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Electrical conductivity and electrochemical performance of cobalt-doped $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ cathode

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ABSTRACT

To develop efficient cathode materials for solid oxide fuel cells (SOFCs) based on $\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2})\text{O}_{3-\delta}$ (BZCY) electrolyte, we have examined a series of cobalt-doped BZCY samples with the intended composition of $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2-x}\text{Co}_x\text{O}_{3-\delta}$ (where $x = 0, 0.02, 0.05, 0.075, 0.1, 0.2$). It is found that the solubility of cobalt is less than 10 mol% and the electrical conductivity of $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2-x}\text{Co}_x\text{O}_{3-\delta}$ decreased with the content of cobalt within this solubility. When the content of cobalt is greater than its solubility, a BaCoO_3 -based phase forms, which markedly increases the conductivity of the sample (e.g., 2.48 S/cm for a composite material with an intended composition of $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Co}_{0.2}\text{O}_{3-\delta}$ at 700 °C). Typical cells with the cobalt-doped BZCY cathode display much-improved performance than cells with other transition metal doped barium cerate ever reported, yielding a polarization resistance of $0.085 \Omega \text{ cm}^2$ at 750 °C.

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1. Introduction

To make solid oxide fuel cell (SOFC) technologies economically competitive, the operating temperature must be reduced so that much less expensive materials may be used in the SOFC systems [1]. Oxide proton conductors, which often exhibit high ionic conductivity [2–10] as well as promising tolerance to sulfur poisoning and coking [1,11,12] at relatively low temperatures have a potential to meet the requirements for a fuel-flexible SOFCs operated at intermediate temperatures. However, the lack of efficient cathode materials that are compatible with the proton conductors results in poor performance at reduced temperatures. It has been reported that a composite cathode with mixed proton, oxygen ion, and electron conductivity could extend reaction zone beyond the electrolyte–electrode interface and hence reduce the charge transfer resistance [13–17]. Ideally, it is more desirable to dope transition metal ions into barium cerate phase to introduce

these mixed conductivities, especially considering its superior compatibility with the electrolyte [18].

Recently, Bi-doped BaCeO_3 and Pr-doped $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ were developed as cathodes for $\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2})\text{O}_{3-\delta}$ and $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ electrolytes, respectively [19–21]. All these mixed conducting cathodes exhibited relatively sluggish electrode kinetics, yielding a cathodic polarization resistance of $0.35 \Omega \text{ cm}^2$ at 800 °C for $\text{Ba}(\text{Pr}_{0.8}\text{Gd}_{0.2})\text{O}_{3-\delta}$. This is attributed primarily to the low electronic conductivity of these cathode materials. Often, materials with high proton conductivity do not have sufficient electronic conductivity to be useful as mixed protonic and electronic conductors ($<0.1 \text{ S/cm}$ at 800 °C) [22]. Shimura et al. [23] studied the effect of transition metal (Mn, Fe and Co) doping into $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ proton conductors. Among the doped samples, Co-doped samples showed the highest conductivity and the lowest activation energy of conduction. However, no information about cathode performance was provided.

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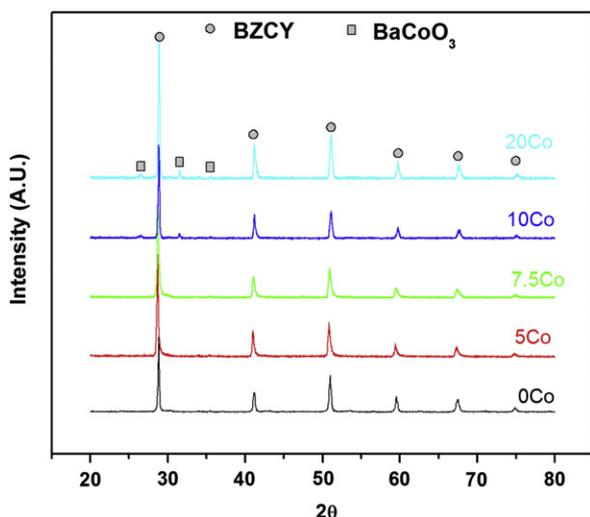


Fig. 1 – XRD patterns of various Co-doped BZCY powders.

In this study, we use Co to replace some B-site cations in Ba ($Zr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$) to enhance its electronic conductivity. The effect of Co concentration on electrical conductivity was characterized by four-probe impedance measurements in dry oxygen. In anode-supported button cells, cathodes based on the material with an intended composition of, $BaZr_{0.1}Ce_{0.7}Y_{0.2-x}Co_xO_{3-\delta}$ demonstrated superior electrocatalytic activity towards oxygen reductions.

2. Experimental

Powders of Co-doped BZCY were synthesized by a conventional solid-state reaction method. The intended compositions of the materials prepared were $BaZr_{0.1}Ce_{0.7}Y_{0.2-x}Co_xO_{3-\delta}$ ($x = 0, 0.02, 0.05, 0.075, 0.1, 0.2$), which were abbreviated as 0Co, 2Co, 5Co, 7.5Co, 10Co, and 20Co, respectively. Stoichiometric amounts of high-purity barium carbonate, zirconium

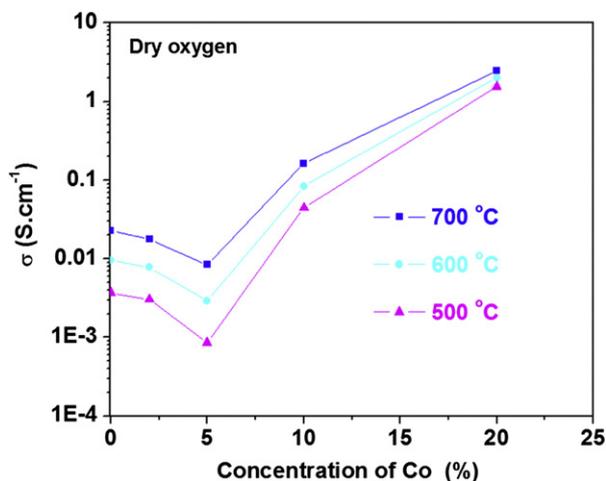


Fig. 2 – Total conductivities of various Co-doped BZCY as a function of the concentration of Co as measured in dry oxygen.

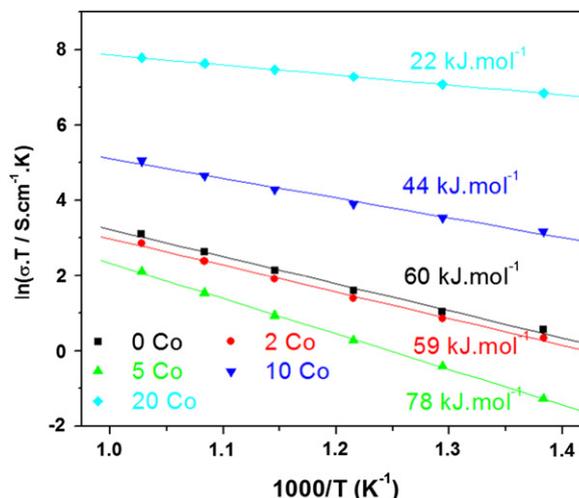


Fig. 3 – Total conductivities in dry oxygen of various Co-doped BZCY as a function of temperature.

oxide, cerium oxide, cobalt oxide, and yttrium oxide powders (all from Aldrich Chemicals) were mixed using ball-milling with stabilized zirconia media in ethanol for 48 h. The resultant mixture was dried at 60 °C for 24 h, followed by calcination at 1100 °C for 10 h. The ball-milling and calcination under same conditions were repeated twice to obtain pure phase. The calcined mixture was then iso-statically pressed into a disk at 274.6 MPa. The disks were then sintered at 1550 °C for 10 h in air to obtain samples with relative density greater than 96%.

The electrical conductivities of Co-doped BZCY samples were evaluated by four-probe impedance measurements. First, the sintered pellets were cut to rectangular bars with a typical dimensions of $2 \times 1 \times 10$ mm. Second, platinum paste was applied to both ends of the bar and fired at 900 °C for 30 min to form working and counter electrodes. Third, two platinum wires were then attached to the bar close to the working and counter electrodes, respectively, as reference electrodes.

NiO-BZCY/BZCY bilayers were fabricated as described elsewhere [24]. A cathode slurry, consisting of Co-doped BZCY, V006 thinner (from Heraeus) and acetone (weight ratio of 1:1:1), was brush-painted on the BZCY surface of the NiO-BZCY/BZCY bilayers, followed by firing at 1000 °C for 3 h. The thicknesses of the anode (NiO-BZCY), electrolyte (BZCY), and cathode were about $\sim 500, 60$ and $20 \mu\text{m}$, respectively. The button cell was mounted on an alumina supporting tube for fuel cell testing at 650–750 °C with humidified hydrogen (3 vol % H_2O) as fuel (The flow rate was 30 mL/min) and stationary air as oxidant.

The phase compositions of the samples were examined by X-ray diffraction (XRD) analysis (PW-1800 system). The microstructure and morphology of various samples were examined using a scanning electron microscope (LEO 1530 field emission SEM). Electrical conductivity of the samples and the cell performances were measured using a Solartron 1286 electrochemical interface and a Solartron 1255 HF frequency response analyzer interfaced by a computer in the frequency range from 1 Hz to 20 MHz.

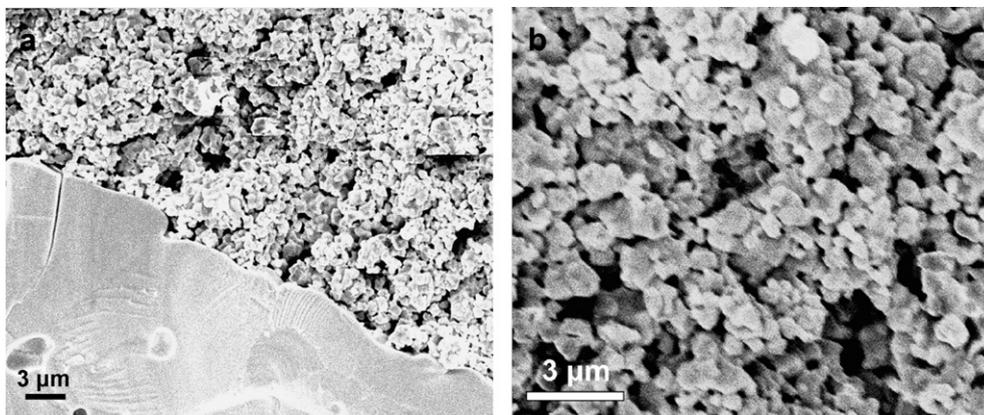


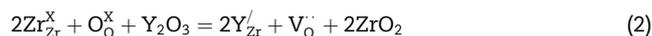
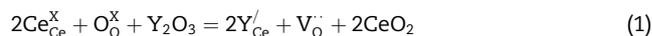
Fig. 4 – Cross-sectional images of BZCC cathode and BZCY electrolyte bilayers (a) interface (b) cathode.

3. Results and discussion

Shown in Fig. 1 are X-ray diffraction patterns of $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2-x}\text{Co}_x\text{O}_{3-\delta}$ ($x = 0, 0.05, 0.075, 0.1$ and 0.2) samples. It is easily seen that no obvious secondary phase was found in BZCY with up to 7.5 mol% of Co content. In addition, the diffraction peaks associated with BZCY phase shifted towards higher angle. The shift is probably a result of smaller ionic radius of Co^{3+} ($R^{\text{III}} = 0.53 \text{ \AA}$) than Ce^{4+} ($R^{\text{IV}} = 0.87 \text{ \AA}$) and Zr^{4+} ($R^{\text{IV}} = 0.72 \text{ \AA}$) [13]. With the increase of Co dopant to

10 mol%, BaCoO_3 -based phase was shown in the XRD pattern and appeared more when 20 mol% Co was doped in B-site. This trend indicates that cobalt formed solid solution in the range of less than 7.5 mol%; further introduction of cobalt resulted in the dissolution of Co from BZCY.

Since cathode is exposed in air or oxygen, it is necessary to investigate the conductivity of various Co-doped BZCY pellets under these conditions. In fact, electrical conductivities of cerate and zirconate are sensitive to partial pressure of oxygen, hydrogen, and water. $\text{BaZr}_x\text{Ce}_{1-x}\text{O}_3$ compounds when doped, typically on the B-site by a lower-valent cation, become oxygen-deficient. The dopant dissolution mechanism leads to the creation of oxygen vacancies as per Equations (1) and (2) (written in Kröger–Vink notation).



Subsequent exposure to humid atmospheres is presumed to lead to the incorporation of protons into the lattice according to Equation (3).



The defect reaction for oxygen incorporation into the lattice (absorption) in dry atmospheres can be written as



This promotes electronic (p-type) conduction, accompanied by consumption of oxygen vacancies at elevated temperatures. However, the electronic conductivity is insufficient for cathode reactions. Transition metal ions are essential to be doped in the B-site to further enhance the electronic conductivity. Fig. 2 represents the conductivities plotted as a function of Co doping concentrations in dry oxygen at 500–700 °C. It was noted that the total conductivities were reduced with increasing Co content and then increased sharply with the further introduction of Co dopants throughout the testing temperatures. For example, the conductivity decreased from 0.023 S/cm for 0Co to 0.008 S/cm for 5Co and reached maxima of 2.48 S/cm for 20Co at 700 °C, a sample with complete replacement of Y by Co in B-site. The

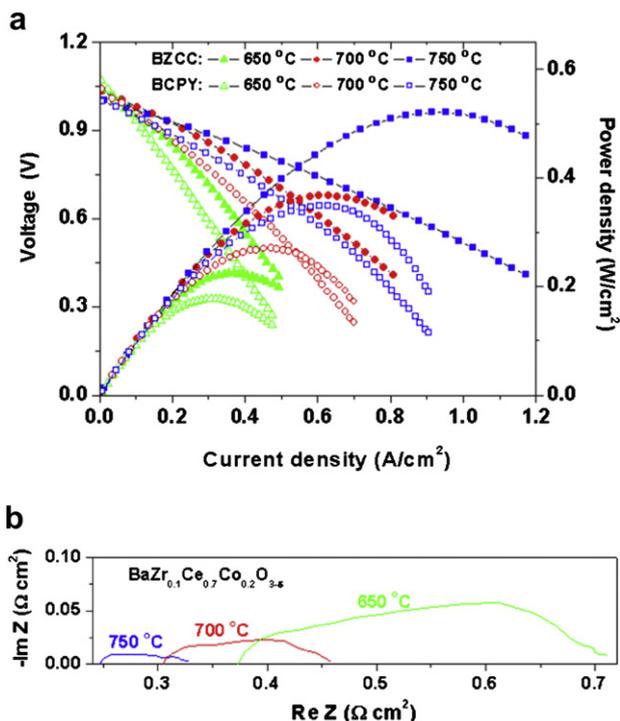


Fig. 5 – (a) Power output characteristics of a typical cell with a composite cathode of intended composition $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Co}_{0.2}\text{O}_{3-\delta}$ (BZCC) and $\text{Ba}(\text{Ce}_{0.4}\text{Pr}_{0.4}\text{Y}_{0.2})\text{O}_{3-\delta}$ (BCPY) cathode at various temperatures. (b) Impedance spectra of a single cell with BZCC cathode measured under open circuit conditions at different temperatures.

decrease in conductivity of BZCY after substitution of Y with small amount of cobalt agrees with the prediction of Kilner [25] and with the experimental results of Shimura for BaCeO₃ system [23]. This behavior was interpreted by the hole-trapping effect of the transition metal 3d orbital. The marked increase of conductivity at high doping level was attributed primarily to formation of BaCoO₃-based phase that is an excellent conductor with high oxygen ion and electronic conductivity [26].

Fig. 3 displays the apparent activation energies of various samples in dry oxygen, which increased slightly with the Co content initially and reached a maximum value for sample with 5% Co dopant. Then a pronounced decrease in activation energy was observed with addition of Co, suggesting a dramatic change in conduction mechanism. The activation energies for the conductivity of 0Co–5Co are in the range of 60–80 kJ mol⁻¹, which are typical values for ionic transport. On the other hand, the 20Co sample has activation energy (22 kJ mol⁻¹) similar to those for doped lanthanum manganite [27], lanthanum cobaltite [28], and BaCoO₃ [29]. These energy barriers are for transport of electronic defects, suggesting that the conduction in the 20Co sample is dominated by electronic transport.

To evaluate the feasibility of Co-doped BZCY conductor as the cathode, anode-supported cells with thin BZCY electrolyte were fabricated. Fig. 4 shows the cross-sectional images of as-prepared composite cathode material with an intended composition of BaZr_{0.1}Ce_{0.7}Co_{0.2}O_{3-δ} (BZCC). The observed strong interface adhesion indicates that the cathode has the unique compatibility with the electrolyte, primarily because BZCC cathode was derived from the BZCY electrolyte. The excellent bonding would yield sufficient electrochemically active sites and sustained stability under the operating conditions. Furthermore, the inter-particle connectivity in the BZCC cathode was suitable; a porous structure was thus obtained, resulting in facile transport of oxygen gas as well as proton, oxygen ion, and electron required for cathode reactions.

Fig. 5a shows the current-voltage characteristics and the corresponding power densities for BZCY-based fuel cells with a composite cathode of intended composition BaZr_{0.1}Ce_{0.7}Co_{0.2}O_{3-δ} (BZCC) and a BaCe_{0.4}Pr_{0.4}Y_{0.2}O_{3-δ} (BCPY) cathode measured at different temperatures. The open circuit voltages (OCV) at 750, 700, and 650 °C are 1.00, 1.04, and 1.07 V, respectively, representing that the BZCY electrolyte is sufficiently dense and exhibits negligible electronic conduction. The single cell with a composite cathode of intended composition BaZr_{0.1}Ce_{0.7}Co_{0.2}O_{3-δ} (BZCC) yielded peak power densities of 0.52, 0.37, and 0.22 W/cm² at 750, 700, and 650 °C, respectively. These power outputs are higher than that of the same cell with BaCe_{0.4}Pr_{0.4}Y_{0.2}O_{3-δ} (BCPY) cathode, specifically, 0.35, 0.27 and 0.18 W/cm² at corresponding temperatures. However, with the Co-doped BZCY cathode in which cobalt content is within the solubility such as BaZr_{0.1}Ce_{0.7}Y_{0.15}Co_{0.05}O_{3-δ}, the cell demonstrated dramatically reduced performance, reaching a peak power density of 0.27 W/cm² at 750 °C. This can be reasonably attributed to the low electronic conductivity of cathodes that inhibited the charge transfer reactions. Moreover, impedance spectroscopy measurements revealed that the cell with a composite

cathode of intended composition BaZr_{0.1}Ce_{0.7}Co_{0.2}O_{3-δ} produced the interfacial resistances of 0.085, 0.16 and 0.35 Ω cm² at 750, 700 and 650 °C, respectively, as shown in Fig. 5b. In contrast, at these temperatures, the polarization resistances for the cell with BaCe_{0.4}Pr_{0.4}Y_{0.2}O_{3-δ} are 0.28, 0.41 and 0.61 Ω cm². Therefore, the markedly increased electrocatalytic activity of BaZr_{0.1}Ce_{0.7}Co_{0.2}O_{3-δ} cathode is ascribed primarily to the enhanced electronic conductivity of this material.

4. Conclusions

This study demonstrated that cobalt-doped BZCY composites are promising cathode materials for BZCY-based SOFCs. Based on the XRD analysis and four-probe conductivity measurements, the solubility of cobalt oxide in BZCY is within the range between 7.5 and 10 mol%. The secondary phase BaCoO₃ offered high electronic conductivity and effectively reduced cathode polarization toward oxygen reduction. Composite materials with an intended composition of BaZr_{0.1}Ce_{0.7}Co_{0.2}O_{3-δ} cathode yielded higher power output than other transition metals doped barium cerate. The cell performance can be further enhanced through decrease of the electrolyte thickness and optimization of cathode microstructures.

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