Short communication

Novel cobalt-free cathode materials BaCe$_x$Fe$_{1-x}$O$_{3-\delta}$ for proton-conducting solid oxide fuel cells

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ABSTRACT

A series of cobalt-free and low cost BaCe$_x$Fe$_{1-x}$O$_{3-\delta}$ (x = 0.15, 0.50, 0.85) materials are successful synthesized and used as the cathode materials for proton-conducting solid oxide fuel cells (SOFCs). The single cell, consisting of a BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{3-\delta}$ (BZCY7)-NiO anode substrate, a BZCY7 anode functional layer, a BZCY7 electrolyte membrane and a BaCe$_x$Fe$_{1-x}$O$_{3-\delta}$ cathode layer, is assembled and tested from 600 to 700 °C with humidified hydrogen ($\sim$3% H$_2$O) as the fuel and the static air as the oxidant. Within all the cathode materials above, the cathode BaCe$_{0.5}$Fe$_{0.5}$O$_{3-\delta}$ shows the highest cell performance which could obtain an open-circuit potential of 0.99 V and a maximum power density of 395 mW cm^{-2} at 700 °C. The results indicate that the Fe-doped barium cerates can be promising cathodes for proton-conducting SOFCs.

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1. Introduction

Solid oxide fuel cells (SOFCs) have attracted much attention worldwide because of the demand for clean, secure, and renewable energy [1,2]. Unfortunately, the expensive SOFC system limits the commercial use for the high operating temperature. The reduction of the working temperature of SOFCs becomes the urgent demand for broad commercialization [3]. Intermediate-temperature SOFCs, especially proton-conducting SOFCs attract much interest for those low operating temperature [2,4]. Proton-conducting SOFCs have some advantages compared with oxygen conducting SOFCs, such as low activation energy [5] and high energy efficiency [6].

One of the major challenges for Proton-conducting SOFCs is a proper compromise between the conductivity and chemical stability. Zuo et al. [7] report a new composition, BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{3-\delta}$ (BZCY7) that exhibits both adequate proton conductivity as well as sufficient chemical and thermal stability over a wide range of conditions relevant to fuel cell operation. BZCY7, at temperatures below 550 °C, displays a very high ionic conductivity for applications of SOFCs.

However, the development of proper cathode materials for proton-conducting SOFCs remains a challenge because the cathode materials sensitively affect the performance of low-temperature SOFCs. Many materials based on cobalt doping in the B site of

perovskite, are synthesized and used as the cathode [8–12]. Nevertheless, the practical applications of these materials often face some problems such as high thermal expansion coefficients (TECs) and high cost of cobalt element. In order to solve these problems, many cobalt-free cathode materials are reported [13–17]. Recently, Zhu et al. have reported the use of iron doped barium cerates as oxygen permeable membrane which shows that the iron doped barium cerates are good mixed conductors [18,19]. Furthermore, the doped barium cerates as the cathode materials have been investigated in our former work and show their advantages which admit the use in the proton-conducting SOFCs [20]. Considering the fact that the barium cerate-based cathode has the advantage of better match for barium cerate electrolyte fuel cells, we synthesize the BaCe$_x$Fe$_{1-x}$O$_{3-\delta}$ by a modified Pechini method and examined the exhibition of their use as a new cathode for a proton-conducting SOFC based on a BZCY7 electrolyte.

2. Experimental

BaCe$_x$Fe$_{1-x}$O$_{3-\delta}$ (x = 0.15, 0.50, 0.85) powders were synthesized by Pechini method. Ba(NO$_3$)$_2$, Ce(NO$_3$)$_3$·6H$_2$O and Bi(NO$_3$)$_3$·5H$_2$O were dissolved at the stoichiometric ratio and citric acid was then added, which was used as complexation agent. Molar ratio of citric acid/metal was set at 1.5. The solution was heated under stirring to evaporate water until it changed into viscous gel and finally ignited to flame, resulting in the white ash. The ash was calcined at 1000 °C for 3 h to form fine BaCe$_x$Fe$_{1-x}$O$_{3-\delta}$ powders. The BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_{3-\delta}$ (BZCY7) powders were also synthesized

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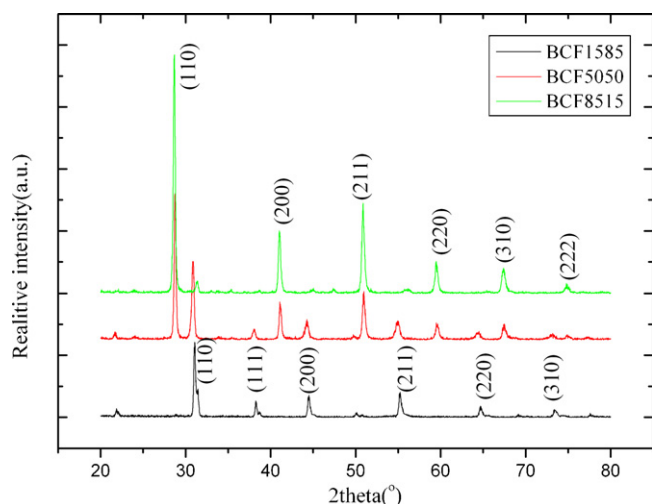
Fig. 1. X-ray diffraction patterns of (a) $BaCe_{0.15}Fe_{0.85}O_{3-\delta}$ (BCF1585), (b) $BaCe_{0.5}Fe_{0.5}O_{3-\delta}$ (BCF5050) and (c) $BaCe_{0.85}Fe_{0.15}O_{3-\delta}$ (BCF8515).

by a Pechini method with the raw material Ba $(NO_3)_2 \cdot 9H_2O$, Ce $(NO_3)_3 \cdot 6H_2O$, Zr $(NO_3)_4 \cdot 4H_2O$ at a proper molar ratio and then calcined at 1000 °C for 3 h. The anode-supported BZCY7 bi-layer (Φ15) was prepared by a dry-pressing method. NiO + BZCY7 + corn starch mixture (60%:40%:20% in weight) was pre-pressed at 200 MPa as substrate about 0.95 mm. Then the anode functional layer about 25 μm (mixture of NiO + BZCY7, NiO:BZCY7 = 50:50%) was pressed onto the substrate. Finally, loose BZCY7 powder was uniformly distributed on to anode substrate, co-pressed at 300 MPa and sintered subsequently at 1350 °C for 5 h to denitrify the BZCY7 membrane. Fine $BaCe_xFe_{1-x}O_{3-\delta}$ (x = 0.15, 0.50, 0.85) powders were mixed thoroughly with a 10 wt.% ethylcellulose–terpineol binder to prepare the cathode slurry, respectively. The three different cathode slurry were painted on the BZCY7 electrolyte membrane respectively, and fired at 1000 °C for 3 h in air to form single cells. The electrode active area was 0.237 cm^2. Ag paste was applied as a current collector for both the anode and cathode. Electrochemical measurements of the fuel cell were performed in an Al_2O_3 test housing placed inside a furnace. Humidified hydrogen ($\sim$3% H_2O) was fed to the anode chamber at a flow rate of 25 mL min^{-1}, while the cathode was exposed to atmospheric air. The anode side was sealed with Ag paste. Fuel cell performance was measured with DC Electronic Load (ITech Electronics model IT8511). Resistances of the cell under open-circuit condition were measured by an impedance analyzer CHI604B (0.1 Hz to 100 KHz). The phase of the obtained thin membrane electrolyte was examined with X-ray diffractometer (XRD) using CuKα radiation by testing the surface of the sintered electrolyte membrane. A scanning electron microscope (SEM, JSM-6301F) was employed to observe the fracture morphology of the assembled cell.

3. Results and discussion

Fig. 1 shows the XRD patterns of the BCF series of oxide powders. $BaCe_{0.15}Fe_{0.85}O_{3-\delta}$ (BCF1585) and $BaCe_{0.85}Fe_{0.15}O_{3-\delta}$ (BCF8515) powders with almost pure perovskite structure were successfully synthesized. As shown in Fig. 1, BCF1585 has a cubic perovskite structure and BCF8515 belongs to the orthorhombic structure. As for $BaCe_{0.5}Fe_{0.5}O_{3-\delta}$ (BCF5050), it is found that the sample comprises two kinds of perovskite oxides mentioned above (BCF1585 and BCF8515).

Fig. 2 shows the cross-sectional view of the single cell after testing. Fig. 2(a)–(c) represent the single cell with the cathode BCF1585, BCF5050 and BCF8515, respectively. As can be seen, the BZCY7 elec-
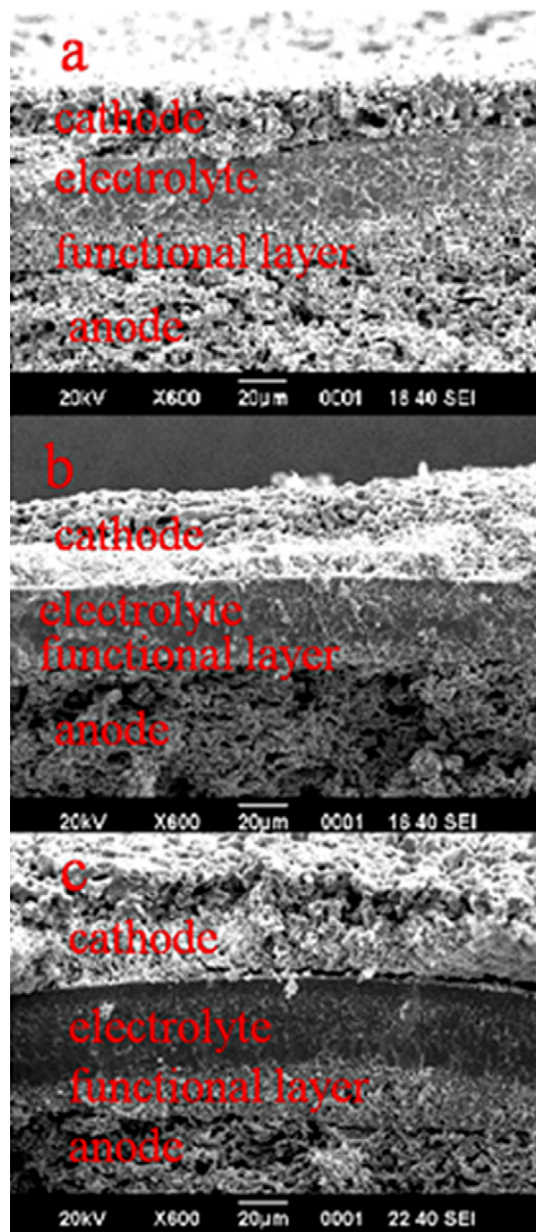
Fig. 2. Cross-section views of the different cells without surface modification after fuel cell testing (a) $BaCe_{0.15}Fe_{0.85}O_{3-\delta}$ (BCF1585), (b) $BaCe_{0.5}Fe_{0.5}O_{3-\delta}$ (BCF5050) and (c) $BaCe_{0.85}Fe_{0.15}O_{3-\delta}$ (BCF8515).

trolyte membranes of the cells are about 25 μm in thickness, and adhere very well to the anode functional layer and the cathode. The anode functional layer is used to optimize the interface of anode and electrolyte, which is about 25 μm in thickness.

Fig. 3 presents the *I*–*V* and *I*–*P* characteristics of the as-prepared cells measuring at 700 °C with humidified hydrogen ($\sim$3% H_2O) as the fuel. The maximum power densities of 395, 255, 150 mW cm^{-2} with the OCV values of 0.986, 0.988 and 0.981 V are obtained for the cell with the cathode BCF5050, BCF1585 and BCF8515, respectively. It can be seen that the cell with the cathode BCF5050 has the highest power densities.

The resistance of the cells under open-circuit conditions, which was investigated by AC impedance spectroscopy at 700 °C, is shown in Fig. 4. The high frequency intercept corresponds to overall electrolyte resistance of the cell including ionic resistance of the electrolyte and some contact resistance associated with interfaces [21]. The low frequency intercept corresponds to the total resistance
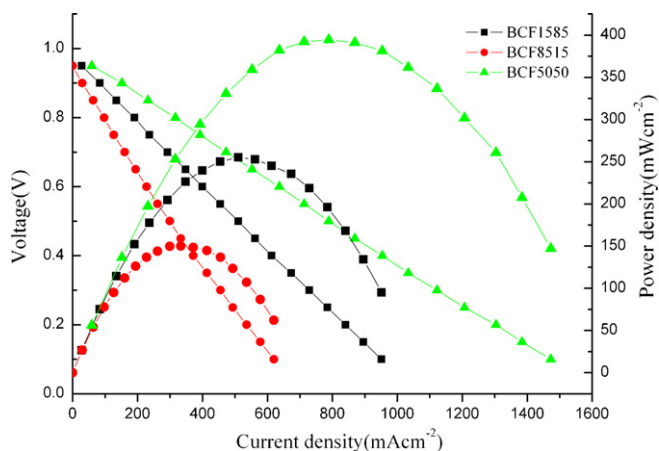
Fig. 3. Performances of the single cells with different cathodes under wet hydrogen atmosphere at 700 °C.

Fig. 5. Performance of the single cell with cathode BCF5050 under wet hydrogen atmosphere at different temperatures.

Fig. 6. (a) Impedance spectra and (b) the interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra of the cell measured with cathode BCF5050 under open-circuit conditions at different temperatures.

of the cell. Therefore, the difference between the high frequency and low frequency intercepts with the real axis represents the total interfacial polarization resistance (R_p) of the cell. As shown in Fig. 4, the cell with cathode BCF5050 has the lowest total resistance 0.58 Ω cm^2 and the lowest R_p 0.17 Ω cm^2 of all the cells mentioned above. The BCF8515 shows poor electronic conductivity while the proton-conducting ability of BCF1585 is little. The BCF5050 which prove to be the mixture of BCF1585 and BCF8515 can avoid the problems above. In the traditional cathodes, the performances of proton-conducting SOFCs are limited by the active sites for oxygen reduction at the interface between the proton-conducting electrolyte and the oxygen ion conducting cathodes. However, the BCF5050 consisting BCF1585 and BCF8515 allows the simultaneous transport of proton, oxygen vacancy, and electronic defects, which effectively extend the "active" sites for oxygen reduction to a large extent and reduce the cathodic polarization resistance. Therefore, the cathode BCF5050 exhibits its advantage and indicates that it is the most conformable cathode for proton-conducting SOFCs in the cathodes above.

Fig. 5 shows the I–V and I–P characteristics of the cell with cathode BCF5050, separately. The cell measuring from 550 to 700 °C with humidified hydrogen ($\sim$3% H$_2$O) as the fuel has a maximum power densities of 395, 276, 192, 111 mW cm^{-2} with the OCV values of 0.986, 1.013, 1.036, 1.054 V, respectively. The performance of the cell with the novel cathode is comparable with the traditional cathodes [22,23].

Fig. 6(a) is the AC impedance spectroscopy of the cell at elevated temperatures. The R_p significantly decreases with the increase of the temperature, typically from 2.12 Ω cm^2 at 550 °C to 0.17 Ω cm^2 at 700 °C. The results indicated that the BCF5050 cathode is a good candidate for operation at or below 700 °C. Further, Fig. 6(b) shows that the cell performance is influenced by the interfacial resistances, especially at temperatures below 550 °C, where the cell performance is essentially determined by the interfacial resistances. At 550 °C, the resistance of the cell is only 0.86 Ω cm^2 while the R_p is about 2.12 Ω cm^2. These results make this type of novel cath-
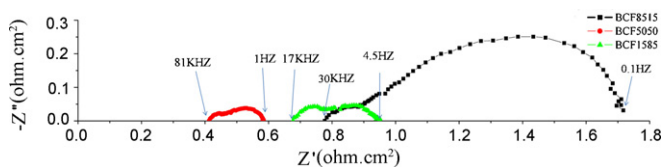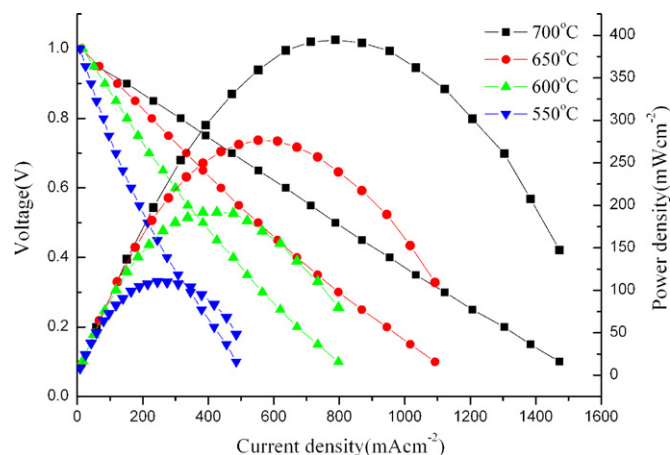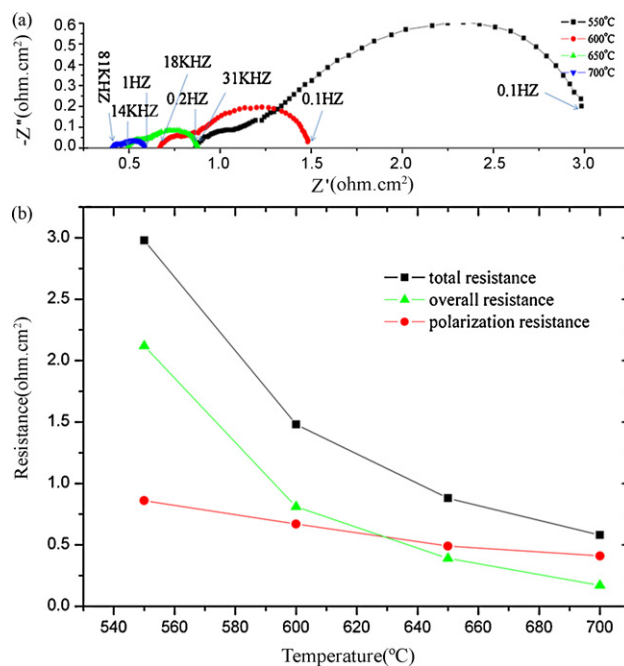
ode interesting for proton-conducting SOFCs working at elevated temperatures.

4. Conclusions

In the present study, a series of cobalt-free and low cost BaCe$_x$Fe$_{1-x}$O$_{3-\delta}$ (x = 0.15, 0.50, 0.85) materials were employed as the cathodes for proton-conducting SOFCs. Among all the cells above, the cell with cathode BCF5050 showed the highest performance which can reach a relatively high power density of 395 mW cm^{-2} at 700 °C. Under the open-circuit condition, the polarization resistance of the electrode was as low as 0.17 Ω cm^2 at 700 °C. Furthermore, the BCF5050 was a mixture of BCF1585 and BCF8515 which can be chemically and thermally compatible to the BaCeO$_3$-based electrolyte for the proton-conducting SOFCs. These results indicated that the cathode BCF5050 was a good cath-

Fig. 4. Impedance spectra of the as-prepared cells measured under open-circuit conditions at 700 °C.

ode material candidate for proton-conducting SOFCs operating at or below 700 °C.

Acknowledgements

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