

# Sintering behavioral and electrochemical performances of LSM-BSB composite cathode for IT-SOFCs

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**Abstract** In this paper,  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3\text{-Ba}_{0.1}\text{Bi}_{0.9}\text{O}_{1.5-\delta}$  (LSM-BSB) composite cathode was prepared and characterized for intermediate temperature solid oxide fuel cells (IT-SOFCs). XRD results show that no reaction occurred between LSM and BSB at 900°C. SEM results show that the LSM-BSB composite cathode formed good contact with YSZ electrolyte after sintered at 900°C for 2 h, which significantly reduced the sintering temperature of cathode. Compared with the LSM-YSZ electrode sintered at 1200°C for 2 h, LSM-BSB electrode exhibits better electrochemical performance. At 800°C, the area specific resistance (ASR) of the LSM-BSB30 electrode is about  $0.168 \Omega\text{cm}^2$ , which is nearly 1.5 times lower than that of LSM-YSZ composite cathode.

**Keywords** Perovskites · Ceramics · Composite cathode · Sintering behavioral · Solid oxide fuel cells

## 1 Introduction

Recently, the development of intermediate temperature solid oxide fuel cells (IT-SOFCs) has attracted lots of attention [1].

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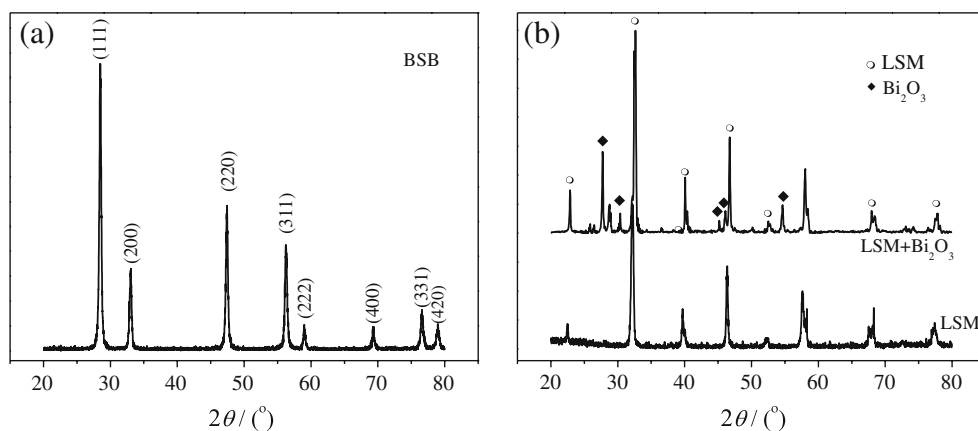
With lower temperature (600–800°C), there is not only a broader scope to search for suitable electrode materials, but also reducing the high temperature requirements of materials. However, with the reduction of operating temperature, the electrochemical properties of traditional cathode materials have also declined [2]. So, one of the important tasks is to find cathode materials used for IT-SOFCs. Now, there are two main ways to solve the problem, one is to develop mixed ionic and electronic conductor materials, such as  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_3$  (LSCF) [3],  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  (BSCF) [4] and some  $\text{K}_2\text{NiF}_4$ -type  $\text{A}_2\text{BO}_4$  materials [5–7]. The other is to fabricate composite cathode through mixing electronic conductor with oxygen-ion conductor, such as LSM-YSZ composite cathode [8], LSM-SDC composite cathode [9]. Via the latter way, higher ion conductivity of oxygen-ion conductor, better electrochemical properties of composite cathode can be obtained. Oxygen-ion conductors based on bismuth oxide have much higher ion conductivity, with respect to other well-known oxygen-ion conductors; the conductivity of bismuth oxide is about two orders of magnitude higher than that of stabilized zirconia [10–12].

In this paper, we prepared BaO stabilized  $\text{Bi}_2\text{O}_3$  (BSB) oxygen-ion conductor and fabricated the LSM-BSB composite cathode. The sintering behavioral and electrochemical properties of LSM-BSB composite cathode on YSZ electrolyte were investigated.

## 2 Experimental

$\text{Ba}_{0.1}\text{Bi}_{0.9}\text{O}_{1.5-\delta}$  (BSB) material was synthesized by EDTA-citric acid process [13]. First,  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Bi}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were mixed according to the stoichiometric compositions of BSB, and dissolved in pure water; then the nitrate solution was mixed with a previously prepared 1 M

**Fig. 1** XRD patterns of powders. (a) BSB powder; (b) LSM-BSB mixture sintered at 900°C for 2 h

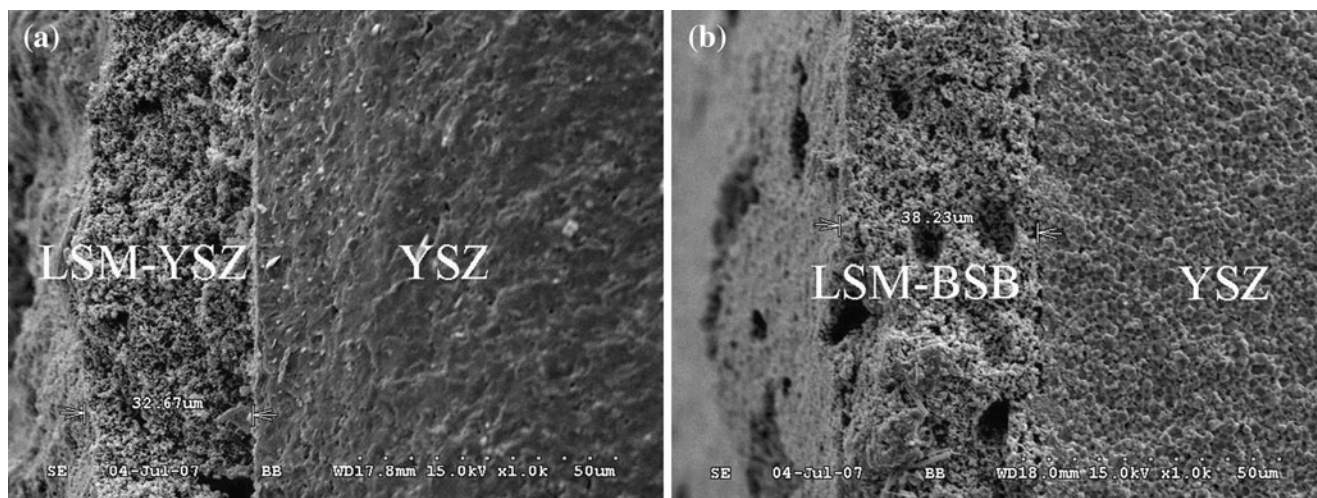


EDTA–NH<sub>4</sub>OH solution. After that, a certain amount of citric acid was introduced, and the mole ratio of the total metal ions : EDTA acid : citric acid was controlled around 1:1:1.5. NH<sub>4</sub>OH was added to adjust the pH value to about 6.0. A brown gel was obtained after the solution was agitated for 12 h at 80°C. This gel was held at 200°C for several hours to remove organics and form a powder precursor. Finally, the BSB precursor was calcined at 750°C for 2 h to obtain the final powders. La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (LSM) powders were prepared via the same process according to Ref. [13], the LSM precursor was calcined at 1000°C for 4 h. The starting materials used in these experiments were analytical reagent grade. As synthesized BSB, LSM powders, and the LSM-BSB mixtures after calcinations were examined by X-ray Diffraction (XRD, Bede D<sup>1</sup>, Cu Kα radiation).

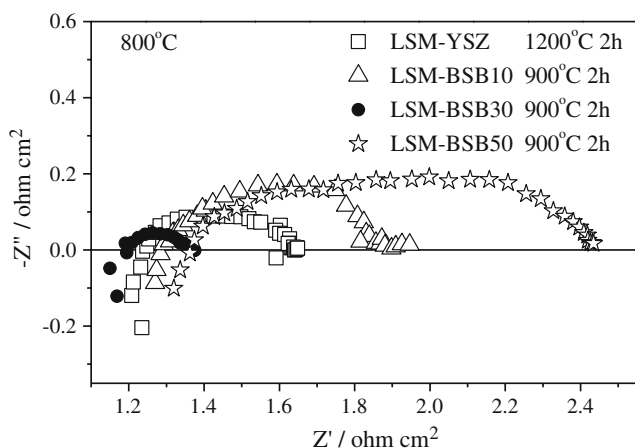
The YSZ (TZ-8Y, Tosoh Co.) powders were pressed into pellets using a stainless steel mold (13 mm in diameter) under about 400 MPa, followed by sintering at 1400°C for 4 h in air to obtain dense electrolyte. The thickness of the

sintered pellets was about 0.4 mm. The LSM-BSB mixtures (0–50 wt.% ratio, named as LSM-BSB<sub>x</sub>, x=0–50) were firstly ball-milled with ethanol media by planetary ball mill for 3 h using an agate jar and zirconia ball media. The rotation speed was 200 rpm. After dried, these mixtures were dispersed in an organic binder and painted on one side of the YSZ pellets, respectively. Then, the pellets were sintered at 900°C for 2 h in air. In order to compare, LSM-YSZ composite cathode was also fabricated and sintered at 1200°C for 2 h in air. The microstructure of the composite electrodes/electrolyte was studied with SEM (Hitachi S-3000 N).

Electrochemical performances were measured with a three-electrode method in air. Prepared cathode on YSZ was used as work electrode (WE). A regular Ag counter electrode (CE) was applied symmetrically opposite to the cathode. An Ag point reference electrode (RE) was attached on the free YSZ surface, 3 mm away from the cathode [14]. The cathodic area was 0.20 cm<sup>2</sup>. Ag grid was printed on the



**Fig. 2** SEM images of the cross section of two composite cathodes after electrochemical test. (a) LSM-YSZ composite cathode sintered at 1200°C for 2 h; (b) LSM-BSB30 composite cathode sintered at 900°C for 2 h.



**Fig. 3** AC impedances of several kind composite cathodes at 800°C

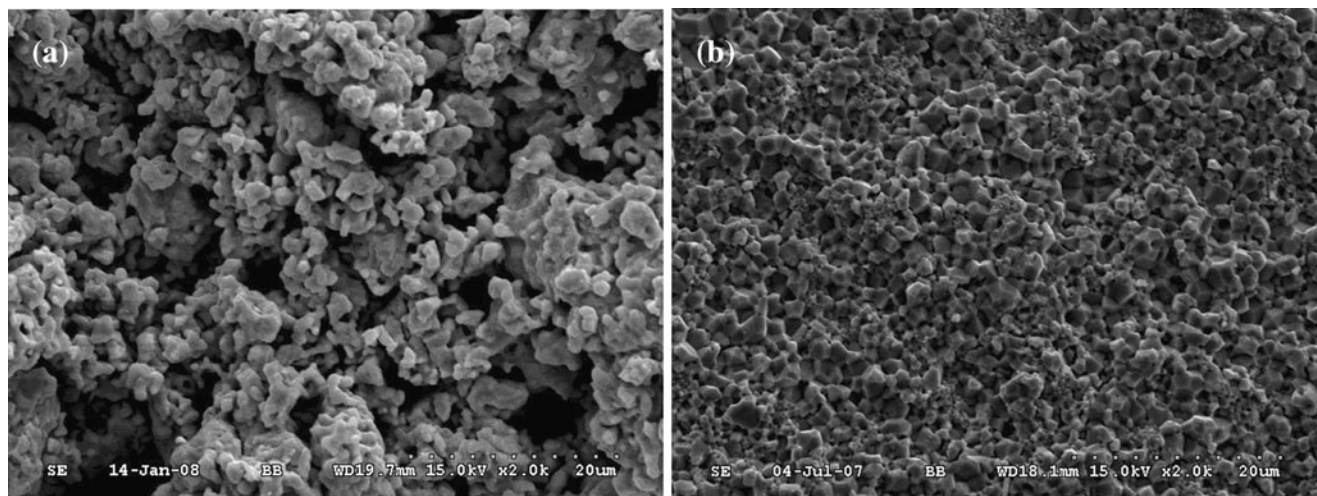
surface of the cathode serving as current collector. AC impedances were carried out with CHI604b electrochemical analyzer in the frequency range of 100 kHz to 0.1 Hz.

### 3 Results and discussion

Figure 1(a) shows the X-ray diffraction pattern of BSB powder. The XRD result indicated the formation of a single phase  $\text{Bi}_2\text{O}_3$  with a cubic fluorite structure. The reactivity of LSM with BSB was further studied. Figure 1(b) shows the XRD pattern of the LSM–BSB mixture prepared by thoroughly mixing LSM with BSB powders in a 1:1 weight ratio, and then sintering at 900°C for 2 h. From the Fig. 1 (b), it can be clearly seen that the main peaks of LSM and BSB were present, except for some unknown peaks between 25° and 40°, indicating that LSM and BSB was chemical compatibility at certain extent.

As we known, sintering temperature has a dramatic effect on the electrode microstructure, which in turn influences the electrode properties. Figure 2 shows cross-sectional images of the interface of the YSZ electrolyte and electrode after electrochemical test. Figure 2(a) is the interface of LSM-YSZ|YSZ electrode sintered at 1200°C for 2 h; Fig. 2(b) is the interface of LSM-BSB|YSZ electrode sintered at 900°C for 2 h. It can be seen that the thicknesses of two kind cathodes were 30~40  $\mu\text{m}$ , and there were enough three phase reaction zone. Compared with Fig. 2(a), it can be seen clearly that there also formed excellent contact between LSM-BSB composite cathode and YSZ electrolyte in Fig. 2(b). The result shows that the cathodic sintering temperature could be reduced through fabricating LSM-BSB composite cathode.

Shown in Fig. 3 is AC impedances LSM-YSZ and LSM-BSB $_x$  ( $x=10, 30, 50$ ) electrode on YSZ electrolyte at 800°C in air under open circuit potential condition. The intercepts of the impedance arcs with the real axis at high frequencies correspond to the resistance of the YSZ electrolyte and lead wires, while the overall size of the arcs can be primarily attributed to cathode area specific resistance (ASR), which is widely used to describe the all resistance terms related to electrode processes. It could be observed that the ASR of LSM-BSB30 composite cathode was 0.168  $\Omega\text{cm}^2$ , which reduced about 1.5 times compared with that of LSM-YSZ composite cathode. Hart et al. [15] found the three-phase reaction zone could be extended after materials with higher ionic conductivity had been used. Murray and Barnett [9] prepared an LSM–GDC (50:50 wt.%) composite cathode on GDC electrolyte and found the cathodic polarization was 0.34  $\Omega\text{cm}^2$  at 750°C, almost 24 times lower than that of the pure LSM cathode (8.19  $\Omega\text{cm}^2$  at 750°C under open-circuit conditions) on the YSZ electrolyte substrate. Zhu et al. [16] reported that an LSCF–SDC composite



**Fig. 4** Surface SEM images of (a) LSM-BSB30 and (b) LSM-BSB50 composite cathode after sintered at 900°C for 2 h

cathode showed a lower polarization resistance of  $0.23 \Omega\text{cm}^2$  on an SDC electrolyte at  $700^\circ\text{C}$ . All these workers supposed that the composite cathode improved the interfacial contact and expanded the TPB, which provided a guide to the improvement of the cathode electrochemical performance. Furthermore, composite cathode with high ionic conductivity is convenient to take place oxygen adsorption, dissociation and diffusion on the cathode surface. The oxygen ionic conductivity of stabilized  $\text{Bi}_2\text{O}_3$  is  $0.193 \text{ Scm}^{-1}$  at  $650^\circ\text{C}$ , while that of YSZ is only  $0.02 \text{ Scm}^{-1}$  at  $800^\circ\text{C}$  [14]. Therefore, LSM-BSB composite cathode can own more excellent electrochemical performance as long as good contact between electrode and electrolyte is obtained after sintering.

From the Fig. 3, we can also see that LSM-BSB electrode showed the best performance after 30 wt% BSB was used. Three phase boundary was not enough when BSB amount was too small, and the electrode interface would be non-uniform after sintering. However, superfluous BSB will cut off the connection of LSM with each other, and finally, influence the electrochemical properties of LSM-BSB electrode, such as the polarization resistance. Figure 4 shows SEM images of the surface of LSM-BSB30 electrode and LSM-BSB50 electrode after sintered at  $900^\circ\text{C}$  for 2 h, respectively. It can be observed that there was no porosity for LSM-BSB50 electrode. There is one reason to explain the phenomenon. The melting point of  $\text{Bi}_2\text{O}_3$  is  $825^\circ\text{C}$ , under sintering temperature. Therefore, at  $900^\circ\text{C}$ , excessive BSB will melt and gather in the electrode surface, and finally lower the porosity of the electrode.

#### 4 Conclusions

The  $\text{Ba}_{0.1}\text{Bi}_{0.9}\text{O}_{1.5-\delta}$  (BSB) oxygen-ion conductor was synthesized via EDTA-citrate process and characterized by XRD.  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3\text{-Ba}_{0.1}\text{Bi}_{0.9}\text{O}_{1.5-\delta}$  (LSM-BSB) composite cathode was prepared and characterized for intermediate

temperature SOFCs (IT-SOFCs). XRD results show that no reaction occurred between LSM and BSB at  $900^\circ\text{C}$ . SEM results show that LSM-BSB electrode formed good contact with YSZ electrolyte after sintering at  $900^\circ\text{C}$  for 2 h, which significantly lowers the sintering temperature of cathode. Compared with the LSM-YSZ electrode sintered at  $1200^\circ\text{C}$  for 2 h, LSM-BSB electrode exhibits better electrochemical performance. At  $800^\circ\text{C}$ , the area specific resistance (ASR) of the LSM-BSB30 electrode is about  $0.168 \Omega\text{cm}^2$ .

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