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Stable $BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ electrolyte-based proton-conducting solid oxide fuel cells with layered $SmBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ cathode

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ABSTRACT

A stable, easily sintered perovskite oxide $BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (BCZYZ) as electrolyte for proton-conducting solid oxide fuel cells with layered $SmBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ (SBSC) cathode is investigated. Thin proton-conducting BCZYZ electrolyte is prepared over porous anode substrate composed of NiO-BCZYZ by the one-step dry-pressing/co-firing method. A laboratory-sized tri-layer cell of NiO-BCZYZ/BCZYZ (∼17 μm)/SBSC is operated from 550 to 700 °C with humidified hydrogen (∼3% H_2O) as fuel and the static air as oxidant. The BCZYZ perovskite electrolyte synthesized by a modified Pechini process is completely dense after sintered at 1250 °C for 5 h, lower than that without Znic dopant about 150 °C. An open-circuit potential of 1.007 V, a maximum power density of 0.306 W cm^{-2}, and a low polarization resistance of the electrodes of 0.11 Ω cm^2 are achieved at 700 °C.

1. Introduction

Solid oxide fuel cell (SOFC) is the most efficient device among the energy technology invented so far for the conversion of chemical fuels directly into electrical power [1,2]. Unfortunately, the expensive SOFC system limits the commercialization for the high operating temperature. In order to widen the materials chosen, decrease material degradation, prolong the lifetime and reduce the cost, the reduction of the working temperature of SOFCs becomes the urgent demand [3]. There is now considerable interest in proton-conducting oxide electrolytes for solid oxide fuel cells. The proton-conducting SOFCs exhibit more advantages than typical SOFCs based on oxygen-ion-conducting electrolyte (SOFC-O^{2-}), such as low activation energy [4] and high energy efficiency [5].

Many perovskite-type oxides show high proton conductivity in a reducing atmosphere. Among the perovskite oxides, doped-barium cerates exhibit mixed proton and oxide-ion-conductivity upon exposure to humid atmosphere [6]. And the proton conductivity can be significantly improved by doping various rare earth ions such as Sm, Y, Yb, Eu, Gd, etc. [7–10]. However, exposure to CO_2 and H_2O containing atmospheres, as would be present in a practical environment, will degrade the material as it reacts to form insulating barium carbonate ($BaCO_3$) and cerium oxide (CeO_2) [11–13]. Compared with doped cerates, doped zirconates possess better chemical stability but lower conductivity. The stability of doped-barium cerates is improved by the introduction of Zr at B site in order to achieve high proton conductivity, as well as sufficient chemical and thermal stability in a wide range of conditions referring to the fuel-cell operation. However, it is difficult to get the electrolyte with high density and high sintering temperatures are always needed. In order to improve sinterability, Babilo and Haile [14] and Tao and Irvine [15] introduced Zn into Y and Zr doped $BaCeO_3$. The reports show the new, stable proton-conducting electrolyte $BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (BCZYZ) by co-doping of Zr and Zn in the lattice could be sintered densely at lower temperatures and the chemical stability was also improved. In this work, 17 μm dense thin membrane BCZYZ electrolyte was fabricated on porous anode support by dry-pressing/co-firing process.

An issue of significant importance for the development of SOFCs is to select a proper cathode material. At present, a key obstacle to reduced-temperature operation of SOFCs is the relatively poor activity of traditional cathode materials for electrochemical reduction of oxygen in the lower temperature range. Many simple perovskite-type mixed ionic–electronic conductors such as doped $LaCoO_3$ [16], $BaCoO_3$ [17], $LaFeO_3$ [18] have been extensively studied as possible cathodes, however not much attention has been paid to the perovskite related structures such as the double or layered perovskites. Layered $SmBaCo_2O_{5+\delta}$ (SBCO) perovskite with an intermediate lanthanide-ion radius ($r_{Sm^{3+}} = 0.964$ Å) may provide a suitable tradeoff of material properties between the catalytic activity and the value of thermal expansion coefficient (TEC) [19]. Zhou et al. [20] and Lin et al. [21] have shown the potential of layered SBCO for cathode application and evaluated the performance of this material working as a cathode in SOFCs. Recently, Irvine

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and co-workers [22] reported a novel layered $SmBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ (SBSC) perovskite, which shows advanced electrochemical properties in doped ceria electrolyte settings, and could be potentially employed as cathode material for SOFC applications. In this work, the layered SBSC synthesized by Pechini method was employed as a new cathode for SOFCs based on a stable, easily sintered BCZYZ electrolyte.

2. Experimental

The $BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (BCZYZ) powders were synthesized by the modified Pechini method with citrate and ethylenediamine tetraacetic acid (EDTA) as parallel complexing agents [23]. Y_2O_3 and ZnO were dissolved in nitric acid first, and calculated amounts of $Ba(NO_3)_2{\cdot}9H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, $Zr(NO_3)_4{\cdot}4H_2O$, were dissolved in EDTA–NH_3 aqueous solution under heating and stirring. The solution was heated to a viscous gel and ignited to flame, resulting in the ash. The resulting ash-like material was afterwards calcined in air at 1100 °C for 5 h. The anode-supported BCZYZ bi-layer was prepared by a dry-pressing method. NiO, BCZYZ and starch mixture (60%:40%:20% in weight) was pre-pressed at 250 MPa as an anode substrate. Then the loose BCZYZ powders synthesized above were uniformly distributed onto the anode substrate, co-pressed at 250 MPa and sintered subsequently at 1250 °C for 5 h to densitify the BCZYZ membrane.

Layered SBSC powder was synthesized using Pechini process with $Sm(NO_3)_3{\cdot}6H_2O$ (99.9%), $Ba(NO_3)_2{\cdot}9H_2O$ (99.9%), $Sr(NO_3)_2$ (99.9%) and $Co(NO_3)_2{\cdot}6H_2O$ (99.9%) as precursors, followed by calcination at 1000 °C for 10 h. The SBSC powders were mixed thoroughly with a 10 wt% ethylcellulose–terpineol binder to prepare the cathode slurry, which was then painted on BCZYZ electrolyte films, and sintered at 1000 °C for 3 h in air to form single cells of NiO-BCZYZ/BCZYZ/SBSC.

The phase identification of the sintered anode–electrolyte bi-layer and prepared cathode powders was carried out with the powder X-ray diffraction by Cu Kα radiation (DX-2000). After being sealed, the single cells were tested in an electrical furnace with humidified hydrogen (~3% H_2O) as a fuel and the static air as oxidant. The cell voltages and output currents of the cells were measured with a digital multimeter (GDM-8145). AC impedance spectroscopy (CHI604b, Shanghai Chenhua) was performed on the cell under open-circuit conditions from 550 to 700 °C. The frequency range was 0.01–10^5 Hz with the signal amplitude of 10 mV. The morphology of the single cell after the electrochemical tests was characterized by a scanning electron microscope (SEM, KYKY-EM3200).

3. Results and discussion

As shown in Fig. 1(a), the as-prepared powder of layered SBSC exhibits a layered perovskite phase structure without any peaks attributable to impurities [12]. Fig. 1 also presents the XRD spectra of anode/electrolyte bi-layer sintered at 1250 °C for 5 h. In Fig. 1(b), the diffraction peaks were identical with those of the barium cerate standard (JCPDS Card No. 82-2425), which were also identical with those of the BCZYZ in literatures [15]. Fig. 1(c) presents the XRD spectra of anode/electrolyte bi-layer sintered at 1250 °C for 5 h. It could be clearly seen that there were only peaks corresponding to NiO and BCZYZ in the anode substrate, which indicated that there were no observable chemical reactions between NiO and BCZYZ in the anodes prepared by dry-pressing/co-sintering.

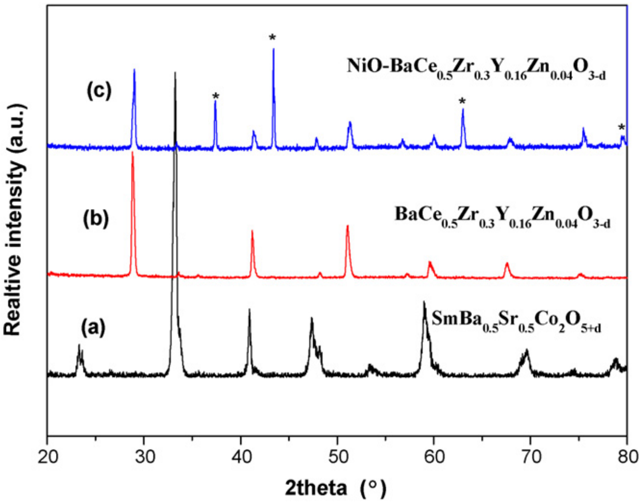

Fig. 1. XRD patterns for (a) the layered $SmBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ (SBSC) perovskite powders, the bi-layer of (b) NiO-BCZYZ anode substrate and (c) BCZYZ membrane. *: NiO.

Fig. 2(a) is the SEM image of surface morphology of BCZYZ electrolyte on the porous anode support after testing. It can be seen that the BCZYZ membrane is completely dense after sintering at 1250 °C. There is no pores and cracks on the surface. The result indicates that it is an effective way to lower sintering temperature greatly by doping Znic as sintering aid. From the cross-section view of tri-layer cell of Ni-BCZYZ/BCZYZ/SBSC (Fig. 2b), it is found that the BCZYZ membrane is only about 17 μm in thickness, and adheres very well to the anode layer and the cathode. No eliminations and cracks were found at the interface of electrode and electrolyte.

The electrochemical performance of the as-prepared cell is experimentally obtained and shown in Fig. 3 under different operating temperature conditions, including *I*–*V* and *I*–*P* curves. The high open-circuit voltages (COVE) of 1.007 V at 700 °C, 1.015 V at 650 °C, 1.021 V at 600 °C, 1.03 V at 550 °C indicate that the electrolyte membrane is sufficiently dense and current leakage is negligible. It is worth pointing out that *I*–*V* curves are almost linear implying that electrode polarization loss is negligible. Since the

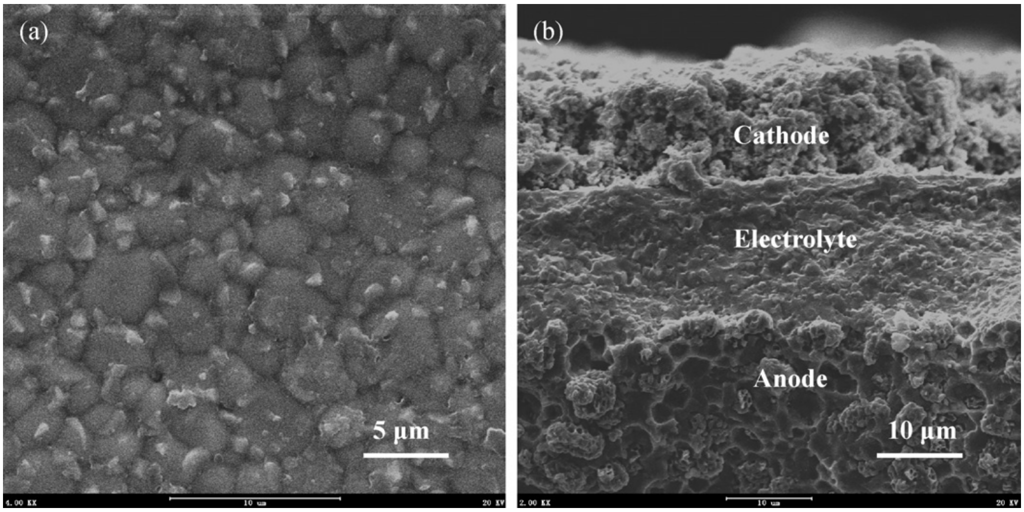

Fig. 2. SEM micrographs of cell after testing: (a) the surface of electrolyte and (b) the cross-section of cell with a 17 μm-thick BCZYZ membrane.

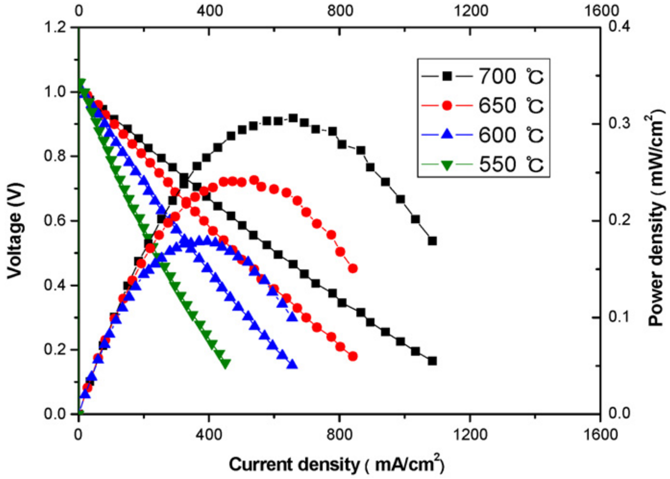

Fig. 3. Performance of the as-prepared cell with humidified hydrogen measured at 550, 600, 650 and 700 °C.

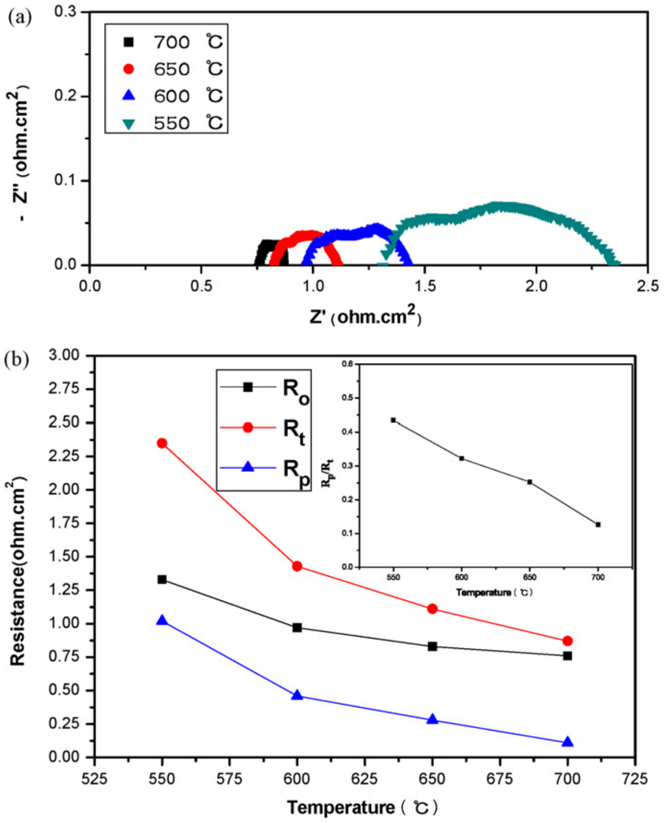

Fig. 4. (a) Impedance spectra and (b) the interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra of the as-prepared cell measured under open-circuit conditions at different temperatures. R_p/R_t is also shown in (b).

conductivity of both anode and cathode materials is higher than that of electrolyte in the as-prepared cell, it can be deduced that the voltage drop of the cell is mainly attributed to the loss across the BCZYZ electrolyte. The maximal power densities were 0.306, 0.242, 0.178 and 0.121 W cm^{-2} at 700, 650, 600 and 550 °C, respectively.

Fig. 4(a) shows the impedance spectra under open-circuit conditions with layered SBSC perovskite working as a cathode in proton-conducting fuel cells. The total cell resistance (R_t), ohmic resistance (R_o), as well as interfacial polarization resistance (R_p) are then determined from the impedance spectra in Fig. 4(a), the results are shown in Fig. 4(b). As one can see, increase operating temperature resulted in a significant reduction of R_p, typically from 1.02 Ω cm^2 at 550 °C to 0.11 Ω cm^2 at 700 °C, respectively. The low polarization resistances indicate that the SBSC cathode is a good candidate for operation at or below 700 °C. Furthermore, the cell performance is influenced by the interfacial polarization resistances, especially at temperatures below 550 °C, where the cell performance is essentially determined by the interfacial polarization resistances. At 550 °C, the polarization resistance of the electrodes is 1.02 Ω cm^2 whereas the resistance of the electrolyte is 1.32 Ω cm^2. The ratio of R_p to R_t increases with the decrease of the operating temperature, from 12.6% at 700 °C to 43.4% at 550 °C, respectively. These analyses indicate that the cell performance is further limited by interfacial polarization resistance with the temperature decrease. It is worthwhile to reduce cathode–electrolyte interfacial resistance for developing proton-conducting solid oxide fuel cells in future studies.

4. Conclusions

A stable, easily sintered BCZYZ electrolyte was fabricated on porous anode support by a simple dry-pressing/co-firing process at 1250 °C, and the thickness of BCZYZ electrolyte was about 17 μm. With layered SBSC perovskite as cathode, a tri-layer single cell of NiO-BCZYZ/BCZYZ/SBSC was assembled and tested from 550 to 700 °C fed with humidified H_2 (∼3% H_2O). The open-circuit voltages and maximum power densities of the cell were 1.007, 1.015, 1.021, 1.03 V and 0.306, 0.242, 0.178, 0.121 W cm^{-2} at 700, 650, 600 and 550 °C, respectively. The polarization resistance of the electrodes was as low as 0.11 Ω cm^2 at 700 °C. The results indicate that the SBSC perovskite cathode is a good candidate for operation at or below 700 °C, and that BCZYZ proton-conducting electrolyte with SBSC cathode is a novel material system for SOFCs.

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