Short communication

Electrochemical performance of $Ba_2Co_9O_{14}$ + SDC composite cathode for intermediate-temperature solid oxide fuel cells

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ABSTRACT

A 50–50 wt.% $Ba_2Co_9O_{14}$ (BCO) + $Sm_{0.2}Ce_{0.8}O_{1.9}$ (SDC) composite was evaluated as a cathode for an intermediate-temperature solid oxide fuel cell (IT-SOFC) operating at 800 °C. The composite was supported on the electrolyte $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$ (LSGM) and its performance for the oxygen-reduction reaction (ORR) was evaluated with a symmetric BCO + SDC|LSGM|BCO + SDC cell, which gave a polarization resistance of 0.068 Ω cm^2 at 800 °C in air. A singe cell with a 300-µm-thick electrolyte and a composite NiO + Gd-doped ceria anode gave a nearly stable $P_{max} \approx 450$ mW cm^{-2} at 800 °C, indicating that with a thinner electrolyte, the composite cathode could provide an IT-SOFC that meets the targeted 500 mW cm^{-2} at 800 °C. The fabrication of the composite cathode versus BCO alone serves two functions: improved adhesion to the electrolyte and an enhancement of the ORR activity.

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1. Introduction

Solid oxide fuel cells (SOFCs) convert chemical energy directly into electrical energy with low environmental impact and good fuel flexibility. Although the energy-conversion efficiency is potentially high, conventional SOFCs are forced to operate above 800 °C, which makes fabrication and maintenance costly and reduces operating life. One requirement for reducing the operating temperature to the intermediate-temperature range 500 °C < T < 800 °C is identification of a cathode that catalyzes a rapid oxygen reduction reaction (ORR) at these temperatures. Cobalt oxides operating on the Co(IV)/Co(III) redox couple in perovskite-related structures have exhibited the highest ORR activities for the IT-SOFC [1–3] because (1) they are mixed oxide-ion/electronic conductors (MIECs), which extends the ORR area from the electrolyte–electrode–air triple-phase boundary to the entire electrode surface, (2) the Co(IV)/Co(III) couple is pinned at the top of the O-2p bands to retain good electronic conductivity under the oxidizing cathode atmosphere, (3) the surface Co(III) are in an intermediate-spin state, which provides a particularly active catalytic reaction for the reduction of adsorbed gaseous O_2 to surface $2O^{2-}$ ions, and (4) they are chemically stable under oxidizing conditions. In this paper, we explored the catalytic activity of a cobalt oxide, $Ba_2Co_9O_{14}$ (BCO), operating in the Co(III)/Co(II) couple.

BCO is the $n = 1$ member of the $Ba_{n+1}Co_nO_{3n+3}(Co_8O_8)$ family of intergrowth compounds [4,5]. As shown in the inset of Fig. 1,

the Ba-containing layers in BCO alternate with the $4CoO_{6/3} = Co_4O_8$ sheets of edge-shared octahedral sites containing high-spin Co(II) coordinated by six low-spin Co(III) in the ratio Co(II)/Co(III) = 1/3. The $Ba_2Co_5O_6$ layers of a unit cell accommodate the two large Ba^{2+} ions with pillars of three face-sharing octahedral sites containing low-spin Co(III) ions. Two high-spin Co(II) in tetrahedral sites also occupy the Ba-containing layers; the tetrahedra share three corners with pillars of octahedral sites and one corner with three octahedra of the Co_4O_8 sheets. BCO has a relatively high electronic conductivity of $\sigma_e > 100$ S cm^{-1} for $T > 430$ °C and exhibits a weak yet reversible oxygen loss/gain upon thermal cycling in air [5], thus making it a possible MIEC. In addition, BCO can retain its crystal structure up to 1000 °C in air. These properties have motivated Rolle et al. [6] to investigate BCO as a potential cathode material for IT-SOFCs. They found that BCO has a good chemical compatibility with the classical electrolytes, YSZ (Y_2O_3-stablized ZrO_2) and GDC (Gd-doped CeO_2), but the cathode adhesion on both electrolytes is rather bad due to the mismatch of their thermal expansion coefficients, i.e. 20×10^{-6} K^{-1} for BCO versus $10–12 \times 10^{-6}$ K^{-1} for both electrolytes. The large thermal expansion of BCO is the result not only of oxygen loss, but also of a low-spin to a higher-spin state transition on the Co(III) ions [7]. Rolle et al. [6] overcame this problem by making composite cathodes of 70 wt.% BCO + 30 wt.% electrolyte; they characterized their electrochemical performances with impedance spectroscopy. With the screen-printed 70 wt.% BCO + 30 wt.% GDC composite, they obtained the lowest polarization resistance R_p (750 °C) = 0.5 Ω cm^2 and an activation energy of ∼1.1 eV. Unfortunately, the single-cell performance, including the I–V curves and the maximum power density based on the BCO composite cathode, were not available in [6]. In addition, the 70:30

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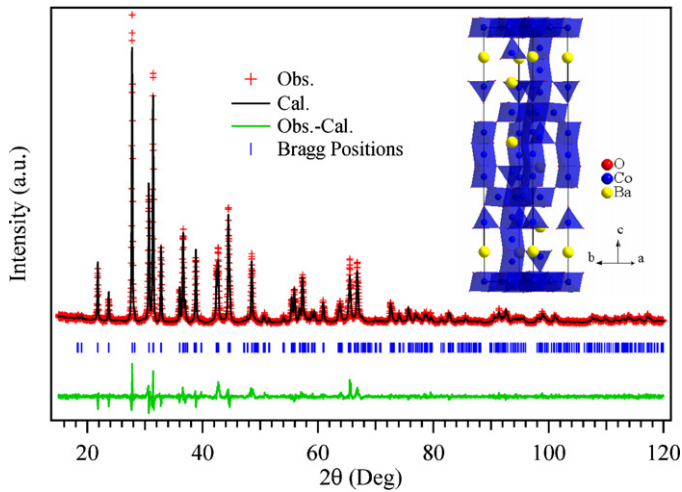E-mail address: jgoodenough@mail.utexas.edu (J.B. Goodenough).

Fig. 1. Rietveld refinement of the powder XRD pattern of the as-prepared BCO sample. Inset displays the crystal structure of BCO.
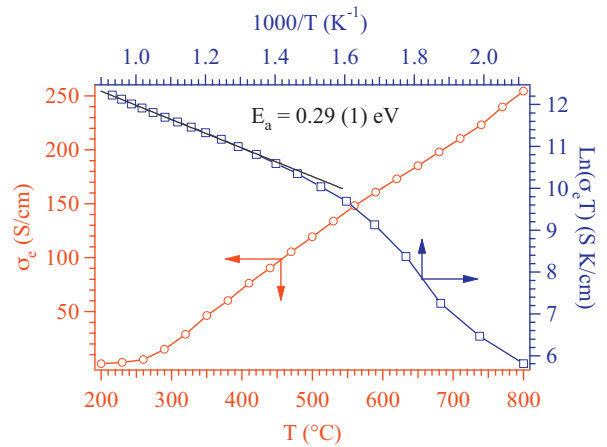

Fig. 2. Temperature dependence of the electronic conductivity $\sigma_e(T)$ and its Arrhenius plot $\ln(\sigma_e T)$ vs $1000/T$. The solid line is the linear fitting to the Arrhenius plot above 450 °C.

weight ratio may not be an optimal one for making the composite cathode as indicated from the relatively high R_p value. Previous studies [8–10] on various composite cathodes have shown that the 50:50 wt.% composite gives the best electrochemical performance. In this short communication, therefore, we have prepared a composite 50 wt.% BCO + 50 wt.% SDC (Sm-doped CeO_2) and evaluated its polarization resistance and electrochemical performance as a SOFC cathode via measurements of impedance spectroscopy and $I–V$ curves at various temperatures; the composite was supported on a $La_{0.8}Sr_{0.2}Ga_{0.83}Mg_{0.17}O_{2.815}$ (LSGM) electrolyte. The R_p values are reduced to 0.133 and 0.068 $\Omega\,cm^2$ at 750 and 800 °C, respectively. A nearly stable maximum power density of $\sim$450 mW cm^{-2} at 800 °C further indicated that BCO can be a potential cathode material for IT-SOFCs.

2. Experimental

Single-phase BCO polycrystalline samples were prepared by a conventional solid-state reaction of a stoichiometric mixture of $BaCO_3$ and Co_3O_4 in air at 900 °C for 5 days with several intermediate grindings. Sm-doped ceria, $Sm_{0.2}Ce_{0.8}O_{1.9}$ or SDC, was obtained via a sol–gel route. The gel formed from the $Sm(NO_3)_3\cdot6H_2O$ and $Ce(NO_3)_3\cdot6H_2O$ solution was first calcined at 400 °C for 10 h and then sintered at 800 °C and 1200 °C for 24 h each in air. The phase purity of the obtained products was examined by powder X-ray diffraction (XRD) with a Philips X'pert diffractometer (Cu Kα radiation, λ = 1.5418 Å) in Bragg–Brentano reflection geometry. The 50 wt.% BCO + 50 wt.% SDC (denoted as BCO + SDC hereafter) composite cathode was prepared by mixing thoroughly fine powders of BCO and SDC obtained by ball-milling in ethanol for 40 min. The particle size of the BCO + SDC powder was in the range of 1–5 μm as seen from scanning electronic microscopy. The chemical compatibility between BCO and SDC was examined by sintering the composite cathode at 850 and 900 °C in air for 10 h. The electrical conductivity of BCO was measured with a standard dc four-probe method in air on a cylindrical rod 6.5 mm in diameter and $\sim$10 mm in length. 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. Electrochemical impedance spectroscopy (EIS) measurements were carried out in air on a symmetrical cell BCO + SDC|LSGM|BCO + SDC with an AC impedance spectroscope (Solartron 1260 FRA) over the temperature range 500–800 °C. For this purpose, the BCO + SDC

composite 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 BCO + SDC cathode was then sintered at 800 °C for 1 h in air. A single electrolyte-supported test fuel cell was fabricated by using a 300-μm-thick LSGM pellet as electrolyte, BCO + SDC composite as cathode, and NiO + GDC as anode. Between the electrolyte and the electrodes, a thin $La_{0.4}Ce_{0.6}O_{2-\delta}$ (LDC) buffer layer was used to prevent interdiffusion of ionic species. Details about the preparation of the LSGM electrolyte and the LDC buffer-layer material have been described elsewhere [11]. The NiO + GDC anode material (composition 60% NiO + 40% GDC10 by weight, surface area 4–8 m^2 g^{-1}) was purchased from Fuel-Cell Materials (www.fuelcellmaterials.com). BCO + SDC, LDC, and NiO + GDC fine powders were made into inks with an organic binder (Heraeus V-006). LDC ink was screen-printed onto both sides of the LSGM disk followed by firing at 1300 °C in air for 1 h. NiO + GDC was subsequently screen-printed onto the LDC layer on one side and baked at 1300 °C in air for 0.5 h. Then, the BCO + SDC was finally screen-printed onto the other side of the LSGM disk and sintered at 900 °C in air for 1 h. The area of the working electrode is 0.24 cm^2. Pt gauze (Alfa Aesar, 52 mesh woven from 0.1 mm-diameter wire, 99.9% metal basis) with a small amount of Pt paste (Heraeus) in separate dots was used as a current collector at both the anode and cathode sides for ensuring contact. A double-layer sealing design was applied in all single-cell tests. The assembled test cell was placed in the hot zone of a vertical furnace with air directly supplied to the cathode surface and dry H$_2$ fuel to the anode surface at a flow rate of 30 mL min^{-1}. The performance measurements were carried out at 800 and 850 °C with an EG&G potentiostat/galvanostat [12].

3. Results and discussion

Fig. 1 shows the powder XRD pattern of the as-prepared BCO sample refined in the rhombohedral $R–3m$ (No. 166) space group with one Ba atom at $6c$ (1/3, 2/3, z), five kinds of Co atoms placed at $3a$ (1/3, 2/3, 2/3), $3b$ (0, 0, 1/2), $6c$, and $9e$ (5/6, 1/6, 2/3) positions, and three oxygen positions, O1 and O3 at $18h$ (x, y, z) and O2 at $6c$. The goodness of refinement illustrated in Fig. 1 confirmed that the obtained BCO sample is single-phase with high quality. The obtained lattice parameters a = 5.6954(1) Å and c = 28.9027(7) Å for our sample are in excellent agreement with those reported previously, i.e. a = 5.6963(8) Å and c = 28.924(6) Å for polycrystalline sample [5] or a = 5.6958(4) Å and c = 28.909(4) Å for a single crystal [4].
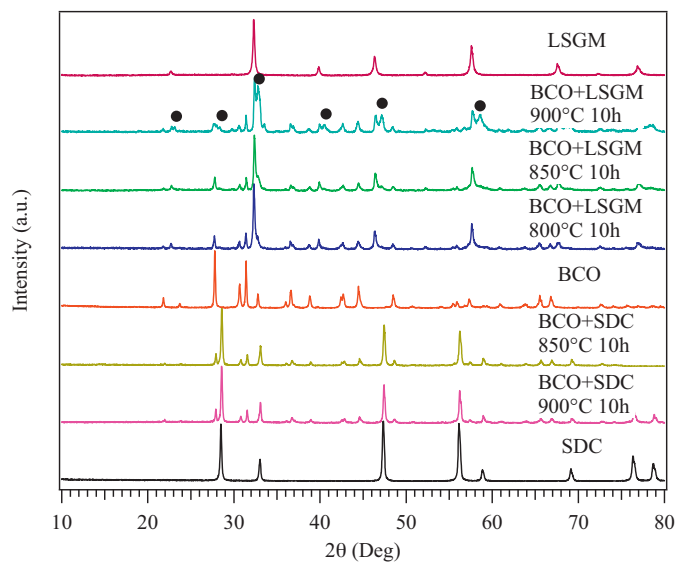
Fig. 3. The XRD patterns of BCO+SDC and BCO+LSGM mixtures sintered at 800–900 °C for 10 h in air together with those of starting materials BCO, SDC and LSGM. The solid circles represent an impurity phase.

Fig. 4. Typical electrochemical impedance spectra of (a) pure BCO cathode and (b) BCO+SDC composite cathode on an LSGM electrolyte measured at 700–800 °C in air. (c) The Arrhenius plots of the polarization resistance R_p for both cathodes and their linear fitting curves.

Displayed in Fig. 2 are the temperature dependence of the electronic conductivity $\sigma_e(T)$ and its Arrhenius plot, $\ln(\sigma_e T)$ versus $1000/T$, for the as-obtained BCO sample measured from 200 to 800 °C in air. In the measured temperature range, BCO exhibited a thermally activated semiconducting behavior with a slope change at $T \approx 350$ °C associated with a low-to-higher spin state transition of the Co^{3+} ions [7]. As previously reported [5], the $\sigma_e(T)$ values exceed $100 \, S \, cm^{-1}$ for $T > 450$ °C and reach $250 \, S \, cm^{-1}$ at 800 °C, signaling a good electronic conductivity. As can be seen in Fig. 2, a linear fitting to the Arrhenius plot above 400 °C yields an activation energy of $E_a = 0.29(1)$ eV, in agreement with the 0.27 eV reported by Ehora et al. [5].

We examined the chemical compatibility of BCO with SDC and LSGM by sintering their mixtures in a 1:1 weight ratio at different temperatures up to 900 °C for 10 h in air. Fig. 3 compared the XRD pattern of the mixtures after sintering together against those of pure BCO, SDC and LSGM. As can be seen, no reaction is evidenced between BCO and SDC up to at least 900 °C, signaling an excellent chemical stability of the BCO+SDC composite cathode in air. On the other hand, the mixture of BCO+LSGM starts to react above 850 °C; a significant amount of impurity phase can be clearly observed in the XRD pattern of BCO+LSGM sintered at 900 °C for 10 h, as is shown by the solid circles in Fig. 3. This fact has thus forced us (1) to choose SDC instead of LSGM as the composite component, (2) to limit the EIS measurements up to 800 °C, and (3) to add an LDC layer in between the BCO+SDC cathode and LSGM electrolyte to prevent an interdiffusion reaction in the electrolyte-supported test fuel cell.

As reported by Rolle et al. [6], we found that the pure BCO cathode screen-printed on the LSGM electrolyte also became detached after sintering at 800 °C for 1 h, presumably as a result of the mismatch of their thermal expansion coefficients. After trying several times, we managed only one time to attach a pure BCO cathode on the LSGM electrolyte for EIS measurement. On the other hand, the cathode adhesion on the electrolyte was improved greatly with the BCO+SDC composite. Fig. 4(a) and (b) displays typical EIS data at 700, 750, and 800 °C in air for pure BCO and the BCO+SDC composite as cathodes. For both cases, the impedance response for oxygen reduction is characterized by one semi-arc at different temperatures. The ohmic loss, i.e., the high-frequency intercept of the arc on the real axis, for the BCO+SDC composite cathode is about 1.5 times
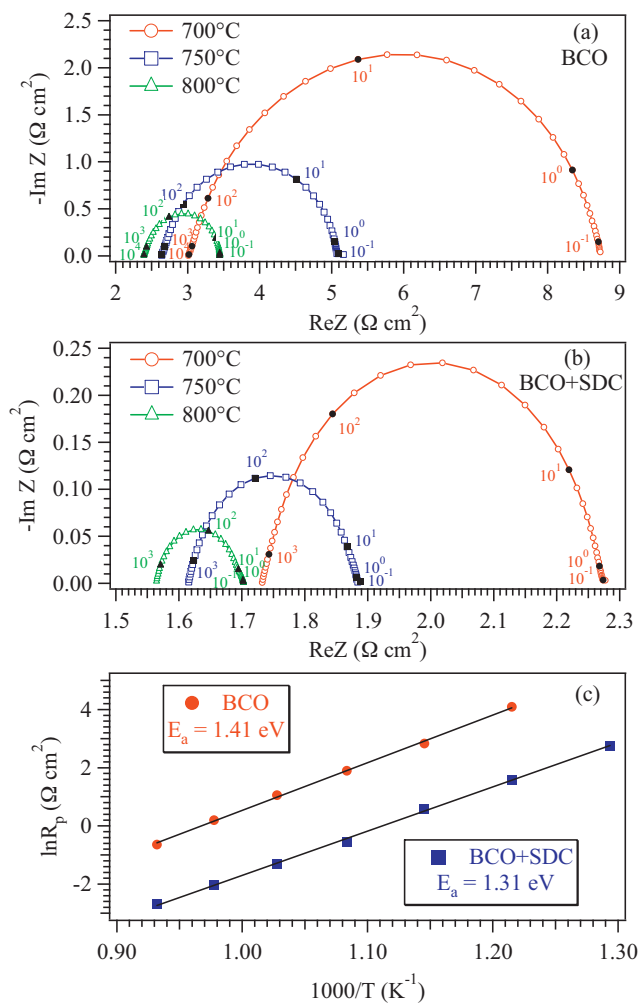
smaller than that of pure BCO, e.g. 1.6 versus 2.4 $\Omega \, cm^2$ at 800 °C, suggesting an improved adhesion on the electrolyte in the presence of SDC. But, the obtained ohmic resistivity for BCO+SDC is about 3 times larger than the theoretical value of the 600-μm thick LSGM electrolyte, presumably due to imperfect interface contact and/or partial delamination during the EIS measurements. From the difference between the low-frequency and high-frequency intercepts of the arc on the real axis, we can obtain the area specific resistance (ASR) of the two interfaces as a result of the oxygen reduction reaction, the oxygen surface/bulk diffusion, and the gas-phase oxygen diffusion. As can be seen, the ASR value reduces significantly with increasing temperature for both cases, but the ASR values of the BCO+SDC composite cathode are nearly one order of magnitude lower than those of pure BCO at the same temperatures. Therefore, the above observation demonstrated the dual function of the SDC: it not only improves the cathode adhesion on the electrolyte, but also enhances the electro-catalytic activity for the ORR. For our 50:50 wt.% BCO+SDC composite cathode, the polarization resistance $R_p = ASR/2$ reaches 0.133 and 0.068 $\Omega \, cm^2$ at 750 and 800 °C, respectively, lower than those reported by Rolle et al. [6] for the 70:30 wt.% BCO+GDC cathode. From the slope of the Arrhenius plot $\ln R_p$ versus $1000/T$ in Fig. 4(c), the activation energies were calculated to be 1.41 and 1.31 eV for the pure BCO and BCO+SDC composite cathode, respectively.
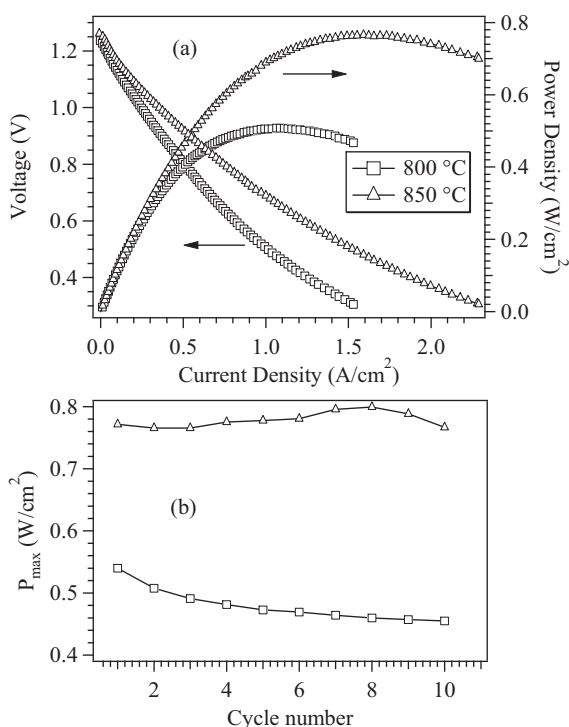
Fig. 5. (a) Cell voltage (left) and power density (right) as a function of the current density and (b) the maximum powder density P_{max} as a function of cycle number for the single fuel cell BCO + SDC|LDC|LSGM|LDC|NiO + GDC at 800 and 850 °C.

Finally, the performance of the BCO + SDC composite cathode was tested in a single cell. Fig. 5(a) depicts the cell voltage (left) and power density (right) as a function of current density for the BCO + SDC|LDC|LSGM|LDC|NiO + GDC single fuel cell operating at 800 and 850 °C with dry hydrogen as fuel and ambient air as oxidant. A high open-circuit voltage (OCV) of ~1.25 V was obtained at both temperatures. The maximum power densities P_{max} reach 520 and 770 mW cm^{-2} at 800 and 850 °C, respectively. At 800 °C, the P_{max} was reached at 0.7 V. Fig. 5(b) gives the P_{max} as a function of redox cycle number. As can be seen, the P_{max} at 800 °C decreases gradually and reaches a constant value of ca. 450 mW cm^{-2} after five cycles. On the other hand, the P_{max} at 850 °C roughly keeps constant at 770 ± 10 mW cm^{-2}. Since the P_{max} is close to the practical requirement of 500 mW cm^{-2} at 800 °C for a single cell with a 300-μm-thick electrolyte [13], the 1:1 BCO + SDC composite can be considered as a potential cathode material for IT-SOFCs.

4. Conclusions

We have synthesized single-phase polycrystalline Ba$_2$Co$_9$O$_{14}$ (BCO) by solid-state reaction and then prepared a composite cathode consisting of 50 wt.% BCO + 50 wt.% SDC, which was found to have an excellent chemical stability up to at least 900 °C in air. The electrochemical performance of this composite cathode was evaluated in a La$_{0.8}$Sr$_{0.2}$Ga$_{0.83}$Mg$_{0.17}$O$_{2.815}$ (LSGM) electrolyte-supported test cell. With a symmetric BCO + SDC|LSGM|BCO + SDC cell for EIS measurements, we obtained a polarization resistance R_p as low as 0.068 Ω cm^2 at 800 °C in air. The maximum power density reaches a nearly stable value of ~450 mW cm^{-2} at 800 °C for a single fuel cell consisting of BCO + SDC|LDC|LSGM|LDC|NiO + GDC with dry hydrogen as fuel, ambient air as oxidant, and a 300-μm-thick LSGM electrolyte. In comparison with a pure BCO cathode, the addition of SDC has two functions: it not only improves cathode adhesion to the electrolyte, but also enhances the electrocatalytic activity for the oxygen reduction reaction. These results demonstrate that the BCO + SDC composite can be a potential cathode material for IT-SOFCs. Further studies on the stability of BCO + SDC cathode in the presence of CO$_2$ at the intermediate temperature range are needed.

Acknowledgement

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