



Short communication

High-performance PrBaCo₂O_{5+δ}–Ce_{0.8}Sm_{0.2}O_{1.9} composite cathodes for intermediate temperature solid oxide fuel cell

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ABSTRACT

PrBaCo₂O_{5+δ}–Ce_{0.8}Sm_{0.2}O_{1.9} (PBCO–SDC) composite material are prepared and characterized as cathode for intermediate temperature solid oxide fuel cells (IT-SOFCs). The powder X-ray diffraction result proves that there are no obvious reaction between the PBCO and SDC after calcination at 1100 °C for 3 h. AC impedance spectra based on SDC electrolyte measured at intermediate temperatures shows that the addition of SDC to PBCO improved remarkably the electrochemical performance of a PBCO cathode, and that a PBCO–30SDC cathode exhibits the best electrochemical performance in the PBCO–xSDC system. The total interfacial resistances R_p is the smallest when the content of SDC is 30 wt%, where the value is 0.035 Ω cm² at 750 °C, 0.072 Ω cm² at 700 °C, and 0.148 Ω cm² at 650 °C, much lower than the corresponding interfacial resistance for pure PBCO. The maximum power density of an anode-supported single cell with PBCO–30SDC cathode, Ni–SDC anode, and dense thin SDC/LSGM (La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_{3–δ})/SDC tri-layer electrolyte are 364, 521 and 741 mW cm^{–2} at 700, 750 and 800 °C, respectively.

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1. Introduction

Reducing the cost of solid oxide fuel cells (SOFCs) is the goal currently pursued by the developers of the world. The decrease of operating temperature would result in reducing reactivity between the cell components and therefore an improvement of fuel cell stability. Furthermore, much cheaper metallic interconnects and more flexible glass gasket sealants may be applied [1]. Therefore, there is a general tendency for SOFCs towards a reduced operating temperature. However, the decrease of operating temperature leads to a significant decrease in electrode activity, especially for the cathode [2–5]. Hence, the development of novel and high-performance cathodes in the intermediate temperature range (500–800 °C) is essential [6].

Recently, a family of oxides such as LnBaCo₂O_{5+δ} (Ln = rare-earth) with the layered or double perovskite-type structure has received widespread attention for its potential application as IT-SOFC cathode. It has been reported that LnBaCo₂O_{5+δ} has a 112-type phase, whose structures are derived from perovskites via ordering of Ln and Ba cations into layers along *c* [7]. Moreover, oxygen atoms can be partially or even completely removed from the lanthanide planes, creating a lot of vacant sites in the crystal lattice,

and the ordered phase can be grown under strongly reducing atmosphere or pure argon [8]. The particular distribution of vacancies in these materials could greatly enhance the diffusivity of oxide ions in the bulk of the material and possibly supply surface defect sites with enhanced reactivity towards molecular oxygen compared with non-ordered perovskites [9]. Among the various LnBaCo₂O_{5+δ} oxides, GdBaCo₂O_{5+δ} (GBCO) has been the most investigated [10–12]. Jacobson and co-workers demonstrated that the oxygen bulk diffusion coefficient and the surface exchange coefficient of PrBaCo₂O_{5+δ} (PBCO) are ~10^{–5} cm² s^{–1} and ~10^{–3} cm s^{–1} in the oxygen flow at 623 K, respectively, which could be 2–3 orders of magnitude higher than the values reported for GBCO [9], suggesting it may perform even better than GBCO as a cathode of IT-SOFCs. More recently, we have reported that anode-supported thin SDC electrolyte SOFC using PBCO as a cathode exhibits high power densities when operated with hydrogen as the fuel and air as the cathode gas [13]. These results indicate that PBCO is a promising cathode material for IT-SOFCs.

It is well known that one commonly used means for optimizing cathode performance is to add an ionically conducting second phase to the electrode material to form a composite cathode. The addition of a highly ionic conductive phase to the electrode layer is effective in improving the electrocatalytic activity of cathode due to enlargement of the electrochemically active area, i.e., the triple phase boundary (TPB), at which the oxygen reduction reaction occurs. With the aim of improving the electrocatalytic activity

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of PBCO and achieving a match of the thermal expansion coefficient between the electrolyte and the cathode, we present here the electrochemical properties of PBCO–SDC composite cathodes. Then, the performance of an NiO–SDC anode-supported single cell with tri-layer SDC/LSGM/SDC electrolyte film using PBCO–30SDC as the cathode, is evaluated.

2. Experimental

Detailed synthesis of $\text{PrBaCo}_2\text{O}_{5+\delta}$ cathode, $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC), NiO–SDC anode and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ (LSGM) electrolytes for this investigation are available elsewhere [13–15]. The PBCO powder obtained was mixed with different amounts of SDC powder (0–50 wt%) to make composite cathodes (denoted here by “PBCO–xSDC”, $x=0$ –50). The cathode powders were mixed with ethyl cellulose and terpineol to obtain well-distributed cathode slurry. Then a half-cell with symmetric cathodes was prepared with the cathode slurry, fabricated on both sides of the SDC electrolyte disk (sintered at 1400 °C for 10 h) and sintered in air at 900 °C for 2 h. The anode-supported SOFC was prepared by co-pressing the NiO–SDC–flour composite powder with the SDC and LSGM powder under 220 MPa into pellets with a diameter of 13 mm and co-sintered at 1400 °C for 4 h to form a dense thin bilayer SDC/LSGM film on the porous NiO–SDC substrate [13]. And SDC slurry was screen-printed onto LSGM film and sintered in air at 1300 °C for 1 h. The SDC buffer layers are introduced to minimize reactions or inter-diffusion between LSGM and the Ni-based anode or the Co-contained cathode [16]. A PBCO–30SDC powder was mixed with ethyl cellulose and terpineol, and screen-printed onto the sintered SDC buffer layer and sintered in air at 900 °C for 2 h.

X-ray diffraction (XRD) (Rigaku-D-Max Ra system) was used to confirm the crystalline structure of the prepared powders. Morphologies of the cathode after electrochemical test were characterized by a scanning electron microscope (SEM, JSM-6480LV, JEOL, Japan). AC impedance spectroscopy of the symmetrical cell was tested under open-circuit conditions using an electrochemical impedance spectrum analyzer (CHI 604C, Chenhua Inc., Shanghai). The frequency range was 0.1–10⁵ Hz with signal amplitude of 10 mV. The single cell attached to one end of an alumina tube with the anode inside by using silver paste for sealing. Hydrogen produced by GCH2500 hydrogen generator (HP) was fed into the alumina tube as fuel with a flow rate of 350 mL min⁻¹, while oxygen in the air was used as oxidant. The fuel cells were tested between 600 and 800 °C. The current–voltage curves of SOFC were obtained using an electrochemical instrument (CHI604C, CH Instruments Inc., China).

3. Results and discussion

Fig. 1 shows the XRD patterns of PBCO–SDC mixtures calcined at 1100 °C for 3 h. For comparison, the patterns of PBCO and SDC powders are also shown in the same figure. The PBCO cathode material has formed a single-phase double perovskite structure after calcinations at 1100 °C (Fig. 1a). The structure of the SDC is the cubic fluorite structure (Fig. 1b). After the PBCO–30SDC mixture has been sintered at 1100 °C for 3 h, the PBCO and SDC still retain their own structures. No reaction products were detected by XRD. It seems that PBCO is a chemically stable cathode material for SOFCs based on SDC when the operating temperature is below 1100 °C.

Fig. 2 reveals the impedance spectra of the symmetrical cells using different cathodes at 700 °C. It is obvious that the addition of an ionically conducting phase SDC to PBCO cathode resulted in a significant reduction of the total interfacial polarization resistances R_p (i.e., the difference between the real axis intercepts of the impedance arcs), typically from 0.259 $\Omega\text{ cm}^2$ for PBCO to less

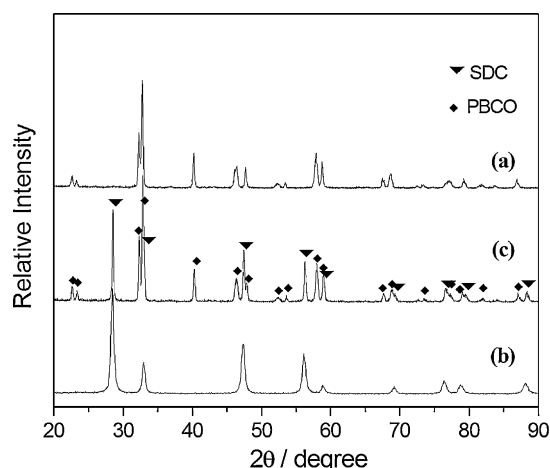


Fig. 1. XRD patterns of (a) PBCO powders, (b) SDC powders and (c) PBCO–30SDC mixture sintered at 1100 °C for 3 h.

than 0.072 $\Omega\text{ cm}^2$ for PBCO–30SDC at 700 °C. CeO_2 -based oxides are known for their ability to store, release and transport oxygen under SOFC operating conditions owing to their high ionic conductivity [14]. The ionically conducting phase SDC, when added to a porous cathode, functions effectively as an oxygen conduction path, greatly extending the electrochemically active reaction sites from the electrode/electrolyte interface region to the bulk of the PBCO electrode, and effectively enhancing the TPBs for the oxygen reduction. Therefore, a decrease in the total interfacial polarization resistance R_p owing to the addition of SDC can be expected.

Fig. 3 shows the relation between the electrode resistance, content of SDC and temperature. It is clear that R_p decreases as the temperature and SDC content increase. Moreover, the R_p is the smallest when the content of SDC is 30 wt%. A further increase in SDC content to a value higher than 30 wt% results in a higher interfacial polarization resistance. This may be due to a decrease in the continuity of the PBCO phase in the composite, and hence a decrease in electrical conductivity [16]. The PBCO electrode containing 30 wt% SDC exhibits the smallest interfacial polarization resistance among the PBCO–xSDC composite cathode, where the values are only about 0.021, 0.035, 0.072, and 0.148 $\Omega\text{ cm}^2$ at 800, 750, 700 and 650 °C, respectively, which is much lower than those of pure PBCO cathode at the corresponding temperatures. Trans-

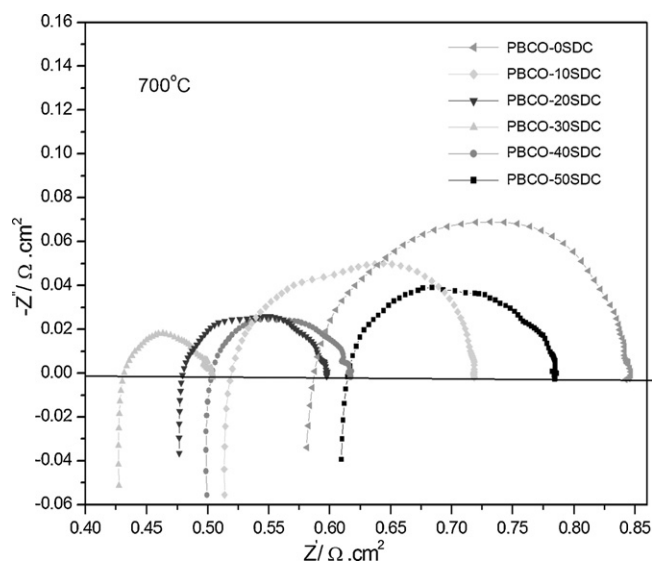


Fig. 2. Impedance spectra of the PBCO–xSDC measured at 700 °C.

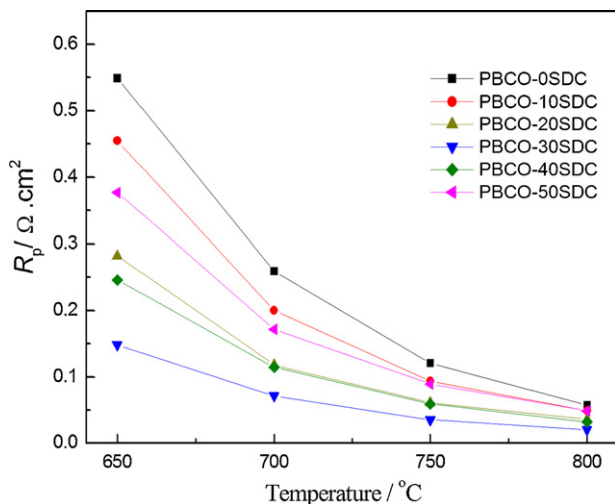


Fig. 3. Change of the polarization resistance with the SDC contents and temperature.

port properties in a composite, such as electrical conductivity, are especially sensitive not only to the amount of each phase, but also to the degree to which phases are connected.

Fig. 4 shows typical cross-SEM images of a PBCO and PBCO-30SDC on a SDC electrolyte sintered at 900 °C for 2 h. It can be seen that the PBCO-30SDC electrode (Fig. 5a) exhibits a homogeneous porous microstructure and shows good bonding and continuous contact with the dense electrolyte pellet, which lead

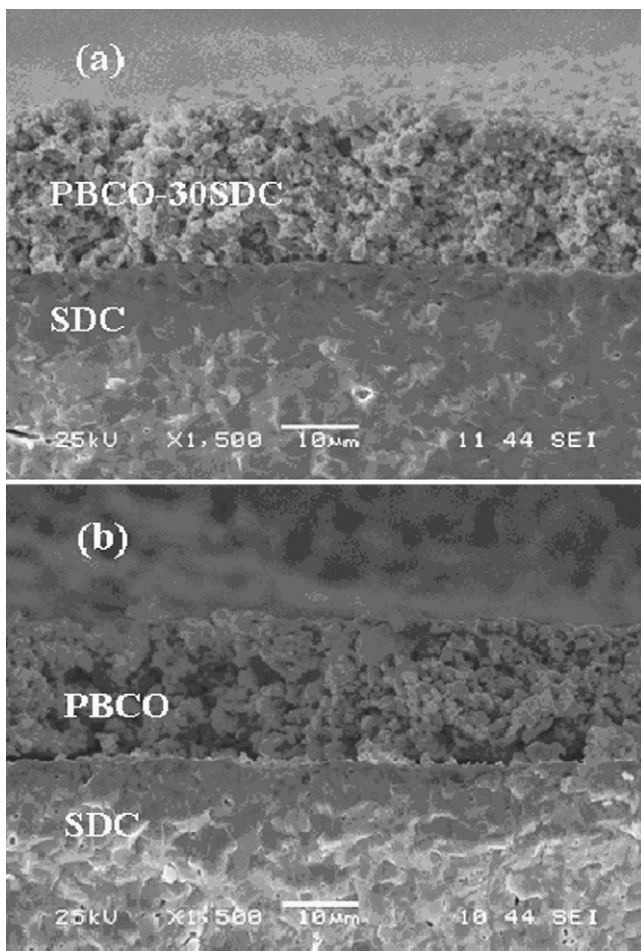


Fig. 4. SEM micrographs of (a) PBCO-30SDC/SDC and (b) PBCO/SDC interfaces.

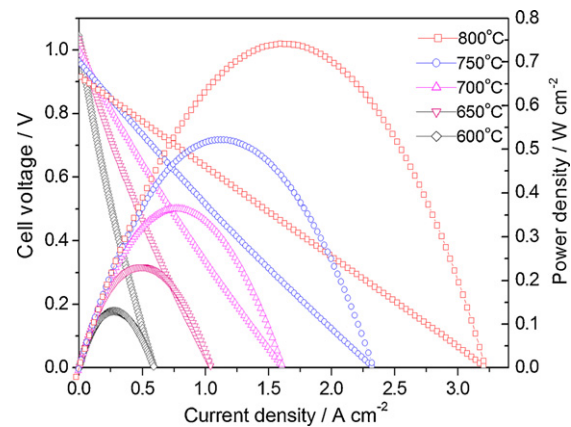


Fig. 5. Performances of the cell with PBCO-30SDC/SDC/LSGM/SDC/Ni-SDC at 600–800 °C.

to the low interfacial polarization resistance. Compared with the PBCO-30SDC cathode, the PBCO cathode shows a significantly high polarization resistance. As seen in Fig. 5b, the PBCO cathode shows poor adhesion between the cathode and SDC electrolyte. The different thermal expansion between the two materials leads to bad bonding at the interface. An insufficient connectivity between electrolyte and cathode leads to a reduction of the real active surface involved in the electrochemical processes.

The cell voltage and the corresponding power density are shown in Fig. 5 as a function of current density for a Ni/SDC anode-supported single cell with tri-layer SDC/LSGM/SDC electrolyte film using PBCO-30SDC as the cathode, measured with hydrogen and air at temperatures from 600 to 800 °C. It can be seen that the values of the open-circuit voltage (OCV) are 1.035, 1.025, 1.005, 0.965 and 0.925 V at 600, 650, 700, 750 and 800 °C, respectively, which is quite similar to those reported by Guo et al. with a LSGM electrolyte and $\text{La}_{0.6}\text{Ce}_{0.4}\text{O}_{1.8}$ (LDC) buffer layer [17]. Here, using SDC as buffer layer, the maximum power densities of the cell with the LSGM electrolyte film reach 130, 231, 364, 521 and 741 mW cm^{-2} at 600, 650, 700, 750 and 800 °C, respectively, illustrating that good performance can be obtained for a single cell using PBCO-30SDC as the cathode and an LSGM film as the electrolyte. The high output performance of single cell also indicates that the SDC buffer layers are effective in preventing the reactions inducing high resistance products between LSGM and NiO or the Co-contained cathode.

4. Conclusions

The electrochemical performances of PBCO-xSDC composite cathode are investigated for potential application in IT-SOFCs. The XRD result shows no reaction product is found between PBCO electrode and SDC electrolyte after heat-treatment at 1100 °C for 3 h. The impedance spectra results indicate that the addition of SDC electrolyte to PBCO greatly improves electrochemical performances of PBCO cathode. PBCO-30SDC electrode exhibits the highest cathode performance among the PBCO-xSDC composite cathode. Using a PBCO-30SDC cathode, the Ni/SDC anode-supported single cell with tri-layer SDC/LSGM/SDC electrolyte membrane achieves excellent performance. These results suggest that PBCO-30SDC is a potential cathode material for use in IT-SOFCs.

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