Short communication

BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ electrolyte-based solid oxide fuel cells with cobalt-free PrBaFe$_2$O$_{5+\delta}$ layered perovskite cathode

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ABSTRACT

A new anode-supported SOFC material system Ni-BZCYYb|BZCYYb|PBFO is investigated, in which a cobalt-free layered perovskite oxide, PrBaFe$_2$O$_{5+\delta}$ (PBFO), is synthesized and employed as a novel cathode while the synthesized BZCYYb is used as an electrolyte. The cell is fabricated by a simple dry-pressing/co-sintering process. The cell is tested and characterized under intermediate temperature range from 600 to 700 °C with humified H$_2$ ($\sim$3% H$_2$O) as fuel, ambient air as oxidant. The results show that the open-circuit potential of 1.006 V and maximal power density of 452 mW cm^{-2} are achieved at 700 °C. The polarization resistance of the electrodes is 0.18 Ω cm^2 at 700 °C. Compared to BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$O$_{3-\delta}$, the conductivity of co-doped barium zirconate–cerate BZCYYb is significantly improved. The ohmic resistance of single cell is 0.37 Ω cm^2 at 700 °C. The results indicate that the developed Ni-BZCYYb|BZCYYb|PBFO cell is a promising functional material system for SOFCs.

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1. Introduction

Intermediate temperature solid oxide fuel cells (IT-SOFCs) could circumvent problems induced by high temperature conditions in yttria stabilized zirconia (YSZ) electrolyte-based SOFCs, such as long-term stability and durability of material systems [1]. However, lowering temperature will significantly increase the ohmic resistance of electrolyte due to poor oxygen-ion conductivity of YSZ.

Recently, proton conducting electrolytes have attracted much attention and show great advantages over oxide-ion conducting ones, such as low activation energy [2] and high energy efficiency [3]. The state-of-the-art proton conducting materials are barium-based perovskite-type oxides, e.g., BaCeO$_3$ and BaZrO$_3$. By suitable doping, these materials may obtain both adequate proton conductivity as well as sufficient chemical and thermal stability over a wide range of SOFC operating conditions, e.g., BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ (BZCYYb) [4]. Particularly compared to other conventional electrolyte materials, e.g., YSZ and GDC, BZCYYb may obtain high conductivity in lower temperature conditions.

In a typical proton conducting electrolyte-based SOFC, hydrogen molecules release electrons and are dissociated into protons at anode electrode. The protons then migrate to cathode side through proton conducting electrolyte. At cathode side, oxygen molecules are dissociated into oxygen-ions with a supply of exter-nal electrons; the combination of protons and ions forms into water molecules at cathode side. Essentially three charge species are involved in cathode electrode, i.e., protons, ions, and electrons. Consequently, the development of cathode materials is very critical for high performance proton conducting SOFCs. Furthermore, lowering operating temperature imposes additional challenges on cathode material selections [5]. Many cobalt-containing perovskite-type mixed ionic-electronic conductors (MIEC), such as La$_x$Sr$_{1-x}$Co$_y$Fe$_{1-y}$O$_{3-\delta}$ (LSCF) [6], Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (BSCF) [7] and Sm$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ (SSC) [8], have been extensively studied as cathode materials due to the fact that the cobalt is beneficial to the activation of oxygen reduction. These cobalt-based cathodes, however, often suffer from problems like poor chemical stability in CO$_2$, high thermal expansion coefficients (TECs), ease of evaporation, as well as high cost of cobalt element [9,10]. Obviously, it is significant to develop cobalt-free cathodes with sufficient catalytic activity at reduced temperatures for IT-SOFCs. Several cobalt-free oxides with simple perovskite structure, such as La$_x$Sr$_{1-x}$FeO$_{3-\delta}$ (LSF) [11] and Ba$_{0.5}$Sr$_{0.5}$Zn$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (BSZF) [9], have been reported as IT-SOFC cathodes.

Recently, layered perovskites have attracted much attention because their A-sites are ordered. 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 [12–15], and consequently improve cathode performance. In this paper, we present a novel proton conducting SOFC material system using BZCYYb as an electrolyte and cobalt-free layered perovskite PrBaFe$_2$O$_{5+\delta}$ (PBFO) as a cathode.

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2. Experimental

2.1. Sample preparation, cell fabrication, and X-ray diffraction measurement

The $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) powders were synthesized using modified Pechini method, where citrate and ethylenediamine tetraacetic acid (EDTA) were employed as parallel complexing agents. Y_2O_3 and Yb_2O_3 was first dissolved in nitric acid under heating; the calculated amount of $Ba(NO_3)_2 \cdot 9H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Zr(NO_3)_4 \cdot 4H_2O$ was dissolved in EDTA-NH_3 aqueous solution. After agitation for a certain time, a proper amount of citric acid was introduced, the molar ratio of EDTA:citric acid:total of metal cations was controlled around 1:1.5:1. After converted into viscous gel under heating and stirring conditions, the solution ignited to flame and resulted in ash. The resulting ash-like material was afterwards calcined at 1100 °C for 5 h in air to form a pure perovskite oxide, and the synthesized BZCYYb powders were then obtained.

The anode-supported BZCYYb bi-layer ($\Phi = 15$ mm) was prepared by a dry-pressing method. The mixture of NiO + BZCYYb + starch (60%:40%:20% in weight) was pre-pressed at 200 MPa and formed into an anode substrate. The anode functional layer (mixture of NiO and BZCYYb, NiO:BZCYYb = 60%:40% in weight) was then pressed onto the substrate. Then loose BZCYYb powder synthesized above was uniformly distributed onto the anode substrate, co-pressed at 250 MPa, and subsequently co-sintered at 1400 °C for 5 h to obtain bi-layer cell with dense BZCYYb membrane.

Layered $PrBaFe_2O_{5+\delta}$ (PBFO) powder was synthesized using Pechini process with Pr_6O_{11}, $Ba(NO_3)_2 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 5H_2O$ as precursors, followed by calcinations at 1000 °C for 5 h. Fine PBF powders were then mixed thoroughly with a Heraeus binder (V-006) to prepare the cathode slurry. The slurry was painted on BZCYYb electrolyte films using brush, which was then sintered at 950 °C for 3 h in air to form single cells of NiO-BZCYYb/BZCYYb/PBFO.

The phase identification of the prepared cathode and electrolyte powders were studied with the powder X-ray diffraction by Cu Kα radiation (D/MAX-3C).

2.2. Electrochemical characterization

Single cells were tested from 600 to 700 °C with humidified hydrogen (~3% H_2O) as fuel and the static air as oxidant. The flow rate of fuel was controlled at 30 ml min^{-1} using a precision flow meter (APEX). The voltage–current curves were recorded by DC load (BK-8500) at the scanning rate of 30 mV s^{-1}. The electrochemical impedance spectra (EIS) were obtained using a Solartron 1260 frequency response analyzer in combination with a Solartron 1287 potentiostat over the frequency range from 0.01 to 10^5 Hz under open-circuit conditions. A scanning electron microscope (SEM, FEI Quanta 200) was used to observe the microstructure of the post-test cells.

3. Results and discussion

As shown in Fig. 1(a), the as-prepared powder of PBFO exhibits a pure layered perovskite phase with orthorhombic lattice geometry of space group (*Pmmm*) [16]. The diffraction peaks are identical with $PrBaCo_2O_{5+\delta}$ reported in the literature by Kim et al. [13]. The replace of Fe at B site did not affect the formation of layered perovskite phase. Fig. 1(b) presents the diffraction patterns of BZCYYb calcined at 1100 °C for 5 h. It can be clearly seen that there are only peaks corresponding to cubic perovskite phase [10].
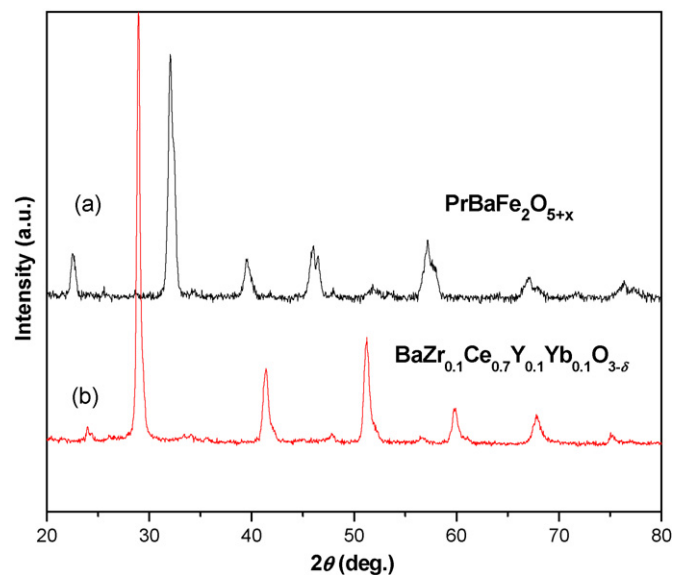

Fig. 1. XRD patterns for (a) the layered $PrBaFe_2O_{5+\delta}$ (PBFO) cathode powders and (b) BZCYYb electrolyte powders.

After electrochemical test, the microstructure of as-prepared tri-layer cell was examined using SEM. One can see from Fig. 2 that the BZCYYb electrolyte membrane is sufficiently dense, and there are no pores or cracks. The thickness of fabricated electrolyte is only about 15 μm, and that of PBFO cathode layer is about 20 μm. The cathode layer adheres to the electrolyte fairly well, which might be due to the replacement of cobalt element with Fe element. The reduction of cobalt element from high valence state to low valence state and the loss of lattice oxygen lead to the high TEC of cobalt-containing cathode material [17], as a result, the replacement of cobalt element with Fe element can potentially mitigate such a high thermal expansion. Furthermore, the microspores are distributed uniformly which is of great benefit to oxygen permeation and reduction at electrolyte–cathode interfaces.

The electrochemical performance of the as-prepared cell was experimentally obtained and shown in Fig. 3 under different oper-
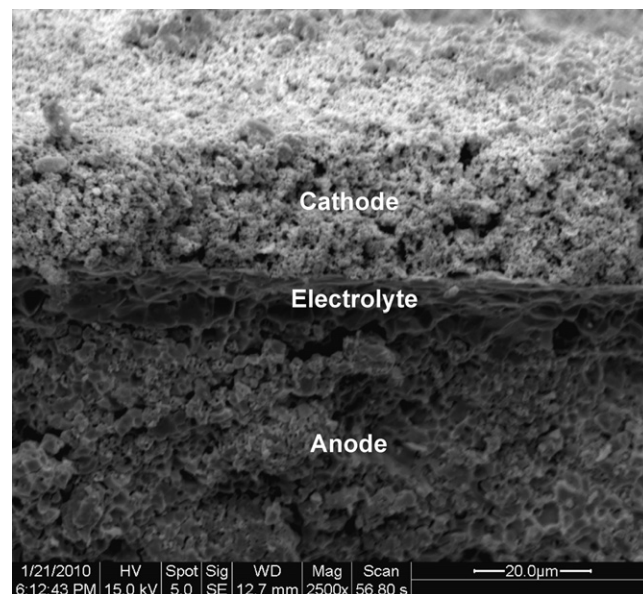

Fig. 2. SEM micrographs of cell after testing: the cross-section of tri-layer cell with a 15 μm-thick BZCYYb membrane.
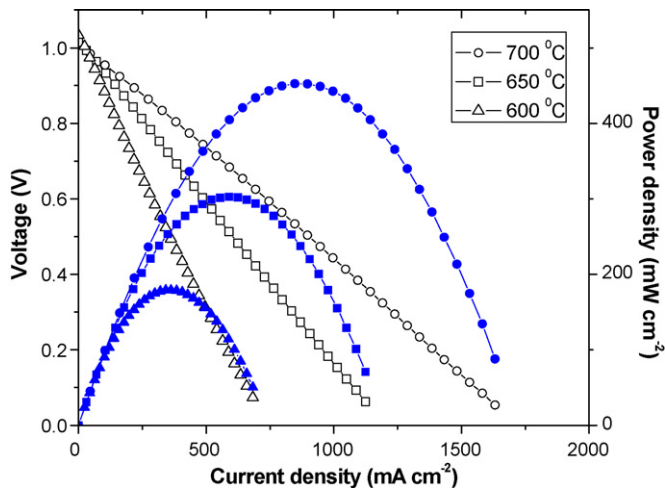
Fig. 3. Performance of the as-prepared cell with hydrogen at different temperatures.

ating temperatures, including *I–V* curve and *I–P* curve. In general, the open-circuit voltage (OCV) of the cell should be close to its theoretic value, and is slightly influenced by operating conditions. Since BZCYYb electrolyte is a mix conductor membrane, a slight electron cross-flow (current leakage) might exist through the membrane, consequently it leads to the fact that the practical OCV is lower than its theoretical value. The higher the current leakage exists, the lower the cell OCV will be. On the other hand, if the electrolyte membrane is not dense, fuel/gas cross-flow might take place, causing lower OCV value as well. One can see from Fig. 3 that peak power densities are 452, 302 and 179 mW cm^{-2} at 700, 650 and 600 °C, respectively; whereas the high open-circuit voltages (OCV) of 1.006 V at 700 °C, 1.015 V at 650 °C, 1.034 V at 600 °C indicate that the electrolyte membrane is sufficiently dense, and the current leakage is negligible. The output power is comparably higher than the reported values of ∼186 mW cm^{-2} for Ni-BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.1}$O$_{3-\delta}$ (BZCY7)/BZCY7/GdBaCo$_2$O$_{5+\delta}$ anode-supported single cell [18] and ∼70 mW cm^{-2} for Ni-BZCY7/BZCY7/SmBaCo$_2$O$_{5+\delta}$ single cell [19].

The polarization processes of Ni-BZCYYb|BZCYYb|PBFO cell is examined using electrochemical impedance spectra (EIS). The impedance spectra of the as-prepared cells are obtained under open-circuit conditions at different temperatures, and are shown in Fig. 4(a). The total cell resistance (R_t), ohmic resistance (R_o), as well as polarization resistance (R_p) are then determined from the impedance spectra in Fig. 4(a), the results are shown in Fig. 4(b). In these spectra, the intercept with the real axis at low frequency represents R_t and the value of the intercept at high frequency is R_o, while the difference of these two values corresponds to R_p. As one can see that increase operating temperature may lead to significant reduction of polarization resistance R_p, typically from 0.86 Ω cm^2 at 600 °C to 0.18 Ω cm^2 at 700 °C, respectively. It is worth noting that the R_p values of single cell with PBFO as cathode are well comparable to those of similar proton conducting cells with cobalt-containing cathodes, such as GdBaCo$_2$O$_{5+\delta}$ [18] (0.16 Ω cm^2 at 700 °C), PrBaCo$_2$O$_{5+\delta}$ [20] (0.15 Ω cm^2 at 700 °C).

As shown in Fig. 4(b), the cell resistance contributed from electrode polarization resistance R_p is larger than that from ohmic resistance (R_o) when the cell is operated at the temperatures below 640 °C. At 600 °C, the polarization resistance is 0.86 Ω cm^2 whereas the ohmic resistance is only 0.58 Ω cm^2. The ratio of R_p to R_t decreases with increasing temperatures, from 57% at 600 °C to 32% at 700 °C, respectively. By co-doping barium zirconate–cerate with Y and Yb, the conductivity of electrolyte was significantly improved. The ohmic resistance of Ni-BZCYYb|BZCYYb|PBFO cell is 0.37 Ω cm^2 at 700 °C as shown in Fig. 4(b), while the BZCYYb electrolyte thick-
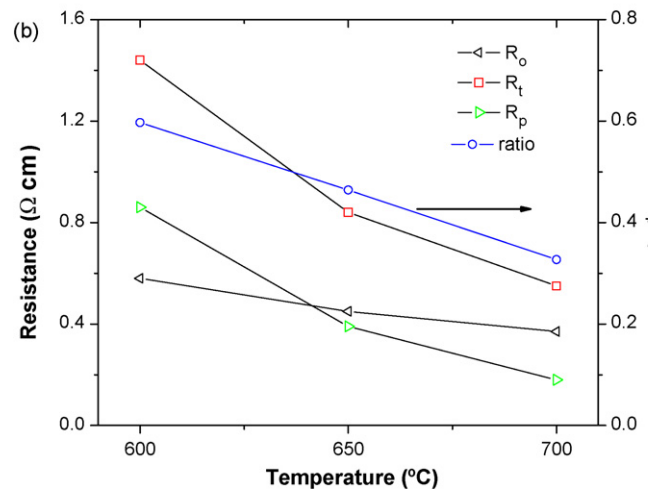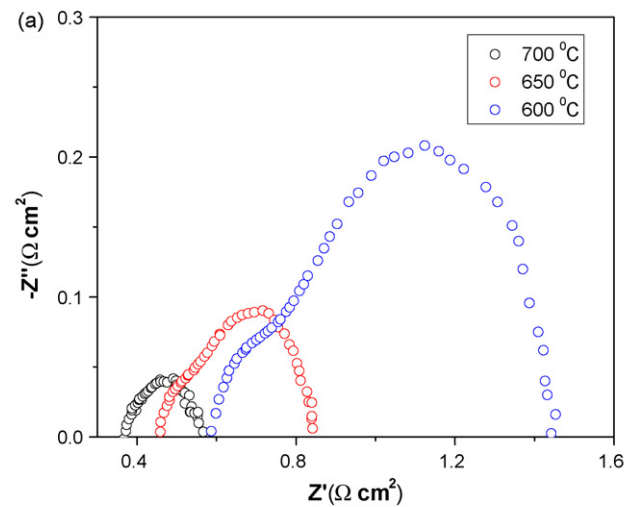

Fig. 4. (a) Impedance spectra and (b) the electrode polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra of the as-prepared cell measured under open-circuit conditions at different temperatures. R_p/R_t is also shown in (b).

ness is about 15 μm as shown in Fig. 2, much lower than that of BZCY7 electrolyte (0.7 Ω cm^2 with thickness 10 μm) [18].

4. Conclusions

A new anode-supported SOFC material system Ni-BZCYYb|BZCYYb|PBFO was investigated, in which a cobalt-free layered perovskite oxide, PrBaFe$_2$O$_{5+\delta}$ (PBFO), was synthesized and employed as a novel cathode while the synthesized BZCYYb was used as an electrolyte. The cell was fabricated by a simple dry-pressing/co-sintering process. The performance of the lab-scale tri-layer cell Ni-BZCYYb|BZCYYb|PBFO was tested and characterized under intermediate temperature range from 600 to 700 °C with humified H$_2$ (∼3% H$_2$O) as fuel, ambient air as oxidant. The results show that the open-circuit potential of 1.006 V and maximal power density of 452 mW cm^{-2} were achieved at 700 °C. The polarization resistance of the electrodes is 0.18 Ω cm^2 at 700 °C. By co-doping barium zirconate–cerate with Y and Yb, the conductivity of electrolyte was significantly improved. The ohmic resistance of the single cell is 0.37 Ω cm^2 at 700 °C. With increasing temperatures, the total cell resistance decreases, among which electrolyte resistance becomes increasingly dominant over polarization resistance.

Acknowledgments

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