

# Novel layered perovskite $\text{GdBaCuFeO}_{5+x}$ as a potential cathode for proton-conducting solid oxide fuel cells

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**Abstract** A layered perovskite  $\text{GdBaCuFeO}_{5+x}$  (GBCuF) was developed as a cathode material for intermediate-temperature solid oxide fuel cells based on a proton-conducting electrolyte of stable  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY). The X-ray diffraction results showed that GBCuF was chemically compatible with BZCY after co-fired at 1,000 °C for 10 h. The thermal expansion coefficient of GBCuF, which showed a reasonably reduced value ( $15.1 \times 10^{-6} \text{ K}^{-1}$ ), was much closer to that of BZCY than the cobalt-containing conductor. The button cells of Ni–BZCY/BZCY/GBCuF were fabricated and tested from 500 to 700 °C with humidified  $\text{H}_2$  (~3 %  $\text{H}_2\text{O}$ ) as a fuel and ambient oxygen as the oxidant. A high open-circuit potential of 1.04 V, maximum power density of  $414 \text{ mW cm}^{-2}$ , and a low electrode polarization resistance of  $0.21 \Omega \text{ cm}^2$  were achieved at 700 °C, with calculated activation energy ( $E_a$ ) of  $128 \text{ kJ mol}^{-1}$  for the GBCuF cathode. The experimental results indicated that the layered perovskite GBCuF is a good candidate for cathode material.

**Keywords** Layered perovskite · Intermediate-temperature solid oxide fuel cells · Thermal expansion coefficient · Polarization resistance

## Introduction

Since high operating temperature (800–1,000 °C) conditions lead to complex material degradation problems, there is an increasing interest in developing intermediate-temperature

solid oxide fuel cells (IT-SOFCs; 400–800 °C), which will cause substantial increases of electrolyte ohmic resistance and electrode polarization losses (particularly for the cathode material) [1, 2]. It is well known that proton-conducting SOFCs have attracted much attention and show great advantages over oxide ion-conducting SOFCs, such as lower activation energy of polarization and higher energy efficiency [3–5].  $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$  (BZCY) can be used as an electrolyte for proton-conducting IT-SOFC development because it shows adequate proton conductivity as well as sufficient chemical and thermal stability over a wide range of SOFC operating conditions [6].

High-performance cathode material development is also one of the critical steps toward IT-SOFCs. In general, oxygen reduction reaction is strongly dependent on oxygen surface absorption and oxide ionic diffusivity in porous mixed ionic–electronic conductor (MIEC) cathode. Many cobalt-containing perovskite-type MIECs, such as  $\text{La}_x\text{Sr}_{1-x}\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-\delta}$  [7] and  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  [8], have been extensively studied as possible cathodes due to the fact that cobalt is beneficial to the activation of oxygen reduction. These cobalt-based cathodes, however, often suffer from problems like poor chemical stability in  $\text{CO}_2$ , high thermal expansion coefficients (TECs), ease of evaporation, as well as high cost of the cobalt element [9, 10].

Clearly, it is significant to develop cobalt-free cathodes with sufficient catalytic activity at reduced temperatures for IT-SOFCs. Recently, layered perovskite materials based on  $\text{GdBaCo}_2\text{O}_{5+x}$  have attracted much attention [11–14] because the ordering A-sites are recognized to be able to greatly enhance the diffusivity of oxygen ion in the bulk of the material by orders of magnitude. In this paper, we present a novel proton-conducting SOFCs material system using BZCY as an electrolyte and cobalt-free layered perovskite  $\text{GdBaCuFeO}_{5+x}$  (GBCuF) as a cathode.

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## Experimental

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

BZCY powders were synthesized using a modified Pechini method, where citrate and ethylenediaminetetraacetic acid (EDTA) were employed as parallel complexing agents [15].  $Y_2O_3$  was dissolved in nitric acid first and the calculated amounts of  $Ba(NO_3)_2 \cdot 9H_2O$ ,  $Ce(NO_3)_3 \cdot 6H_2O$ , and  $Zr(NO_3)_4 \cdot 4H_2O$  were dissolved in EDTA– $NH_3$  aqueous solution under heating and stirring. An appropriate amount of citric acid was added into the solution. Ammonia was added into the solution until the pH value was about 6. The solution was heated while stirring until it was converted into a viscous gel. The viscous gel is then ignited to flame, resulting into ash. The resulting ash-like material was calcined afterwards in air at 1,000 °C for 5 h to form pure perovskite oxide; synthesized BZCY powders were then obtained. The anode-supported BZCY bilayer was prepared using a dry-pressing method. The mixture of NiO+BZCY+starch (60:40:20 % in weight) was pre-pressed at 200 MPa and formed into an anode substrate. Then, loose BZCY powder synthesized above was uniformly distributed onto the anode substrate, co-pressed at 250 MPa, and subsequently co-sintered at 1,400 °C for 5 h to obtain a dense BZCY membrane.

Layered GBCuF powder was synthesized using the Pechini process with  $Gd_2O_3$ ,  $Ba(NO_3)_2 \cdot 9H_2O$ ,  $Fe(NO_3)_3 \cdot 5H_2O$ , and  $Cu(NO_3)_2$  as precursors, followed by calcinations at 900 °C for 3 h. Fine GBCuF powders were then mixed thoroughly with a 6 wt% ethylcellulose–terpineol binder to prepare the cathode slurry. The slurry was painted on a BZCY electrolyte film, which was then sintered at 900 °C for 3 h in air to form single cells of NiO–BZCY/BZCY/GBCuF.

Phase identification of the sintered electrolyte and the prepared cathode powders was done using a Dandong Fangyuan X-ray diffractometer (DX-2000) with a Cu–K $\alpha$  radiation source; the diffraction angle range ( $2\theta$ ) was 20–80°. In order to measure the TECs of GBCuF, GBCuF powders were pressed into slats at 200 MPa. After sintering at 1,250 °C for 5 h, the samples (about 15 mm in length, 5 mm in width, and 1.45 mm in thickness) for the TEC test were attained. Thermal expansion of the specimen was measured from 30 to 900 °C using a dilatometer (DIL 402C) at a heating rate of 10 K  $min^{-1}$  in air.

### Electrochemical characterization

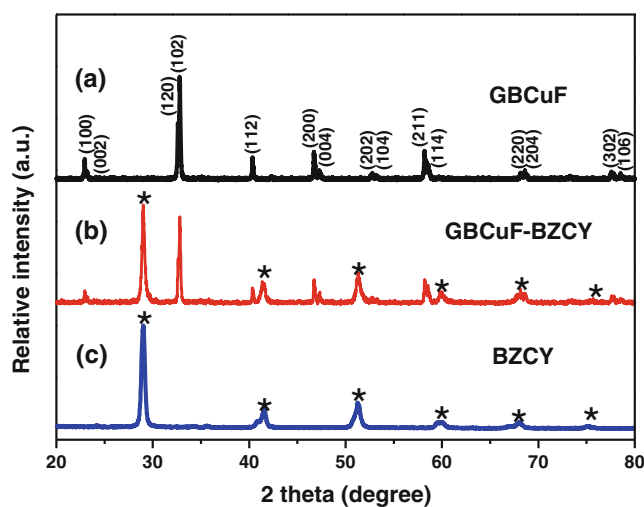
Single cells were tested from 500 to 700 °C in a home-developed cell testing system with humidified hydrogen (~3 %  $H_2O$ ) as fuel and static air as the oxidant, respectively. The flow rate of fuel gas was about 40 ml  $min^{-1}$ . The cell voltages and output current of the cells were measured with

digital multi-meters (GDM-8145). AC impedance spectroscopy (Chi604c, Shanghai Chenhua) with a frequency range of 0.1 Hz–100 MHz was performed on the cell under open-current conditions from 500 to 700 °C. A scanning electron microscope (SEM) was used to observe the microstructure of the cells after testing.

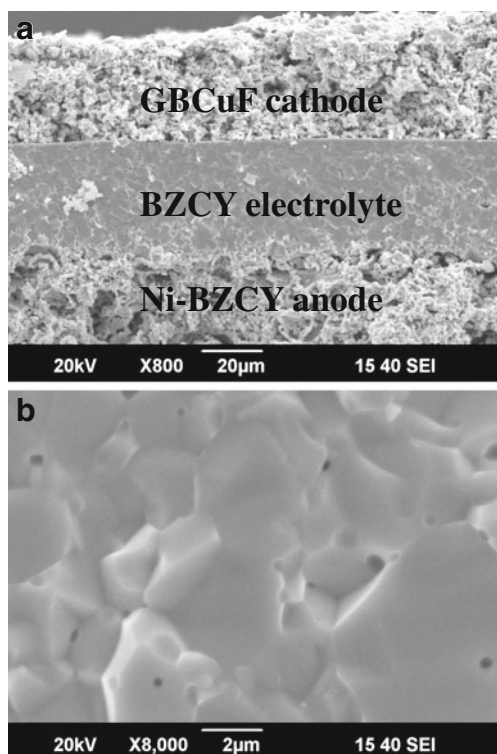
## Results and discussion

As shown in a in Fig. 1, the as-prepared powder of layered  $GdBaCuFeO_{5+x}$  (GBCuF) exhibits a layered perovskite phase structure without any peaks attributable to impurities [12, 16]. Figure 1 (part b) shows the X-ray diffraction (XRD) pattern of the chemical compatibility of the GBCuF cathode with  $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$  (BZCY) electrolyte, which was investigated by mixing thoroughly with a 1:1 weight ratio and then sintered at 1,000 °C for 10 h. Pure GBCuF contains a layered perovskite phase structure, while BZCY contains a perovskite-type structure; they are different structures. The result revealed that no obvious interface reaction appeared for the GBCuF–BZCY composites heated up to 1,000 °C, with no new identifiable peaks or shift of peaks, thus indicating excellent chemical compatibility. Figure 1 (part c) also presents the XRD pattern of the electrolyte membrane which has only peaks corresponding to BZCY sintered at 1,400 °C for 5 h.

After electrochemical test, the microstructure of the as-prepared trilayer cell of NiO–BZCY/BZCY/GBCuF was examined using SEM. One can see from Fig. 2 that the BZCY electrolyte membrane is sufficiently dense and that there are no pores or cracks. The cathode layer adheres to the electrolyte fairly well. The thickness of the fabricated



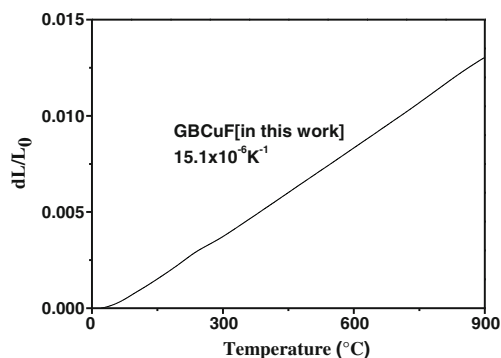
**Fig. 1** XRD diffraction patterns of the layered  $GdBaCuFeO_{5+x}$  (GBCuF) perovskite powders (a), the GBCuF–BZCY composite sintered at 1,000 °C for 10 h (b), and  $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$  (BZCY) membrane (c)



**Fig. 2** SEM images of the cross-section of the trilayer cells after testing (a) and the BZCY electrolyte (b)

electrolyte is only about 35 µm; that of the GBCuF cathode layer is about 25 µm. This excellent configuration favors the gas transport and electrochemical reactions, which would induce a decrease in the polarization resistance of the electrodes; hence, a high electrochemical performance can be expected.

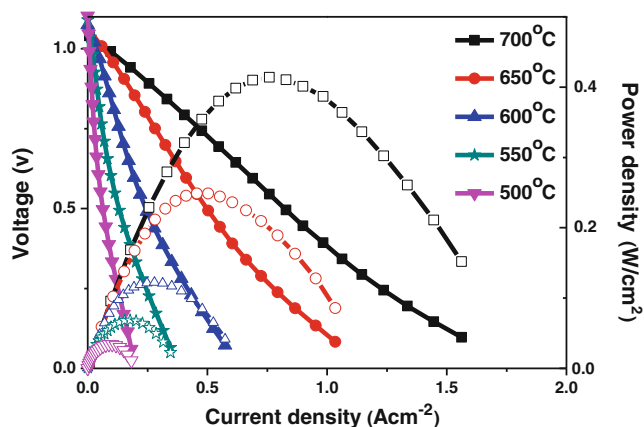
Thermal compatibility is a critical issue for cobalt-rich cathodes, which in general exhibit higher thermal expansion coefficient (TEC) values in the operation temperature regime. Generally, the high TEC of these cobalt-based cathodes is mainly related to the spin state transition of cobalt and the loss of oxygen at elevated temperatures. The reduction of the cobalt element from a high valence state to a low valence state and the loss of lattice oxygen led to the high TEC of the cobalt-containing cathode material [17]. As a result, replacement of the cobalt element with Fe and Cu elements can potentially mitigate such a high thermal expansion. As shown in Fig. 3, the TEC of GBCuF is  $15.1 \times 10^{-6} \text{ K}^{-1}$ . The mismatch of TECs between the electrolyte and the cathode will result in delamination at the cathode/electrolyte interface or cracking of the electrolyte because of stress developed upon heating and cooling. It is clear that the TEC of GBCuF is much closer to that of BZCY ( $10.2 \times 10^{-6} \text{ K}^{-1}$ ) [18]. Besides, it is also much lower than that of another cobalt-free cathode material such as  $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_3$  [19]. This implies that GBCuF might be a suitable cathode based on BZCY electrolyte for IT-SOFCs.



**Fig. 3** Thermal expansion of the samples of GBCuF and GBCuF-SDC at a heating rate of  $10 \text{ °C min}^{-1}$  in air

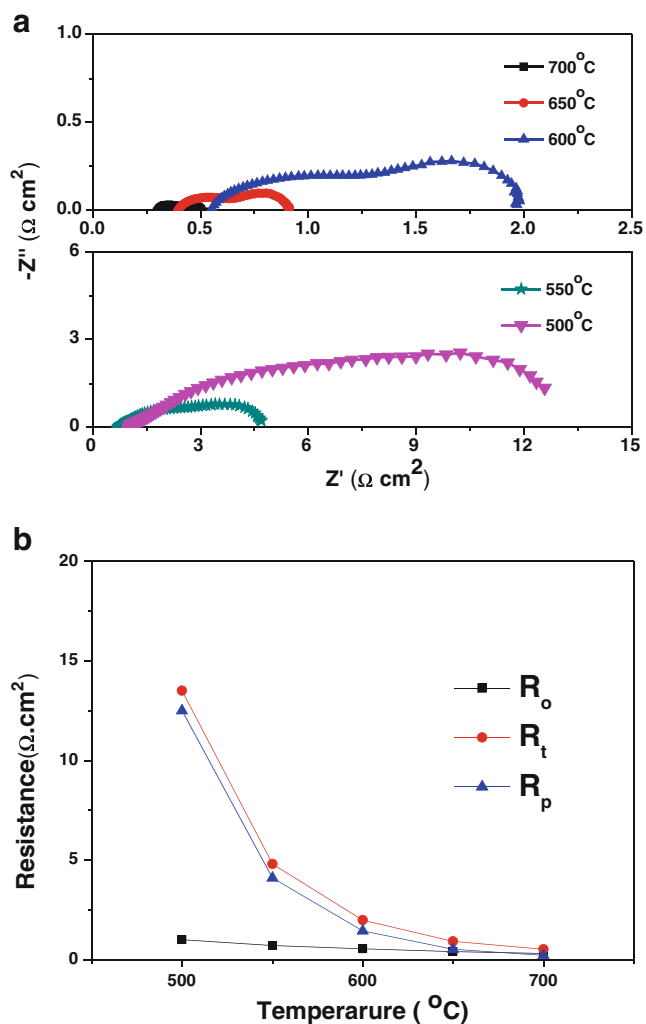
The electrochemical performance of the as-prepared cell is experimentally obtained and shown in Fig. 4 under different operating temperatures, including the  $I-V$  and  $I-P$  curves. Under ideal conditions, voltage does not change with the current change, but a straight line parallel to the  $x$ -axis. In fact, the voltage decreases with the current density increasing, which is mainly due to ohmic losses, concentration losses, and activation losses. Since the BZCY electrolyte is a mix conductor membrane, a slight electron cross flow (current leakage) might exist through the membrane, consequently leading to the practical open-circuit voltage (OCV) being lower than its theoretical value. The maximum power densities are 414, 249, 122, 69, and 34  $\text{mW cm}^{-2}$  at 700, 650, 600, 550, and 500 °C, respectively. Whereas the high OCVs of 1.04 V at 700 °C and 1.10 V at 600 °C indicate that the electrolyte membrane is sufficiently dense, the current leakage is negligible. It is worth noting that the  $I-V$  curves are almost linear, implying that there is little activation loss related to the high catalytic activity of GBCuF.

The polarization processes of NiO-BZCY/BZCY/GBCuF cells are examined using electrochemical impedance spectra. The impedance spectra of the as-prepared cells are obtained



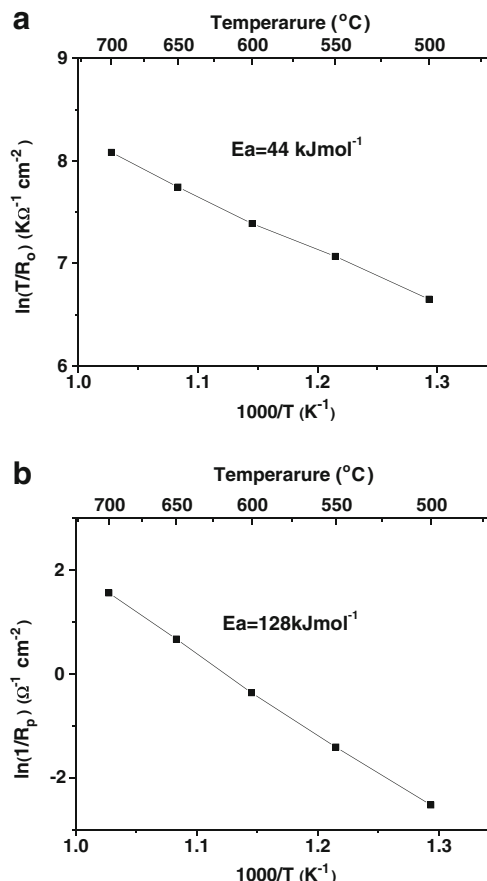
**Fig. 4**  $I-V$  and  $I-P$  curves of the NiO-BZCY/BZCY/GBCuF single cell with humidified hydrogen as the fuel at 500–700 °C. Solid pattern represents the left y-axis; hollow pattern represents the right y-axis

under open-circuit conditions at different temperatures and are shown in Fig. 5a. In these Nyquist plots, the intercepts with the real axis at low frequencies represent the total cell resistance ( $R_t$ ) of the cell and the value of the intercept at high frequency is ohmic resistance ( $R_o$ ), which can approximately be considered as the electrolyte resistance, while the difference of the two values corresponds to the polarization resistance ( $R_p$ ) of the two interfaces: the cathode–electrolyte interface and the anode–electrolyte interface. As expected, the increase of the measurement temperature resulted in a significant reduction of the polarization resistance. For state-of-the-art porous anode materials, it brings negligible polarization loss due to the high catalytic activity of the Ni metal and the fact that hydrogen is light and relatively easy to transport in porous anode. Consequently, the polarization loss in anode electrode is treated as negligible in the following analysis. The total cell resistance ( $R_t$ ), ohmic resistance ( $R_o$ ), as well as



**Fig. 5** a Electrochemical impedance plot of the tested cell under open-circuit conditions at 500–700 °C. b Total cell resistances ( $R_t$ ), interfacial polarization resistances ( $R_p$ ), and ohmic resistances ( $R_o$ ) obtained from the impedance spectra at different temperatures

polarization resistance ( $R_p$ ) are then determined from the impedance spectra in Fig. 5a. The results are shown in Fig. 6b. The intercepts with axes at high frequencies and low frequencies represent the electrolyte resistance ( $R_o$ ) and total resistance ( $R_t$ ) of the cell, respectively. The interfacial polarization resistance ( $R_p$ ) of the cell can be calculated as the difference between  $R_t$  and  $R_o$ . The  $R_p$  values of the cell were 0.21, 0.51, 1.44, 4.1, and 12.5  $\Omega \text{ cm}^2$  at 700, 650, 600, 550, and 500 °C, respectively. It is dominated by the cathode–electrolyte interface, whereas the resistance of the anode–electrolyte is negligible, if assuming that the bulk resistance of the cell mainly comes from the electrolyte BZCY layer. As shown in Fig. 6a, the activation energy ( $E_a$ ) with a value of 44  $\text{kJ mol}^{-1}$  is obtained, which is similar to that of the proton-conducting electrolyte, while for  $E_a$  of the GBCuF cathode, the nearly linear dependence of natural logarithm of  $1/R_p - 1/T$  was used to calculate the activation energy ( $E_a$ ). The value of  $E_a$  is 128  $\text{kJ mol}^{-1}$ , less than the other  $E_a$  values reported in the literature [20], e.g.,  $E_a=164 \text{ kJ mol}^{-1}$  for  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  and  $E_a=183 \text{ kJ mol}^{-1}$  for  $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ . It is obvious that GBCuF exhibits an unusually high activity for oxygen activation and mobility. It was also reported by Taskin et al. [14] that



**Fig. 6** a Arrhenius plots of the simulated ohmic resistances ( $R_o$ ). b Temperature dependence of the simulated polarization resistance  $R_p$  for cells

oxygen diffusion in layered perovskites becomes very fast at relatively low-temperature conditions. The results indicated that GBCuF has considerable catalytic activity for operation at the intermediate temperature range.

## Conclusions

In conclusion, a layered perovskite, GdBaCuFeO<sub>5+x</sub> (GBCuF), was developed as a cathode material for intermediate-temperature solid oxide fuel cells based on the proton-conducting electrolyte of stable BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> (BZCY). The XRD results showed that GBCuF was chemically compatible with BZCY after co-fired at 1,000 °C for 10 h. The TEC of GBCuF, which showed a reasonably reduced value (15.1×10<sup>-6</sup> K<sup>-1</sup>), is much closer to that of BZCY than the cobalt-containing conductor, as expected. The button cells of Ni-BZCY/BZCY/GBCuF were fabricated and tested from 500 to 700 °C with humidified H<sub>2</sub> (~3 % H<sub>2</sub>O) as a fuel and ambient oxygen as the oxidant. An open-circuit potential of 1.04 V, maximum power density of 414 mW cm<sup>-2</sup>, and a low electrode polarization resistance of 0.21 Ω cm<sup>2</sup> were achieved at 700 °C, with calculated activation energy (*E*<sub>a</sub>) of 128 kJ mol<sup>-1</sup> for the GBCuF cathode. The experimental results indicated that the layered perovskite GBCuF is a good candidate for cathode materials.

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