

Performance of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ -CGO-Ag cathode for IT-SOFCs

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Abstract

Single phase $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) was synthesized successfully at 1000 °C by solid reaction method. The dependence of thermal expansion and electrical conductivity on temperatures were studied. Electrochemical properties of pure BSCF cathode and BSCF + CGO (20 mol% Gd_2O_3 -doped CeO_2) composite cathode on CGO electrolyte at intermediate temperatures were investigated by using AC impedance analyzer. Additionally, a composite cathode of BSCF containing 30 wt.% CGO and a small quantity of Ag was prepared and studied, which shows the lowest area specific resistance ($<0.1 \Omega \text{ cm}^2$ at temperatures higher than 700 °C), being a high potential candidate of cathode for intermediate temperature SOFCs (IT-SOFCs, working at 800 °C or lower temperatures).

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1. Introduction

Solid oxide fuel cells (SOFCs) are attracting more and more attention, as a new electric power generation system with less emission of pollutant, lower noise, and high energy conversion efficiency. At present time, intermediate temperature SOFCs (IT-SOFCs) represent the research mainstream in the realm of fuel cell. An issue of significant importance for the development of IT-SOFCs is the selection of an appropriate cathode material. In the past, $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ with high electronic conductivity is used as cathode materials because of its low chemical reactivity and close thermal expansion with YSZ, which is the normally used electrolyte at 900–1000 °C. However, cathode polarization of $\text{La}_{1-y}\text{Sr}_y\text{MnO}_{3-\delta}$ becomes large at reduced temperatures, so that it is necessary to develop more active cathode materials in order to accelerate the commercialization of SOFCs.

Recently, Shao et al. reported a new cathode material $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) for low-temperature SOFCs [1]. In Shao's work, an interfacial polarization resistance as low as $0.06 \Omega \text{ cm}^2$ and a peak power density of 1010 mW cm^{-2} at 600 °C was reported for BSCF cathodes on Samaria-doped ceria (SDC) electrolyte, showing that BSCF was an excellent cath-

ode material for reduced-temperature SOFCs. However, other detailed properties, such as thermal expansion and electrical conductivity of BSCF, have not been reported by Shao. Shao's cathode powder was synthesized by a sol-gel method called combined citrate and EDTA complexing method [2]. However, for practical use of BSCF, more convenient and economical method, such as solid reaction method, should be developed, and more detailed physical and electrochemical properties of BSCF should be studied.

In the present work, we successfully synthesized single phase BSCF by solid reaction method and measured its thermal expansion and electrical conductivity. Then we focused on the investigation of electrochemical properties of pure BSCF cathode and BSCF + CGO composite cathode on CGO electrolyte at intermediate temperature with AC impedance measurements, expecting to find the optimal cathode sintering temperature and the most appropriate ratio between BSCF and CGO.

2. Experimental

2.1. Powder synthesis and characterization

Powder of BSCF was prepared from BaCO_3 , SrCO_3 , CoCO_3 and Fe_2O_3 of 99.9% purity in air by only one step solid reaction. The initial powders were mixed in a planetary ball mill for 3 h and heated at 1000 °C in air for 6 h. Then product was re-milled again for 1 h to break agglomeration, then dried and sieved with a grading sieve (#150 mesh). The obtained powder was subjected to X-ray diffraction with a Rigaku XRD diffractometer at room temperature, and found

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to be a single phase of cubic perovskite structure with the lattice parameter $a = 0.399$ nm.

2.2. Measurements of thermal expansion behavior and electrical conductivity

To measure the thermal expansion and electrical conductivity, the obtained powder was pressed uniaxially with a \varnothing 5 mm die and sintered at 1150 °C in air for 12 h. Furthermore, in order to compare the thermal expansion behavior between BSCF and CGO, two additional cylindrical specimens were prepared, one was pure CGO (from Rare-chem. Hi-Tech. Co. Ltd., China) sintered at 1450 °C for 5 h, another was the composite of 70 wt.% BSCF and 30 wt.% CGO sintered at 1150 °C for 12 h. Obtained cylindrical specimens, \sim 4 mm in diameter and more than 15 mm in length, were first used to measure the density by standard Archimedes method, showing more than 95% of relative density. Thermal expansion behavior was measured then with a dilatometer, NETZSCH DIL 402PC. Electrical conductivity was measured by the four-probe DC technique, using Pt paste as electrodes.

2.3. Sample preparation

CGO pellets of about 1.5 mm thick and 16 mm in diameter were prepared by uniaxially pressing of CGO powder. The pellets were subsequently sintered at 1450 °C for 5 h in air. Pure BSCF cathodes were screen-printed onto the CGO electrolyte and fired at 1050, 1100 and 1150 °C in air for 3 h, which were denoted as PB1050, PB1100, PB1150, respectively. The composite cathodes were sintered at 1100 °C in air for 3 h after screen-printed onto the CGO electrolyte, and denoted, for example, as CB3070 for the cathode with 30 wt.% CGO and 70 wt.% BSCF. Wang et al. reported that the performance of LSCF + CGO composite cathode could be improved dramatically by adding some proper amount of Ag [3]. In order to test whether this applies to BSCF cathode, an additional cathode CB3070 was coated by AgNO_3 solution, denoted as Ag-CB3070 (with an Ag content of \sim 4.5 mg cm^{-2}). For all these cathodes with \sim 0.916 cm^2 area, Pt paste was deposited on the opposite side as a counter electrode and a Pt reference electrode was placed on the CGO electrolyte surface of about 3 mm from the cathode by applying Pt paste, then sintering in air at 800 °C for 1 h. Interfacial polarization resistance was determined with three-electrode configuration using AC impedance spectroscopy (ZAHNER IM6e) and evaluated quantitatively with area specific resistance (ASR) which is the difference between the real-axis intercepts of the impedance plots and calibrated with area.

3. Results and discussion

3.1. Measurements of thermal expansion behavior and electrical conductivity

Fig. 1 compares the thermal expansion curves of the three specimens in air. It is interesting that the slope increase abruptly at about 650 °C and 700 °C for curve 1 and curve 2, respectively. The reason of this abrupt variation may be attributed to structural phase transition or generation of oxide ion vacancy [4], which needs further investigation. Additionally, it is obvious that pure BSCF has a much larger thermal expansion than that of CGO. Detailed calculation shows that the average thermal expansion coefficient (TEC) of pure BSCF between 30 °C and 850 °C is $18.53 \times 10^{-6} \text{ K}^{-1}$, while that of CGO is $13.11 \times 10^{-6} \text{ K}^{-1}$. Therefore large expansion mismatch may influence the long-term stability of cathode, causing some degradation. Fortunately, TEC could be reduced with the addition of CGO. The expansion mismatch is much smaller between CGO electrolyte and the composite cathode of 70 wt.% BSCF and 30 wt.% CGO. At low temperature

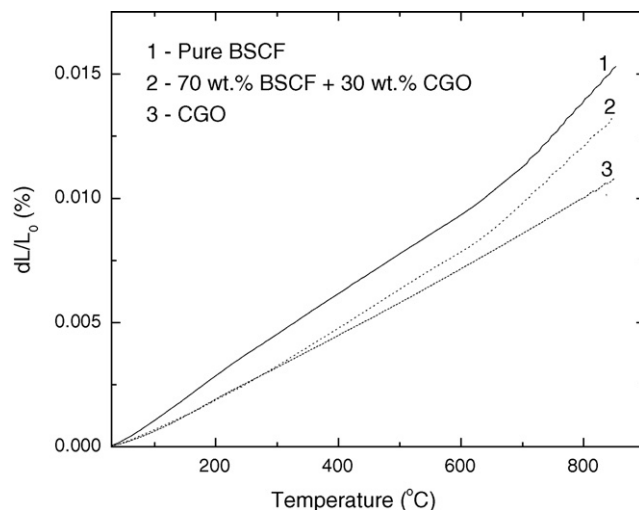


Fig. 1. Three specimens' thermal expansion curves in air.

range the shape of their curves are nearly the same. The average TEC for the composite of 70 wt.% BSCF and 30 wt.% CGO between 30 °C and 850 °C is 16.11 K^{-1} , closer to that of CGO, which may improve the long-term stability of the cathode.

Fig. 2 shows the electrical conductivity of BSCF in the temperature range of 200–900 °C in air. Comparing with the conductivity of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ [5], BSCF conductivity is much lower and only about 43 S cm^{-1} at 800 °C. However, BSCF indeed exhibits an excellent performance, which may result from the high rate of oxygen diffusion through it [1,2]. Unlike typical cathodes, the A-site cation of BSCF perovskite is an alkaline-earth species with 2+ valence rather than a rare-earth element with 3+ valence, therefore the charge balance may lead to much more oxygen vacancies in BSCF than in the typical cathodes, such as LSCF, then result in a higher oxide ion conductivity in BSCF than in LSCF.

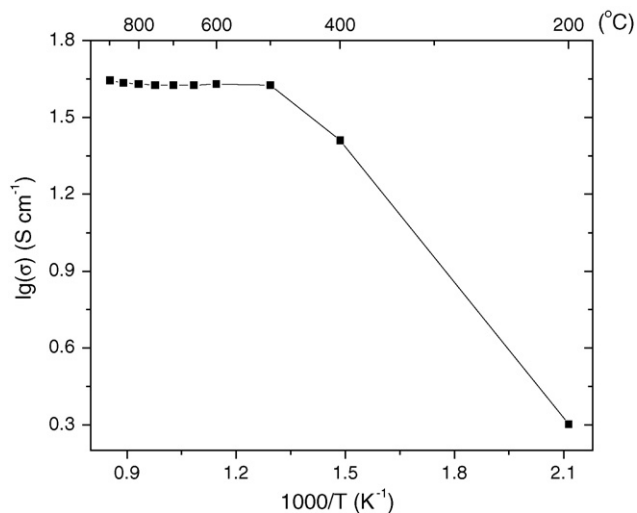


Fig. 2. Electrical conductivity of BSCF between 200 °C and 900 °C in air.

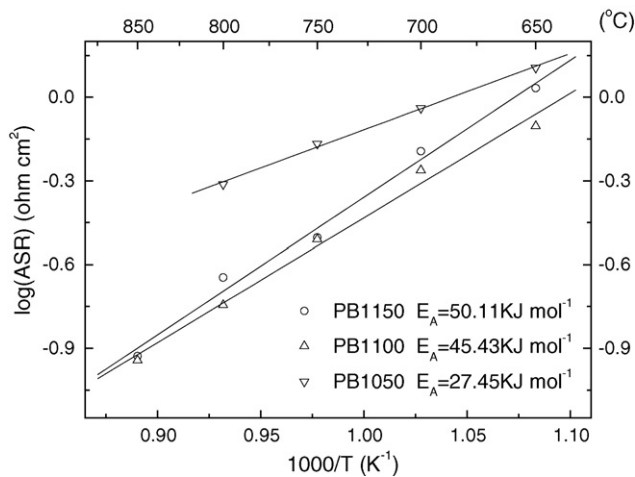


Fig. 3. Arrhenius plot of ASR for pure BSCF cathodes sintered at various temperatures in air.

3.2. Measurements of area specific resistance

Fig. 3 shows the Arrhenius plot of area specific resistance for pure BSCF cathodes sintered at various temperatures in air. The lowest ASR was achieved for the cathode sintered at 1100 °C, at which the cathode got a good adhesion with the electrolyte and at the same time the grain size of BSCF did not become too big. In fact, we found a small quantity of cathode PB1050 had desquamated after the test, which did not happen for cathodes PB1100 and PB1150.

Fig. 4 shows the Arrhenius plot of ASR for various composite cathodes in air. The cathode PB1100 is also included for comparison. Obviously, the ASR of PB1100 is the lowest, meaning that the introduction of CGO decreased the pure-BSCF cathode performance. In [1], Shao only mentioned that composite SDC+BSCF cathodes yielded lower power densities than pure BSCF cathodes, which was because the oxygen ion conductivity of BSCF was higher than that of SDC. However, maybe there are also some other reasons for that phenomenon. Comparing with some typical cathode materials,

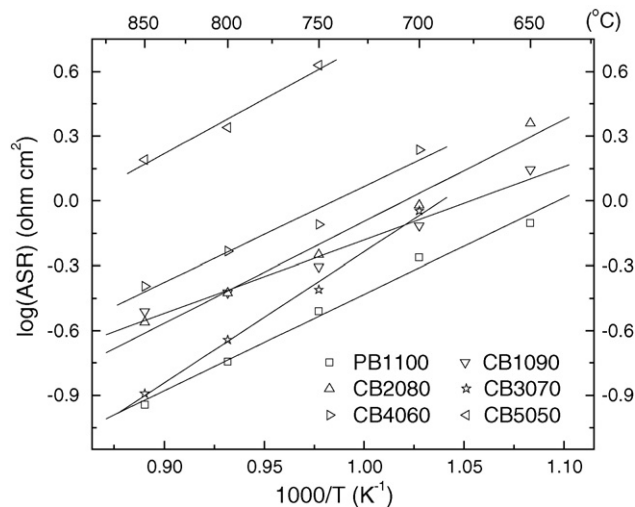


Fig. 4. Arrhenius plot of ASR for various composite cathodes in air.

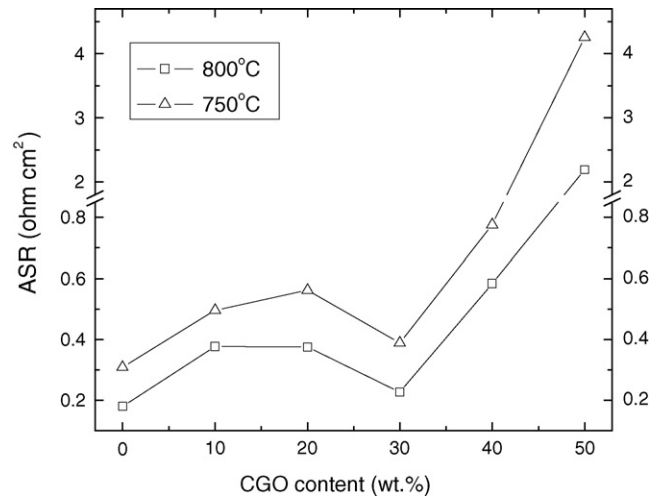


Fig. 5. ASR of BSCF+CGO composite cathodes with various CGO contents measured at 750 °C and 800 °C in air.

the electrical conductivity of BSCF is very low, which will become even lower by adding some CGO. The relatively low electrical conductivity of BSCF+CGO composite material should influence the current collection and the process of charge transfer for the whole cathode, which may also be responsible for the worse performance of the BSCF+CGO composite cathodes. However, the decrease in performance for the composite cathodes with ≤ 30 wt.% CGO content at 750 °C and 800 °C is only a little (shown in Fig. 5). Additionally, Fig. 5 shows that the ASR of BSCF+CGO composite cathodes appears to increase sharply when CGO content increases from 30 wt.% to 40 wt.%. In fact, we usually prefer to use the composite cathodes [6–11], because the addition of fine electrolyte powder will suppress the growth of cathode grain size therefore sustaining the porosity and increasing the three phase boundary (TPB) length, meanwhile decreases the thermal expansion mismatch between cathode and electrolyte therefore keeping a better interface adhesion between cathode and electrolyte. Considering all above-mentioned reasons, the cathode CB3070

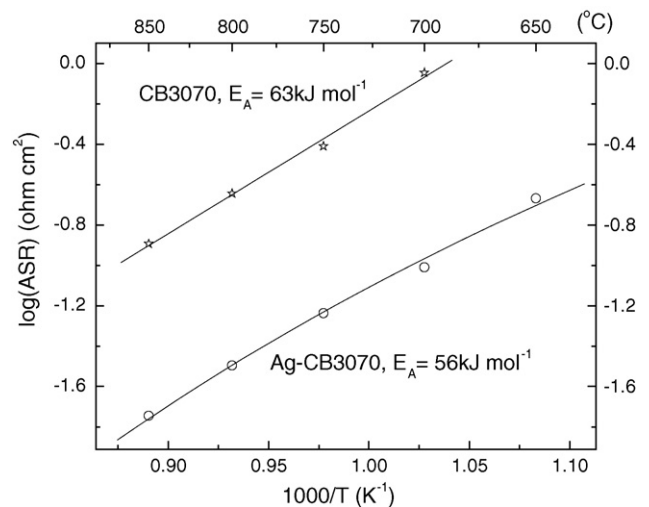


Fig. 6. Arrhenius plot of ASR for CB3070 and Ag-CB3070.

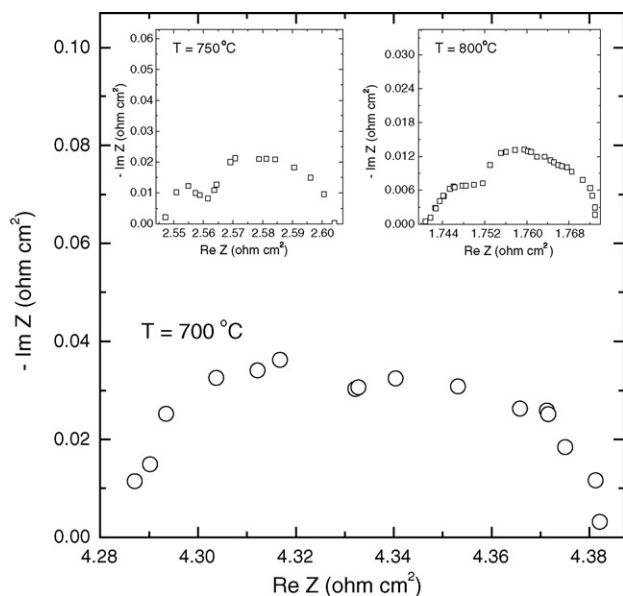


Fig. 7. Impedance spectroscopy of cathode Ag-CB3070 at various temperatures in air.

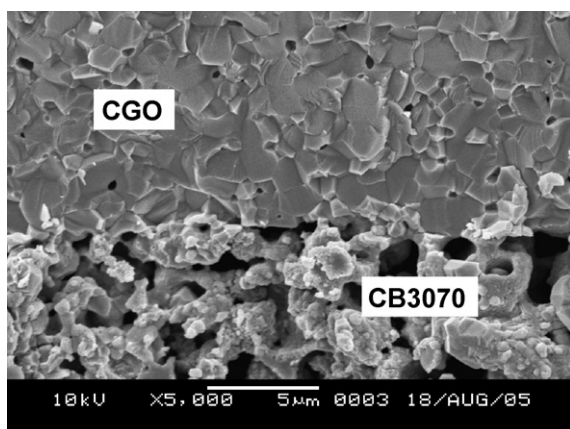


Fig. 8. A cross-sectional view (SEM micrograph) of cathode CB3070.

has the highest potential as the candidate of cathode material for IT-SOFCs, though the electrochemical performance of which is still a little worse than that of pure BSCF cathode (PB1100).

Fortunately, the performance of cathode CB3070 became much better by adding some proper amount of Ag (namely Ag-CB3070, shown in Fig. 6). For the cathode CB3070 with a relatively low electrical conductivity, the introduction of Ag will provide a much better path for current collection and improve the process of charge transfer, which should contribute mostly to the excellent performance of Ag-CB3070. Fig. 7 shows the impedance spectroscopy of cathode Ag-CB3070 in air at various temperatures, the ASR of which is considerably small

($0.1 \Omega \text{ cm}^2$ at temperatures higher than $700^\circ\text{C}</math>). Fig. 8 shows a cross-sectional view (SEM micrograph) of cathode CB3070. As shown in Fig. 8, at the interface between the solid and gas phases there exist pores of $1\text{--}2 \mu\text{m}$ in diameter, while the grain size in solid phase seems larger. It is widely accepted that keeping the nano and submicron structural cathode is the key to obtain an excellent performance [12,13]. But it should be noted that it is very difficult to prepare the nano and submicron structural powder by solid reaction method. So the good performance of cathode Ag-CB3070 achieved in this work is still very exciting to us. It is believed that the structure of cathode Ag-CB3070 can be still optimized, such as dispersing the CGO and Ag particles more effectively in the cathode, which will further promote the cathode performance and provide a bright prospect for the practical application of cathode Ag-CB3070.$

4. Conclusions

Single phase BSCF was synthesized successfully at 1000°C by solid reaction method. The average TEC of pure BSCF in the temperature range of $30\text{--}850^\circ\text{C}$ was $18.53 \times 10^{-6} \text{ K}^{-1}$ (much higher than that of CGO), which could be reduced to 16.11 K^{-1} by introduction of 30 wt.% CGO. The electrical conductivity of BSCF was all the same level ($\sim 43 \text{ S cm}^{-1}$) from 500°C to 900°C . The lowest ASR of pure BSCF cathodes in air was achieved for the cathode sintered at 1100°C . The introduction of CGO decreased the pure-BSCF cathode performance slightly, and the ASR of BSCF + CGO composite cathodes appeared to increase sharply when CGO content increased from 30 wt.% to 40 wt.%. It was very exciting that the performance of cathode CB3070 was improved dramatically by adding some proper amount of Ag. The ASR of Ag-CB3070 was less than $0.1 \Omega \text{ cm}^2$ at temperatures higher than 700°C . So the cathode Ag-CB3070 is a high potential candidate of cathode for IT-SOFCs.

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