



Short communication

In situ drop-coated $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte-based proton-conductor solid oxide fuel cells with a novel layered $\text{PrBaCuFeO}_{5+\delta}$ cathode

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ABSTRACT

In order to develop a simple and cost-effective route to fabricate proton-conductor intermediate-temperature SOFCs, a dense $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) electrolyte was fabricated on a porous anode by in situ drop-coating. The $\text{PrBaCuFeO}_{5+\delta}$ (PBCF) composite oxide with layered perovskite structure was synthesized by auto ignition process and examined as a novel cathode for proton-conductor IT-SOFCs. The single cell, consisting of PBCF/BZCY/NiO-BZCY structure, was assembled and tested from 600 to 700 °C with humidified hydrogen (~3% H_2O) as the fuel and the static air as the oxidant. An open-circuit potential of 1.01 V and a maximum power density of 445 mW cm^{-2} at 700 °C were obtained for the single cell. A relatively low interfacial polarization resistance of 0.15 Ωcm^2 at 700 °C indicated that the PBCF is a promising cathode for proton-conductor IT-SOFCs.

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1. Introduction

Solid oxide fuel cells (SOFCs) have attracted much attention worldwide as future green energy conversion devices [1,2] because of their high-energy efficiency and low impact on the environment [3,4]. As we know, the proton-conductor SOFCs have some advantages compared with oxide-ion conductor SOFCs, such as forming water at the cathode side and low activation energy of electrolyte [5]. However, the expensive cost of the SOFCs system limits the commercial use for high operating temperature. Lowering the operating temperature of SOFCs from high temperature (about 1000 °C) to intermediate-temperature (500–700 °C) can significantly improve materials' compatibility, reduce the capital cost and prolong the operational lifetime [6]. Unfortunately, the performance of these intermediate-temperature SOFCs (IT-SOFCs), especially proton-conductor IT-SOFCs is strongly dependent on the property of the cathode–electrolyte interface, since the polarization resistance increases rapidly as the temperature decreases [7].

Accordingly, the development of proper cathode material for proton-conductor IT-SOFCs in order to reduce cathode–electrolyte interface polarization remains a challenge. Recently, $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) that exhibits both adequate proton conductivity as well as sufficient chemical and thermal stability over a wide range of conditions relevant to fuel cell operation has been exten-

sively applied as electrolyte material for SOFCs [8]. In addition, many simple perovskite-type mixed ionic–electronic conductors such as doped $\text{Nd}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Cu}_{0.2}\text{O}_{3-\delta}$ [9], $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cu}_{0.2}\text{O}_{2.5-\delta}$ [10] and LaFeO_3 [11] have been extensively studied as cathodes for IT-SOFCs, however, not much attention has been paid to the layered perovskite structure. Among the various layered $\text{LnBaCo}_2\text{O}_{5+\delta}$ oxides, $\text{PrBaCo}_2\text{O}_{5+\delta}$ has the highest bulk diffusion coefficient and surface exchange coefficient, suggesting it may perform better than others as cathodes for proton-conductor IT-SOFCs [12]. However, to our knowledge, these cathodes, Co occupying the whole of B-sites, often suffer some problems like poor chemical stability in CO_2 and high thermal expansion coefficients (TECs) in practical long-term application. Therefore, in order to avoid these disadvantages and improve the performance ulteriorly, more attention should be paid to the B-sites ions. In this work, the ceramic material of $\text{PrBaCuFeO}_{5+\delta}$ (PBCF) synthesized by auto ignition process was examined as a new cathode in proton-conductor IT-SOFCs based on a BZCY electrolyte.

2. Experimental

2.1. Preparation of $\text{PrBaCuFeO}_{5+\delta}$ and $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ powders

$\text{PrBaCuFeO}_{5+\delta}$ (PBCF) powders were prepared by auto ignition process. $\text{Pr}(\text{NO}_3)_3$, $\text{Ba}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ were dissolved at the stoichiometric ratio in distilled water to form an aqueous solution, and then citric acid was added with the ratio of citric acid/metal mole of 1.5:1, which was used as complexation

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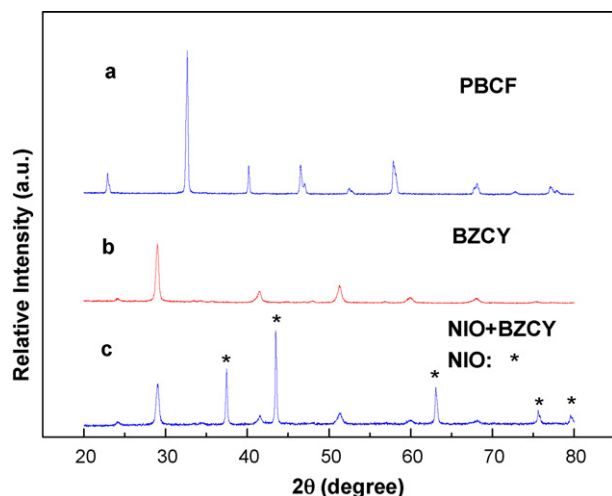


Fig. 1. XRD diffraction patterns of (a) $\text{PrBaCuFeO}_{5+\delta}$ (PBCF), (b) $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) membrane and (c) NiO-BZCY anode substrate (*NiO).

agent. 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 subsequently calcined at 950°C for 2 h to obtain fine PBCF powders. The $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) powders were also synthesized by auto ignition process with the raw materials $\text{Ba}(\text{NO}_3)_2$, $\text{Zr}(\text{NO}_3)_4$, $\text{Ce}(\text{NO}_3)_3$ and $\text{Y}(\text{NO}_3)_3$ at a proper molar ratio and then calcined at 1000°C for 2 h.

2.2. Fabrication of the fuel cell with $\text{PrBaCuFeO}_{5+\delta}$ as the cathode

To make a single cell, a mixed powder of NiO + BZCY + corn starch (in a weight ratio of 60:40:20) was pressed at 200 MPa (25 mm in diameter and 0.5 mm thick) and then sintered at 800°C for 2 h to form an anode substrate. Then the BZCY layer was subsequently drop-coated [13] on the porous anode surface in air at room temperature. The electrolyte layer and anode support were then co-fired at 1400°C for 5 h. After that, fine PBCF powder was mixed thoroughly with a 10 wt% ethylcellulose-terpineol binder to prepare the cathode slurry, which was painted on the BZCY electrolyte membrane, and fired at 950°C for 3 h in air to form a single cell. In addition, the electrode active area was 0.237 cm^2 .

2.3. Characterization of the cell performance

The cell components were selected as follows: PBCF/BZCY/NiO-BZCY measured by X-ray diffraction (PW-1730). Ag paste was applied onto the cathode surface as current collector. Single cells were tested from 600 to 700°C in a home-developed-cell-testing system. Humidified hydrogen ($\sim 3\%$ H_2O) was fed to the anode chamber at a flow rate of 60 ml min^{-1} , while the cathode was exposed to atmospheric air. The cell voltages and output current of the cells were measured with digital multi-meters (GDM-8145). AC impedance spectroscopy (Chi604c, Shanghai, Chenhua) was performed on the cell under open-current conditions from 600 to 700°C . A scanning electron microscope (SEM) was used to observe the microstructure of the cells after testing.

3. Results and discussion

As shown in Fig. 1(a), the as-prepared powder of $\text{PrBaCuFeO}_{5+\delta}$ (PBCF) exhibits a layered perovskite phase structure, which is consistent with the data reported by Zhou et al. [14]. Fig. 1 also represents the XRD spectra of anode/electrolyte bi-layer sin-

tered at 1400°C for 5 h. It is obvious that there were only peaks corresponding to $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) in electrolyte membrane (Fig. 1(b)) and to NiO and BZCY in the anode substrate (Fig. 1(c)), which gave no evidence for the formation of other substance.

In order to investigate PBCF as a cathode material for proton-conductor IT-SOFCs, the single PBCF/BZCY/NiO-BZCY cell was prepared. Micrograph of cross-sectional view of the single cell after electrochemical tests is provided in Fig. 2(a). It is evident that the PBCF cathode has a fine porous microstructure. Moreover, the visual appearance of the electrolyte/cathode interface in the micrograph indicates distinctly that the cathode displays good adhesion to the dense BZCY, which is about $15\ \mu\text{m}$ in thickness. Fig. 2(b) illustrates morphology of the electrolyte fractured surface, which is quite dense. In addition, the size of the crystal is about $2\ \mu\text{m}$. The results above demonstrate that the in situ reaction-sintering drop-coated process followed by a heat treatment at a relatively low temperature (1400°C) to fabricate dense BZCY electrolyte membrane on porous anode support is successful.

Fig. 3 presents the I - V and I - P characteristics of the cell measuring from 600 to 700°C with humidified hydrogen ($\sim 3\%$ H_2O) as the fuel. The maximum power densities of 445 , 305 , and 201 mW cm^{-2} with the OCV values of 1.01 , 1.02 , and 1.03 V are obtained at 700 , 650 , and 600°C , respectively, hinting that the electrolyte membrane is sufficiently dense. It is unambiguously pointed out that the cell with PBCF cathode has higher power density than the values (270 and 148 mW cm^{-2} at 700 and 600°C) reported by Zuo et al. [8].

In order to intensively evaluate the performance of layered PBCF working as a cathode for proton-conductor IT-SOFCs, resistances of the cells under open-circuit conditions surveyed by AC impedance spectroscopy are shown in Fig. 4. The high frequency intercept corresponds to the ohmic resistance of the cell (R_b), including ionic resistance of the electrolyte, electronic resistance of the electrodes and some contact resistance associated with interfaces, while the low frequency intercept corresponds to the total resistance of the cell (R_{total}). Therefore, the difference between the high frequency and low frequency intercepts with the real axis represents the total interfacial polarization resistance (R_p) of the cell, including the cathode-electrolyte interface resistance and the anode-electrolyte interface resistance. As expected, the increase of the measuring temperature resulted in a significant reduction of the interfacial resistances, typically from $0.76\ \Omega\text{ cm}^2$ at 600°C to $0.15\ \Omega\text{ cm}^2$ at 700°C . As compared to the fuel cell with uniform anode and electrolyte but different single phase cathode materials such as: $\text{BaCe}_{0.5}\text{Bi}_{0.5}\text{O}_{5+\delta}$ [15], $\text{SmBaCo}_2\text{O}_{5+\delta}$ [16] and $\text{GdBaCo}_2\text{O}_{5+\delta}$ [17], the interfacial resistance of the cell with PBCF cathode is lower at or below 700°C . So, it is concluded that the interfacial resistance of PBCF-BZCY is lower than other cathodes for identical anode-electrolyte interface resistances among the cells. The above results indicate that the layered PBCF may be more suitable for intermediate-temperature operation. It should be noted that Fig. 4 consists of two semicircles. The semicircle at high and intermediate frequencies decreases remarkably with increasing temperature. According to Adler et al. [18], impedance at high and intermediate frequencies is related to ion and electron transfer at the electrode, electrolyte, and collector/electrode interfaces, while the impedance at low frequencies is associated with non-charge transfer, such as surface exchange and gas-phase diffusion inside and outside the electrode layer. Therefore, reducing the temperature might lead to low ion transfer and cause the semicircle at high and intermediate frequencies to decrease remarkably.

Further, in Fig. 5 is shown the total cell resistance, the interfacial resistance and electrolyte resistance as determined from the impedance spectra. Both the electrolyte resistance and polarization resistances decreased with the increase of temperature and the interfacial resistances exceeded the resistances of the electrolyte

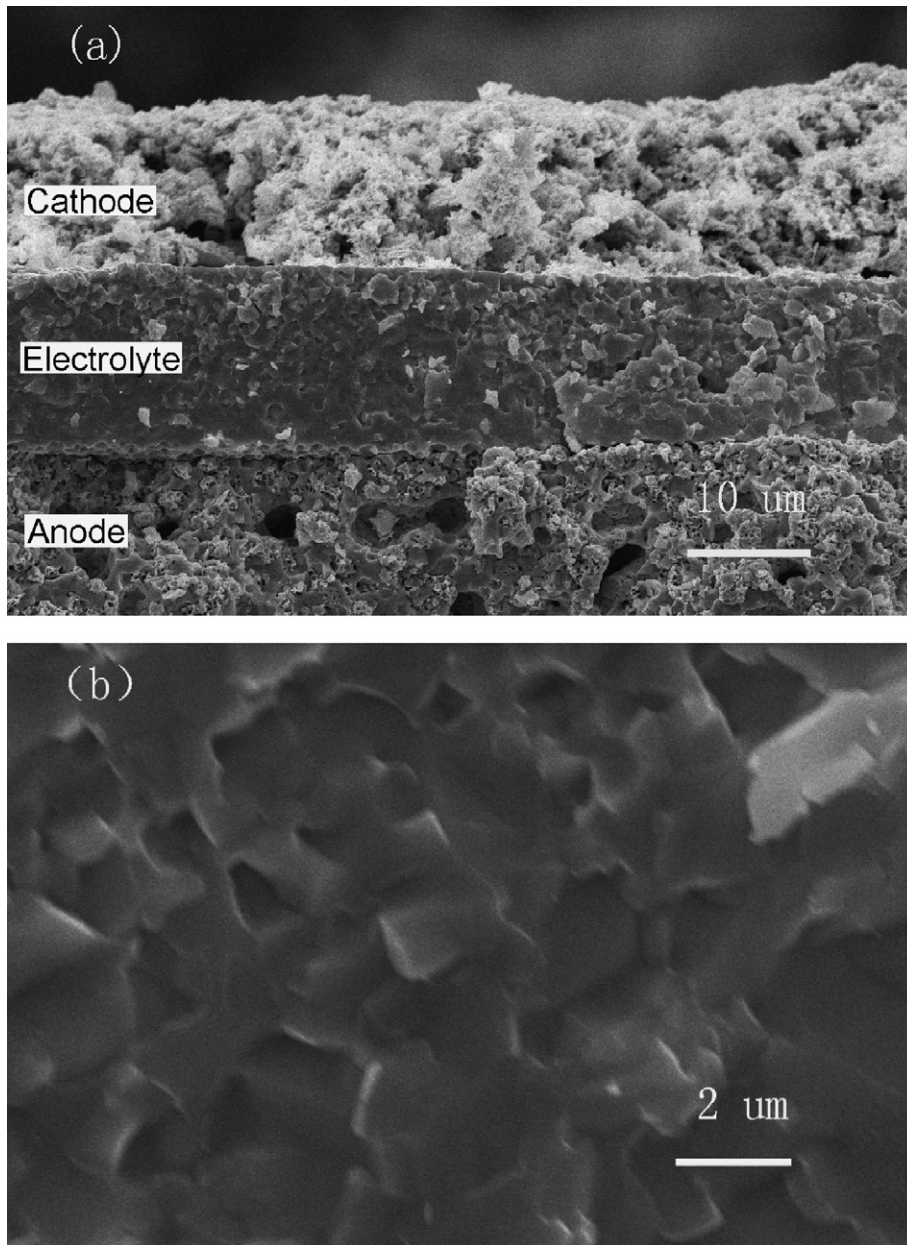


Fig. 2. Cross-section views of the cells without surface modification after fuel cell testing (a) single cell (b) electrolyte surface.

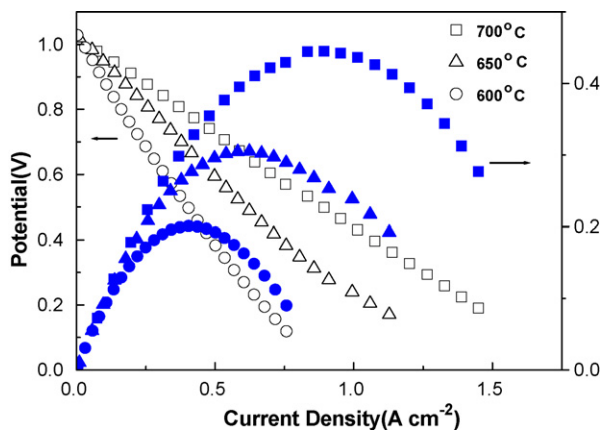


Fig. 3. Cell performance of a single cell (PBCF/BZCY/NiO-BZCY) under wet hydrogen atmosphere at 600–700 °C.

at temperature below 650 °C, suggesting that the cell performance is essentially determined by the interfacial resistances. So we can deduce that development of proper cathode materials is a grand challenge for developing the low-temperature proton-conductor SOFCs.

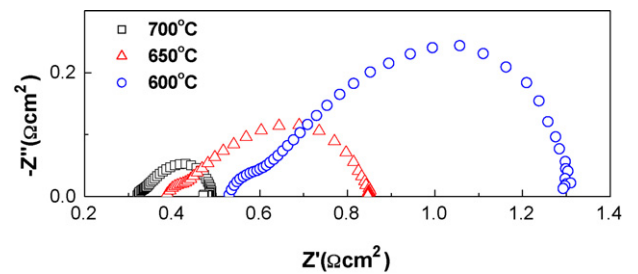


Fig. 4. Impedance spectra of the single cell measured under open-circuit condition.

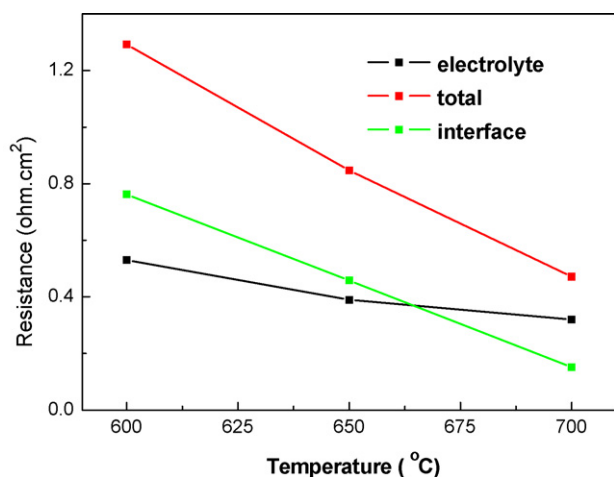


Fig. 5. The interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra of the tri-layer cell measured under open-circuit conditions at different temperatures.

4. Conclusions

A dense $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) electrolyte was fabricated on a porous anode by in situ drop-coating in order to develop a simple and cost-effective route to fabricate proton-conductor IT-SOFCs. In this study, a new single phase PBCF, instead of the traditional dual phase composite cathode materials, was prepared by auto ignition process. The maximum power density of the PBCF/BZCY/NiO-BZCY cell with about 15 μm thick electrolyte was 445 mW cm^{-2} at 700 °C.

A relatively low interfacial polarization resistance of 0.15 $\Omega \text{ cm}^2$ at 700 °C indicated that the PBCF is a promising cathode for proton-conductor IT-SOFCs.

Acknowledgments

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