

Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) and La_{0.6}Ba_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LBCF) cathodes prepared by combined citrate-EDTA method for IT-SOFCs

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Abstract

The potential candidates for IT-SOFCs cathode materials, Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) and La_{0.6}Ba_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LBCF), were synthesized by the combined citrate-EDTA method. The BSCF and LSCF aqueous precursors solutions were prepared from Sr(NO₃)₂, Ba(NO₃)₂, La(NO₃)₃·6H₂O, Co(NO₃)₂·6H₂O, Fe(NO₃)₃·9H₂O, citric acid and EDTA-NH₃. BSCF precursor solutions with different pH values were dried at 130 °C and subsequently calcined at various temperatures. Symmetrical electrochemical cells consisting of porous BSCF or LBCF electrodes and a GDC electrolyte were fabricated by the screen-printing technique, and the cathode performance of the interfaces between the porous electrode (BSCF or LBCF) and GDC electrolyte was investigated at intermediate temperatures (500–700 °C) using AC impedance spectroscopy. The pH value of the precursor solution did not affect the phase evolution behavior of the BSCF powder. On the other hand, it appears that a low pH value results in the calcined BSCF powder having a more porous microstructure. The cathode performances of the BSCF and LBCF electrodes were sensitive to the powder preparation conditions. The BSCF electrode prepared from the precursor solution with a pH value of 8 showed low polarization resistance, and its area specific resistances (ASR) were 1.1, 0.15 and 0.035 Ω cm² at 500, 600 and 700 °C, respectively. On the other hand, the cathode polarization resistances of the LBCF electrode were slightly higher than those of the BSCF electrode.

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1. Introduction

The fuel cell is an environmental-friendly energy conversion device which generates electricity directly from the chemical energy released by an oxidation and reduction reaction. Fuel cell systems show very high efficiency compare to other energy generation systems such as gas turbines, because they convert energies without any intermediate thermal energy being generated [1,2]. Since Grove introduced the first fuel cell operation which used sulfuric acid as an electrolyte in 1839 [3], many different kinds of fuel cells have been developed, such as the proton exchange membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), molten carbonate fuel cell (MCFC), and phosphoric acid fuel cell (PAFC). The solid oxide fuel cell (SOFC), which is also referred to as the ceramic fuel cell, was devel-

oped much later than Grove's system, after Nernst discovered solid oxide electrolytes [4,5]. In SOFCs, all of the components in the system are in the solid state, including the electrolyte, and a higher temperature is needed to operate them because, in general, solid state electrolytes only show sufficient ion conduction at high temperatures. The SOFCs have various advantages such as the lack of need for a separate reformer or noble metal catalyst, their multi-fuel capability [6] and cogeneration [7].

Conventional SOFCs are operated at temperatures of around 1000 °C. This high operating temperature, however, leads to many disadvantages, although hybrids of SOFCs with turbine engines show better efficiency at high temperature. At temperatures as high as 800–1000 °C, the materials incur damage caused by their chemical and physical instability, so that the choice of components that can be used for the fabrication and subsequent operation of the SOFCs is quite limited. For example, lanthanum chromite-based interconnectors, which are very expensive and difficult to fabricate or machine, are required for high temperature (800–1000 °C) SOFCs. If operating tempera-

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tures as low as 600–800 °C were to be used, inexpensive ferritic stainless steel (Fe–Cr alloy) could be used for the interconnectors [8,9] and the chemical, physical, thermal and mechanical durability of all of the components, such as the interconnectors, electrodes, electrolytes, and sealants, would be enhanced [10–12]. On the other hand, using such a low operating temperature causes a decrease in the ion conductivity of the electrolytes and an increase in the cathode resistance. Therefore, ceria-based electrolytes, such as gadolinia doped ceria (GDC) or scandia stabilized zirconia (ScSZ), are normally used, because they show better ion conductivity in this lower temperature range than yttria stabilized zirconia (YSZ) which is widely used as the electrolyte for high temperature SOFCs. In addition, other types of cathodes designed to improve the cathode performance at intermediate temperatures of around 600–800 °C have received a great deal of attention [13,14]. Recently, there was a report that $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ showed excellent performance as the cathode material in conjunction with a ceria-based electrolyte at reduced temperatures compared to conventional cathode materials [15].

In this study, we fabricated symmetrical electrochemical cells consisting of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) or $\text{La}_{0.6}\text{Ba}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LBCF) electrodes and a GDC electrolyte. The BSCF and LBCF powders were synthesized by the combined citrate-EDTA complexing method. The phase evolution behavior, microstructure of the synthesized powders and the cathode performance of the BSCF/GDC/BSCF and LBCF/GDC/LBCF cells were investigated.

2. Experimental procedure

2.1. Powder synthesis

The BSCF powders were synthesized by the combined EDTA-citrate method [16]. First, 0.04 mol of ethylenediaminetetraacetic acid (EDTA) was mixed with 40 ml of 1N NH_4OH solution to make NH_3 -EDTA buffer solution. Then, 0.01 mol of $\text{Ba}(\text{NO}_3)_2$, 0.01 mol of $\text{Sr}(\text{NO}_3)_2$, 0.016 mol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.004 mol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added to the buffer solution. Next, 0.06 mol of anhydrous citric acid was added and the pH value was adjusted to 6, 8 or 10 by adding further amounts of 1N NH_4OH solution. In this study, we referred to the BSCF, which was prepared from the solutions with pH values of 6, 8 and 10, as BSCF1, BSCF2 and BSCF3, respectively. Each solution was kept on a hotplate at 100 °C and stirred until gelation took place. Approximately one day later, the gelled BSCF-contained samples were baked in a drying oven at 130 °C for one day. Finally, the samples were calcined at various temperatures, viz. 550, 650, 750, 850 and 950 °C, for 4 h.

The LBCF powders were synthesized by the same method. To prepare the LBCF precursor, we used 0.012 mol of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 0.008 mol of $\text{Ba}(\text{NO}_3)_2$, 0.004 mol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.016 mol of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The pH value of the solution used for the preparation of the LBCF was adjusted to 6 using NH_4OH . Both the BSCF and LBCF powders calcined at 950 °C were ball-milled by 5 μm zirconia balls for 10 h to break up any agglomerations which formed during the

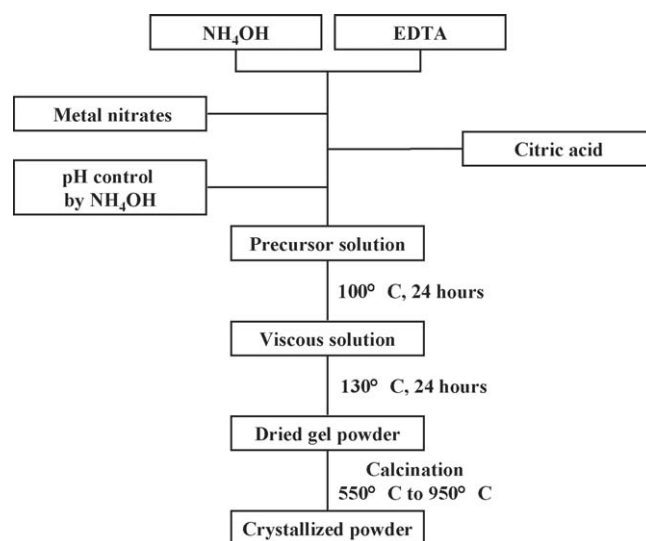


Fig. 1. Flow chart of experimental procedure.

calcination at high temperature. Fig. 1 shows the preparation flow chart.

2.2. Cell preparation

Symmetrical electrochemical cells consisting of porous BSCF or LBCF and a GDC electrolyte were fabricated. Uniaxially pressed disks of GDC ($\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$) powder, which was purchased from Anan Kasei, were sintered at 1400 °C for 4 h in air. 0.5 cm^2 BSCF or LBCF electrodes were screen printed on both sides of GDC electrolyte disks with a diameter of 12 mm and a thickness of 1 mm. The electrode pastes were prepared by mixing the 950 °C-calcined BSCF or LBCF powder with an organic vehicle at a weight ratio of 5:5. Then, the pastes were printed twice on each side of the electrolyte disk. A current-collector platinum layer containing 15 wt% GDC powder was further coated onto each of the electrodes. The symmetrical cells were calcined at 1000 °C for 2 h in air.

2.3. Characterization

The phase identification of the BSCF and LBCF powders, which were calcined at various temperatures, was performed with a powder diffractometer (DMAX-2500, Rigaku Co. Ltd., Japan) with Ni-filtered $\text{Cu K}\alpha$ radiation. The thermal decomposition behavior was examined using a DTA/TG thermal analyzer in air with a heating rate of 10 °C from room temperature to 900 °C. The morphologies of the as-synthesized and ball-milled powders were observed by scanning electron microscopy (SEM, JSM-5500, JEOL, Japan). The cross sections of the symmetrical cells having either an LBCF or BSCF electrode were observed by field emission scanning electron microscopy (FE-SEM, S-4200, Hitachi, Japan). For the AC impedance spectroscopy measurement, platinum wires were connected to the Pt meshes, which were in contact with the current collecting Pt layers. AC impedance spectroscopy was performed, with an excitation potential of 50 mV, over a frequency range from 1 MHz to 0.1 Hz,

generated by an impedance analyzer (1260A Impedance analyzer, Solartron, UK) and an electrochemical interface (1287A Potentiostat, Solartron, UK).

3. Results and discussion

The XRD patterns of the BSCF and LBCF powders are shown in Fig. 2. The three kinds of BSCF powders prepared from the precursor solutions with different pH values exhibited almost the same crystallization behavior. This result suggests that the pH value of the precursor solution does not affect the chelation between the constituent cations and EDTA or citric acid. In our previous study, it was found that the chelation between the cations and glycine strongly depended on the pH value of the precursor solution [16]. A highly acidic precursor solution increased the temperature at which a single phase was formed. When the gelled powders were calcined at a temperature higher than 850 °C, second phase-free single phase perovskite could be obtained in the case of the BSCF.

On the other hand, the perovskite phase appeared at temperatures as low as 550 °C, although only small peaks, which were attributed to the perovskite LaCoO_3 phase, were observed and the crystallinity increased with increasing calcination temperature. That the temperature at which the perovskite phase appeared was low is interesting and important, since this implies that one can synthesize the LBCF powder with weak agglomeration at low temperatures.

Fig. 3 shows the DTA/TG curve of the gelled BSCF1 powder which was dried at 130 °C for 24 h. A small endothermic peak is present at 200 °C as a consequence of the loss of the residual

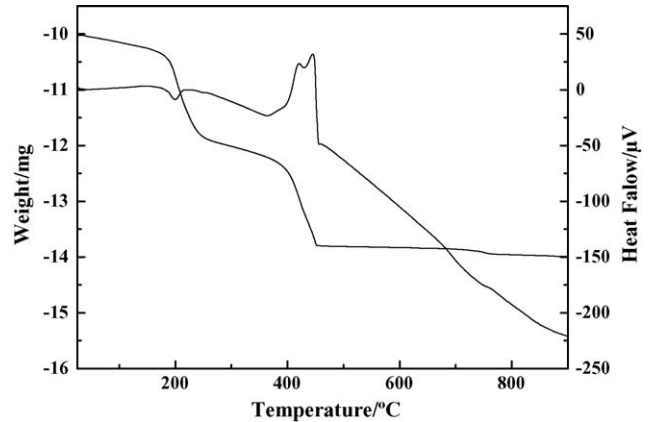


Fig. 3. TG/DTA curves of the gelled BSCF1 powder prepared from the precursor solution with a heating rate of 10 °C min⁻¹.

and hydrated water, as well as the charation of the gelled powder. From 350 to approximately 460 °C, two strong exothermic peaks were observed which seemed to be associated with the decomposition/oxidation of the metal-chelates and the reaction between the chelates, producing intermediate oxide phases. As is evident in Fig. 2(a–c), in the case of the BSCF, the crystalline phases start to appear at 550 °C.

The SEM photographs of the as-calcined and ball-milled BSCF and LBCF powders are shown in Figs. 4 and 5, respectively. It can be seen from Fig. 4(a–d) that the powders calcined at 950 °C were strongly agglomerated. At 750 °C where the perovskite phase starts to appear and crystallize, agglomerated particles were formed. As the calcination temperature

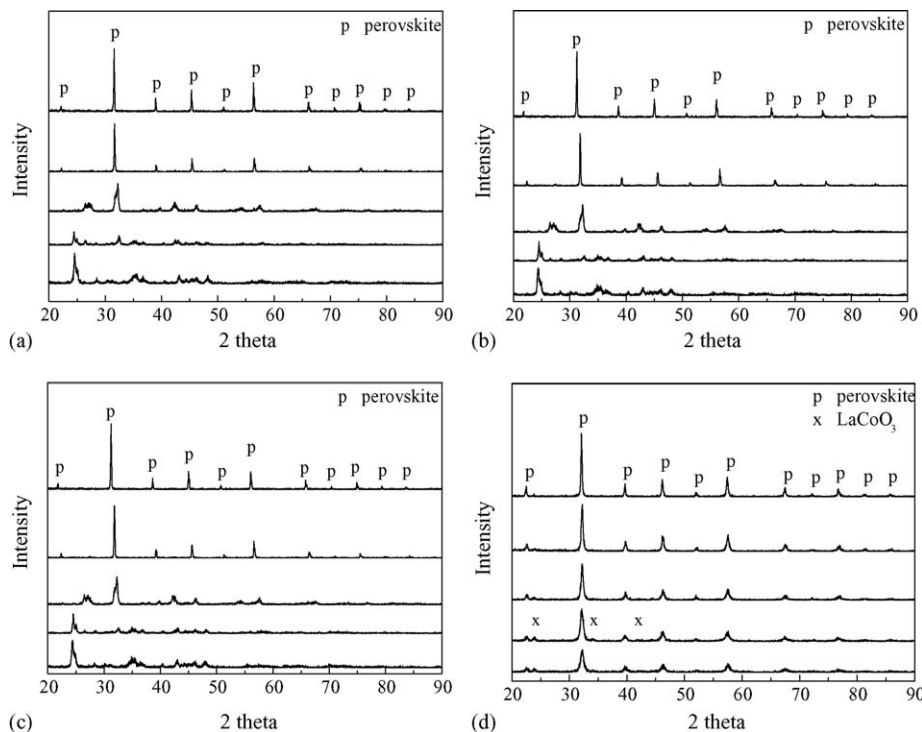


Fig. 2. XRD patterns of BSCF1 (a), BSCF2 (b), BSCF3 (c) and LBCF (d) powders prepared by the combined citrate-EDTA method.

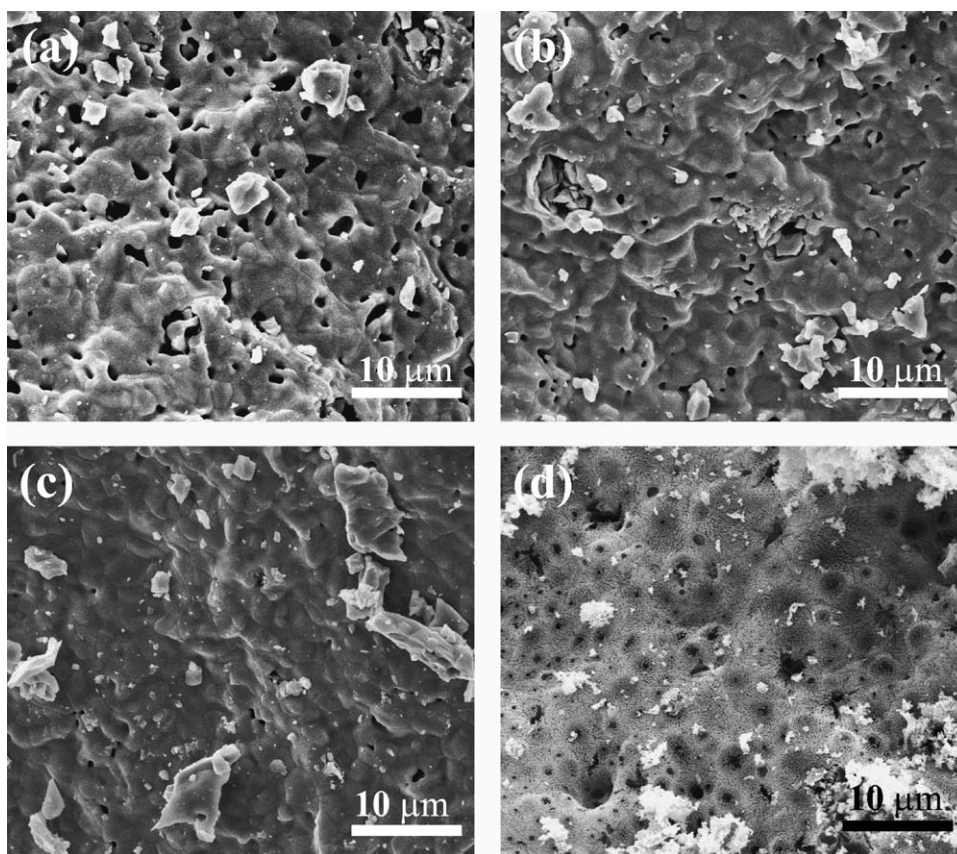


Fig. 4. SEM photographs of BSCF1 (a), BSCF2 (b), BSCF3 (c) and LBCF (d) powders which were calcined at 950 °C for 4 h.

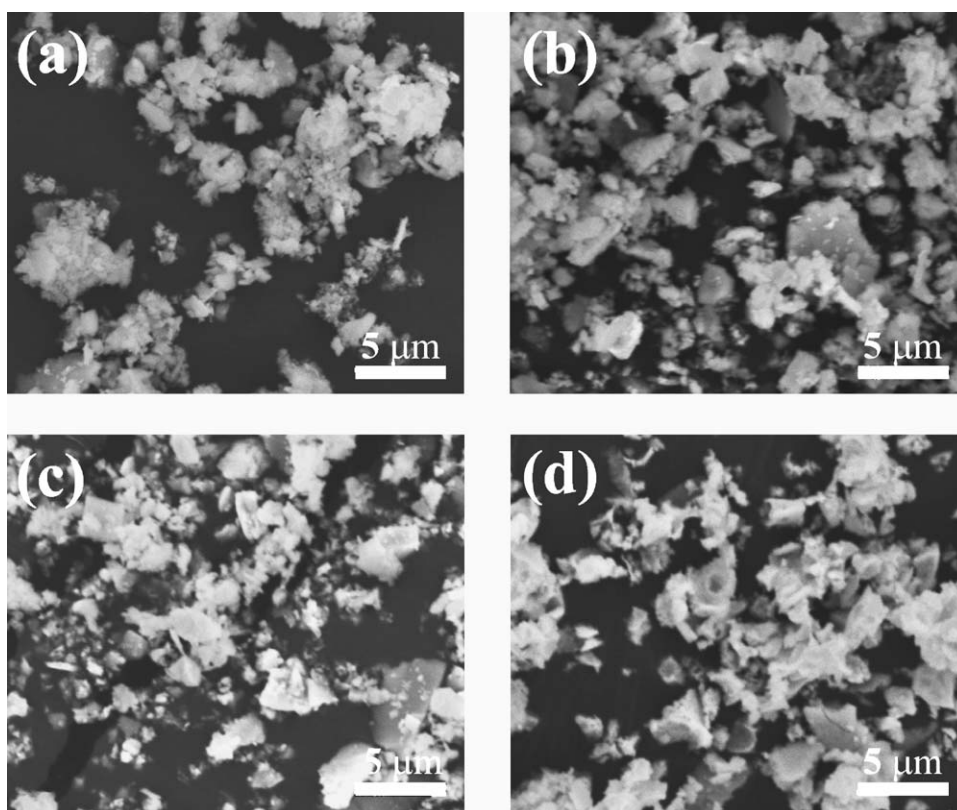


Fig. 5. SEM photographs of BSCF1 (a), BSCF2 (b), BSCF 3 (c) and LBCF (d) powders which were calcined at 950 °C for 4 h and ball-milled for 10 h.

was increased up to 950 °C, the sintering between the weakly agglomerated particles proceeded, producing dense and strongly agglomerated BSCF or LBCF particles. In comparing Fig. 4(d) with (a–c), the LBCF particles showed a more porous and finer microstructure than the BSCF particles, because the crystallization temperature of the LBCF was much lower than that of the BSCF, as described above.

The microstructure of the BSCF powder prepared from the precursor solution with the highest pH value (BSCF3) is denser than that of the BSCF powder prepared from the precursor solution with the lowest pH value (BSCF1). These observations support the hypothesis that one can control the morphology of the BSCF powder by varying the pH value of the precursor solution. After ball-milling for 10 h, the particle sizes of the BSCF and LBCF were significantly reduced to a few micrometers, although the ball-milled BSCF and LBCF were not seen to show a homogeneous particle size distribution. Therefore, ball-milling conditions should be further optimized.

The cross sections of the BSCF and LSCF electrodes sintered at 1000 °C for 2 h were observed by SEM. Typical images are shown in Fig. 6. The BSCF or LBCF electrodes and the platinum electrode were approximately 15–20 μm thick. The GDC electrolyte exhibited good interfacial contact with both the BSCF and LBCF electrodes, with no signs of delamination. According to Wang et al. [17,18] and Hayashi et al. [19], thermal expansion coefficient of BSCF is similar to that of the GDC elec-

trolyte. Therefore, no exfoliation of the electrodes was observed in this study. Both the electrodes and platinum current collecting layer showed sufficiently porous microstructures, whereas the GDC electrolyte was relatively dense (96% of the theoretical density).

Fig. 7 shows the impedance spectra of the BSCF and LBCF electrodes, measured at 700, 600 and 500 °C, in air. The BSCF showed better electrocatalytic activity than the LBCF. This tendency could be observed at all operating temperatures. Among the different BSCF electrodes, the BSCF2 electrode that was prepared from the precursor solution with a pH of 8 showed the best area specific resistance (ASR). The ASR values of the BSCF2 and LBCF electrodes were estimated to be approximately 0.035 and 0.1 Ω cm², respectively, at an operating temperature of 700 °C.

Since the ionic conductivity of Gd_{0.1}Ce_{0.9}O_{2-δ} was estimated to be ~0.02 S cm⁻¹ at 600 °C, the ohmic resistances should be 10 Ω, based on the assumption that the thickness of the electrolyte was 0.1 cm, the area of the electrode was 0.5 cm² and the resistance due to the electronic resistance of the electrodes and current collecting Pt layers can be ignored. As can be seen in Fig. 7(b), the ohmic resistances of the cells ranged from 10.5 to 12.5 Ω for the BSCF/GDC/BSCF cells at 600 °C, which is similar to the calculated values, suggesting that our processing method and materials are adequately optimized.

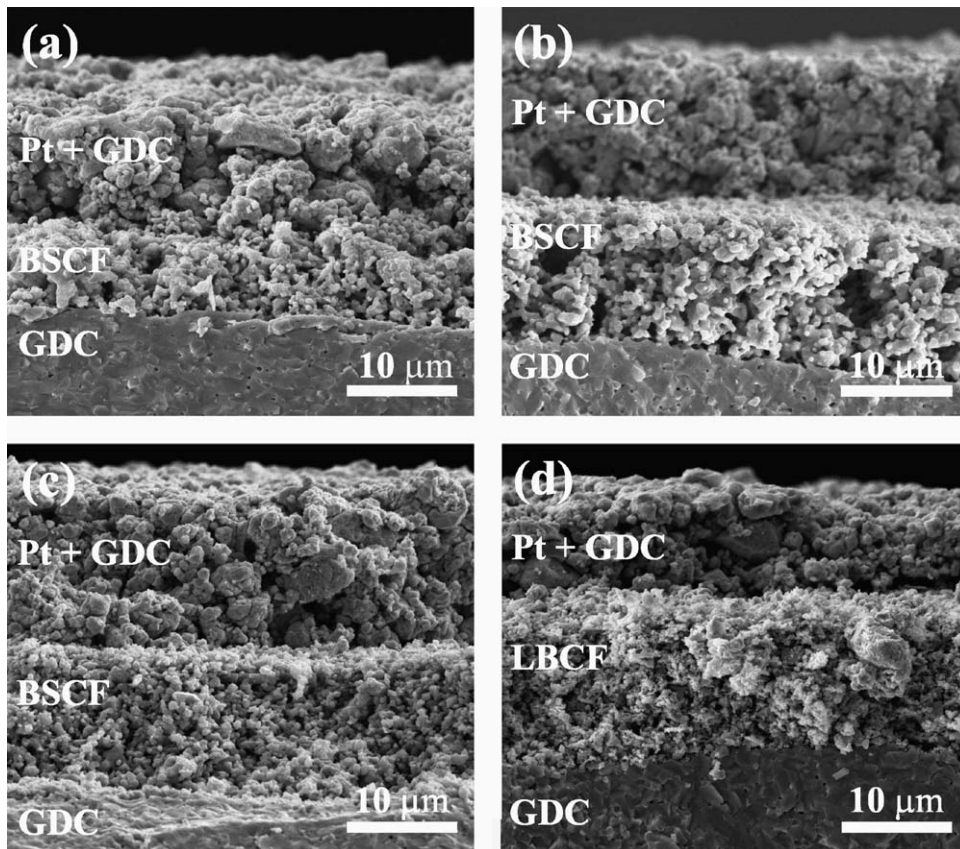


Fig. 6. Cross section SEM photographs of BSCF1/GDC (a), BSCF2/GDC (b), BSCF3/GDC (c) and LBCF/GDC (d) symmetrical cells showing the electrode-electrolyte interfaces.

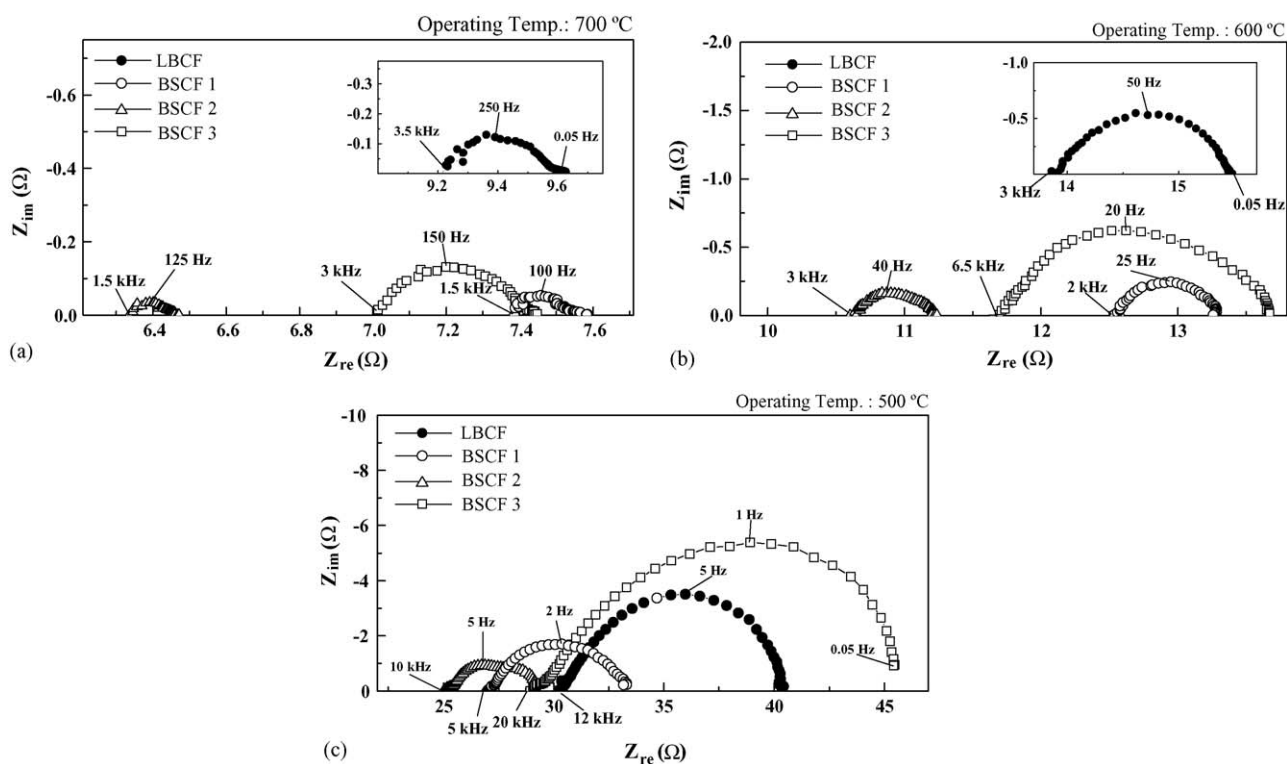


Fig. 7. Impedance spectra of BSCF/GDC/BSCF and LBCF/GDC/LBCF symmetrical cells. The operating temperature was 700 °C (a), 600 °C (b) and 500 °C (c).

From the polarization resistance versus temperature relationship shown in Fig. 8, the activation energy can be calculated. The activation energy was 100, 98, 109 and 106 kJ mol⁻¹ for the BSCF1, BSCF2, BSCF3 and LBCF electrodes, respectively. These values are much lower than those of other cathode materials. For example, the activation energy for LSCF was estimated to be 135–142 kJ mol⁻¹ in our previous reports [7,16]. Thus,

BSCF or LBCF would be expected to show much lower polarization resistances than LSCF, especially at lower temperatures.

The excellent performance obtained for the BSCF electrode can be attributed to its high oxygen ion conductivity. In fact, the oxygen ion diffusion coefficient of the BSCF electrode is $7.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is much higher than that of other cathode materials having the perovskite structure [15,20]. In addition, the activation energies for oxygen ion diffusion and the oxygen surface exchange reaction are known to be 42 ± 2 and $113 \pm 11 \text{ kJ mol}^{-1}$, respectively. Shao et al. [15] reported that the activation energy of polarization resistance was 116 kJ mol⁻¹ in the temperature range of 400–725 °C, which is a similar value to that of the oxygen surface exchange reaction. The results obtained in this study are quite consistent with those obtained in previous reports by other researchers, and thus the rate determining step of the electrode reaction might well be an oxygen surface exchange reaction.

4. Conclusion

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) and $\text{La}_{0.6}\text{Ba}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LBCF), which are potential candidates for the cathode materials of IT-SOFCs, were synthesized by the complexing EDTA-citrate method. Single phase perovskite could be obtained by calcining the gelled BSCF and LBCF powders at temperatures above 850 °C. The phase evolution behavior of the BSCF did not depend on the pH value of the precursor solution, while the BSCF powder prepared from the precursor solution with the highest pH value showed the densest

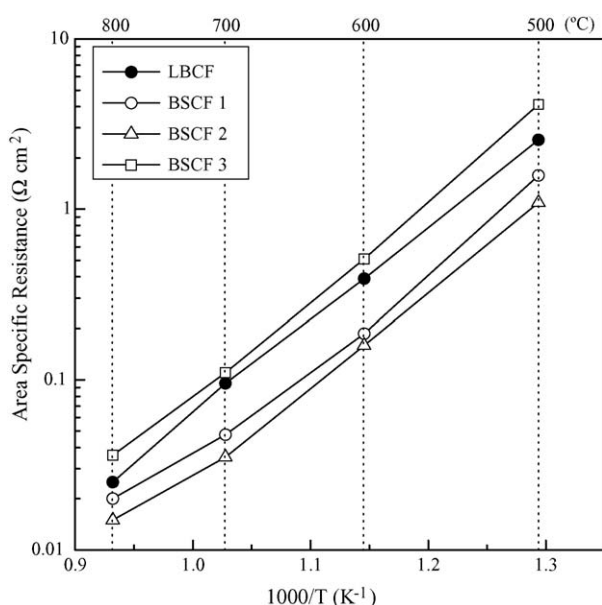


Fig. 8. The area specific resistance (ASR) of the LBCF/GDC and BSCF/GDC cells as a function of temperature.

microstructure. Based on the impedance spectra obtained from the BSCF and LBCF cathodes, BSCF2 which was prepared from the solution with a pH value of 8 was found to be the best electrode. The area specific polarization resistances of the BSCF2 electrode were 0.15 and 0.035 $\Omega \text{ cm}^2$ at 600 and 700 °C, respectively. In the case of the LBCF electrode, the ASR values were 0.38 and 0.095 $\Omega \text{ cm}^2$ at 600 °C and 700 °C, respectively. The excellent performances observed for the BSCF and LBCF cathodes were attributed to their having higher oxygen ion conductivities than the other perovskite cathode materials.

Acknowledgements

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