



## Short communication

Novel layered perovskite oxide PrBaCuCoO<sub>5+δ</sub> as a potential cathode for intermediate-temperature solid oxide fuel cells

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## ARTICLE INFO

## Article history:

Received 31 July 2009

Accepted 9 August 2009

Available online 15 August 2009

## Keywords:

Cathode

Thermal expansion coefficient

Electrochemical performance

## ABSTRACT

A novel layered perovskite oxide PrBaCuCoO<sub>5+δ</sub> (PBCCO) is employed as a potential cathode for intermediate-temperature solid oxide fuel cells (IT-SOFCs). Thermal expansion and electrochemical performance on samarium-doped ceria (SDC) electrolyte are evaluated. The thermal expansion coefficient (TEC) of PrBaCuCoO<sub>5+δ</sub> (PBCCO) is close to that of SDC electrolyte and electrical conductivity of PrBaCuCoO<sub>5+δ</sub> (PBCCO) reaches the general required value of cathode material. Symmetrical electrochemical cell with the configuration of PrBaCuCoO<sub>5+δ</sub> (PBCCO)/SDC/PrBaCuCoO<sub>5+δ</sub> (PBCCO) applied for the impedance studies, the area specific resistance of PrBaCuCoO<sub>5+δ</sub> (PBCCO) cathode is as low as 0.047 Ω cm<sup>2</sup> at 700 °C. A maximum power density of 791 mW cm<sup>-2</sup> is obtained at 700 °C for the single cell consisting of PrBaCuCoO<sub>5+δ</sub> (PBCCO)/SDC/NiO–SDC. Preliminary results indicate that PrBaCuCoO<sub>5+δ</sub> (PBCCO) is especially promising as a cathode for IT-SOFCs.

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## 1. Introduction

As a promising energy conversion device, solid oxide fuel cells (SOFCs) have attracted widespread attention due to its high efficiency, fuel flexibility and environmental benefits, and now it is on the way to practical application and commercialization [1,2]. Nowadays, lowering the operation temperature of SOFCs from high temperature (~1000 °C) to intermediate-temperature (600–700 °C) can not only significantly improve materials' compatibility for the SOFCs system, but also reduce the capital costs of production and application [3]. However, a key obstacle to reduced-temperature operation of SOFCs is the poor activity of traditional cathodes such as La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> (LSM) [4].

Accordingly, the development of alternative cathode with high electrochemical performance is indispensable to make intermediate-temperature SOFCs (IT-SOFCs) technology successful. Recently, Zhang et al. have reported that among the LnBaCo<sub>2</sub>O<sub>5+δ</sub> oxides examined, PrBaCo<sub>2</sub>O<sub>5+δ</sub> (PBCO) has the highest bulk diffusion coefficient and surface exchange coefficient [5], implying it may perform better than others as promising cathodes for IT-SOFCs.

However, to our knowledge, these cathodes, Co occupying the whole of B-sites, often suffer some problems like high thermal expansion coefficients (TECs) in practical long-term applications.

Therefore, in order to reduce disadvantages and improve the performance, much attention should be paid to the B-sites ions. In this work, the ceramic powder with a composition of PrBaCuCoO<sub>5+δ</sub> (PBCCO) synthesized by auto ignition process was examined as a novel cathode for IT-SOFCs based on samarium-doped ceria (SDC) electrolyte.

## 2. Experimental

PrBaCuCoO<sub>5+δ</sub> (PBCCO) powders were prepared by auto ignition process. Pr(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Ba(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were dissolved at the stoichiometric ratio and citric acid was then added, which was used as complexation agent. Molar ratio of citric acid/metal was set at 1.5. After that, this solution was stirring on a heating plate until it changed into black foam and finally ignited to flame, forming the primary powders. The as-synthesized powders were then calcined at 950 °C for 3 h to remove the carbon residue and obtain the desired PrBaCuCoO<sub>5+δ</sub> (PBCCO) phase measured by X-ray diffraction (PW-1730).

Thermal expansion of the specimen was measured from 30 to 1000 °C using a dilatometer (SHIMADZU50) at a heating rate of 10 °C min<sup>-1</sup> in air and Electrical conductivity of PrBaCuCoO<sub>5+δ</sub> (PBCCO) was studied using the standard DC four-probe technique on H.P. multimeter (Model 34401) from 400 to 800 °C in air.

Symmetrical electrochemical cells with the configuration of PrBaCuCoO<sub>5+δ</sub> (PBCCO)/SDC (Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub>)/PrBaCuCoO<sub>5+δ</sub> (PBCCO) and PrBaCo<sub>2</sub>O<sub>5+δ</sub> (PBCO)/SDC (Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub>)/PrBaCo<sub>2</sub>O<sub>5+δ</sub> (PBCO) applied for the impedance research

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were measured by electrochemical instrument (CHI604C 0.1 Hz–100 kHz) from 600 to 700 °C in air. Morphology and microstructure of symmetrical electrochemical cells after one thermal cycling were observed by scanning electron microscopy (SEM, FEI XL30).

The single cell was fabricated by a dry-pressing process utilizing SDC powders prepared by the glycine–nitrate method and calcined at 600 °C for 2 h [6]. To make a single cell, a mixed powders of NiO+SDC+starch (in a weight ratio of 65:35:20) were pressed at 200 MPa as a substrate (25 mm in diameter and 0.5 mm thick), SDC powders were then added, distributed uniformly, and co-pressed onto the substrate at 250 MPa. The bilayer was subsequently sintered at 1300 °C for 5 h, resulting in an SDC film of about 30 μm thick on the NiO–SDC substrate. Fine PrBaCuCoO<sub>5+δ</sub> (PBCCO) powders were mixed thoroughly with a 10 wt% ethylcellulose–terpineol binder to prepare the cathode slurry, which was painted on the SDC electrolyte membrane to form a single cell. Afterwards, the cell was fired at 950 °C for 3 h in air. Electrochemical characterizations were performed from 600 to 700 °C under ambient pressure. The single cell performance was tested using an electrochemical instrument (CHI604C) with hydrogen as fuel and ambient air as oxidant.

### 3. Results and discussion

As shown in Fig. 1a, the prepared powder of PrBaCuCoO<sub>5+δ</sub> (PBCCO) calcined at 950 °C for 3 h exhibits layered perovskite phase which is consistent with the data reported by Zhou et al. [7], indicating that the layered perovskite structure is well developed after calcination. Fig. 1 also presents the XRD spectra of electrolyte/anode bilayer sintered at 1250 °C for 5 h. It is obvious that there were only peaks corresponding to SDC in the electrolyte membrane (Fig. 1b) and to NiO and SDC in the anode substrate (Fig. 1c) with no peaks attributable to impurities detected.

As shown in Fig. 2, the thermal expansion coefficient of PrBaCuCoO<sub>5+δ</sub> (PBCCO) and PrBaCo<sub>2</sub>O<sub>5+δ</sub> (PBCO) is  $15.2 \times 10^{-6} \text{ K}^{-1}$  and  $24.1 \times 10^{-6} \text{ K}^{-1}$ , respectively. The mismatch of TEC between the electrolyte and cathode will result in delamination at the cathode/electrolyte interface, or cracking of the electrolyte because of the stress developed upon heating and cooling [8]. It is clear that the TEC of PrBaCuCoO<sub>5+δ</sub> (PBCCO) is much closer to that of SDC ( $\sim 12 \times 10^{-6} \text{ K}^{-1}$  [9]) than PrBaCo<sub>2</sub>O<sub>5+δ</sub> (PBCO) as expected. This implies that PrBaCuCoO<sub>5+δ</sub> (PBCCO) might be more suitable as a cathode based on SDC electrolyte for IT-SOFCs.

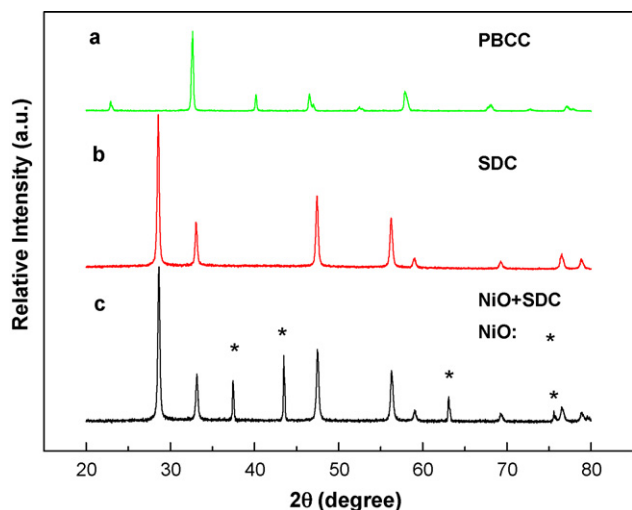


Fig. 1. XRD patterns of (a) PrBaCuCoO<sub>5+δ</sub> (PBCCO), (b) Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub> (SDC) membrane and (c) NiO–SDC anode substrate (\*: NiO).

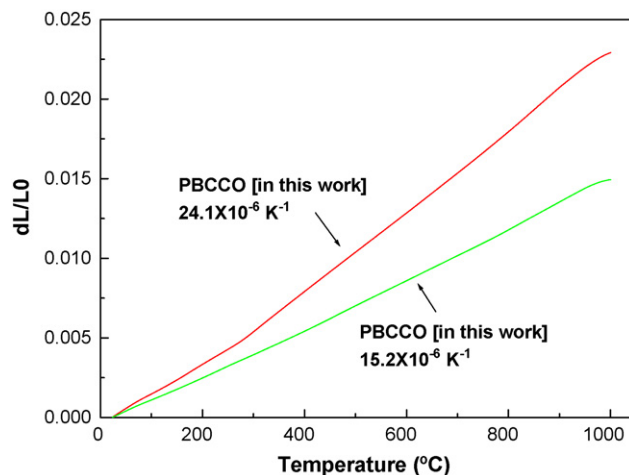


Fig. 2. Thermal expansion of different samples of PrBaCuCoO<sub>5+δ</sub> (PBCCO) and PrBaCo<sub>2</sub>O<sub>5+δ</sub> (PBCO) in air.

Fig. 3 shows the electrical conductivity behaviors of the PrBaCuCoO<sub>5+δ</sub> (PBCCO) sample versus the temperature when exposed to an air atmosphere. For cathodes of IT-SOFCs, the general required value for the electrical conductivity is about  $100 \text{ S cm}^{-1}$  at the operating temperature [10]. The electrical conductivity of PrBaCuCoO<sub>5+δ</sub> (PBCCO) reaches the above standard absolutely within the 400–800 °C temperature range, though it is slightly lower than PrBaCo<sub>2</sub>O<sub>5+δ</sub> (PBCO) [5]. A similar behavior of LaBaCuCoO<sub>5+δ</sub> has been reported by Zhou et al. [7]. Therefore, the electrical conductivity of PrBaCuCoO<sub>5+δ</sub> (PBCCO) as a cathode is acceptable for application in IT-SOFCs.

Symmetric cells were prepared with SDC serving as the electrolyte. Fig. 4 shows the typical impedance spectra of the symmetrical cells from 600 to 700 °C in air. The high frequency intercept corresponds to overall electrolyte resistance of the symmetric cell including ionic resistance of the electrolyte, while the low frequency intercept corresponds to the total resistance of the symmetric cell. Therefore, the difference between the high frequency and low frequency intercepts with the real axis represents the area specific resistance (ASR) of the two interfaces [11]. It is clear that the ASR significantly reduces with the increasing temperature. It is worthy to note that the ASR of the PrBaCuCoO<sub>5+δ</sub> (PBCCO) cathode is  $0.207 \Omega \text{ cm}^2$  at 600 °C,  $0.101 \Omega \text{ cm}^2$  at 650 °C and  $0.047 \Omega \text{ cm}^2$  at 700 °C, respectively. Compared with the ASR of PrBaCo<sub>2</sub>O<sub>5+δ</sub>

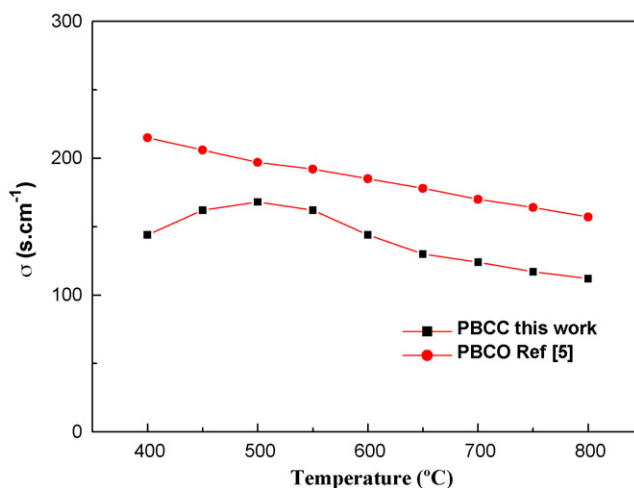


Fig. 3. Temperature dependence of the conductivity for PrBaCuCoO<sub>5+δ</sub> (PBCCO) sample in air.

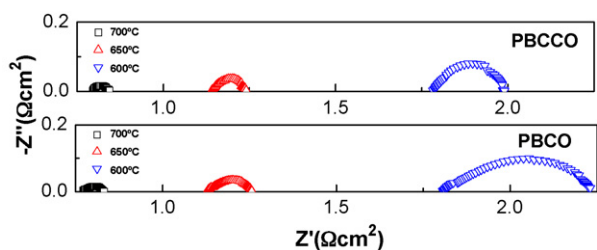


Fig. 4. Impedance spectra of the  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO) and  $\text{PrBaCo}_2\text{O}_{5+\delta}$  (PBCO) cathodes with SDC serving as the electrolyte measured at 600–700 °C.

(PBCO) that is  $0.061 \Omega \text{ cm}^2$  at 700 °C in this work, the  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO) cathode displays somewhat lower interfacial resistance, which might be due to the better connection between cathode and electrolyte shown in Fig. 5. As shown in Fig. 5a, the mismatch of TEC between the  $\text{PrBaCo}_2\text{O}_{5+\delta}$  (PBCO) and SDC results in delamination at the cathode/electrolyte interface only after one thermal cycling, while the SDC electrolyte membrane adheres very well to the  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO) cathode layer after one thermal cycling in Fig. 5b. Moreover, the ASR of  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO) is lower than some traditional cathodes, such as:  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ ,  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ ,  $\text{GdBaCo}_2\text{O}_{5+\delta}$ ,  $\text{SmBaCo}_2\text{O}_{5+\delta}$  [12–15], though a little higher than  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$  [2] and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$  [16]. This implies that  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO) should be a highly potential material as IT-SOFCs cathode with high electrocatalytic activity.

In order to further investigate  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO) as a cathode for IT-SOFCs, the single  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO)/SDC/NiO–SDC cell was prepared. Fig. 6 presents the  $I$ – $V$  and  $I$ – $P$  characteristics

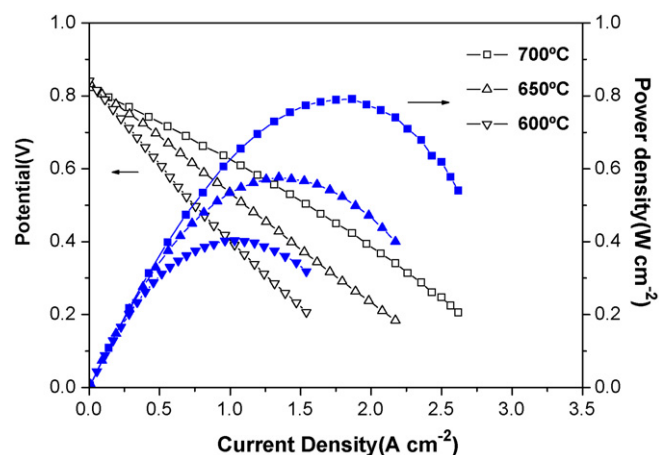


Fig. 6. Cell performance of a single cell (PBCCO/SDC/NiO–SDC) under wet hydrogen atmosphere at 600–700 °C.

of the cell measuring from 600 to 700 °C with humidified hydrogen (about 3%  $\text{H}_2\text{O}$ ) as the fuel. The maximum power densities of the cell is  $791 \text{ mW cm}^{-2}$  at 700 °C and  $403 \text{ mW cm}^{-2}$  at 600 °C, respectively. Obviously, the performance of the cell with the single phase cathode is well compared with other composite cathodes, which are measured under almost the same conditions, such as:  $\text{Pr}_{0.7}\text{Sr}_{0.3}\text{Co}_{0.9}\text{Cu}_{0.1}\text{O}_{3-\delta}$ – $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  [17] and  $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_{3-\delta}$ – $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$  [18]. High power densities demonstrate that  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO) may be a promising single phase cathode for IT-SOFCs, which is in good agreement with the results of impedance measurement discussed above.

#### 4. Conclusions

In this study, a novel single phase oxide  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO) was prepared by auto ignition process for IT-SOFCs. Thermal expansion coefficient was suitable for SDC electrolyte and electrical conductivity of  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO) reached the general required value of cathode materials. The ASR of  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO) cathode on SDC electrolyte investigated by the electrochemical instrument (EIS) was as low as  $0.047 \Omega \text{ cm}^2$  at 700 °C, which displayed high performance. The maximum power density of the  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO)/SDC/NiO–SDC cell with about  $30 \mu\text{m}$  thick electrolyte was  $791 \text{ mW cm}^2$  at 700 °C. The above results indicated that the  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO) cathode could be a good candidate for the next generation solid oxide fuel cells.

#### Acknowledgments

The authors gratefully acknowledge the support of this research by National Natural Science Foundation of China under contract (No. 50572099 and No. 50730002) and National High-tech R&D Program of China (Grant No.: 2007AA05Z157).

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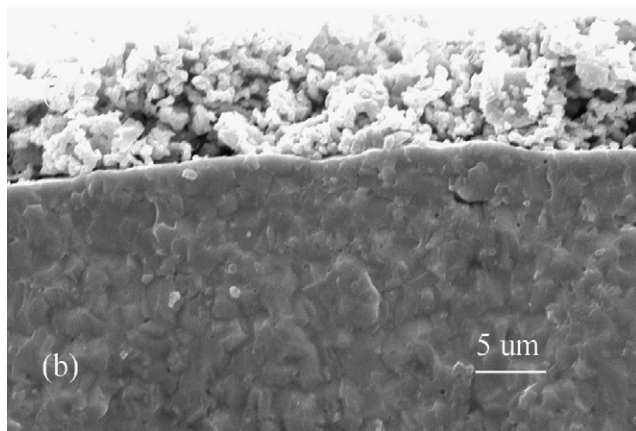
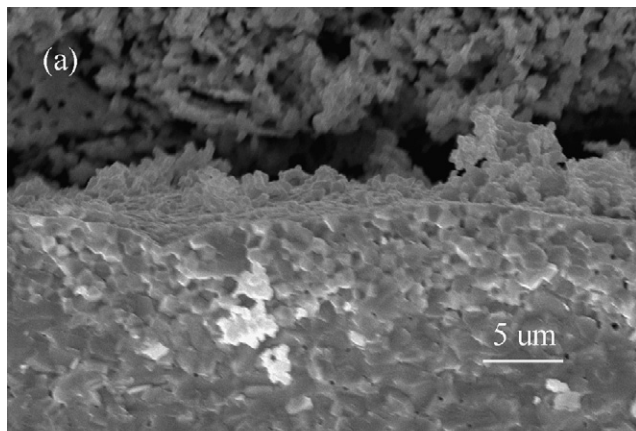


Fig. 5. Cross-section views of the cathode/electrolyte interface on symmetrical electrochemical cells after once testing (a)  $\text{PrBaCo}_2\text{O}_{5+\delta}$  (PBCO) and (b)  $\text{PrBaCuCoO}_{5+\delta}$  (PBCCO).

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