Tests

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NiO-SDC composite powders were deposited by the screen printing technique onto LSGM pellets. LSGM pellets with 13 mm diameter and 0.5 mm thickness were used for polarization measurements, and the pellets with 32 mm diameter and 0.5 mm thickness were used for other experiments. The green anode was sintered at different temperatures of 1200, 1250, 1300, and 1350°C for 2 h. NiO in the anode was reduced to Ni under fuel atmosphere. LSCo cathode was screen printed and sintered on the opposite side of the LSGM pellet. The cells were sintered at different temperatures of 950, 1000, 1050, and 1200°C for 4 h. The effective electrode area was 0.785 cm² for electrode polarization measurements, and 2 cm² for the other tests. Pt wires, wound around the LSGM pellet and fixed with platinum paste, were used as a reference. The single cell tests were carried out at 800°C. Air was used as an oxidant, and 3 % moisturized hydrogen gas (H₂ + 3% H₂O) was used as fuel. For the electrochemical characterization, the current-interruption technique was used to measure iR free polarization loss. After the cell tests, the microstructures were observed by scanning electron microscopy (SEM, Hitachi S-800).

RESULTS AND DISCUSSION

Initial Performance of Single Cells

Fig. 1 shows the anodic polarization (iR-free) measured at 800°C with 300 mA/cm² as a function of sintering temperature. Clearly, the anodic performance is dependent on the sintering temperature in the range of 1200°C to 1350°C. The lowest anodic polarization of about 27 mV at 300 mA/cm² was obtained for the anode sintered at 1300°C. The microstructure of the anode sintered at 1300°C is considered to have Ni grain skeleton with well-connected SDC grains finely dispersed over the Ni grain surfaces (Fig. 2). This microstructure seems to result from the use of the NiO-SDC composite powder, because it is strongly influenced by the starting powder characteristics.

![Fig. 1. Anodic polarization vs. current density as a function of sintering temperature.](image-url)

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Fig. 2. Microstructure of the Ni-SDC cermet anode sintered at 1300°C.

Fig. 3. Anodic polarization vs. Ni content in Ni-SDC cermet.

Fig. 3 shows the dependence of anodic polarization on Ni content in Ni-SDC, using Ni-SDC sintered at 1250°C for current density of 300 mA/cm². The best results were obtained for the anode with Ni content of around 50 vol.%. The microstructure of the anode is considered to have good connection between Ni-Ni, SDC-SDC, and Ni-SDC grains, so that the number of active sites at the boundary between Ni, SDC, and H₂ gas increases.
Fig. 4. Cathodic polarization vs. current density as a function of sintering temperature.

Fig. 4 shows the cathodic polarization (iR-free) measured at 800°C with 300 mA/cm² as a function of sintering temperature. Similar to the case of the anode, the cathodic performance is dependent on the sintering temperature in the range of 950 to 1200°C. The lowest cathodic polarization of 24 mV at 300 mA/cm² was obtained for the cathode sintered at 1000°C. The cathode sintered at 1000°C consisted of well-bonded particles. Each agglomerated particle is an aggregate of small particles (Fig. 5). Well-connected agglomerates allow utilization of a large surface area of the porous electrode for reduction.
of O₂ to O²⁻, and therefore measured cathodic polarization was very low.

Selecting 1300°C as the sintering temperature for the anode and 1000°C for the cathode, we constructed a single SOFC. The electrode area was 2 cm² in this case. Ni content in Ni-SDC was 48%. Fig. 6 shows the I-V and I-P curves. The maximum power density was 0.51 W/cm², which was a good initial performance for a 0.5 mm thick electrolyte at 800°C. This result is better than the cell using YSZ as an electrolyte, Ni-YSZ cermet as an anode, and La(Sr)MnO₃-YSZ composite as a cathode, whose performance was reported to be 0.37 W/cm² at 1000°C with the microstructure-optimized electrodes(17).

**Long Term Stability**

After we obtained the good initial property of intermediate temperature SOFC with microstructures-optimized electrodes for LSGM electrolyte, life time cell tests were performed to evaluate the compatibility of the electrodes with respect to LSGM electrolyte. Fig. 7 shows the time dependence of the electrode polarizations for a single cell test at 800°C with 300 mA/cm². The anodic polarization was stable during the course of the operation. This is probably due to the microstructure with a few small SDC grains dispersed on the surface of the Ni grains, which prevents Ni grains from sintering and making contact directly with LSGM electrolyte. In contrast, the cathodic polarization rapidly increased with time. After about 300 h of operation, the cathodic polarization was more than five times higher that initial performance. The deterioration of the cell performance is considered to be mainly due to the increase of the cathodic polarization.
LSCO powder prepared by spray pyrolysis method was not calcined in order to prevent the grain growth before sintering onto the electrolyte. Since the omission of calcination might have given rise to the deterioration of the cell performance, possibly due to some diffusion at the cathode and electrolyte interface, LSCO powder was calcined in air at 1000°C for 4 h prior to the sintering. From XRD patterns, the calcination appeared to promote the crystal growth of LSCO. The microstructures of the uncalcined and calcined powders are shown in Fig. 8. The spherical shape of LSCO powder changed to a rather rugged shape by calcination, which indicated sintering and crystal growth in progress.

Fig. 7. Anodic and cathodic polarization during the long term stability test.

Fig. 8. Microstructures of (a) uncalcined and (b) calcined LSCO powders.
Fig. 9. Operation time dependence of the cathodic polarization of the single cell using calcined and uncalcined LSCo powder at 800°C with 300 mA/cm².

For the cathode prepared using the calcined LSCo powder, life time cell testing was performed at 800°C and the current density of 300 mA/cm². Fig. 9 shows the time dependence of the cathodic polarization for a single cell. It is clearly shown that the

Fig. 10. Operation time dependence of the cathodic polarization of the single cell using calcined La₁₋ₓSr₉CO₃ powders at 800°C with 300 mA/cm².
increase in cathodic polarization with the calcined LSCo powder was much slower. The cathodic polarization at about 300 h operation with 300 mA/cm² using calcined LSCo powder was 50 mV, which was 110 mV lower than the case of uncalcined cell.

After obtaining the improved result mentioned above, the effect of the La/Sr ratio of A site cations in perovskite type LSCo was investigated using calcined LSCo powders. The difference of the La/Sr ratio across the interface of cathode and electrolyte could also bring interface diffusion of the elements. The result obtained using LSCo10 instead of using LSCo, however, showed that there was not a clear effect (Fig. 10). This indicates that La/Sr ratio is not a dominant factor in the cathodic polarization increase.

The variation of the cell voltage using calcined LSCo powder at the current density of 300 mA/cm² is shown in Fig. 11. The cell voltage degradation rate was about 3%/1000h. The long term stability was extensively improved compared with the cell using uncalcined LSCo (the degradation rate: about 36%/1000h). Further investigation is needed to enhance the stability and the power density.

CONCLUSIONS

The intermediate temperature SOFC with La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₂.₈₅ electrolyte (thickness: 0.5 mm), La₀.₆Sr₀.₄CoO₃ cathode, and Ni-(CeO₂)₀.₈(SmOₓ)₀.₂ cermet anode showed a fairly good initial performance. Spray pyrolysis technique was used to synthesize the electrode materials and the optimization of the sintering temperature gave the lowest polarization of 27 mV for the anode and 24 mV for the cathode with 300 mA/cm². Moreover, about 50% Ni content in Ni-SDC cermet anode was found to make the anodic polarization the lowest. The high maximum power density of 0.51 W/cm² at 800°C was better than those for the conventional SOFC with yttria-stabilized zirconia (YSZ) electrolyte, Ni-YSZ cermet anode, and La(Sr)MnO₃-YSZ cathode at 1000°C. Long term cell test at 800°C with 0.3 A/cm² showed that the cathodic polarization increased with operation time. Calcination of LSCo powder prior to the sintering onto the electrolyte was effective to improve the stability of the cell.
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