



Short communication

A mixed proton, oxygen ion, and electron conducting cathode for SOFCs based on oxide proton conductors

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ABSTRACT

A composite cathode, consisting of $\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2})\text{O}_{3-\delta}$ (BZCY) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF), has shown high catalytic activity toward oxygen reduction, demonstrating a peak power density of 855 mW cm^{-2} at 750°C . The chemical compatibility between BZCY and LSCF is excellent since there was no evidence of chemical reaction between the two after being fired at 1100°C for 10 h. The stability of the composite cathode is further shown in single cells operated at 750 and 600°C for 100 h without observable degradation in performance.

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1. Introduction

Development of new materials for SOFCs to be operated at low temperatures is vital to effectively reduce the cost of SOFC technologies [1,2]. Proton conductors are promising electrolytes for low temperature SOFCs due to their low activation energy for proton transport [3–6]. Recently, a new composition of oxide proton conductor, $\text{Ba}(\text{Zr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2})\text{O}_{3-\delta}$ (BZCY), is reported to exhibit both high proton conductivity and sufficient chemical and thermal stability over a wide range of conditions relevant to fuel cell operation [7–9]. However, the performance of cells based on oxide proton conductors is still inadequate for practical applications [3], due primarily to the lack of proper cathode materials compatible to the electrolytes [8]. The well-studied oxygen ion–electron conducting cathodes for SOFCs based on oxygen ion conductors have been used as cathodes for fuel cells based on proton conducting electrolytes; however, the electrode reaction mechanism has not been well understood and the cathodic overpotentials are much larger than what is acceptable [10–12]. For example, $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC) was used as the cathode for Y-doped barium cerate, yielding an overpotential of $\sim 350 \text{ mV}$ at a current density of 100 mA cm^{-2} at 600°C [10], far exceeding the overpotential of an SSC cathode on an SDC

electrolyte, $\sim 35 \text{ mV}$ under the same conditions [13]. While layered perovskite $\text{SmBaCo}_2\text{O}_{5+x}$ is a superior cathode for cells based on oxygen ion conductors [14,15], it showed relatively high cathodic polarization resistances when applied to BZCY electrolyte [12]. The marked difference is attributed to the limited electrochemically active reaction sites (electrode/electrolyte interface) when an oxygen ion and electron conducting cathode is used as electrode for a proton conducting electrolyte.

Electrochemical stability of cathode is another issue which impedes the development of SOFCs based on oxide proton conductors. Little information is available on the durability of cells based on the BZCY electrolyte. For an electrolyte with complicated components such as BZCY, it is difficult to develop a compatible cathode. It was found that a secondary phase $\text{La}_2\text{Zr}_2\text{O}_7$ was formed during processing at 1100°C between LaMnO_3 (La_2NiO_4) and BaZrO_3 [16]. Undesirable reactions between the components of a composite cathode may degrade the strength, electrical, catalytic, and electrochemical performance.

In this communication, we report the unique properties of a proton, oxygen ion, and electron conducting cathode consisting of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and BZCY. This mixed conducting cathode greatly increases the number of active sites, facilitating the electrochemical reactions involving H^+ , O^{2-} and e' or h^* . Further, no additional reaction products were identified after firing BZCY–LSCF powders mixture even at 1100°C for 10 h. A typical cell with BZCY electrolyte and BZCY–LSCF composite cathode has demonstrated peak power densities of 855, 522, and 215 mW cm^{-2} at 750, 650, and 550°C , respectively.

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2. Experimental

BZCY powders were prepared by a solid state reaction method as described elsewhere [7]. BZCY–NiO supported BZCY bilayers were fabricated by a co-pressing and co-firing method. Proper amount of starch (12 wt.%) was added into NiO and BZCY mixture (weight ratio of 65:35) which was then co-pressed with BZCY powders. The bilayer was then fired at 1350 °C for 6 h. The thickness of the anode and the electrolyte layers are around 500 and 55 μm , respectively.

LSCF powders were synthesized using a citrate process. 1 M precursor solution with $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (from Alfa Aesar) in stoichiometric ratio was added drop by drop in a 3 M citric acid solution under vigorous stirring. The pH value of the solution was adjusted to about 8 by ammonia. The solvent in the solution was then evaporated at 50–80 °C for about 2 h to form a sol, followed by drying in an oven at 120–160 °C for 1 h to form a gel, which was finally fired at 800 °C for 2 h.

BZCY and LSCF powders (weight ratio of 3:7), V006 thinner (from Haurreus), and acetone were then mixed in weight ratio of 1:1:1 to form cathode slurry. The slurry was brush-painted on BZCY surface of a NiO–BZCY/BZCY bilayer, followed by firing at 1000 °C for 3 h. The composite cathode is $\sim 25 \mu\text{m}$ thick.

The phase composition of the composite cathodes fired at 1000–1200 °C for 10 h was examined using X-ray diffraction (XRD) analysis (PW-1800 system, $2\theta = 20\text{--}80^\circ$). The morphologies of the electrodes before and after operation were examined using a scanning electron microscope (SEM, Hitachi S-800).

The electrochemical performances of the cells were tested at 550–750 °C with humidified hydrogen (3 vol.% H_2O) as fuel and stationary air as oxidant. All standard electrochemical experiments were performed using a Solartron 1286 electrochemical interface and a Solartron 1255 HF frequency response analyzer. The interfacial resistances of a single cell (anodic and cathodic polarization) were determined from impedance spectroscopy under open circuit conditions.

3. Results and discussion

The oxygen reduction reaction on a cathode of SOFCs based on oxygen ion conductors has been extensively studied [17–21]. It is well known that mixed ionic and electronic conducting (MIEC) cathode on an oxygen ion conducting electrolyte could expand the electrochemically active reaction sites from the triple phase boundary (TPB) to the cathode surface, as shown in Fig. 1(a). However, when applying an MIEC on a proton conducting electrolyte, the oxygen reduction can only take place at the interface where electrode, electrolyte, and the gas phase are in contact and where the access to oxygen, proton, and electrons are met for the reduction reaction as indicated in Fig. 1(b). The limited reaction sites may lead to large electrode polarization resistance. This could explain why pure SSC cathode exhibits poor electrochemical performance (an overpotential of 350 mV at a current density of 100 mA cm^{-2} at 600 °C) on Y-doped barium cerate electrolyte [10]. In order to expand reaction zone beyond the interface, a potential cathode material must be able to conduct proton, oxygen ions and electrons. A mixed proton, oxide ion and electron conducting cathode extends the TPB from the interface to the entire cathode, thereby greatly accelerating the charge transfer reaction. From these points of view, a fuel cell based on proton conducting electrolyte using this mixed conducting cathode should reduce the resistance to oxygen reduction reactions. Unfortunately, a single-phase proton, oxygen ion and electron conductor with significant electronic conductivity is not yet developed [22]. Thus, a composite cathode consisting of a proton conductor and a mixed oxygen ion and electron conductor (MIEC) may facilitate simultaneous transport of proton,

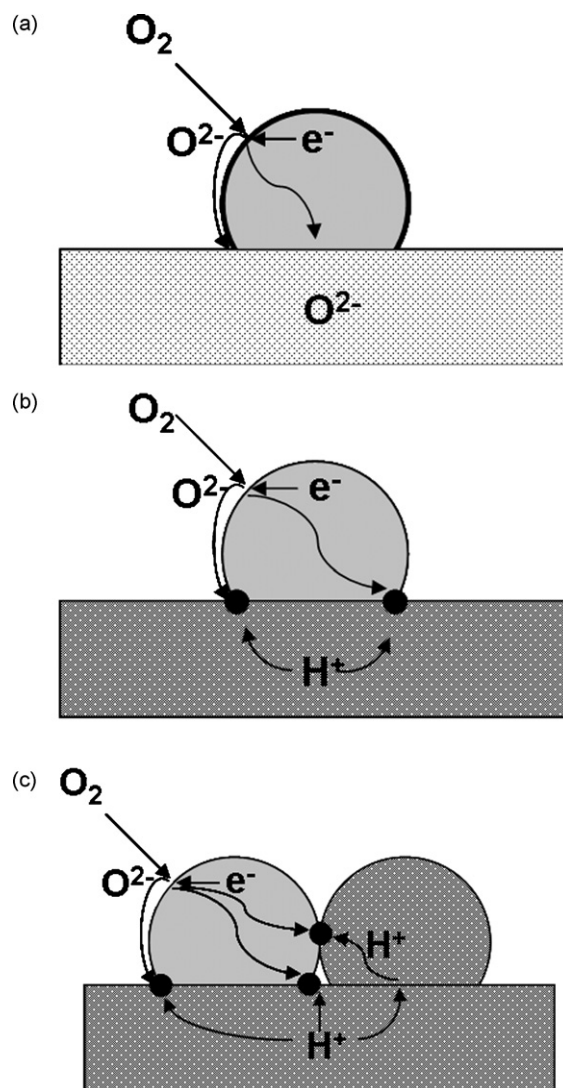


Fig. 1. Schematic illustration of oxygen reduction reaction sites (a) a mixed oxygen ion–electron conducting cathode on oxygen ion conducting electrolyte; (b) a mixed oxygen ion–electron conducting cathode on a proton conducting electrolyte, and (c) a mixed proton–oxygen ion–electron conducting cathode on a proton conducting electrolyte. The circles denote electrochemically active reaction sites.

oxide ion, and electron for the oxygen reduction, as schematically shown in Fig. 1(c). The other advantage of this concept is that well-developed MIECs can be mixed with a proton conductor to tailor the properties. In this study, LSCF was mixed with BZCY to form a composite cathode that transport proton, oxide ion, and electron, exhibiting very low polarization resistance and high power density.

The pairing of proton conducting electrolytes with proper electrode materials is significant to achieving high performance SOFCs. Shown in Fig. 2 are some typical X-ray diffraction patterns for BZCY, LSCF, and BZCY–LSCF powder mixtures taken before and after firing at 1000–1200 °C for 10 h. As can be seen, no obvious secondary phase appears in the BZCY–LSCF system when the firing temperature is 1100 °C. Further, the linear thermal expansion coefficient of BZCY ($11.2 \times 10^{-6} \text{K}^{-1}$) is similar to that of LSCF ($15.3 \times 10^{-6} \text{K}^{-1}$) [23,24]. Thus, LSCF is a chemically and thermally compatible with BZCY electrolyte under the conditions studied.

Fig. 3(a) shows the dependence of cell voltages and power densities on cell operating current densities at different temperatures for BZCY-based fuel cells using BZCY–LSCF and LSCF cathodes. The

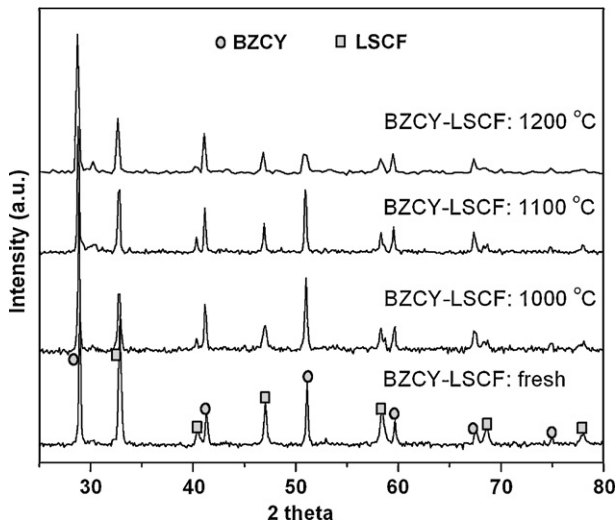


Fig. 2. Typical XRD patterns of BZCY, LSCF, and BZCY–LSCF mixture before and after firing at 1000–1200 °C for 10 h.

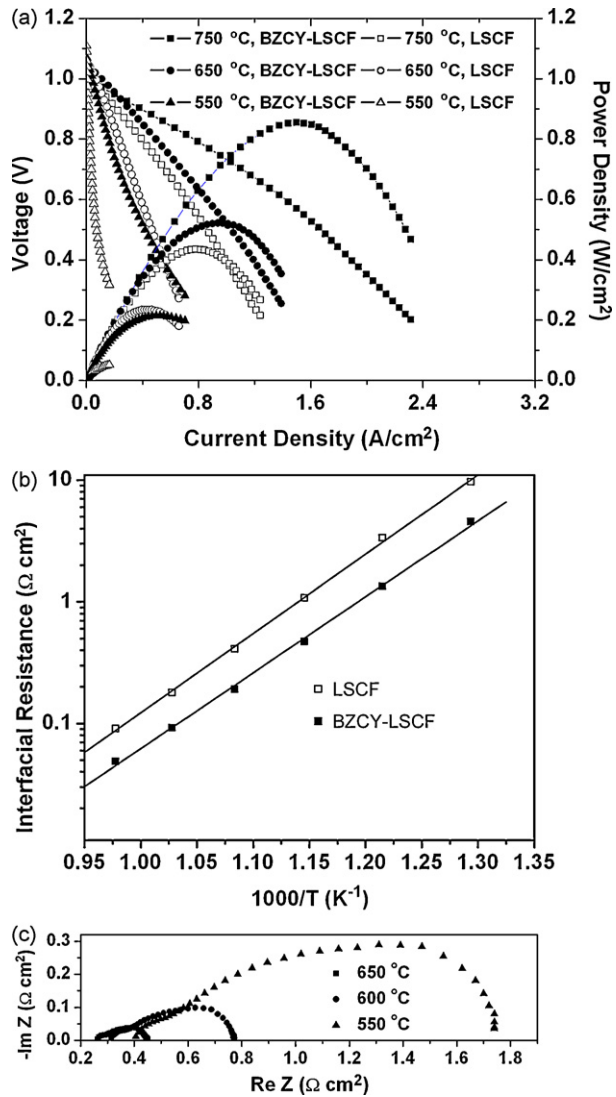


Fig. 3. (a) $V-I$ characteristics for BZCY-based anode-supported cells with BZCY–LSCF and LSCF cathodes as measured in humidified (3% H_2O) H_2 at 550–750 °C; (b) polarization resistances of the cells with LSCF and BZCY–LSCF cathode; (c) impedance spectra of a single cell with BZCY–LSCF cathode measured under open circuit conditions at different temperatures.

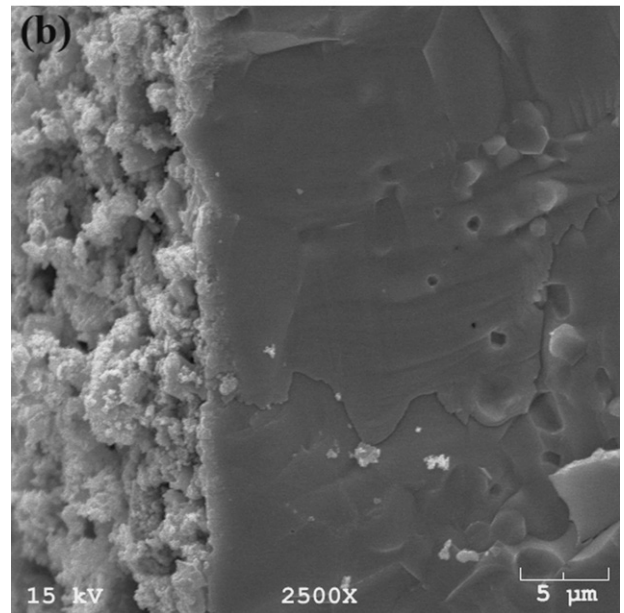
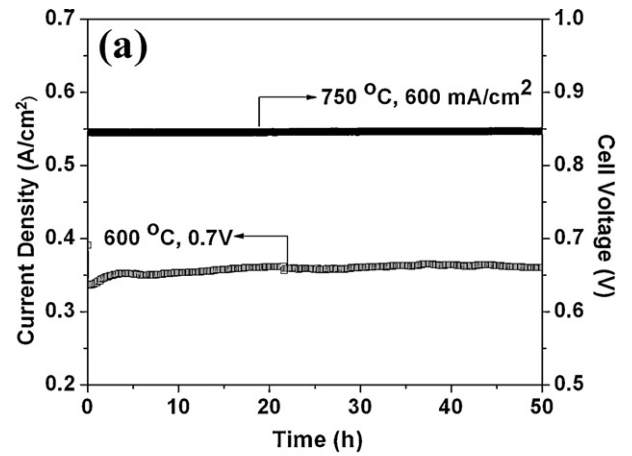


Fig. 4. (a) Performances of the cells with BZCY electrolyte and BZCY–LSCF cathode tested at a constant current density of 600 $mA cm^{-2}$ at 750 °C and at a constant cell voltage of 0.7 V at 600 °C; (b) a cross-sectional view of the porous BZCY–LSCF cathode after operation at 600 $mA cm^{-2}$ and 750 °C and 0.7 V and 600 °C for 100 h.

open circuit voltages (OCV) at 750, 650, and 550 °C are 1.01, 1.06, and 1.11 V, respectively. This indicates that the BZCY electrolyte is sufficiently dense and exhibits negligibly small electronic conduction. More importantly, BZCY–LSCF composite cathode produced much higher power output than the LSCF cathode under the same operating conditions. The peak power densities were ~855, 522, and 215 $mW cm^{-2}$ at 750, 650, and 550 °C, respectively. These performances are surprisingly high for a cell based on a 55 μm thick electrolyte, even better than that based on an oxygen ion conductor (e.g., 26 μm thick GDC electrolyte and GDC–SSC cathode showed 330 and 205 $mW cm^{-2}$ at 650 and 550 °C, respectively) [25]. In contrast, the cell with the LSCF cathode displayed 435, 235, and 81 $mW cm^{-2}$ at 750, 650, and 550 °C, respectively.

Fig. 3(b) summarizes the polarization resistances of typical cells with BZCY–LSCF and LSCF cathodes measured at different temperatures. Obviously, BZCY–LSCF exhibits much lower cathodic polarization resistances than the LSCF cathode in all cases. The polarization resistances of cells with BZCY–LSCF are estimated to be only 0.19, 0.47, and 1.34 Ωcm^2 at 650, 600, and 550 °C, respectively, comparable to those of the GDC–LSCF composite cathode on GDC electrolyte (0.13, 0.33, and 1.24 Ωcm^2 at 650, 600, and

550 °C, respectively), as shown in Fig. 3(c) [26]. SEM examination of fresh BZCY–LSCF and LSCF cathodes reveals that their surface and cross-sectional morphologies are very similar, suggesting that the remarkable improvement in performance is due primarily to the superior catalytic activity of BZCY–LSCF cathode.

It is critical to evaluate durability of the cells with BZCY electrolyte and BZCY–LSCF cathode. Any instability of BZCY at high water activities and deterioration of electrode may lead to degradation in fuel cell performance. Fig. 4(a) shows the performance of cells operated at 600 mA cm⁻² and 750 °C and at 0.7 V and 600 °C. The cell voltage and current density were relatively stable and there was no obvious degradation in performance at both high and low temperatures, implying superior chemical stability of BZCY, steady electric characteristics of electrode, and strong bonding between electrolyte and electrode, as shown in Fig. 4(b).

4. Conclusions

SOFCS based on oxide proton conductor BZCY electrolyte and BZCY–LSCF composite cathode have produced high and steady power densities at reduced temperatures. The mixed conducting composite cathode demonstrated much-improved catalytic activity toward oxygen reduction than LSCF cathode. It appears that the addition of BZCY considerably increases the number of electrochemical reaction sites and expands them from the electrode/electrolyte interface to the entire surface of cathode. Moreover, LSCF is chemically compatible with BZCY even when firing at 1100 °C for 10 h, leading to both phase stability and superior adhesion with electrolyte. The preliminary durability testing indicated the practical viability of this promising composite cathode.

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