



Short communication

## Investigation of cobalt-free perovskite $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_{3-\delta}$ as a cathode for proton-conducting solid oxide fuel cells

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## ABSTRACT

Cobalt-free perovskite  $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_{3-\delta}$  (BLF) was synthesized. The conductivity of BLF was measured with a DC four-point technique. The thermal expansion coefficient of the BLF was measured using a dilatometer. The  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY7) electrolyte based proton conducting solid oxide fuel cells (SOFCs) were fabricated. A composite cathode with BLF+BZCY7 was used to mitigate the thermal expansion mismatch with the BZCY7 electrolyte. The polarization processes of the button cell  $\text{NiO-BZCY7/BZCY7/BLF+BZCY7}$  were characterized using the complicated electrochemical impedance spectroscopy technique. The open circuit voltage of 0.982 V, 1.004 V, and 1.027 V was obtained at 700 °C, 650 °C, and 600 °C, respectively, while the peak power density of 325  $\text{mW cm}^{-2}$ , 240  $\text{mW cm}^{-2}$ , and 152  $\text{mW cm}^{-2}$ , was achieved accordingly.

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## 1. Introduction

Solid oxide fuel cell (SOFC) has attracted great attentions due to the fact that SOFC is able to convert the chemical energy of fuels to electrical energy in an efficient and clean way. The most widely studied SOFCs are based on yttria stabilized zirconia (YSZ) electrolyte. Since the conductivity of YSZ electrolyte will be significantly reduced at lower operating temperatures, resulting in poor cell performance, YSZ electrolyte based SOFC is generally operated in very high temperatures (800–1000 °C). Nevertheless, the high temperatures lead to various degradation problems [1,2]. To overcome these issues, intermediate temperature SOFCs are resorted in recent years [3,4].

It is generally recognized that the cathode is the critical component limiting SOFC performance [5,6]. A good cathode material should have high catalytic activity, high conductivity, and good compatibility with electrolyte. To increase the catalytic activity, the element cobalt is usually doped into the cathode materials. However, the cobalt is expensive rare material, and the chemical stability of cobalt containing cathode materials is poor at  $\text{CO}_2$ -containing atmosphere [7,8]. Clearly, it will be very significant to develop cobalt-free cathode materials with sufficient catalytic activity at low-temperatures for intermediate temperature SOFCs. Several cobalt-free oxides with perovskite structure have been studied as cathode materials, such as  $\text{La}_{0.3}\text{Sr}_{0.7}\text{FeO}_{3-\delta}$  [9],

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Zn}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  [10],  $\text{PrBaFe}_2\text{O}_{5-\delta}$  [11], and  $\text{GdBaFe}_2\text{O}_{5-\delta}$  [12]. It has been reported that the perovskite  $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_{3-\delta}$  (BLF) shows very good property for oxygen permeation at high temperature of 900 °C [13,14]. The feasibility of BLF as a cathode material is not examined yet, particularly for intermediate temperature SOFCs.

In this paper, BLF as a cathode material is investigated for intermediate temperature SOFCs with proton conducting electrolyte of  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY7). The conductivity of BLF is measured. The chemical and thermal compatibilities between BLF and BZCY7 are examined. The electrochemical performances of the cells  $\text{NiO-BZCY7/BZCY7/BZCY7+BLF}$  are characterized.

## 2. Experimental

### 2.1. Sample preparation, cell fabrication, and X-ray diffraction measurement

The BZCY7 powder was synthesized using citrate–nitrate sol–gel combustion method.  $\text{Y}_2\text{O}_3$  was dissolved in nitric acid in a beaker; the calculated amounts of  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Zr}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  were dissolved in a distilled water in another beaker; the solutions were mixed, stirred and heated; then citric acid was added. The molar ratio of citric acid to metal ions was 1.5:1. The ammonia was added into the solution until the pH value was about 8. The solution was heated while stirring until it was converted to a viscous gel. The viscous gel is then ignited to flame, resulting in the ash. The obtained ash-like powders were calcined at

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1000 °C for 5 h to form pure perovskite oxide, and the synthesized BZCY7 powders were obtained.

The mixture of NiO, BZCY7, and starch (60%:40%:20% in weight) was prepressed at 200 MPa to form an anode substrate with the diameter of 15 mm. The loose BZCY7 powder was uniformly distributed onto anode substrate, co-pressed at 250 MPa, and subsequently sintered at 1400 °C for 5 h to densify the BZCY7 membrane.

BLF powder was synthesized using Pechini process with  $\text{La}_2\text{O}_3$ ,  $\text{Ba}(\text{NO}_3)_2$ , and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as precursors, followed by calcinations at 1000 °C for 10 h. The powders of BLF and BZCY7 (70:30 in weight) were mixed thoroughly with 6 wt% ethylecellulose–terpineol binder to prepare cathode slurry. The slurry was then painted on BZCY7 electrolyte films, which was sintered at 1000 °C for 3 h in air to form single cells.

The phase identification of the sintered anode–electrolyte bilayer and the prepared cathode powders were studied using X-ray diffraction (XRD) with Cu K radiation (D/Max-gA, Japan).

## 2.2. Measurements of electrical conductivity and thermal expansion

The BLF and BLF + BZCY7 powders were pressed into bars and then sintered at 1100 °C. The electrical conductivity of BLF in air was measured from 100 to 800 °C using a standard DC four-probe technique with a H.P. multimeter. The thermal expansions of the BLF and BLF + BZCY7 bars were measured using a dilatometer (SHIMADZU50).

## 2.3. Electrochemical characterization

Single cells were tested from 600 to 700 °C with humidified hydrogen (3%  $\text{H}_2\text{O}$ ) as a fuel and the static air as an oxidant. The flow rate of the fuel was controlled at  $50 \text{ ml min}^{-1}$  using a precision flow meter (APEX). The voltage–current curves were recorded by Scribner890 ZV at the scanning rate of  $50 \text{ mV s}^{-1}$ . The electrochemical impedance spectra (EIS) were obtained using a Solartron 1260 frequency response analyzer in combination with a Solartron 1287 potentiostat over the frequency range from 0.1 Hz to  $10^5$  Hz under the open circuit voltage conditions. A scanning electron microscope (SEM) was used to observe the microstructure of the post-test cells.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of BLF powder and the mixture of BLF and BZCY7 powders after calcination at 1000 °C. As shown in Fig. 1(a), the as-prepared powder BLF exhibits a well-developed crystallization and all of the peaks can be well indexed as a cubic

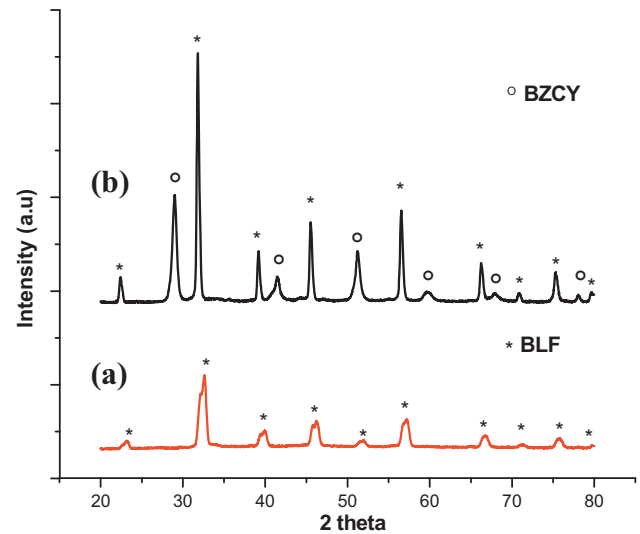


Fig. 1. The powder X-ray diffraction patterns of (a)  $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_{3-\delta}$ ; (b) mixture of  $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_{3-\delta}$  and  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  powders calcined at 1000 °C for 3 h.

perovskite structure. The lattice constant calculated from XRD is about 4.03 Å, consistent with the results reported by Kida on the  $\text{Ba}_{1-x}\text{La}_x\text{FeO}_{3-\delta}$  systems [15]. From Fig. 1(b), it can be clearly seen that the peaks are corresponding to BZCY7 and BLF, respectively, no peaks contributing to other phases, indicating that there are no large scale crystalline reaction products between BZCY7 and BLF, and they are chemically compatible at high temperatures.

Fig. 2(a) shows the temperature dependent electrical conductivities of the BLF sample when exposed to an air atmosphere. The conductivity increases from 0.3 to  $11.6 \text{ S cm}^{-1}$  when the temperature increases from 100 °C to 450 °C, then decreases from 11.6 to  $3.8 \text{ S cm}^{-1}$  when the temperature further increases from 450 °C to 800 °C. Shown in Fig. 2(b) is the linear relation between  $\ln(\sigma T)$  versus  $1000/T$  obtained from electronic conductivity data. The activation energy  $E_a$  of BLF (range from 450 °C to 800 °C) is about 0.085 eV.

The thermal expansion coefficients (TEC) of BLF and the BLF + BZCY7 (BLF:BZCY7 = 70:30 in weight) composite samples are shown in Fig. 3. It has been reported that the TEC of BZCY7 is about  $10.2 \times 10^{-6} \text{ K}^{-1}$  [16], however, the measured TEC value of BLF is about  $28.4 \times 10^{-6} \text{ K}^{-1}$ , indicating that there is a significant thermal expansion mismatch problem between BLF cathode and BZCY7 electrolyte. When the BLF is composited with BZCY7, the TEC value of BLF + BZCY7 is about  $22.4 \times 10^{-6} \text{ K}^{-1}$  as shown in Fig. 3, indicating that better thermal matching can be achieved between

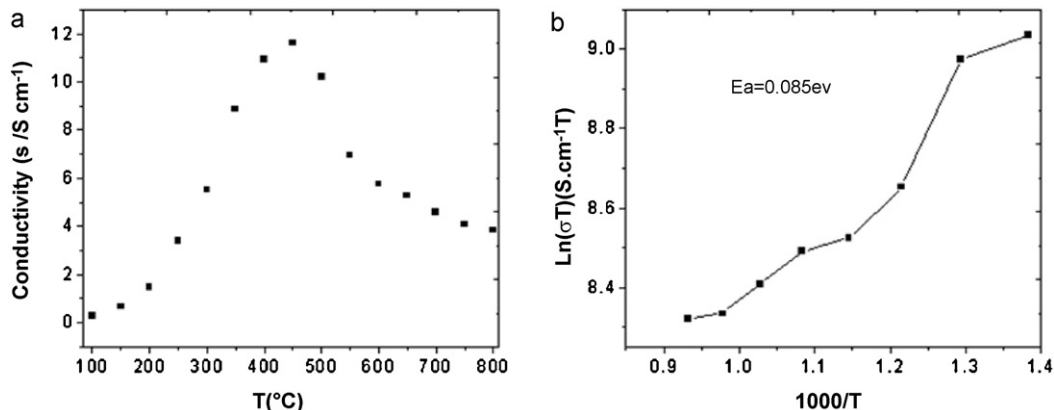
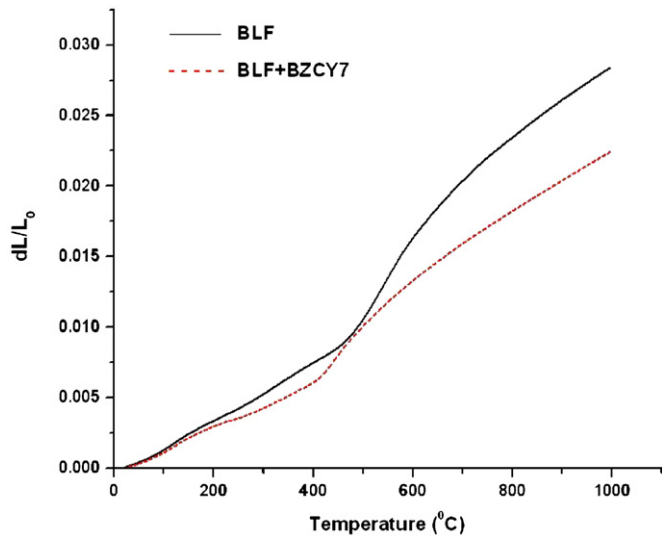


Fig. 2. The temperature dependent of electrical conductivity of the BLF sample (a) at 100–800 °C in air; (b) with  $\ln(\sigma T)$  versus  $1000/T$  (450–800 °C).

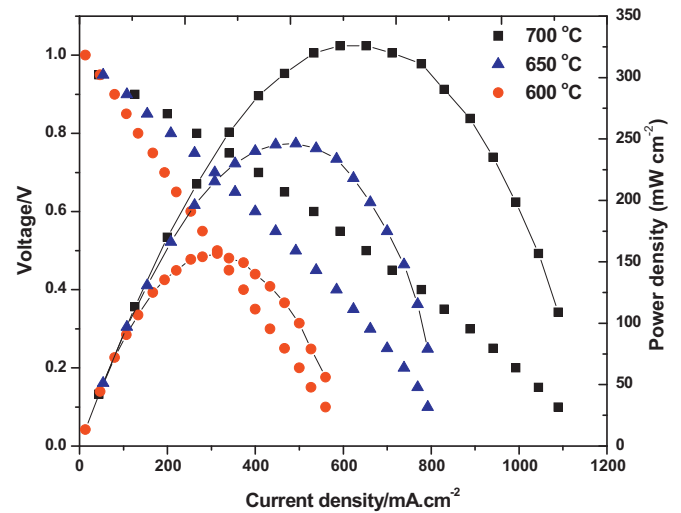


**Fig. 3.** Thermal expansion ( $dL/L_0$ ) curves of  $Ba_{0.95}La_{0.05}FeO_{3-\delta}$  and  $Ba_{0.95}La_{0.05}FeO_{3-\delta} + BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$  in the temperature range of 20–1000 °C in air.

the composite cathode and the electrolyte. Consequently, it will reduce the possibility of occurrence of delaminations or cracks at the cathode/electrolyte interface.

**Fig. 4(a)** shows the SEM images of the cross-section of the cell Ni + BZCY7/BZCY7/BLF + BZCY7. The thickness of BZCY7 electrolyte is about 15  $\mu\text{m}$ . The electrolyte adheres very well to the anode and the cathode without any delaminations or cracks, indicating that it is feasible to use composite cathode to improve the thermal compatibility between the electrolyte and the cathode. **Fig. 4(b)** presents the cross-sectional image of the electrolyte. It can be seen that the electrolyte is pretty dense without any pores.

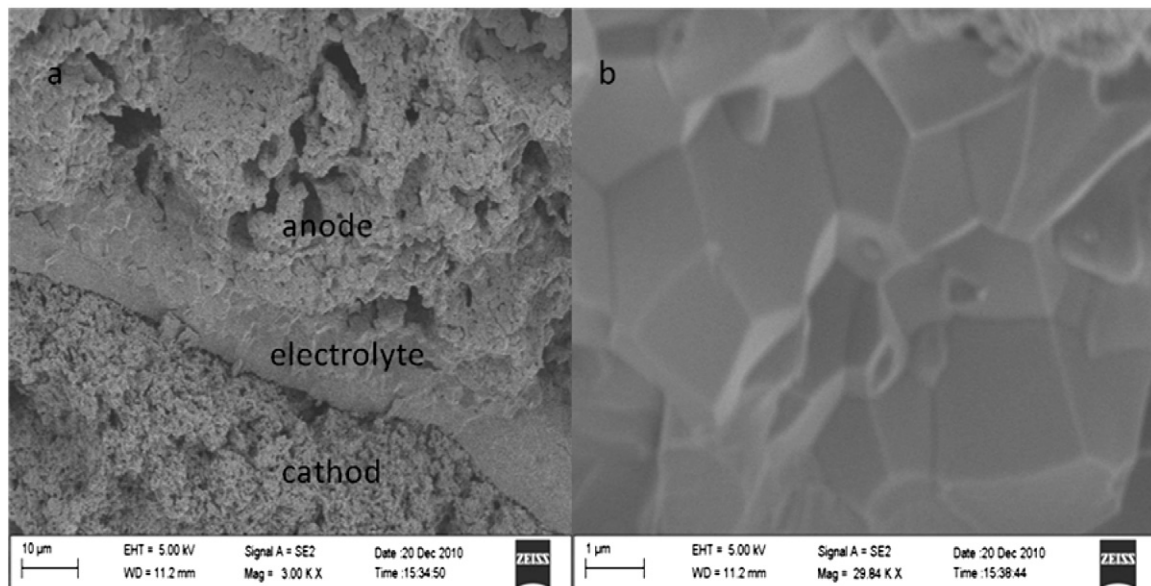
The polarization and power density curves of the cell Ni + BZCY7/BZCY7/BLF + BZCY7 were measured from 600 °C to 700 °C as shown in **Fig. 5**, in which the humidified hydrogen ( $\sim 3\%$   $H_2O$ ) was used as a fuel while the cathode was exposed to the ambient air. The open circuit voltages of 0.982 V, 1.004 V,



**Fig. 5.** Performance of the as-prepared cell with hydrogen at different temperatures.

and 1.027 V were achieved at temperatures of 700 °C, 650 °C, and 600 °C, respectively. The corresponding peak power density reaches 325  $\text{mW cm}^{-2}$  at 700 °C, 240  $\text{mW cm}^{-2}$  at 650 °C, and 152  $\text{mW cm}^{-2}$  at 600 °C, respectively.

The cell Ni + BZCY7/BZCY7/BLF + BZCY7 was characterized using electrochemical impedance spectroscopy. **Fig. 6** shows the impedance spectra measured under open circuit voltage conditions at different temperatures. The low frequency intercept represents the cell total resistance ( $R_t$ ). The high frequency intercept is the cell ohmic resistance ( $R_{ohm}$ ). Subtracting  $R_{ohm}$  from  $R_t$  leads to the cell total polarization resistance, including the contributions from both the anode and cathode. Results show that the cell total polarization resistance reaches 0.17  $\Omega \text{cm}^2$ , 0.42  $\Omega \text{cm}^2$ , and 1.08  $\Omega \text{cm}^2$  at 700 °C, 650 °C, and 600 °C, respectively. Accordingly the cell ohmic resistance is 0.55, 0.64, and 0.75  $\Omega \text{cm}^2$ . It is observed from **Fig. 4(a)** that the thickness of the electrolyte membrane is about 15  $\mu\text{m}$ , the conductivity of the BZCY membrane is then calculated as  $2.7 \times 10^{-3} \text{ S cm}^{-1}$ ,  $2.34 \times 10^{-3} \text{ S cm}^{-1}$  and  $2 \times 10^{-3} \text{ S cm}^{-1}$  at 700 °C, 650 °C and 600 °C, respectively. The conductivity results



**Fig. 4.** Cross-sectional SEM micrograph of the cell without surface modification after fuel cell testing (a) a tri-layer single cell; (b) electrolyte.

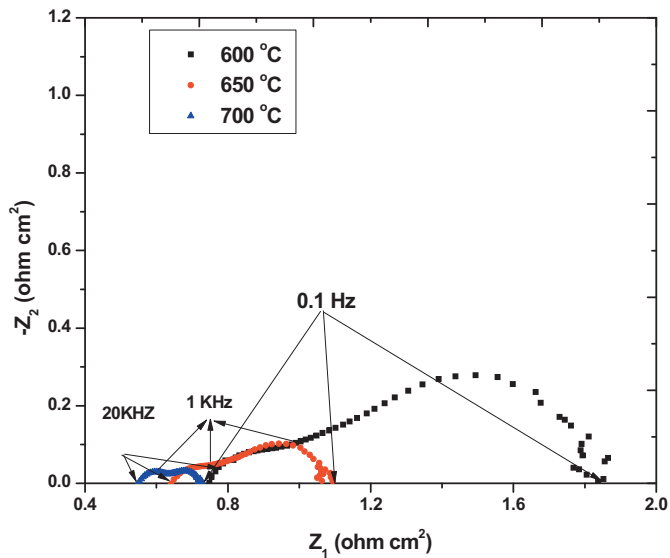


Fig. 6. Impedance spectra of a single cell under open-current conditions at different temperatures.

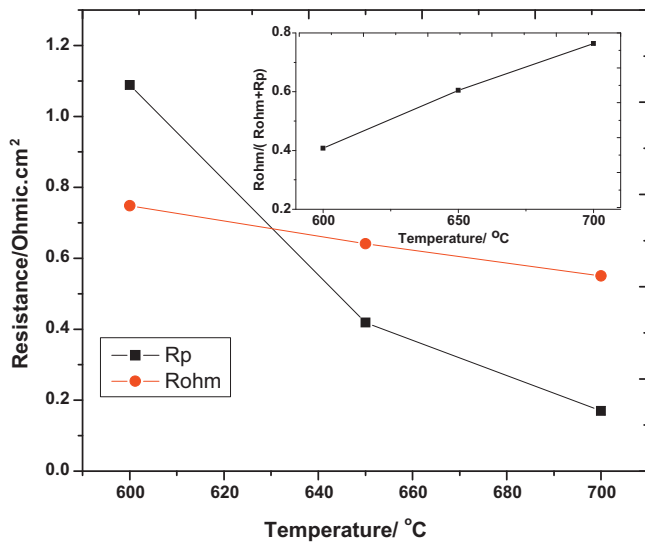


Fig. 7. The ohmic ( $R_{ohm}$ ) and polarization ( $R_p$ ) resistances of the tested single cell determined from impedance spectroscopy under open circuit conditions at different temperatures. Inset: the  $R_{ohm}/(R_{ohm} + R_p)$  ratio at different temperatures.

are a little bit higher than those reported by Sun et al. under comparable conditions [17]. Two arcs can be clearly identified from Fig. 6, indicating that at least two processes are involved. The low frequency arc could be attributed to the anode while the high fre-

quency could be attributed to the cathode. Both arcs decrease with increasing operating temperatures from 600 °C to 700 °C. Fig. 7 shows the variations of resistances with respect to temperature. Both the ohmic resistance and polarization resistance decrease with increasing the operating temperatures. However, the ratio of ohmic resistance with respect to the cell total resistance increase with increasing the temperatures, indicating that the resistance contributed from polarizations decreases in the total cell resistance.

#### 4. Conclusions

A cobalt-free perovskite oxide,  $Ba_{0.95}La_{0.05}FeO_{3-\delta}$  (BLF) was investigated as a novel cathode material for BZCY7 electrolyte based proton conducting SOFCs. The electronic conductivity of BLF is strongly dependent on the operating temperatures. A composite cathode of BLF + BZCY7 facilitates to mitigate the thermal expansion mismatch between the cathode and the electrolyte. The maximum power density of  $325 \text{ mW cm}^{-2}$  was achieved at 700 °C for the cell Ni + BZCY7/BZCY7/BLF + BZCY7.

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