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Cobalt free $SrFe_{0.95}Nb_{0.05}O_{3-\delta}$ cathode material for proton-conducting solid oxide fuel cells with $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ electrolyte

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Abstract

A novel cobalt-free cubic perovskite $SrFe_{0.95}Nb_{0.05}O_{3-\delta}$ (SFNb) was synthesized and investigated as cathode for proton-conducting solid state fuel cell (H-SOFC) with $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) as the electrolyte. Anode supported NiO-BZCY/BZCY/SFNb cell was fabricated and the performance was investigated. A peak power density of 538 mW cm^{-2} and a low polarization resistance of 0.23 Ω cm^2 were obtained at 650°C with hydrogen as the fuel and air as the oxidant. No obvious cell degradation was observed during the 50 h test. All the results indicated that the cobalt-free SFNb oxide is a promising cathode material for H-SOFCs.

Key words: Proton-conducting solid oxide fuel cell, cobalt-free, cubic perovskite, cathode, ceramics.

1. Introduction

Proton-conducting solid oxide fuel cells (H-SOFC) have attracted much attention in recent years. Compared with oxygen-ion conducting solid oxide fuel cells, this type of fuel cell has several advantages, such as simpler fuel-recycling instruments[1], a lower active energy of proton transport[2] and a much lower working temperature range of 400–650°C[3, 4]. Among all the proton conductors, $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) exhibits both adequate proton conductivity and sufficient chemical stability over a wide range of temperature, and has been widely used as electrolyte of H-SOFC[4].

Accordingly, the development of proper cathode materials for H-SOFC in order to reduce interface polarization of cathode and BZCY electrolyte is of great importance. Many cobalt-containing perovskite oxides have been used as cathodes for H-SOFCs[5, 6]. However, those oxides often suffer from problems like high thermal expansion coefficients, high cost of cobalt and the poor stability under humid atmosphere. Therefore, it is desirable to develop the cobalt-free cathodes with good electrocatalytic activity for H-SOFCs. Strontium ferrite $SrFeO_{3-\delta}$ is a promising perovskite oxide with high mixed oxygen ionic and electronic conductivities, which may have potential application in H-SOFC. However, $SrFeO_{3-\delta}$ usually exhibits a transformation from a cubic structure into a brownmillerite structure of $SrFeO_{2.5}$ which is not favorable for application for low oxygen ion conduction[7]. In order to stabilize the cubic perovskite structure, many efforts have been made. It was reported that the cubic phase $SrFeO_{3-\delta}$ oxide could be stabilized by partial substitution of Fe-sites with other elements such as Mo, Ti or Nb[8-10]. Recently, the Nb-doped $SrFeO_{3-\delta}$ perovskites ($SrNb_xFe_{1-x}O_{3-\delta}$) have been reported as good oxygen-permeable membrane materials and excellent cathode materials for oxygen-ion conducting solid oxide fuel cells[10, 11]. However, details about the electrochemical properties of Nb-doped $SrFeO_{3-\delta}$ perovskite as an oxygen reduction electrocatalyst for H-SOFCs are still unclear. Herein, as a first study, we investigated the performance of $SrFe_{0.95}Nb_{0.05}O_{3-\delta}$ (SFNb) as a cobalt-free cathode for proton-conducting SOFC.

2. Experimental

2.1. Powder preparation

BZCY and NiO powders were prepared by a modified citrate combustion method[12]. The SFNb powder was prepared by a solid-state reaction. Appropriate amounts of $SrCO_3$, Fe_2O_3 and Nb_2O_5 were weighed and ball-milling with ethanol for 2 h in the high energy ball milling machine, then dried in the oven for 4h, after that the composite were calcined repeatedly at 1000 and 1200°C for 10 h with intermediate grindings, respectively.

2.2. Fabrication of the single cells

To make a single cell, a mixed powder composed of NiO+BZCY+corn starch (in a weight ratio of 60:40:20) were pressed at 200 MPa (15 mm in diameter and 0.5 mm thick) and then calcined at 800°C for 2 h to form an anode substrate. Then the electrolyte suspension containing 6% BZCY was subsequently coated on the porous anode surface by a spray-painting method. The electrolyte layer and the anode substrate were then co-sintered at 1450°C for 5 h. After that, the cathode slurry was sprayed onto the central surface of the electrolyte and fired at 1000°C for 2h in air to form a single cell. The effective cathode area of the cell was ~0.48 cm^2. The final sintered cell had a diameter of ∼1.2 cm and anode thickness of ∼400 μm.

2.3 Characterization and cell testing

Single cell was sealed onto glass tube with silver paste for cell performance evaluation. Ag paste and Ag wires were used for current collection in the cell. The phase composition of the sintered powders were analyzed by XRD (XRD, Rigaku Smartlab), and the microstructure of the single cell were observed by a scanning electron microscope (SEM, JEOL 6490). The performance of fuel cell was measured from 450 to 650°C by homemade testing system, with dry H_2 (100 $mLmin^{-1}$) as fuel and air as oxidant. The electrochemical impedance spectra were measured by a Solartron 1260A frequency response analyzer with a Solartron 1287 potentiostat under open-circuit from 0.1 Hz to 10^6 Hz with AC amplitude of 10mV.

3 Results and discussion

Figure 1a shows the refined diffraction patterns of the as-prepared SFNb powder. A well-formed perovskite structure in space group Pm-3m with unit cell data of a = 3.88 Å is observed. The low converged reliability factors (Rp = 4.25 %, Rwp = 5.49 %, $\chi 2$ = 1.50) indicate a good fitting between the experimental and calculated patterns. Compatibility of BZCY and SFNb has also been studied, and the XRD patterns of mixed powders after co-firing at 1100°C for 2 h are shown in Figure 1b. No other phase can be observed in the mixture, demonstrating that SFNb is suitable for cathode on BZCY electrolyte.

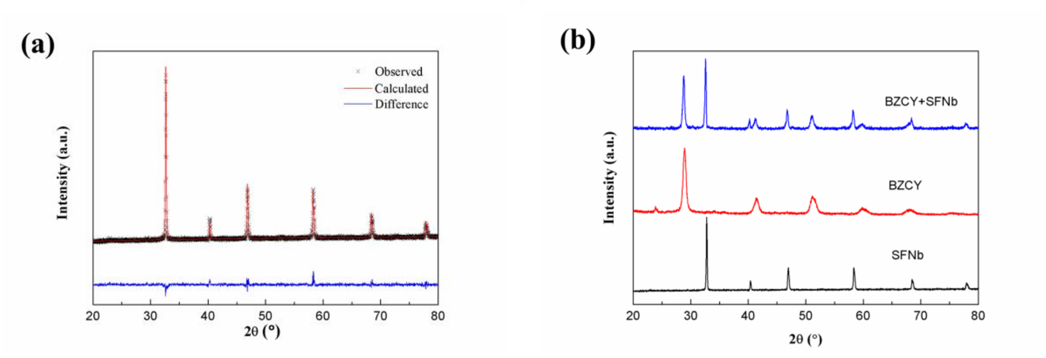

Fig.1. (a) refined diffraction patterns of SFNb. (b) XRD patterns of SFNb, BZCY, BZCY+SFNb oxides at room temperature.

In order to investigate the performance of the cell with SFNb as cathode, an anode supported fuel cell (NiO–BZCY/BZCY/SFNb) has been fabricated. Figure 2a shows the micrograph of the cross-sectional view of the cell after test. A dense electrolyte with thickness of ~20 μm is observed, indicating that spray-painting is an effective way to fabricate electrolyte. The thickness of the porous cathode is ~15 μm and no crack can be found at the interface between cathode and electrolyte (Figure 2b).

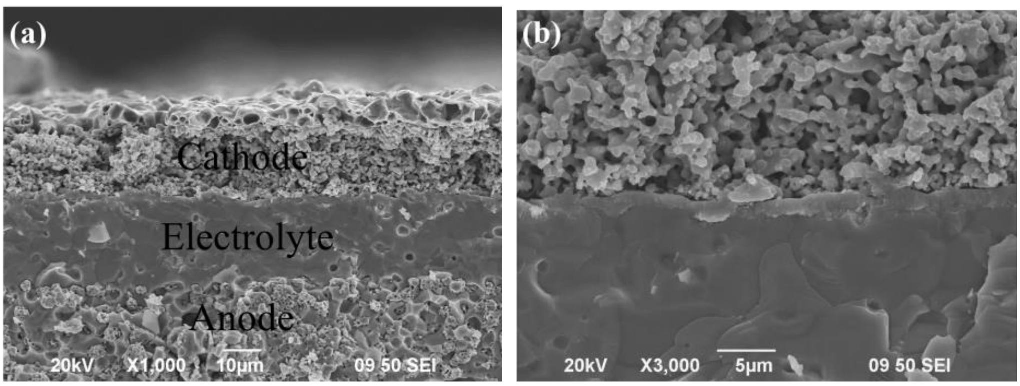

Fig.2. SEM images of (a) the cross-section view of the single cell, (b) close-up image of the interface of cathode and electrolyte after test.

Figure 3a shows the I-V and I-P curves of the anode-supported cell in the temperature range of 450–650°C. The open circuit voltages (OCVs) were observed to be from 1.07 V to 1.00 V, indicating a densified electrolyte, which is corresponding to the SEM images. Maximum power densities of 538, 428, 341,220 and 161 $mWcm^{-2}$ were obtained at 650, 600, 550,500 and 450°C respectively. The performances are better than the Sb doped $SrFeO_{3-\delta}$ oxide, which achieved the maximum power densities of 310 and 94 mWcm^{-2} at 650 and 550°C respectively [12]. The outputs obtained in the present work are also much higher than some other cobalt-free cathodes (such as $La_{0.6}Sr_{0.4}Fe_{1-x}Nb_xO_{3-\delta}$[13]and layered perovskite $GdBaFeNiO_{5+\delta}$[14]). The high performance may be related to the low polarization resistance as shown in Figure 3b. The total interfacial polarization resistance of the cell (the difference between the high and low frequency intercept) decreased with the increasing of temperature as expected. Polarization resistances were measured as 0.23, 0.35, 0.54, 1.13, 2.15 Ω cm^2 at 650, 600, 550, 500 and 450°C respectively which are lower than some other cobalt-free cathodes under similar conditions[14, 15]. The low polarization resistances indicate that SFNb is a promising cathode for intermediate temperature H-SOFC. Also the stability of the cell is evaluated under a constant current density of 140 mA cm^{-2} at 550°C for over 50 h, no obvious degradation was observed. This indicates that the cathode is steady under testing condition.

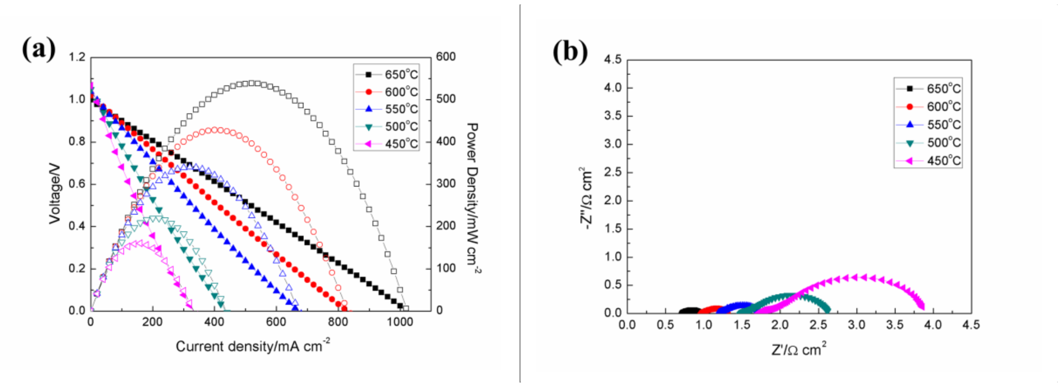

Fig.3. (a) I-V and I-P curves for single cell at different temperatures, (b) impedance spectra of the single cell under open circuit voltage conditions.

4 Conclusions

In this study, a cobalt-free cubic perovskite $SrFe_{0.95}Nb_{0.05}O_{3-\delta}$ (SFNb) was fabricated and applied as cathode in H-SOFC with BZCY as electrolyte. The anode-supported NiO-BZCY/BZCY/SFNb single cell exhibited excellent performance with hydrogen as the fuel and air as the oxidant. Peak power densities of 538, 428, 341, 220 and 161 mW cm^{-2} were obtained at 650, 600, 550, 500 and 450°C respectively. The durability test of the cell lasted over 50 h and the output kept stable. The results indicate that cobalt-free SFNb is an excellent candidate cathode for proton conducting SOFC at intermediate temperature.

Acknowledgements

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Figure captions:

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