Short communication

Sr$_{0.7}$Ho$_{0.3}$CoO$_{3-\delta}$ as a potential cathode material for intermediate-temperature solid oxide fuel cells

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ABSTRACT

The oxygen-deficient perovskite Sr$_{0.7}$Ho$_{0.3}$CoO$_{3-\delta}$ (SHCO) operates on the Co(III)/Co(II) redox couple rather than the usual Co(IV)/Co(III) couple for an oxygen reduction reaction(ORR) cathode of an intermediate-temperature solid oxide fuel cell (IT-SOFC). The room-temperature XRD pattern of SHCO prepared by solid-state reaction can be indexed in the tetragonal *I4/mmm* space group with unit-cell parameters a = 7.617 Å, and c = 15.293 Å. SHCO exhibits an electrical conductivity with values larger than 488 S cm^{-1} over the temperature range 560–800 °C. The area specific resistance (ASR) of a SHCO cathode measured on a La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{2.815}$ (LSGM) electrolyte reaches a relatively low value of 0.14 Ω cm^2 at 800 °C in air. With a 300-μm-thick LSGM disk as the electrolyte and NiO-GDC as the anode, a cell with the SHCO cathode exhibited maximum power densities of 1274, 756, and 493 mW cm^{-2} at 850, 800, and 750 °C, respectively, with hydrogen as fuel and ambient air as oxidant. Cross-section scanning-electron-microscopy measurements confirmed the porous microstructure of the electrodes and good electrode-buffer layer-electrolyte adherence in a single test cell. The ORR activity of a SHCO cathode operating on the Co(III)/Co(II) couple approaches that of the best cathodes operating on the Co(IV)/Co(III) couple, and higher-spin Co(III) ions provide a compatible thermal expansion.

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1. Introduction

A solid oxide fuel cell (SOFC) is an electrochemical device that can convert chemical energy directly into electrical energy; it has the merits of high energy-conversion efficiency, low environmental impact and good fuel flexibility [1,2]. Much effort in recent years has been devoted to lowering the operating temperatures of SOFCs to the intermediate-temperature (IT) range 500–800 °C not only to reduce the cost of fabrication and maintenance but also to prevent degradation of the cell performance [3]. In this respect, cathode materials with mixed ionic-electronic conductivity and excellent electrocatalytic activity for the oxygen reduction reaction deserve special attention [4,5]. Recently, the oxygen-deficient perovskite Sr$_{0.7}$Y$_{0.3}$CoO$_{2.63}$ (SYCO), which operates on the Co(III)/Co(II) couple rather than the Co(IV)/Co(III) couple, has been observed [6] to be a cathode material that exhibits promising performance for IT-SOFCs and to have a compatible thermal expansion owing to all Co in a higher spin state. The electrical conductivity reaches values higher than 700 S cm^{-1} for T > 500 °C in air, and the area specific resistance (ASR) of SYCO on an LSGM electrolyte exhibits a relatively low value

of 0.11 Ω cm^2 at 800 °C. As a result, with a 300-μm-thick LSGM disk as the electrolyte and NiO-GDC as the anode, a cell with the SYCO cathode exhibited a maximum power density of 927 mW cm^{-2} at 800 °C with pure H$_2$ as fuel and air as oxidant. Previous studies have shown that a structure similar to that of SYCO can be formed with other rare-earth substituted Sr$_{1-x}$Ln$_x$CoO$_{3-\delta}$ (Ln = rare earth) samples, but the stability range depends sensitively on the ionic radius of the Ln^{3+} ion. It remains unclear whether an excellent electrochemical performance can be found in other Ln^{3+}-substituted samples isostructural with SYCO. In this present study, we have replaced Y^{3+} with Ho^{3+} and investigated the electrochemical performance of Sr$_{0.7}$Ho$_{0.3}$CoO$_{3-\delta}$ as a cathode for IT-SOFCs.

2. Experimental procedure

2.1. Sample preparation and characterizations

Polycrystalline Sr$_{0.7}$Ho$_{0.3}$CoO$_{3-\delta}$ (SHCO) was prepared from a stoichiometric mixture of SrCO$_3$, Co$_3$O$_4$ and Ho$_2$O$_3$ [8]. The mixtures were ground and sintered at 1100 °C for 12 h followed by re-grinding and another firing at 1100 °C for 48 h in air. The obtained product was characterized by powder X-ray diffraction (XRD) for phase identification with a Philips X'pert diffractometer (Cu Kα radiation, λ = 1.5418 Å) in Bragg-Brentano reflection

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geometry. The XRD data were recorded in the 2θ range of 20–90° with an increment of 0.02° and a dwell time of 10 s.

2.2. Electrical conductivity and electrochemical impedance spectra measurements

The dc electrical conductivity of SHCO was measured in air with the Van Der Pauw method [9,10] in the temperature range 200–800 °C. SHCO powder was pressed into a pellet with a diameter of 6.25 mm and a thickness of 0.7 mm; it was then sintered at 1100 °C for 6 h. Pt wire and Pt paste were used to make the four probes. At each temperature point, an *I–V* scan from −100 mA to 100 mA with a step of 10 mA was performed, and the electrical conductivity was calculated from the slope of the obtained straight line.

The electrochemical impedance spectra (EIS) were measured with an electrochemical interface (1287 potentiostat and 1260 Frequency response analyzer, Solartron Analytical, Farnborough, Hampshire, U.K.). The ac impedance spectra were performed on the symmetrical cell SHCO/LSGM/SHCO under open-current conditions from 550 to 800 °C in the frequency range 10^6–10^{-2} Hz with a signal amplitude of 10 mV. For this purpose, the SHC cathode with an area of 0.25 cm^2 was screen-printed onto both sides of a dense LSGM electrolyte pellet of 600 μm thickness. After drying, the SHCO cathode was sintered at 1050 °C for 1 h in air. Pt meshes with Pt wires were attached to each electrode with a thin coating of dilute Pt paste and Pt paste in separate dots for ensuring contact.

2.3. Preparation of single-cells

Single test cells were fabricated by an electrolyte-supported technique. A 300-μm-thick LSGM disk was used as the electrolyte [3,11], commercial NiO-GDC was used as the anode, SHCO was the cathode, and La$_{0.4}$Ce$_{0.6}$O$_{2-\delta}$ (LDC) was used as a buffer layer between the electrode and the electrolyte [11,12]. The LDC buffer layer prevents unwanted interface phases arising from a reaction between cathode and electrolyte that impede O^{2-} transport across the interface. The buffer layer is not needed in the symmetrical cells that are used to determine the ASR at the O$_2$/cathode interface. LDC, NiO-GDC and SHCO were made into a paste with a commercial binder (V-006, Heraeus). LDC paste was screen-printed onto two sides of the LSGM disk followed by firing at 1300 °C for 1 h. NiO-GDC was subsequently screen-printed on one side of the LSGM and fired at 1300 °C for 0.5 h. SHCO was finally screen-printed on the other side of the LSGM and fired at 1050 °C for 1 h. The working electrode area of the cell was 0.28 cm^2. The single cell was sealed onto one end of an alumina tube with glass powder and then placed into a vertical furnace with air directly supplied to the cathode surface and hydrogen to the anode surface. Before testing, the anode was exposed to 5% H$_2$/Ar for 40 min at 800 °C and then purged with hydrogen for 20 min. The performance measurements were carried out at 750, 800, and 850 °C.

3. Result and discussion

The XRD pattern of the Sr$_{0.7}$Ho$_{0.3}$CoO$_{3-\delta}$ sample shown in Fig. 1 indicates that a single phase is formed. The patterns could be indexed on the basis of a tetragonal *I4/mmm* structure with unit-cell parameters a = 7.617 Å, and c = 15.293 Å, which are in agreement with those in the literature [8].

Fig. 2 shows the temperature dependence of the electrical conductivity (left) and resistivity (right) of the SHCO pellet. With increasing temperature, the conductivity of SHCO first increases rapidly to a maximum value of 512 S cm^{-1} at 560 °C and then decreases slowly, but keeps above 488 S cm^{-1} up to 800 °C. Such a high electrical conductivity satisfies the general requirement for
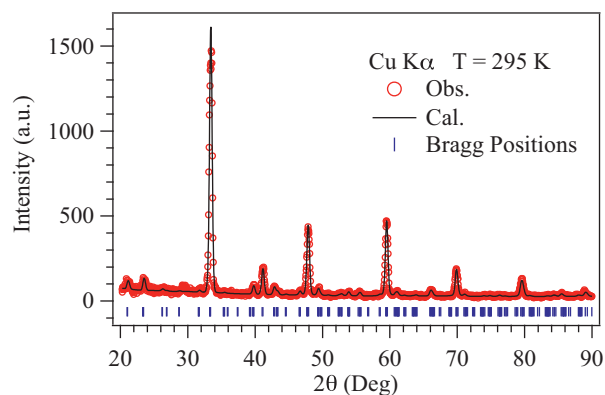

Fig. 1. The X-ray diffraction patterns of the Sr$_{0.7}$Ho$_{0.3}$CoO$_{3-\delta}$ sample.

the cathode materials of a SOFC, i.e. σ_e > 100 S cm^{-1} at the operating temperature [7]. Similar to Sr$_{0.7}$Y$_{0.3}$CoO$_{2.63}$, the Arrhenius plot of ln(σT) vs 1000/T does not produce a single straight line owing to an increase in oxygen loss in a narrow temperature range about 650 K.

Fig. 3 displays typical impedance spectra of the SHCO|LSGM|SHCO cell obtained at different temperatures in air. The impedance response is characterized by a single arc. The high-frequency intercept of the electrode impedance on the real axis is the total resistance of the electrolyte. The difference between the low-frequency and the high-frequency intercepts on the real axis corresponds to the area specific resistance (ASR) of the two cathode–electrolyte interfaces. ASR represents the overall cathodic resistance related to the oxygen reduction, oxygen surface/bulk diffusion, and the gas-phase oxygen diffusion. As can be seen, the ASR value reduces significantly with increasing temperature and reaches 0.14 Ω cm^2 at 800 °C, which is lower than that required for the cathode ASR and suggests that a SHCO cathode has high electrocatalytic activity for the oxygen reduction reaction at intermediate temperatures. The corresponding activation energy, calculated from the slope of Fig. 3(b), is 160.4 kJ mol^{-1}.

Displayed in Fig. 4 are the cell voltage and power density as a function of current density for the single test cell NiO-GDC|LDC|LSGM|LDC|SHCO operating at different temperatures with dry hydrogen as fuel and ambient air as oxidant. Each data point was recorded about 30 min after the cell reached a steady state. In general, the open-circuit voltage (OCV) of the cell should be close to its theoretical value and slightly influenced by operating conditions. As shown in Fig. 4, the maximum power densities (P_{max}) of 1274, 756, and 493 mW cm^{-2} with the open-circuit
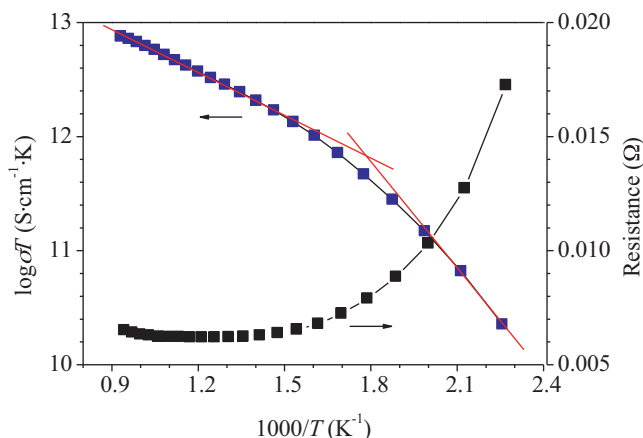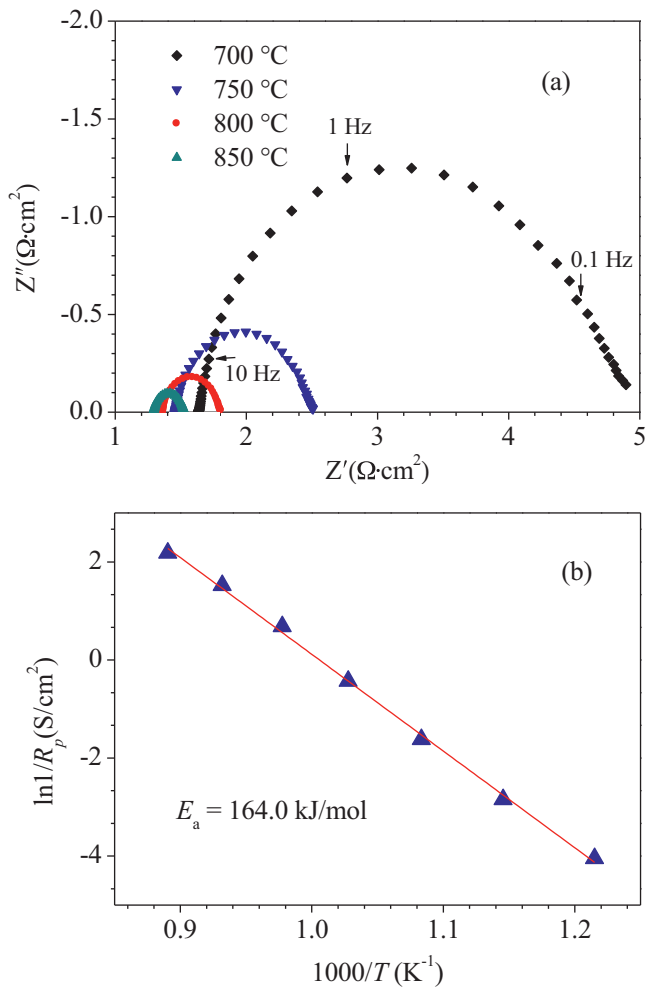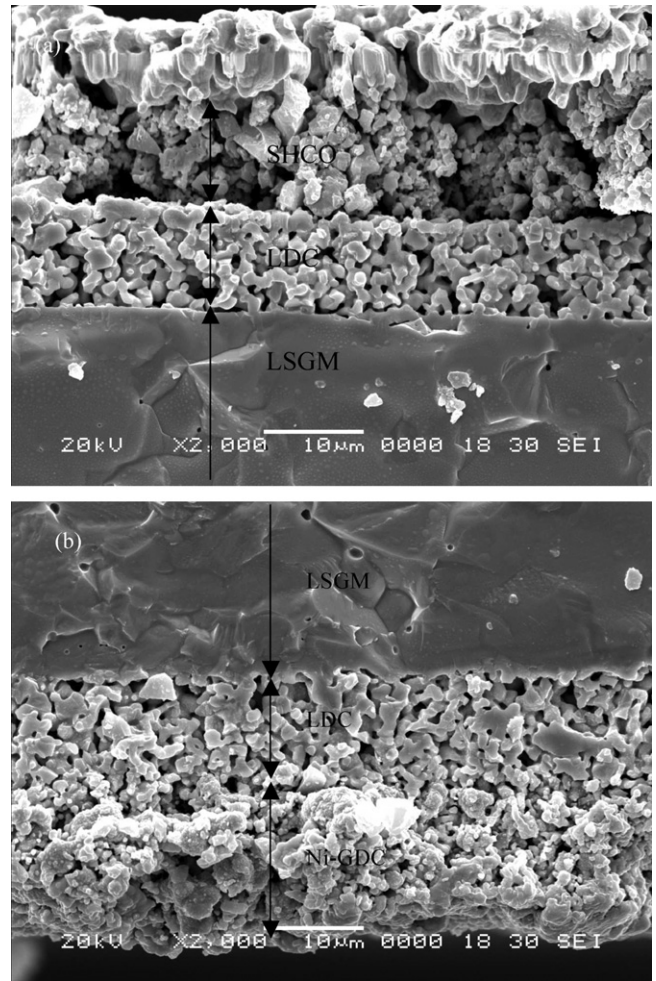

Fig. 2. Temperature dependence of the conductivity and resistance for SHCO pellet.

Fig. 3. (a) Impedance spectra of the symmetrical cell with the configuration of SHC/LSGM/SHC under OCV conditions at different temperatures. (b) Arrhenius plot of the polarization resistance of a SHC cathode on LSGM electrolyte.

Fig. 5. SEM micrograph of (a) the SHCO/LDC/LSGM cross-section and (b) the Ni-GDC/LDC/LSGM cross-section after test.

voltage (OCV) values of 1.2863, 1.2895, and 1.2917 V were obtained at 850, 800, and 750 °C, respectively.

Fig. 5(a) and (b) shows the cross-section SEM micrographs of electrode-electrolyte interfaces after testing. From the SEM images, the electrolyte layer is fairly dense without obvious pores and cracks. The thicknesses of the LDC, SHCO and Ni-GDC layers are estimated to be 10, 10 and 15 μm, respectively; the mean grain and particle sizes for LDC, SHCO and Ni-GDC are about 2 μm. Furthermore, the cathode SHCO exhibits porosity.

4. Conclusions

The oxygen-deficient perovskite $Sr_{0.7}Ho_{0.3}CoO_{3-\delta}$ (SHCO), which operates on the Co(III)/Co(II) couple rather than the Co(IV)/Co(III) couple, has been evaluated as a potential cathode material for IT-SOFCs in the present study. It can be easily prepared with standard solid state reaction as a single phase with tetragonal $I4/mmm$ symmetry. A high electrical conductivity and a relatively low polarization resistance can be obtained for a SHCO cathode at intermediate temperatures; and with higher-spin cobalt, the thermal expansion is compatible. In an electrolyte-supported single test cell, the SHCO cathode exhibited maximum power densities of 1274, 756, and 493 mW cm^{-2} with the OCV values of 1.2863, 1.2895, and 1.2917 V at 850, 800, and 750 °C, respectively.
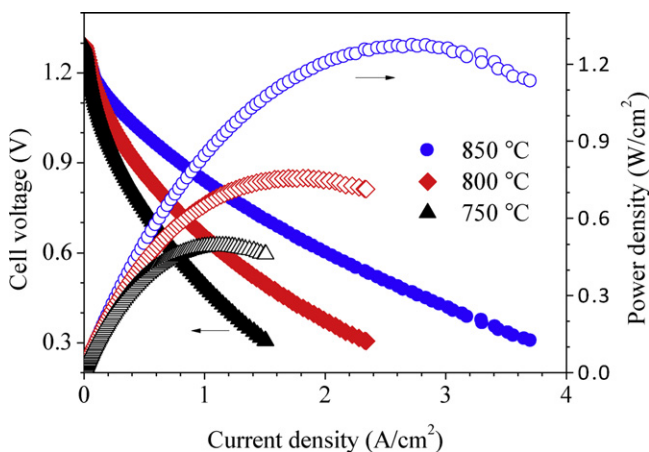
Fig. 4. Typical current–voltage characteristics and corresponding power densities measured at different temperatures.

References

[1] H.Y. Tu, Y. Takeda, N. Imanishi, O. Yamamoto, Solid State Ionics 117 (1999) 277–281.
[2] M. Dokiya, Solid State Ionics 152 (2002) 383–392.
[3] Y.H. Huang, R.I. Dass, Z.L. Xing, J.B. Goodenough, Science 312 (2006) 254–257.
[4] T. Kawada, J. Suzuki, M. Sase, A. Kaimai, K. Yashiro, Y. Nigara, J. Mizusaki, K. Kawamura, H. Yugami, J. Electrochem. Soc. 149 (2002) E252–E259.
[5] S.B. Adler, Chem. Rev. 104 (2004) 4791–4843.
[6] Y. Li, J.B. Goodenough, Chem. of Mater. (2011), doi:10.1021/cm202542q.
[7] M. Ji-Woong, M. Yoshitake, S. Won-Seon, K. Kunihito, Mater. Sci. Eng. B 85 (2001) 70–75.
[8] S.Ya. Istomin, O.A. Drozhzhin, G. Svensson, E.V. Antipov, Solid State Sci. 6 (2004) 539–546.
[9] L.J. Van der Pauw, Philips Research Report, 1958.
[10] A. Esquirol, N.P. Brandon, J.A. Kilner, M. Mogensen, J. Electrochem. Soc. 151 (2004) A1847–A1855.
[11] K.Q. Huang, J.B. Goodenough, J. Alloys Compd. 454 (2000) 303–304.
[12] K.Q. Huang, J.B. Goodenough, J. Electrochem. Soc. 148 (2001) A788–A794.