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A bi-layer cathode based on lanthanum based cobalt- and iron-containing perovskite and gadolinium doped ceria for thin yttria stabilized zirconia electrolyte solid oxide fuel cells

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Abstract

Composite cathodes based on $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) are investigated for lower operating temperature (<750 °C) applications of a solid oxide fuel cell (SOFC). To enhance a charge transfer, a bi-layer SOFC cathode is proposed, which has a LSCF–$Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) composite layer and a pure LSCF layer. The bi-layer cathode SOFC shows a current density of 0.65 A cm^{-2} at 0.8 V and 660 °C, which is higher than a LSCF–GDC composite single-layer cathode SOFC cell of 0.35 A cm^{-2}. The charge transfer polarizations in the bi-layer cathode SOFC are 0.14 Ω cm^2 and 0.35 Ω cm^2 at 760 °C and 660 °C, respectively, which are lower than those in the single-layer cathode cell of 0.23 Ω cm^2 and 0.66 Ω cm^2. The impedances characterized with a fitting model show that the lowered charge transfer polarization in the bi-layer cathode is a dominant factor in reducing the total polarization of SOFC.

Keywords: E. Fuel cells; Electrochemistry; Electrical conductivities; Oxide

1. Introduction

The development of solid oxide fuel cells (SOFCs) for intermediate temperature (IT, 600–800 °C) operations have been considered as the most promising future component related to energy generation for power plants and distributed power systems. For operation at IT, perovskite-based compounds having the general formula of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) with a Gd-doped ceria (GDC)-based interlayer have been reported to be very effective owing to their high ionic conductivity and catalytic activity [1–6]. In LSCF-based cathodes, electrochemical reactions occur at both the triple phase boundary (LSCF and oxygen gas) and the surface of LSCF. To enhance the ionic conductivity and prevent the coarsening of the cathode, the addition of a second phase such as GDC has been reported and many studies have confirmed that the formation of a composite cathode can beneficially reduce the polarization resistance of a pure LSCF cathode [7–18]. Even if LSCF has a good ionic conductivity, its electronic conductivity is much more relevant for SOFC cathode. So the addition of other materials, such as GDC, which has a high ionic conductivity, is effective in increasing the overall charge transfer of the composite electrode LSCF–GDC. This phenomenon is attributed to the extension of the three-phase boundary (TPB) of the electrolyte (ionic conductor), cathode (electronic conductor) and gas phase (oxygen or air used as an oxidant). Additional benefits include better adhesion and thermal expansion match to the electrolyte layer or interlayer [19]. Composite electrodes commonly containing 40–60 wt% of electrolyte materials are characterized to have low electronic conductivity, which can be resolved using a design of bi-layer electrodes of the cathode functional layer and the current collector layer. The cathode functional layer, which directly contacts the electrolyte, needs to have good thermal and chemical compatibility with the electrolyte and provide high electrochemical activity for oxygen reduction. The outer current collector layer, on the other

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hand, is usually composed of high electronic conductive materials to facilitate a uniform current distribution along the cathode and to help the electrons transfer from the outer circuit to the TPB of the cathode functional layer [20]. Similar to bi-layer cathode, multilayer cathode and functionally graded composite cathode are fabricated through inserting layers with different cathode/electrolyte ratios to guarantee a smooth transition from one cathode material to another cathode material [21] or from one electrolyte material to another electrolyte material [22,23]. With the $Sm_{0.2}Ce_{0.8}O_{2-\delta}$ (SDC) as an electrolyte, the addition of SDC to LSCF shows the improvement of the adhesion of the cathode layer to electrolyte layer, and the thickness of the composite layer should be optimized to minimize the ohmic and polarization resistance and maximize the cell performance [24]. This enhanced performance of both a composite and a layered cathode is a function of sintering temperature, microstructure (such as the grain size and porosity), and composition of LSCF and GDC.

In this study, LSCF synthesized via a complex method with an inorganic nano-dispersant is used for cathode, and a bi-layer cathode based on nanocrystalline LSCF is proposed to enhance the electrical conductivity for thin yttrium stabilized zirconia (YSZ) electrolyte SOFCs. The bi-layer cathode includes a LSCF–GDC composite layer and a LSCF layer. LSCF–GDC layer comes into contact with a GDC interlayer and a LSCF layer with a current collector. LSCF layer in the bi-layer cathode is expected to provide higher electronic conductivity than LSCF–GDC composite layer, and is likely to be beneficial for enhancing an electronic transfer. SOFC with the bi-layer cathode electrode is characterized in terms of its fuel cell performance and impedances, and compared with the single-layer cathode SOFC. The performances of SOFC are characterized by the equivalent circuit developed with five RQ (resistance and constant phase in series) and the fitted results are compared with experiment data and the five RQ elements are characterized. The characterized impedances are studied to clarify the effects of the bi-layer cathode design in SOFCs.

2. Experimental procedures

The LSCF cathode materials, with a surface area of $80\ m^2\ g^{-1}$, were synthesized using the method described in a previous work [25]. The GDC materials, with a surface area of $15\ m^2\ g^{-1}$, were purchased from ANAN Kasei. Metal precursors of lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$, YAKURI, 97%), strontium nitrate ($Sr(NO_3)_2$, JUNSEI, 97%), cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, JUNSEI, 97%), and ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$, JUNSEI, 97%) were used for the LSCF perovskite powders. Ethylenediaminetetraacetic acid powder (YAKURI) and crystallized citric acid (DUKSAN), each with a purity level higher than 99.5%, were used as the raw materials for chelation. As previous work [25], a homogeneous metal nitrate solution was prepared by dissolving lanthanum nitrate, strontium nitrate, cobalt nitrate, and ferric nitrate into a deionized water with a mole ratio of 6:4:2:8. Next, solid citric acid was added to the mixed metal nitrate solution, followed by EDTA powder. The solution was then heated in a water bath at 70 °C until it became clear, at which point 5 g of HI BLACK170 carbon black was added as an inorganic nano-dispersant. The mixture was reheated until a magnetic bar immersed in the solution stopped rotating. The remaining mixture was dried overnight at 80–120 °C in a vacuum oven to remove the residual water. The dried mixture was crushed and calcined at 700 °C for 5 h to form a perovskite phase and to remove any organic compounds and inorganic nano-dispersants.

The anode-supported cells of $32 \times 22\ cm^2$, which consist of Ni-YSZ of 900 μm as a support, Ni-YSZ of 20 μm as an anode functional layer, and YSZ of 10 μm as an electrolyte, were prepared by a tape-casting and co-firing method at 1370 °C for 3 h. GDC of 1 μm as an interlayer was formed onto the YSZ electrolyte by an aerosol deposition method with the carrier gas, compressed air dried through a dehumidifying filter, in the aerosol chamber evacuated using a rotary pump. The anode supported SOFCs were cut into circles with diameters of 2.6 cm from a 32×22 cm plate.

The composite cathodes were prepared with LSCF-based nanocrystalline powders (surface area of $80\ m^2\ g^{-1}$) and GDCs (surface area of $15\ m^2\ g^{-1}$). For preparing LSCF–GDC composite cathode, LSCF and GDC were mixed together in ratios of 50:50 wt% with organic binder solution, ethyl cellulose, and di-ethylene glycol butyl ether with α-terpinol. The bi-layer cathode is fabricated by screen-printing of LSCF–GDC paste on the GDC interlayer followed by the drying in oven at 120 °C. After drying, the LSCF paste is printed and the bi-layer cathode is sintered at 900 °C for 3 h. The thickness of each layer is controlled by the number of prints done. For the bi-layer cathode, a paste with LSCF and GDC was printed twice onto a GDC interlayer and a LSCF paste was then printed once onto the LSCF–GDC composite layer. After printing the LSCF–GDC composite and the LSCF layer, the SOFC was sintered at 900 °C for 3 h. The active cathode area was $0.785\ cm^2$. The SOFC with a single-layer consisted of only a LSCF–GDC composite layer. A paste of LSCF and GDC was printed three times onto a GDC interlayer, followed by drying in oven at 120 °C and sintering at 900 °C for 3 h. The fabricated cells were assembled and sealed with Cerama bond^{TM} 571 from AREMCO in a ceramic jig to measure current–voltage characteristic and impedances. The ceramic jig is shown in Fig. 1. Pt paste and mesh was used for current collecting. The cells were heated to 780 °C in 9 h and the anode reduction was performed with $300\ cc\ min^{-1}$ of 97% H_2–3% H_2O for 3 h. The fuel cell performances and the impedances were characterized and analyzed with 300 cc min^{-1} of 97% H_2–3% H_2O and 1000 cc min^{-1} of air. The impedance was measured with the WEIS system from