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Letter

A cubic $BaCo_{0.8}Nb_{0.1}Fe_{0.1}O_{3-\delta}$ ceramic cathode for solid oxide fuel cell

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ABSTRACT

A novel ceramic solid oxide fuel cell cathode $BaCo_{0.8}Nb_{0.1}Fe_{0.1}O_{3-\delta}$ (BCNF) was synthesized by a solid-state reaction at 1000 °C for 10 h. XRD results demonstrate BCNF is in possession of excellent structure stability in cubic phase. Chemical stability test shows it is also adequately stable against $CO_2 + H_2O$ at intermediate temperature. The conductivity of BCNF reaches 10–17 S cm^{-1} in air from 700 to 900 °C. Besides, the electrode polarization is only 0.1 Ω cm^2 in air which is significantly lower that of $La_{0.5}Sr_{0.5}MnO_{3-\delta}$ cathode in the same symmetric cell based on $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ electrolyte at 700 °C. The corresponding fuel cell performance with BCNF cathode based on anode-supported $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ electrolyte with H_2 as fuel and air as oxidizer reaches 413 mW cm^{-2} at 700 °C.

1. Introduction

Solid oxide fuel cells (SOFCs) have been extensively studied as advanced power generation devices because of their high energy conversion efficiency, low environmental impact, and good fuel flexibility [1,2]. Among all the SOFC cathodes, some perovskite oxides based on cobalt, such as $BaCoO_3$, display the most excellent performance compared with manganese- and chromium-based cathodes at intermediate temperature because of the outstanding catalytic activity of cobalt to oxygen as well as desirable mixed conductivity of these cobalt-based ceramic oxides [3–5]. The A-site fully occupied by Ba^{2+} with large ionic size enables fast rate of surface oxide–oxide exchange reaction in cubic structure [6,7] which determines the total cathode performance. However, these $BaCoO_3$-based cathodes have been proved to be instable in structure as they change from cubic phase at high temperature to hexagonal structure at room temperature simultaneously accompanied by the change of oxygen vacancy from disordering to ordering, which greatly decreases the catalytic activity as well as ionic conductivity. In addition, these cathodes are instable in the presence of $CO_2 + H_2O$ at intermediate temperatures because unfavorable reactions take place to form carbonates and then lead to degradation in the cathode performance [8]. In the process of searching for stable cobalt-based cathodes, high-valance cations, such as Zr^{4+} [8], Sn^{4+} [6] and Ti^{4+} [6], have been proved to effective dopant ions in B-site to stabilize cobalt-based cathodes. The high-valance ions lead to high oxygen nonstoichiometry, $3-\delta$, which is closely related to the structure stability of pervoskite. Besides, these cations with high electro-negativity can stabilize the cubic pervoskite as well.

Thus, it is reasonable to assume that Nb^{5+} with the similar ionic size and high electro-negativity compared with Co^{3+} can be considered as a possible dopant to stabilize cobalt-based cathode. In this study, we partially substitute 10% Nb^{5+} together with 10% Fe^{3+} for Co^{3+} in B-site to modify the structure stability and chemical stability. The doping of Fe^{3+} is to make the thermal expansion compatible with current electrolytes. The phase stability, chemical stability and electrode polarization of $BaCo_{0.8}Fe_{0.1}Nb_{0.1}O_{3-\delta}$ (BCNF) were studied; and a single solid oxide fuel cell based on BCNF cathode was tested.

2. Experimental

$BaCo_{0.8}Nb_{0.1}Fe_{0.1}O_{3-\delta}$ (BCNF) was synthesized by solid-state reaction at 1000 °C [9]. In the process, $BaCO_3$, $CoCO_3$, Nb_2O_5 and Fe_2O_3 were ball-milled in ethanol, dried at 100 °C and then fired at 1000 °C for 10 h. XRD was performed to analyze the phase structure. In order to further check the phase stability at higher temperatures, BCNF powder was quenched to room temperature for immediate XRD test after heating in air at 1000 °C for 24 h. For the chemical stability study, BCNF powder was exposed and heated in mixed atmosphere ($3\%CO_2/3\%H_2O/94\%Ar$) at 700 °C for 5 and 10 h, respectively. XRD was performed to detect the phase changes. BCNF powder was pressed into disk followed by a heat treatment at 1150 °C for 5 h. Conductivity of $BaCo_{0.8}Nb_{0.1}Fe_{0.1}O_{3-\delta}$ was tested by four-terminal DC in air from 600 to 900 °C at an interval of 50 °C.

The electrode polarization in symmetric cell based on $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BCZY) was tested at 700 °C in air. BCZY powder was fabricated by a combustion method as described in our previous work [10] and then pressed into disk in thickness of 2 mm followed by heat treatment at 1400 °C for 5 h. Cathode slurry consisting of 65% BCNF and 35% BCZY in weight ratio was applied onto both sides of BCZY disk and subsequently fired at 1100 °C for 3 h to assemble a symmetric cell. Silver paste was printed onto both cathode surfaces and fired at 550 °C for 30 min to form current collectors. The interfacial polarization was recorded with

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AC impedance (CHI604C, Chenhua, Shanghai) at 700 °C. For comparison, another symmetric cell with $La_{0.5}Sr_{0.5}MnO_{3-\delta}$ cathode was also made and tested under the same conditions. After that, a half cell with BCZY electrolyte membrane supported by NiO + BCZY anode substrate was fabricated by a spray coating method as described elsewhere [10]. With BCNF cathode, single cell was assembled with and without Ag current collectors and tested with humidified hydrogen (3% H_2O) as fuel at 700 °C.

3. Results and discussions

It is deemed that the cubic phase of cobalt-based cathodes is instable because of the phase change from cubic phase at higher temperature to hexagonal structure at room temperature simultaneously accompanied by the change of oxygen vacancy from disordering to ordering to decrease cathode performance [6,7]. Here we try to dope 10% Nb^{5+} into B-site to stabilize the cubic phase. As shown in Fig. 1(a), BCNF prepared with solid-state reaction at 1000 °C is in a single cubic phase. The space group is $Pm\bar{3}m$ and the cell parameter is 4.088 Å with the corresponding cell volume 68.318 Å^3. In order to check the phase stability at higher temperature, some BCNF powders were quenched at 1000 °C after heated at this temperature for 24 h. As shown in Fig. 1(b), BCNF still keeps its original structure and displays no changes in cell parameter. Thus, the donor substitution of 10% Nb^{5+} for Co in B-site demonstrates excellent stabilization effect for cubic pervoskite structure, which may be due to the high-valance Ta^{5+} increases the oxygen nonstoichiometry, $3-\delta$, to stabilize the cubic phase. As presented in introduction part, cobalt-based cathodes are also instable in the presence of $CO_2 + H_2O$ where unfavorable reactions take place and lead to a degradation in the fuel cell performance [8]. For the chemical stability test, BCNF powder was heat-treated at 700 °C with $3\%CO_2/3\%H_2O/94\%Ar$ flowing for 5 and 10 h, respectively. As shown in Fig. 1(c), no phase change was observed for BCNF after corrosion for 5 h. Partial Nb^{5+} substitution for Co^{3+} decreases the sensitivity to $CO_2 + H_2O$. The small introduction of Nb^{5+} into lattice may provide adequate benefit to the overall thermodynamics to render carbonation unfavorable in short-term performance. However, a weak peak corresponding to barium carbonates appears in XRD shown in Fig. 1(d) after corrosion for 10 h, indicating that BCNF may be not completely stable in the presence of $CO_2 + H_2O$ at intermediate temperature for long time.

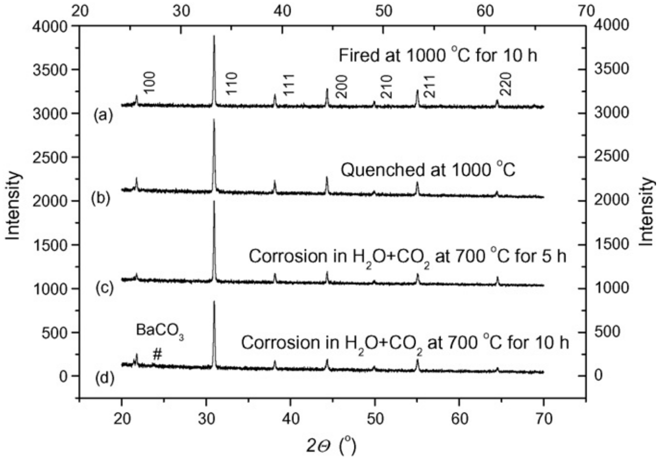

Fig. 1. XRD spectra of $BaCo_{0.8}Nb_{0.1}Fe_{0.1}O_{3-\delta}$ (BCNF): (a) fired at 1000 °C; (b) quenched at 1000 °C; (c) corrosion in $3\%CO_2/3\%H_2O/94\%Ar$ at 700 °C for 5 h; (d) corrosion in $3\%CO_2/3\%H_2O/94\%Ar$ at 700 °C for 10 h.

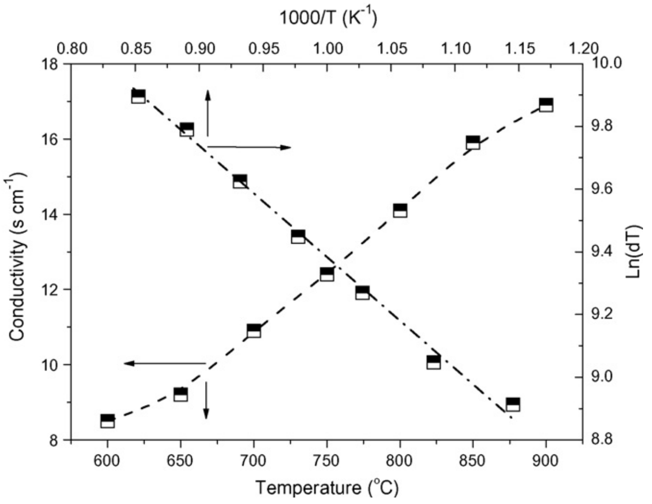

Fig. 2. Conductivity of $BaCo_{0.8}Nb_{0.1}Fe_{0.1}O_{3-\delta}$ (BCNF) as function of temperature.

Fig. 2 shows the conductivity of BCNF in air as function of temperatures. As shown in the figure, the conductivity reaches 10 S cm^{-1} at 700 °C and 17 S cm^{-1} at 900 °C, which is lower than that of reported Co- and Fe-based cathode under the same conditions [11,12]. This could be attributed to that the highly electronegative Nb^{5+} decreases the conductivity. Fig. 3 shows the cathode polarization in symmetric cell at 700 °C recorded with AC impedance. The theoretical intercept with real axis at high frequency represents the electrolyte resistance (R_2) of the symmetric cell and the other intercept at low frequency corresponds to the total polarization resistance (R_1) of cell. Thus, 50% of electrode polarization was considered as cathode polarization. As shown in Fig. 3, the BCNF polarization is just 0.1 Ω cm^2 at 700 °C which is much lower than 0.8 Ω cm^2 for traditional $La_{0.5}Sr_{0.5}MnO_3$ cathode, indicating the desirable performance of BCNF cathode. Besides, it is comparable to the reported cobalt-based cathodes, but much better than the reported manganese- or cobalt-based cathodes [12]. Fig. 4 shows the microstructure of a single anode-supported fuel cell with BCNF cathode and BCZY electrolyte membrane after testing. It can be seen that the BCNF cathode layer adheres to electrolyte very well indicating the desirable thermal compatibility. However, the cathode layer is not porous enough, which may increase cathode polarization. Fig. 5 shows the performance of single cell with BCNF cathode. The OCV reaches 1.01 V at 700 °C, which is a little lower than the theoretical value. This could be due to the electronic con-

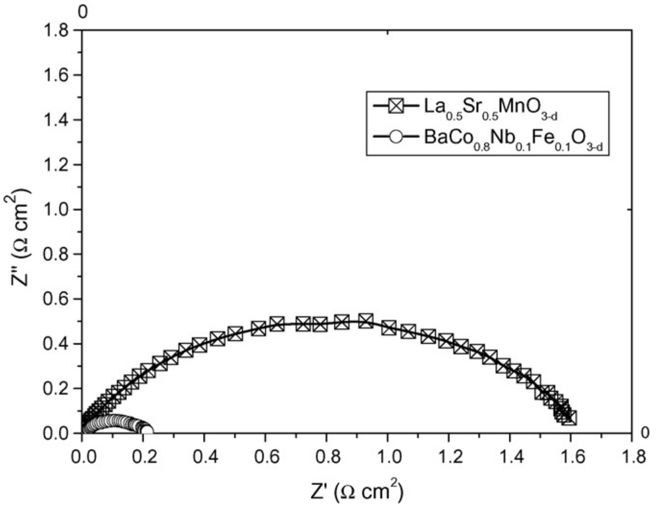

Fig. 3. Electrode polarization of $BaCo_{0.8}Nb_{0.1}Fe_{0.1}O_{3-\delta}$ (BCNF) in symmetric cell.

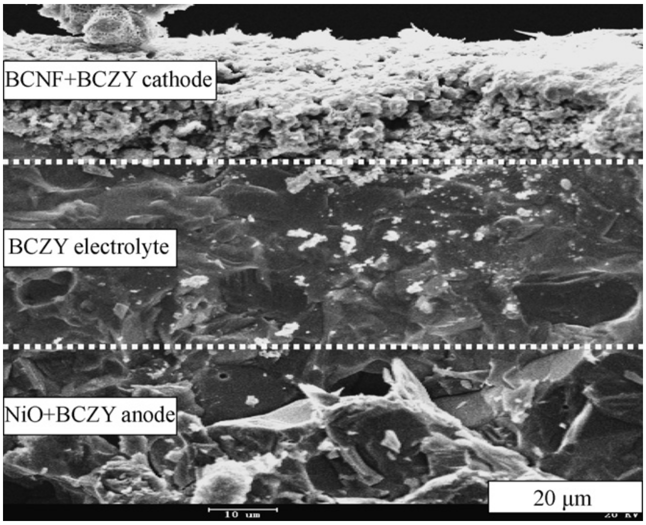

Fig. 4. SEM photo of $BaCo_{0.8}Nb_{0.1}Fe_{0.1}O_{3-\delta}$ (BCNF) on anode-supported $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ electrolyte.

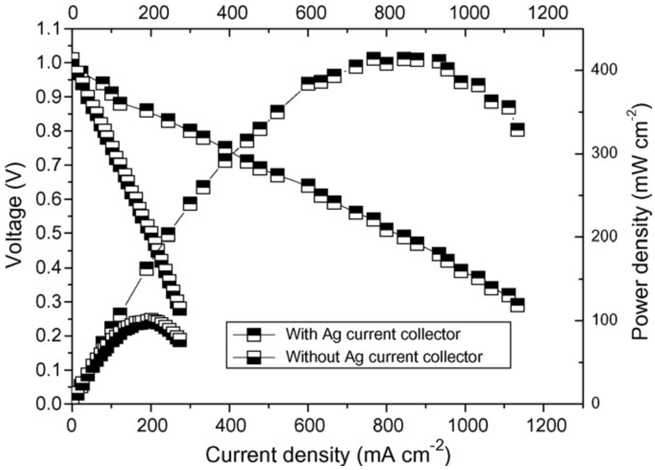

Fig. 5. Performance of fuel cell with $BaCo_{0.8}Nb_{0.1}Fe_{0.1}O_{3-\delta}$ (BCNF) cathode.

duction of proton conductor. The corresponding maximum power density reaches 413 mW/cm^2 at 700 °C with (3% H_2O) hydrogen as fuel and static air as oxidizer. For comparison, a single cell was tested under the same conditions without Ag paste as current collector. The OCV reaches the same value but the performance only reaches 98 mW cm^{-2} which is significantly lower than the above value. This implies BCNF could not be utilized as cathode as well as cathode current collector because of the insufficient mixed conductivity. In summary, BCTF can be considered as a good cathode candidate for intermediate temperature solid oxide fuel cells.

4. Conclusion

In this study, we aim to provide a novel cathode $BaCo_{0.8}Nb_{0.1}Fe_{0.1}O_{3-\delta}$ (BCNF) for intermediate temperature solid oxide fuel cells. XRD study demonstrates that the donor substitution of 10% Nb^{5+} for Co^{3+} in B-site not only demonstrates the outstanding stabilization effect for cubic perovskite structure but also increases the chemical stability against carbonation in the presence of CO_2 and H_2O at intermediate temperature. Besides, BCTF shows adequate mixed conductivity and desirable cathode polarization at intermediate temperature. A fuel cell with BCNF cathode and $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ electrolyte (20 µm in thickness) generates maximum 413 mW cm^{-2} at 700 °C with (3% H_2O) hydrogen as fuel and air as oxidizer.

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