



Short communication

Electrochemical performance of $\text{PrBaCo}_2\text{O}_{5+\delta}$ layered perovskite as an intermediate-temperature solid oxide fuel cell cathode

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ABSTRACT

$\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) powder was prepared by a combined EDTA and citrate complexing method. The electrochemical performance of PBCO as a cathode for intermediate-temperature solid oxide fuel cells (IT-SOFCs) was evaluated. A porous layer of PBCO was deposited on a 42 μm thick electrolyte consisting of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC), prepared by a dry-pressing process. A fuel cell with a structure PBCO/SDC/Ni-SDC provides a maximum power density of 866, 583, 313 and 115 mW cm^{-2} at 650, 600, 550 and 500 $^\circ\text{C}$, respectively, using hydrogen as the fuel and stationary air as the oxidant. The total resistance of the cell was about 0.41, 0.51, 0.57 and 0.77 Ωcm^2 , respectively. This encouraging data identifies PBCO as a potential cathode material for IT-SOFCs.

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1. Introduction

Solid oxide fuel cells (SOFCs) are considered as one of the most promising energy conversion devices because of their high efficiency, low pollutant emission and flexibility with respect to fuel. From the viewpoint of cost reduction and long-term stability, it is necessary to lower the operating temperature. However, a key obstacle to reduced-temperature operation of SOFCs is the poor activity of traditional cathode materials for electrochemical reduction of oxygen in this temperature range [1,2]. Therefore, there are current efforts aimed at finding cathode materials that are electrolyte-compatible and have the fast oxygen diffusion and surface exchange kinetics necessary for low electrode resistance.

In recent years, many simple perovskite mixed ionic–electronic conductors, such as doped LaCoO_3 , BaCoO_3 and LaFeO_3 , have been extensively studied as possible cathodes in SOFCs [1,3]. It has been reported that the oxygen kinetics in perovskites with an ordered structure type, such as the double and layered perovskites, are significantly faster than in the corresponding disordered perovskites [4], suggesting the potential application of ordered perovskites as cathodes in SOFCs. $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) has been reported to adopt an oxygen-deficient double perovskite structure with orthorhombic symmetry [5]. The studies on $\text{PrBaCo}_2\text{O}_{5+\delta}$ by Maignan et al. [6] have shown that, in this structure, the Ba cations do not have a random distribution on the A perovskite sites but are ordered

in alternating (001) layers. Moreover, the oxygen vacancies are mainly located in the $[\text{PrO}]_x$ rare earth planes. 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 [7]. Frontera et al. [8] have observed facile oxygen uptake in $\text{PrBaCo}_2\text{O}_{5+\delta}$ powders at temperatures as low as 200 $^\circ\text{C}$. Kim et al. [4] also found that $\text{PrBaCo}_2\text{O}_{5+\delta}$ has unusually rapid oxygen transport kinetics at low temperatures (300–500 $^\circ\text{C}$). According to preliminary results, $\text{PrBaCo}_2\text{O}_{5+\delta}$ appears to be an attractive cathode material for IT-SOFCs.

Recently, Kim et al. [4] have shown the potential of $\text{PrBaCo}_2\text{O}_{5+\delta}$ for application in cathodes of IT-SOFCs, obtaining values of 0.15 Ωcm^2 for the area specific resistance of PBCO-GDC composite cathodes in contact with a GDC electrolyte at 600 $^\circ\text{C}$ in symmetrical cell systems. However, to our knowledge, the performance of PBCO cathodes as part of a whole fuel cell has not been reported to date. This paper seeks to address this issue by evaluating the performance of this material when it is used as a cathode in a standard anode-supported SOFC.

2. Experimental

A PBCO powder was prepared by a combined EDTA and citrate complexing method. Stoichiometric amounts of Pr_6O_{11} (99.99%), $\text{Ba}(\text{NO}_3)_2$ (99.5%) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.9%) were used as starting materials. The Pr_6O_{11} was dissolved completely in concentrated nitric acid (65–68%), and the $\text{Ba}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2$ were dis-

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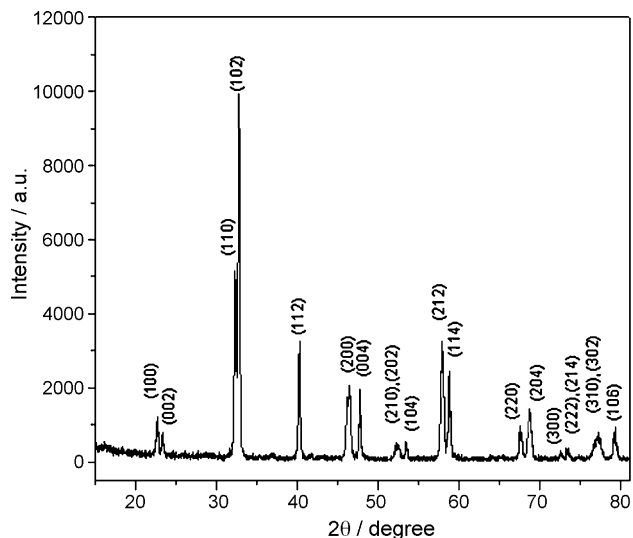


Fig. 1. XRD patterns of PBCO powder after calcinations at 1100 °C for 10 h in air.

solved in distilled water. The solutions were then mixed together. An EDTA-ammonia aqueous solution and solid citric acid were then added to the mixed solution in sequence at an EDTA: citric acid: metal ions mole ratio of 1:2:1. The mixed solution was subsequently stirred at 150 °C until it formed a glutinous colloid. The colloid was dried at 250 °C for several hours and calcined at 1000 °C for 10 h in air to obtain the cathode powder.

A $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) powder was prepared by a glycine-nitrate method. Stoichiometric amounts of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (A.R.) and Sm_2O_3 (A.R.) were used as starting materials. The Sm_2O_3 was dissolved completely in concentrated nitric acid (65–68%), and the $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in distilled water. The solutions were then mixed together, and glycine was added as a complexant. The mixture was heated on a hotplate, and was finally converted to a pale yellow ash. The SDC powder was then obtained by calcining the ash at 600 °C for 4 h.

A NiO powder was prepared by an ammonia precipitation method as described elsewhere [9]. The NiO and SDC powders obtained were mixed in a weight ratio of 60:40 and ball-milled for 20 h using ethanol as the medium. As a pore former, 15 wt% flour was then added to the mixture, which was subsequently ball-milled

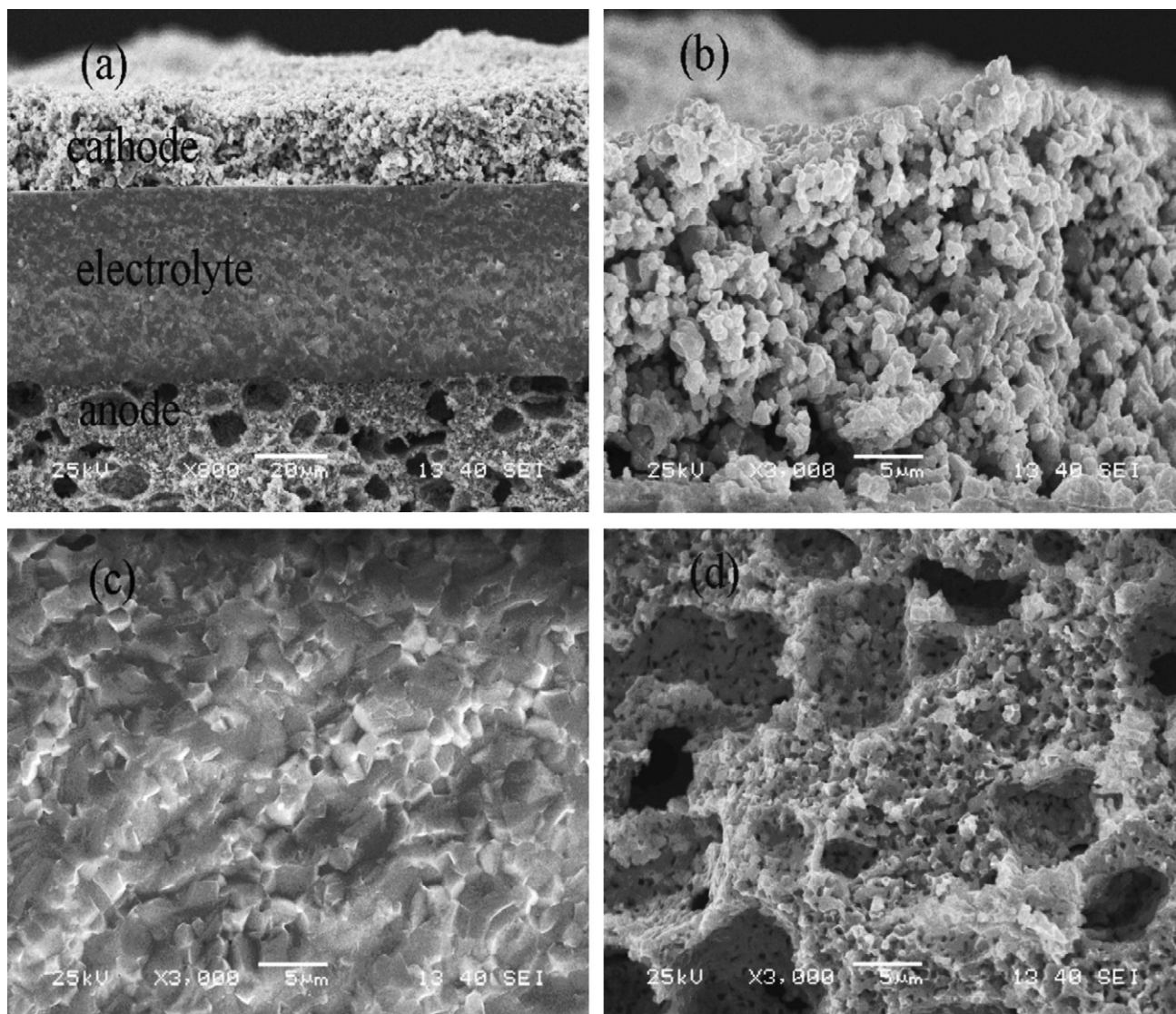


Fig. 2. Cross-sectional views (SEM micrographs) of (a) a single cell, (b) the porous PBCO cathode, (c) the dense SDC electrolyte, and (d) the porous Ni-SDC anode.

for another 2 h. After drying, the anode powder was pressed under 100 MPa into pellets with a diameter of 13 mm to be used as anode substrates. To prepare thin SDC films on the anode substrates, the prepared SDC powder was added to the anode substrate through a screen (silk net, 180 mesh), and then co-pressed at 220 MPa to obtain a green bilayer. The green bilayer was subsequently sintered at 1400 °C for 4 h to form a dense SDC electrolyte film.

The PBCO powder was mixed with ethyl cellulose and terpineol, and screen-printed onto the sintered SDC films and sintered in air at 950 °C for 2 h. Silver paste was applied to the anode and cathode surfaces to serve as current collectors, followed by attachment of two silver wires to each electrode to serve as current and voltage leads. The single cell made in this way was sealed onto one end of an alumina tube with silver paste. The performance of the cell was tested from 500 to 650 °C. Hydrogen (100 ml min⁻¹) was used as the fuel at the anode side, and air as the oxidant at the cathode side.

X-ray diffraction (XRD) (Rigaku-D-Max Ra system, with Cu K α radiation, operated at 12 kW) was used to confirm the crystal structure of the prepared powders. AC impedance spectroscopy measurements were carried out on single cells under open-circuit conditions using an electrochemical impedance spectrum analyzer (CHI 604C, Chenhua Inc., Shanghai). The frequency range was 0.1–10⁵ Hz with a signal amplitude of 10 mV. The morphologies of the cathodes after electrochemical tests were characterized by a scanning electron microscope (SEM, JSM-6480LV, JEOL, Japan). The single-cell performance was tested at temperatures from 500 to 650 °C.

3. Results and discussion

An XRD pattern of the synthesized PBCO powder after calcination at 1100 °C for 10 h is shown in Fig. 1. The X-ray pattern of the PBCO matches well with the diffraction data for the double perovskite phase. This indicates that a single crystalline phase of PBCO was successfully obtained after calcination, which is consistent with the data reported elsewhere [4–6].

Fig. 2 shows cross-sectional SEM micrographs of each cell component. As can be seen from Fig. 2a, the thickness of the PBCO cathode layer is about 20 μ m and the thickness of the SDC film is about 42 μ m. The SDC film adheres well to both the PBCO cathode and the Ni-SDC anode substrate. The SDC film (Fig. 2c) seems very dense except for a few pinholes or isolated voids, and no cross-film cracks are observed. In contrast to the dense electrolyte film, both the cathode (Fig. 2b) and the anode (Fig. 2d) are highly porous. The presence of sufficient porosity is important for electrodes in order to allow rapid transport of gaseous reactants and to provide abundant sites for electrochemical reactions.

The cell voltage and the corresponding power density are shown in Fig. 3 as a function of current density for a single cell, measured with hydrogen and air at temperatures from 500 to 650 °C. The open-circuit voltage (OCV) obtained in the work described here was about 0.816 V, which is obviously lower than the theoretical value, i.e. 0.989 V at 600 °C [10]. According to the report of Zhang et al. [11], a thinner electrolyte film will not only reduce the cell resistance, but will also enhance the possibility of electrolyte defects such as pinholes or microcracks spanning the entire electrolyte thickness. The pinholes observed in the cross-section of the SDC film may cause gas leakage across the electrolyte film and thus lower the cell's OCV.

With hydrogen as the fuel and ambient air as the oxidant, the maximum power density of a single cell was 866, 583, 313 and 115 mW cm⁻² at 650, 600, 550 and 500 °C, respectively. It is gratifying that the performance of the present cell at 600 °C is higher

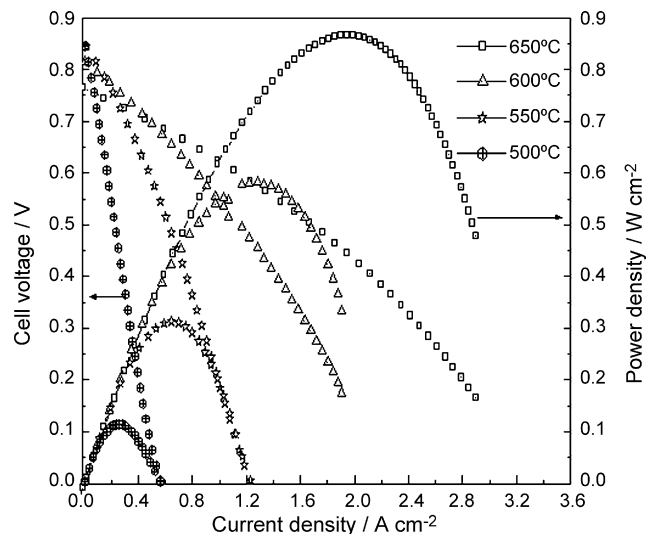


Fig. 3. Performances of the cell with PBCO cathode at 500–650 °C.

than that obtained with an SOFC with a Pr_{0.7}Sr_{0.5}Co_{0.9}Cu_{0.1}O_{3- δ} cathode and an anode-supported SDC film at 650–750 °C [12]. Since the two cells have similar structures, and similar ceria-based electrolyte films prepared via dry pressing, the distinct difference in power density can be ascribed to the cathode used. The present cell exhibits a much higher power output than that obtained with a Pr_{0.7}Sr_{0.5}Co_{0.9}Cu_{0.1}O_{3- δ} cathode, which implies that PrBaCo₂O_{5+ δ} possesses a better cathode performance than that of Pr_{0.7}Sr_{0.5}Co_{0.9}Cu_{0.1}O_{3- δ} .

Fig. 4 shows impedance spectra of a cell in the open-circuit condition at temperatures ranging from 500 to 650 °C. The total resistances, the electrode interfacial resistances and the ohmic resistances, as determined from the impedance spectra at different temperatures, are shown in Table 1. It can be seen that the electrode interfacial resistance is higher than the ohmic resistance from 500 to 650 °C. This implies that the interfacial resistance is more significant and that the quality of the electrode has more effect on the performance of the cell [13]. According to previous studies [14,15],

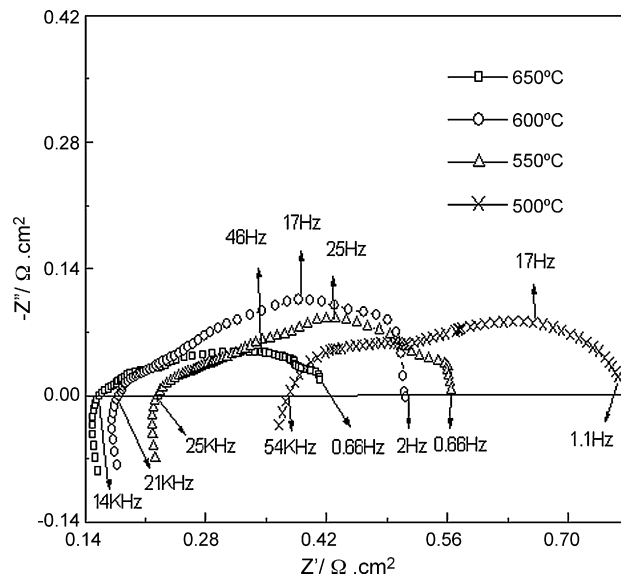


Fig. 4. Impedance spectra of the single cell (PBCO/SDC/NiO-SDC) measured under open-circuit condition.

Table 1
Impedance spectra values for single cell PBCO/SDC/NiO-SDC ($\Omega \text{ cm}^2$)

Temperature	500 °C	550 °C	600 °C	650 °C
Interface resistance	0.3935	0.3413	0.3307	0.2559
Ohmic resistance	0.3754	0.224	0.1788	0.1579
Total resistance	0.7689	0.5653	0.5095	0.4138

the interfacial resistance is dominated by the cathode–electrolyte interface, and the resistance of the anode–electrolyte interface is negligible. Therefore reduction of the cathode–electrolyte interfacial resistance will be important for improving the performance of such cells in further studies.

4. Conclusion

A $\text{PrBaCo}_2\text{O}_{5+\delta}$ cathode for potential application in IT-SOFCs has been reported. Dense SDC electrolyte films have been successfully fabricated on anode substrates by a dry-pressing process. An anode-supported single cell based on a $42 \mu\text{m}$ SDC electrolyte film has been assembled, using the $\text{PrBaCo}_2\text{O}_{5+\delta}$ material as the cathode, and tested at low temperatures with hydrogen as the fuel and ambient air as the oxidant. The maximum power density obtained was 866, 583, 313 and 115 mW cm^{-2} at 650, 600, 550 and 500°C , respectively, and the total resistance of the cell was 0.41, 0.51, 0.57 and $0.77 \Omega \text{ cm}^2$, respectively. The power outputs obtained are encouraging and indicate that $\text{PrBaCo}_2\text{O}_{5+\delta}$ is a promising cathode material for IT-SOFCs.

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