INFLUENCE OF COMPOSITION/MICROSTRUCTURE OF COMPOSITE CATHODE ON ELECTRICAL PERFORMANCE OF ANODE-SUPPORTED SOLID OXIDE FUEL CELLS

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ABSTRACT

The electrical performance of anode-supported 5 x 5 cm² single cells with LSM+YSZ/LSCo composite cathode was measured at 750°C using hydrogen as a fuel. The maximum power density in this work was 360 mW/cm² at 750°C with a composite cathode of La0.78Sr0.22Mn1.2O3+δ/YSZ(6/4)/La0.6Sr0.4CoO3. In the case of addition of stoichiometric LSM where Mn was not present in excess, the cell performance with LSM calcined at 800°C was higher than with LSM calcined at 1000°C. In the case of composite cathode using LSM with an excess amount of Mn, cell performance had a maximum value when using LSM calcined at 1000°C. Also LSM+YSZ/ LSCo composite cathodes showed lower cathodic overpotential than those without LSCo. The results indicate that the LSCo current collecting layer improves performance of LSM+YSZ composite cathode although LSCo slightly reacts with YSZ. It seems that the excess amount of Mn decreases electrode resistance and cathodic overpotential by reducing the reaction of LSCo with YSZ and improving the ionic conductivity of LSCo.

INTRODUCTION

Since the efficiency of SOFCs depends significantly on the ionic conductivity of the electrolyte component, thin electrolyte (anode-supported) solid oxide fuel cells are expected to show relatively higher performance at a lower operating temperature (below 800°C) (1). In the planar-type solid oxide fuel cells, the benefit of lowering operating temperature for SOFC stacks is an increase in the possibility of practical application of SOFC power generation system. Also the production cost of an anode-supported SOFCs system is lowered because of less expensive interconnecting materials, and sufficient endurance of the stack is guaranteed at reduced temperature because the component materials of SOFC single cells would be thermodynamically more stable.

The electrical performance of anode-supported single cells depends on processing variables such as microstructure and composition of electrolyte and electrodes. In YSZ-thin-electrolyte SOFCs, cathode material is usually a mixture of strontium-doped lanthanum manganite (LSM) and yttria-stabilized zirconia (YSZ) (2,3). However the LSM+YSZ cathode is known to have a high value of cathodic overpotential for use in the intermediate temperature range due to smaller values for the ionic conductivity and oxygen surface exchange coefficient (4,5). Alternatively, LSCo which has been
known for high performance cathode at intermediate temperature precludes co-firing with YSZ electrolytes (7). The present work investigated the influence of a composite cathode consisting of LSM+YSZ/LSCO on the electrical performance in thin zirconia-electrolyte single cells. The composite cathodes were prepared by screen-printing LSM+YSZ paste and fired at 1100°C for 2 hours, and thereafter LSCO current collecting layer was screen-printed and dried on the surface of LSM+YSZ cathode. The measurements of cell performance at different composition and microstructure of LSM+YSZ cathode materials were conducted at 750°C from anode-supported 5 × 5 cm² SOFC single cells fabricated by the slurry coating method. The microstructure was examined and the performance of cathode was studied by means of I-V characteristics and the current interrupt technique.

EXPERIMENTAL

Fabrication of Cells

For anode substrates, nickel oxide powder and yttria-stabilized zirconia powder (ZrO₂+8Y₂O₃, 8YSZ) were primarily mixed and milled together at a weight ratio of 50:50, thus preparing a powder mixture. Then 24 vol% graphite powder as a pore-former and organic binder were mixed in the powder mixture with ethylalcohol, and the mixture was dried in an oven to form a starting material. The NiO+8YSZ powder mixture was compacted by a rectangular steel mold and pre-sintered at 1400°C for an hour to prepare a pre-sintered anode substrate. A porous anode substrate, or a fuel electrode having a porosity of 40%, was then produced. The size of this porous anode substrate was about 6 × 6 cm², with a thickness of 2 mm. Thereafter 8YSZ was coated on the substrate by slurry coating and sintered at 1500°C for 2 hours to make a dense electrolyte layer with a thickness of about 20 μm. The cell size was reduced after this to 5 × 5 cm² and the thickness of the cell substrate was about 1.8 mm. The electrolyte layer was created on top of the substrate and on the edge in all four directions to prevent gas leakage from the porous substrate layer. On the surface of the electrolyte (8YSZ) layer, the paste mixtures of LSM (La₀.₇₈Sr₀.₂₂MnxO₃, x=1.0 and 1.2) and 8YSZ (raw or calcined at 1400°C) with a weight ratio of 70:30, 60:40, and 50:50, respectively, were printed for a thickness of 40 μm and heat-treated at 1100°C for 2 hours, thus producing an anode-supported single cell with an activate cathode area of 4 × 3.3 cm² and a Pt reference electrode area of 4 × 0.4 cm² with a distance between each other of 0.3 cm as shown in Fig. 1.

Measurement of Cell Performance

LSM or LSCO raw materials were synthesized by the citrate method using a citric acid to metallic nitrate ratio of 1.5. The LSCO powder was calcined at 1100°C for 8 hours. As shown Table 1, LSM powder was also calcined at 800°C for an hour and 1000°C for 8 hours. X-ray diffraction patterns were analyzed to confirm that the powder consisted of the single LaSrCoO₃ or LaSrMnO₃ perovskite phase (Fig. 5). Each anode-supported single cell with composite cathode ((LSM+YSZ)/LSCO) was prepared by printing LSCO paste on top of the fired LSM+YSZ cathode surface. After drying the paste, each single cell was installed into an Inconel cell holder (hosing) without platinum paste. In the anode side Ni mesh was used to measure cell voltage and in the cathode side Pt mesh of the same area as cathode to measure cell voltage. All the single cells with different composition cathode were tested at 750°C under the same operating condition. The gas was supplied to electrodes from channels in the
Inconel cell holder, and the flow rates were controlled by mass flow controllers. The anode was fed with hydrogen of 150 sccm and steam of 3% humidity (vapor pressure at room temperature), and in the cathode side air was supplied at 600 sccm. During the operation, cell voltage between anode (or the reference electrode) and cathode was measured and recorded with a digital multimeter. Current-voltage characteristics were measured by adjusting current in an electronic loader connected into each side of the Inconel holder. The current interrupt technique was used to measure cell resistance and overpotentials recorded in a digital oscilloscope.

RESULTS AND DISCUSSION

Most fabricated single cells had a defect of slightly convex camber because the shrinkage of 8YSZ electrolyte is smaller than that of anode substrate in the final sintering stage, before the LSM+YSZ cathode was printed, when NiO+YSZ anode substrate and thin 8YSZ electrolyte were co-fired. Final sintering temperature must be adjusted to minimize the difference of the shrinkage of electrolyte and anode substrate depending on cell size. Defects in the anode side can be easily removed by grinding and polishing, but the camber of the cathode side causes a degradation of cell performance by incomplete contact between electrode and interconnector. Therefore the current collecting layer is needed to allow for better contact between cathode and interconnector (or Pt mesh). We did not use Pt paste as the current collecting layer because it is not used in practical application of SOFCs. LaSrCoO₃ perovskite materials are known as good cathode conductors (4,5,7), and therefore La₆Sr₄CoO₃ (LSCO) paste was screen-printed with a thickness of 120 μm as a current collecting layer before measuring the cell.

Fig. 2(a) shows the I-V and I-P curves obtained from 5 × 5 cm² anode-supported single cells with different cathode composites. In the case of La₀.₇₈Sr₀.₂₂Mn₁.₂O₃⁺8YSZ(6:4)/La₀.₆Sr₄CoO₃ noted by HL12Z4C, the maximum power density is 360 mW/cm² at 750°C with 150 sccm H₂ as a fuel and 600 sccm air as an oxidant. As shown in Fig. 2(b) the cathodic overpotential of La₀.₇₈Sr₀.₂₂Mn₁.₂O₃⁺8YSZ(6:4) is relatively lower than the others. Since all the conditions except the cathode materials were identical during the cell measurement, cell performance should depend on only cathodic overpotential of LSM+YSZ/LSCO composite in each cell. When Pt paste or LSCO was not used, cathodic overpotential was higher than others as shown in Fig. 2(b). Poor contact at the cathode surface may be a reason that LSM+YSZ cathode without LSCO paste (open symbols in Fig 2(b)) shows a higher value of cathodic overpotential. Addition of the LSCO current collecting layer improves cathodic performance or electrical contact of LSM+YSZ cathode. From Fig. 2, the cell with Mn-excess LSM calcined at high temperature (1000°C) shows a good performance of 360 mW/cm² while the same cell calcined at low temperature (800°C) shows a performance of 180 mW/cm². On the other hand, the cell without an excessive amount of Mn in LSM calcined at high temperature (1000°C) shows a performance of 180 mW/cm² and the same cell calcined at low temperature (800°C) shows 280 mW/cm². We can infer from these results that cathodic overpotential of fine-grained LSM+YSZ/LSCO composite cathode is lower than that of coarse-grained cathode, which has been already known (2,3). With an excess amount of Mn in the LSM+YSZ/LSCO composite cathode, however, coarse-grained LSM calcined at high temperature shows lower cathodic overpotential than that of LSM calcined at low temperature. Note that the maximum power density is reasonably high (360 mW/cm²) in the case of HL12Z4C as shown in Fig. 2(a). It is believed that the
excess Mn influences the cathodic overpotential in SOFCs with LSCo composite cathode because it lowers overpotential by reaction with LSCo in cathode.

Fig. 3 shows ohmic and non-ohmic losses of anode-supported single cells in the case of La_{0.78}Sr_{0.22}Mn_{1.2}O_3+8YSZ(6:4)/La_{0.8}Sr_{0.2}CoO_3 (HL12Z4C). The total cell resistance was calculated from ohmic loss (IR) by the current interrupt technique and YSZ IR drop estimated from a conductivity value of 20 μm 8% YSZ. The total ohmic loss of this cell was 0.31 Ω cm² including the resistance of YSZ electrolyte of 0.1 Ω cm² (6). As shown in Fig. 3, in anode-supported SOFCs the loss of cell voltage is mainly related to not only the ohmic loss but also to cathodic overpotential (η_c). For comparison, L10Z4C shows higher internal resistance of 0.34 Ω cm², and the increase of 0.03 Ω cm² is probably related with cathode electrical resistance. The higher electrical resistance of composite cathode leads to higher cathodic overpotential resulting in lower cell performance compared to those of HL12Z4C (Fig. 2(a)).

Fig. 4 shows I-V and I-P characteristics with some LSM+YSZ/LSCo composite cathode with excess Mn in LSM calcined at 1000°C. It has been known that cathodic overpotential of LSM+YSZ composite electrode is closely related to the connectivity of LSM+YSZ particles to each other and depends on their size ratio (2,3). Because the three phase boundary is dependent on the particle size of LSM and YSZ, cell performance of a 5:5 mixture (HL12Z5C) is higher than that of a 7:3 mixture (HL12Z3C) as shown in Fig. 4. In addition, for cells using YSZ calcined at 1400°C, the cell performance of a 5:5 mixture (HL12Z5S) is higher than that of a 6:4 mixture (HL12ZS4C).

Fig. 5 shows XRD patterns recorded from starting cathode powders of La_{0.78}Sr_{0.22}Mn_{1.2}O_3 and La_{0.78}Sr_{0.22}Mn_{1.2}O_3 calcined at 800°C and 1000°C respectively. Data (e) and (f) in Fig. 5 are those of composite cathode LSM+YSZ where the LSCo layer was removed after the cell test. In these data, the peak of Mn-excess second phase appeared when LSM was prepared by the citrate method except for HL10Z4. When they were calcined at 800°C, chemical composition is inhomogeneous even though L10Z4 shows the peak of Mn-excess second phase. This phase in HL12Z4 with excess Mn decreases electrode resistance and cathodic overpotential due to lowered reactivity of LSCo with YSZ. It is also known that the cathode performance is enhanced by the presence of both electronic and ionic conduction and acceptor doped cobaltites such as LaSrCo_0.8Mn_0.2O_3.8 which exhibit high values for both electronic and ionic conductivities (7,8). Therefore excess Mn decreases cathodic overpotential of composite cathode to diffuse into the LSCo layer. This also explains the result of Fig. 2(a) where the HL12Z4C cell has the higher performance than HL10Z4C and L10Z4C. It seems that the performance of L10Z4C is higher than that of HL10Z4C due to not only LSM of smaller particle size but also the Mn-excess effect resulting from chemical inhomogeneity. The composite cathode using Mn-excess LSM calcined at 800°C (L12Z4C) has higher chemical inhomogeneity from the XRD patterns shown in Fig. 5. This chemical inhomogeneity contributes to an extreme Mn-excess condition which decreases the kinetics of electrocatalytic reduction of oxygen. Therefore the L12Z4C cell has lower performance than others as shown in Fig. 2(a).

As a result, the performance of LSM+YSZ cathode was enhanced with LSCo as a current collecting layer. The excess Mn inhibits the deterioration reaction of LSCo with YSZ and decreases overpotential of composite cathode by incorporating into
LSCo and increasing ionic conductivities of LSCo. When these LSM+YSZ/LSCo composite cathodes were used for anode-supported single cells, excellent results for long-term performance about 1000 hours were obtained (9).

SUMMARY

The electrical performance of anode-supported 5 × 5 cm² single cells with several different LSM+YSZ/LSCo composite cathodes was measured at 750°C with hydrogen as a fuel. The maximum power density of cells fabricated in this work was 360 mw/cm² at 750°C with La₀.₇₈Sr₀.₂₂Mn₁₀O₃+8YSZ/La₀.₇₀Sr₀.₃₀CoO₃ composite cathode. The results indicate that the LSCo current collecting layer improves performance of LSM+YSZ composite cathode although LSCo slightly reacts with YSZ. With stoichiometric amounts of Mn, cell performance with LSM calcined at 800°C is higher than that calcined at 1000°C. It seems that fine-grained cathode in stoichiometric LSM has lower overpotential than coarse-grained cathode. On the other hand, with excess amounts of Mn, coarse-grained cathode (calcined at 1000°C) has lower cathodic overpotential. It seems that the excess amount of Mn decreases electrode resistance and cathodic overpotential by reducing the reaction of LSCo with YSZ and improving the ionic conductivity of LSCo at interface of LSCo/LSM+YSZ.

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Table 1. Starting materials of (LSM+YSZ)/LSCO composite cathodes.

| Cathode Sample # | Calcination temp. of LSM | Composition of $\text{La}_{x_72}\text{Sr}_{x_22}\text{Co}_x\text{O}_3$ | Wt. ratio of LSM : 8YSZ | Current collector |
|------------------|--------------------------|-------------------------------------------------|-------------------------|------------------|
| L10Z4            | 800°C, 1h                | X=1.0                                           | 6:4                     | without LSCO     |
| L10Z4C           | 800°C, 1h                | X=1.0                                           | 6:4                     | $\text{La}_{x_6}\text{Sr}_{x_4}\text{Co}_x\text{O}_3$ |
| L12Z4C           | 800°C, 1h                | X=1.2                                           | 6:4                     | $\text{La}_{x_6}\text{Sr}_{x_4}\text{Co}_x\text{O}_3$ |
| HL10Z4C          | 1000°C, 8h               | X=1.0                                           | 6:4                     | $\text{La}_{x_6}\text{Sr}_{x_4}\text{Co}_x\text{O}_3$ |
| HL12Z4C          | 1000°C, 8h               | X=1.2                                           | 7:3                     | $\text{La}_{x_6}\text{Sr}_{x_4}\text{Co}_x\text{O}_3$ |
| HL12Z5C          | 1000°C, 8h               | X=1.2                                           | 5:5                     | $\text{La}_{x_6}\text{Sr}_{x_4}\text{Co}_x\text{O}_3$ |
| HL12Z1S4C        | 1000°C, 8h               | X=1.2                                           | 6:4                     | $\text{La}_{x_6}\text{Sr}_{x_4}\text{Co}_x\text{O}_3$ |
| HL12Z1S5C        | 1000°C, 8h               | X=1.2                                           | 5:5                     | $\text{La}_{x_6}\text{Sr}_{x_4}\text{Co}_x\text{O}_3$ |

HL= calcined LSM at high temp., L=$\text{La}_{x_6}\text{Sr}_{x_4}\text{Mn}_x\text{O}_3$, Z= 8YSZ, ZS= calcined 8YSZ at 1400°C, C= $\text{La}_{x_6}\text{Sr}_{x_4}\text{O}_3$

Fig. 1. Photographs of the anode-supported SOFC: (a) appearance of a $5 \times 5$ cm$^2$ single cell with cathode and reference electrode and (b) microstructure (cross-section view).
Fig. 2. Performance of the anode-supported single cell using hydrogen as a fuel at 750°C: (a) I-V and I-P characteristics with (LSM+YSZ)/LSCo composite cathode and (b) cathodic overpotential in (a) with open symbols representing the cathode of La$_{0.78}$Sr$_{0.22}$Mn$_{1.0}$O$_{3}$+8YSZ(6:4) (specimen # L10Z4) without LSCo.
Fig. 3. Performance of the anode-supported single cell using hydrogen as a fuel at 750°C: ohmic and non-ohmic loss in case of La$_{0.78}$Sr$_{0.22}$Mn$_{1.2}$O$_3$+8YSZ (6:4)/LSCo composite cathode (specimen # HL12Z4C): total resistance calculated from the ohmic drop (IR) and YSZ IR drop estimated from conductivity value of 20 μm 8% YSZ.

Fig. 4. I-V and I-P characteristics with LSCo/LSM+YSZ composite cathode of which Mn excess LSM calcined at 1000°C.
Fig. 5. XRD patterns recorded from starting cathode powders of La$_{0.78}$Sr$_{0.22}$Mn$_2$O$_3$ and La$_{0.78}$Sr$_{0.22}$Mn$_2$O$_3$ calcined at 800°C and 1000°C: (e) and (f) are those of composite cathode LSM+YSZ where the LSCo layer was removed after the cell test.
STUDY ON NOVEL COMPOSITE CATHODE MATERIALS DOPED WITH Bi$_2$O$_3$ FOR SOFC

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ABSTRACT

In order to decrease the sintering temperature and increase the electrode properties, Bi$_2$O$_3$ was employed as an addition to composite cathode material based on lanthanum manganite(LSM) and lanthanum cobaltite (LSC), and the composite material could be prepared at 1050°C in a short time. XRD result shows that it is a composite material without any obvious reaction between Bi$_2$O$_3$ and the LSM matrix. The material doped by 15wt% Bi$_2$O$_3$ had the highest conductivity. The conductivity of composite materials is lower than that of LSM and LSC without Bi$_2$O$_3$ addition. SEM photographs show a suitable microstructure for SOFC usage. Electrochemical polarization test shows that the exchange current density improved by the addition of Bi$_2$O$_3$. This improvement can be attributed to the increase of contact area between the electrolyte Bi$_2$O$_3$ and the LSM or LSC, and the sintering temperature has been decreased by Bi$_2$O$_3$ melt. These materials have been tested in SOFCs and show good properties.

INTRODUCTION

Solid oxide fuel cells (SOFCs) have been attracting great attention as a promising new method for electrical power generation and because of its advantages, such as high total efficiency and no pollution [1]. Basic unit of a SOFC consists of three layers: anode, electrolyte and cathode [1]. Since cathode is one of the key components of SOFCs, a cathode with high performance, for example, high electrical and ionic conductivity and oxygen catalysis is necessary. Some complex oxides with perovskite structures (for example, LaMnO$_3$, LaCoO$_3$) have been employed as cathodes of SOFCs[1, 2]. However, during fabrication and operation at high temperatures, the diffusion and reaction at the interface between the cathode and electrolyte would generate some compounds, such as SrZrO$_3$ and La$_2$Zr$_2$O$_7$ to decrease the properties of SOFC[1, 3, 4]. So it is necessary to seek some new cathode materials which are easy to be fired and have high electrochemical performance. In order to get new materials, one can either find some new material systems, dope some elements into the conventional materials or design