



Short communication

A cobalt-free $\text{SrFe}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ cathode material for proton-conducting solid oxide fuel cells with stable $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ electrolyte

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ABSTRACT

A cobalt-free cubic perovskite oxide $\text{SrFe}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ (SFSb) is investigated as a novel cathode for proton-conducting solid oxide fuel cells (H-SOFCs). XRD results show that SFSb cathode is chemically compatible with the electrolyte $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) for temperatures up to 1000 °C. Thin proton-conducting BZCYYb electrolyte and $\text{NiO-BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (NiO-BZCYYb) anode functional layer are prepared over porous anode substrates composed of NiO-BZCYYb by a one-step dry-pressing/co-firing process. Laboratory-sized quad-layer cells of NiO-BZCYYb/NiO-BZCYYb/BZCYYb/SFSb are operated from 550 to 700 °C with humidified hydrogen (~3% H_2O) as fuel and the static air as oxidant. An open-circuit potential of 0.996 V, maximum power density of 428 mW cm^{-2} , and a low electrode polarization resistance of 0.154 Ωcm^2 are achieved at 700 °C. The experimental results indicate that the cobalt-free SFSb is a promising candidate for cathode material for H-SOFCs.

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1. Introduction

Currently, proton-conducting solid oxide fuel cells (H-SOFC), of which the water is formed at the cathode, have attracted tremendous attention because of some advantages over those cells with oxygen-ion conducting solid oxide fuel cells (O-SOFC) such as simpler fuel-recycling instruments [1,2] and a lower active energy of proton transport which ensures that the H-SOFCs operate at an intermediate-to-low-temperature range of 400–650 °C. In order to develop new electrolyte for insufficient conductivity at such low operating temperatures, several proton-conducting oxides were found to have attractive ionic conductivity at reduced temperature [1,3,5]. At temperatures below 750 °C, $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) showed the highest ionic conductivity, at 500 °C, for example, the ionic conductivity of BZCYYb was about $1.2 \times 10^{-2} \text{ S cm}^{-1}$, that of $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ was $9 \times 10^{-3} \text{ S cm}^{-1}$, and the ionic conductivity of GDC was $5 \times 10^{-3} \text{ S cm}^{-1}$. Besides, BZCYYb possesses rapid transport of both protons and oxide ion vacancies and resists deactivation by sulfur and coking for sulfur oxidation and hydrocarbon cracking and reforming [4].

Accordingly, the development of alternative cathode material for proton-conductor IT-SOFCs in order to reduce

cathode–electrolyte interface polarization remains a challenge. Efforts have been devoted to lowering the cathode polarization resistance for H-SOFCs by introducing novel cathode materials to meet the demand for commercialization [5–9]. Recently, Aguadero et al. [10] have reported that a tetragonal perovskite phase by doping the $\text{SrCoO}_{3-\delta}$ system with 10% of Sb was stabilized in the cobalt position obtaining good properties as a mixed conductor to be used as a cathode material in IT-SOFCs, which can be explained because the oxide with the cubic phase showed the highest electronic and oxygen ionic conductivity among the various phase structures of $\text{SrCoO}_{3-\delta}$ with a maximum reported total electrical conductivity of $\sim 160 \text{ S cm}^{-1}$ at $\sim 950 \text{ °C}$ [11]. However, to our knowledge, cobalt-based cathodes often encountered some problems like high thermal expansion coefficient and poor stability [12,13]. Therefore, it is desirable to develop the cobalt-free cathodes with good electrocatalytic activity for proton-conductor IT-SOFCs. To the best of our knowledge, the performance of a novel cobalt-free $\text{SrFe}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ (SFSb) as potential cathode has not been reported to date. In this work, the ceramic material of $\text{SrFe}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ (SFSb) synthesized by auto-ignition process was examined as a new cobalt-free cathode for a protonic SOFC with a BZCYYb electrolyte.

2. Experimental

The $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) powders were synthesized by an EDTA–citrate complexation process as described previously [14], where citrate and ethylenediamine tetraacetic

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acid (EDTA) were employed as parallel complexing agents. $\text{Ba}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Y_2O_3 , and Yb_2O_3 were dissolved at the stoichiometric ratio in distilled water to form an aqueous solution, and then 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 was ignited to flame and form the primary powders. The as-synthesized powders were subsequently calcined at 1000°C for 3 h to form a pure perovskite oxide, and the synthesized BZCYb powders were then obtained. The $\text{SrFe}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ powders were also synthesized by auto-ignition process with the raw materials Sb_2O_3 , $\text{Sr}(\text{NO}_3)_2$, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at a proper molar ratio and then calcined at 950°C for 3 h.

The anode-supported BZCYb bi-layer (φ 15 mm) was prepared by a dry-pressing method. The mixture of NiO + BZCYb + 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 BZCYb, NiO:BZCYb = 60%:40% in weight) was then pressed onto the substrate. Finally loose BZCYb 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 dense BZCYb membrane. Fine SFSb powders were mixed thoroughly with a 6 wt% ethylcellulose-terpineol binder to prepare the cathode slurry, which was then painted on BZCYb electrolyte films, and sintered at 950°C for 3 h in air to form a quad-layer cell of NiO-BZCY/NiO-BZCYb/BZCYb/SFSb.

The phase identification of the sintered anode-electrolyte bi-layer and prepared cathode powders and the phase reaction between electrode and electrolyte were studied with the powder X-ray diffraction by Cu-K α radiation (D/Max-gA, Japan), of which the detection limit is under 5%. Single cells were tested from 550 to 700°C in a home-developed-cell-testing system with humidified hydrogen ($\sim 3\%$ H_2O) as fuel and the static air as oxidant, respectively. The flow rate of fuel gas was about 40 ml min^{-1} . 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 550 to 700°C . A scanning electron microscope (SEM, JEOL JSM-6400) was used to observe the microstructure of the cells after testing.

3. Results and discussion

As shown in Fig. 1 (spectrum a), the XRD pattern of SFSb powders sintered at 950°C for 3 h in air. It can be seen that the crystallization SFSb oxide is a cubic perovskite structure without any peaks attributable to impurities. The partial substitution of Sb at B site did not affect the formation of cubic perovskite phase. Fig. 1 also presents the XRD spectra of anode/electrolyte bi-layer sintered at 1350°C for 5 h. It can be clearly seen that there are only peaks corresponding to $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYb) in electrolyte membrane (Fig. 1 (spectrum c)) and to NiO and BZCYb in anode substrate (Fig. 1 (spectrum b)). There is no evidence pointing to the formation of other substance.

To assess the phase reaction between electrode and electrolyte is undesirable for the long-term stability of H-SOFCs (Fig. 2). The chemical compatibility of SFSb cathode with BZCYb electrolyte was investigated by mixing thoroughly SFSb with BZCYb in a 1:1 weight ratio, and then sintered at 1000°C for 10 h as well as SFSb cathode with SDC electrolyte. There are no new peaks identifiable or shift of XRD peaks in the patterns indicating that there is no significant reaction between SFSb and electrolytes. These results reveal that SFSb has a good chemical compatibility with BZCYb and SDC electrolytes. It is well indicated that addition of a sufficient

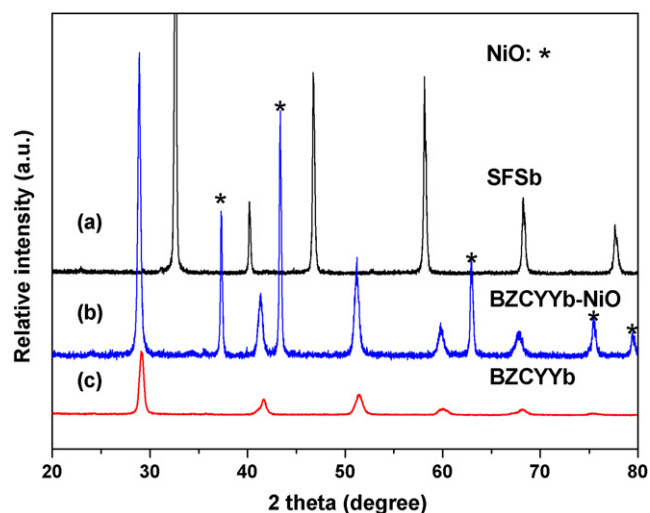


Fig. 1. XRD diffraction patterns of (a) $\text{SrFe}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ (SFSb), (b) $\text{NiO}-\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (NiO-BZCYb) anode substrate (*NiO), and (c) $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYb) membrane.

amount of electrolyte to the SFSb cathode to form the composite cathode, results in a significant improvement in the matching between the electrolyte and the cathode and the higher performance output [15–17].

Fig. 3 shows the SEM micrograph of the cross-sectional views of BZCYb electrolyte and the as-prepared quad-layer cells with SFSb cathode on the porous anode support. It can be seen that the BZCYb membrane is completely dense and the grains are quite uniform without obvious pores and cracks in Fig. 3a. From Fig. 3b, it can be observed that the adhesion of the SFSb cathode to the BZCYb electrolyte seems to be excellent. The results demonstrate that a dense and crack-free BZCYb electrolyte membrane can be successfully fabricated with a heat treatment at a quite low temperature (1350°C) on porous anode support. Therefore, the cathode performance would be further enhanced through optimizing the SFSb cathode microstructures.

To determine its performance in real fuel-cell conditions, the electrochemical performance of the as-prepared quad-layer $\text{NiO}-\text{BZCYb}/\text{NiO}-\text{BZCYb}/\text{BZCYb}$ ($\sim 25\ \mu\text{m}$)/SFSb ($\sim 25\ \mu\text{m}$) cell using humidified hydrogen ($\sim 3\%$ H_2O) as the fuel and static ambient air as the oxidant is experimentally obtained under different operating temperatures, including $I-V$ curve and $I-P$ curve. It is

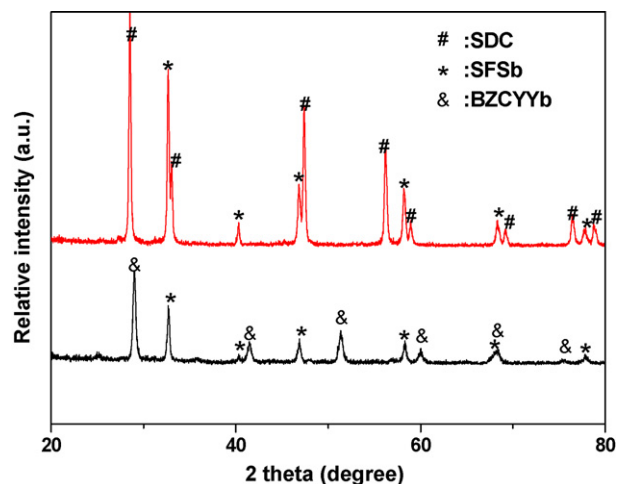


Fig. 2. The phase reaction between SFSb and BZCYb or SDC electrolytes sintered at 1000°C for 10 h, respectively.

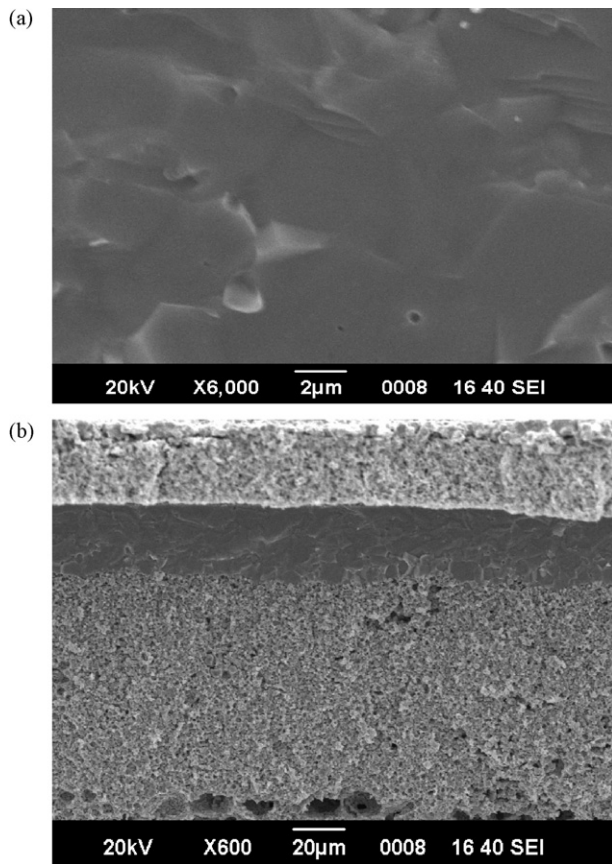


Fig. 3. SEM images of (a) the cross-section of BZCYYb electrolyte and (b) the cross-section views of the quad-layer NiO–BZCYYb/NiO–BZCYYb/BZCYYb/SFSb after testing.

well known that the open-circuit voltage (OCV) of the cell should be close to its theoretic value of 1.1 V, and is slightly influenced by operating conditions. However, BZCYYb electrolyte is a mix conductor membrane and if the electrolyte membrane is not dense, fuel/gas cross flow might take place, causing lower OCV value as well. As shown in Fig. 4, the maximum power densities of 428, 310, 200, and 94 mW cm⁻² with the OCV values of 0.996, 1.008, 1.021, and 1.048 V are obtained at 700, 650, 600, and 550 °C for the SFSb cathode, respectively. It is worth noting that the high open-circuit voltages indicate that the BZCYYb electrolyte membrane is sufficiently dense and a good cell performance can be obtained using the cobalt-free cathode with BZCYYb electrolyte.

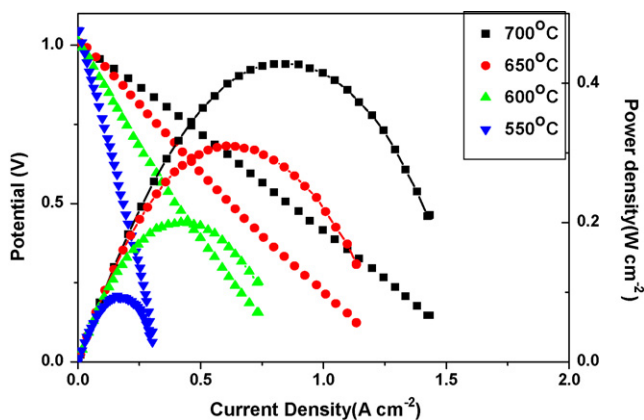


Fig. 4. Performance of the quad-layer cell NiO–BZCYYb/NiO–BZCYYb/BZCYYb/SFSb with hydrogen at different temperatures.

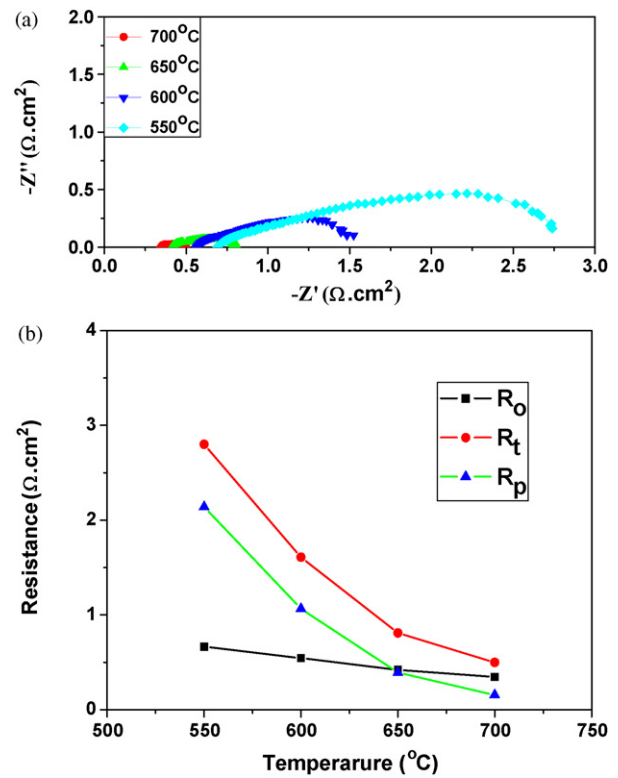


Fig. 5. Impedance spectra for (a) the quad-layer cell with SFSb cathode at various temperatures under OCV conditions. (b) The total cell resistances (R_t), interfacial polarization resistances (R_p), and electrolyte resistances (R_o) obtained from impedance spectra at different temperatures of the quad-layer cell with SFSb cathode.

In order to intensively evaluate the performance of cobalt-free SFSb working as cathodes for H-SOFC, resistances of the cells under open-circuit conditions surveyed by AC impedance spectroscopy are shown in Fig. 5. In these spectra, the intercepts with the real axis at low frequencies represent the total resistance of the cell and the value of the intercept at high frequency is the electrolyte resistance, while the difference of the two values corresponds to the sum of the resistance of the two interfaces: the cathode–electrolyte interface and the anode–electrolyte interface [18]. The total cell resistance (R_t), ohmic resistance (R_o), as well as interfacial polarization resistance (R_p) are then obtained from the impedance spectra in Fig. 5a, the results are shown in Fig. 5b. As expected, the increase of the measurement temperature resulted in significant reduction of interfacial polarization resistance R_p , typically from 2.14 Ω cm² at 550 °C to 0.154 Ω cm² at 700 °C, respectively. The low R_p values indicated that the cobalt-free SFSb cathode exhibited high electrochemical activity for operation at intermediate temperature range in practical fuel cell system. Moreover, the cell performance would be further enhanced through optimizing the SFSb cathode microstructures and using composite cathode with BZCYYb film as the electrolyte.

In Fig. 6 the fit obtained for impedance spectra of the quad-layer cell NiO–BZCYYb/NiO–BZCYYb/BZCYYb/SFSb at 600 °C under OCV conditions is shown. The equivalent circuit that best fits the data is shown as inset in this figure where R_1 , R_2 and R_3 are ohmic resistance, diffusion in the perovskite, and dissociative adsorption on the electrode surface, respectively [19]. The R_2 and R_3 have constant phase elements (CPE) in parallel to simulate the distribution of relaxation time in the real system. Both semicircles are overlapped, with difficulties the analysis of the results obtained for each process. As shown in Fig. 6, R_3 is much smaller than R_1 and R_2 , implying that dissociative adsorption on the electrode surface is

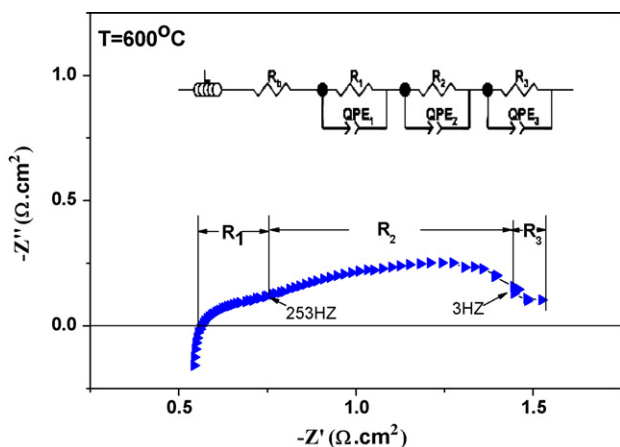


Fig. 6. Experimental and fit Nyquist plots for impedance spectra of the quad-layer cell NiO-BZCYyb/NiO-BZCYyb/BZCYyb/SFSb at 600 °C under OCV conditions. The equivalent circuits adopted for fitting the EIS data are inside the Nyquist plots.

relatively faster compared with ohmic resistance and diffusion in the perovskite at 600 °C.

4. Conclusions

In this work, a cobalt-free cubic perovskite oxide $\text{SrFe}_{0.9}\text{Sb}_{0.1}\text{O}_{3-\delta}$ (SFSb) was investigated as a novel cathode for proton-conducting solid oxide fuel cells (H-SOFCs). XRD results showed that SFSb cathode was chemically compatible with the electrolyte $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYyb) for temperatures up to 1000 °C. Thin proton-conducting BZCYyb electrolyte and $\text{NiO-BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (NiO-BZCYyb) anode functional layer were prepared over porous anode substrates composed of NiO-BZCYyb by a one-step dry-pressing/co-firing process. Laboratory-sized quad-layer cells of NiO-BZCYyb/NiO-BZCYyb/BZCYyb/SFSb were operated from 550 to 700 °C with humidified hydrogen ($\sim 3\% \text{H}_2\text{O}$) as fuel and the static air as oxidant. The maximum power densities of 428, 310, 200, and 94 mW cm^{-2} with the OCV values of 0.996, 1.008, 1.021, and 1.048 V were obtained at 700, 650, 600, and 550 °C for

the SFSb cathode, respectively. And a low polarization resistance of $0.154 \Omega \text{cm}^2$ was achieved at 700 °C. With temperature increases, the total cell resistance decreases, among which electrode resistance becomes increasingly dominant over polarization resistance. The experimental results indicate that the cobalt-free SFSb was a promising candidate for cathode material for H-SOFCs.

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