Short communication

Novel cobalt-free cathode materials $BaCe_xFe_{1-x}O_{3-\delta}$ for proton-conducting solid oxide fuel cells

Zetian Tao, Lei Bi, Zhiwen Zhu, Wei Liu*

Laboratory of Advanced Functional Materials and Devices, Department of Materials Science and Engineering, University of Science and Technology of China, Jinzai Road 96, Hefei, Anhui 230026, People's Republic of China

A B S T R A C T

A series of cobalt-free and low cost $BaCe_xFe_{1-x}O_{3-\delta}$ ($x = 0.15, 0.50, 0.85$) 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 $BaCe_xFe_{1-x}O_{3-\delta}$ cathode layer, is assembled and tested from 600 to 700 °C with humidified hydrogen (~3% H_2O) 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.

© 2009 Elsevier B.V. All rights reserved.

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 $BaCe_xFe_{1-x}O_{3-\delta}$ 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

$BaCe_xFe_{1-x}O_{3-\delta}$ ($x = 0.15, 0.50, 0.85$) powders were synthesized by Pechini method. $Ba(NO_3)_2$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$ 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 $BaCe_xFe_{1-x}O_{3-\delta}$ powders. The $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY7) powders were also synthesized
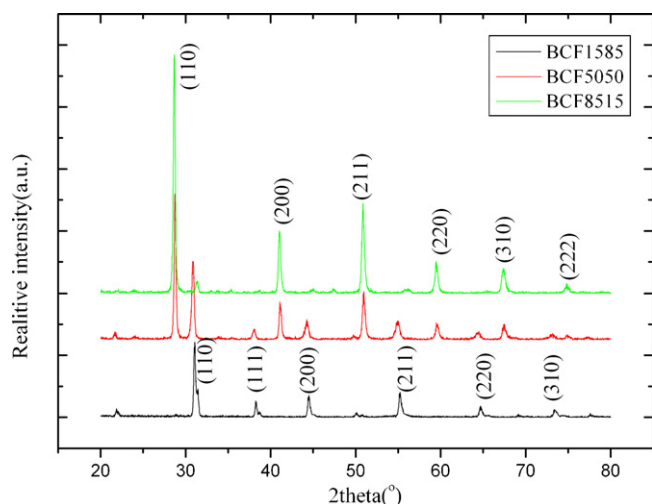
Fig. 1. X-ray diffraction patterns of (a) $BaCe_{0.15}Fe_{0.85}O_{3-\delta}$ (BCF1585), (b) $BaCe_{0.5}Fe_{0.5}O_{3-\delta}$ (BCF5050) and (c) $BaCe_{0.85}Fe_{0.15}O_{3-\delta}$ (BCF8515).

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 (∼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-
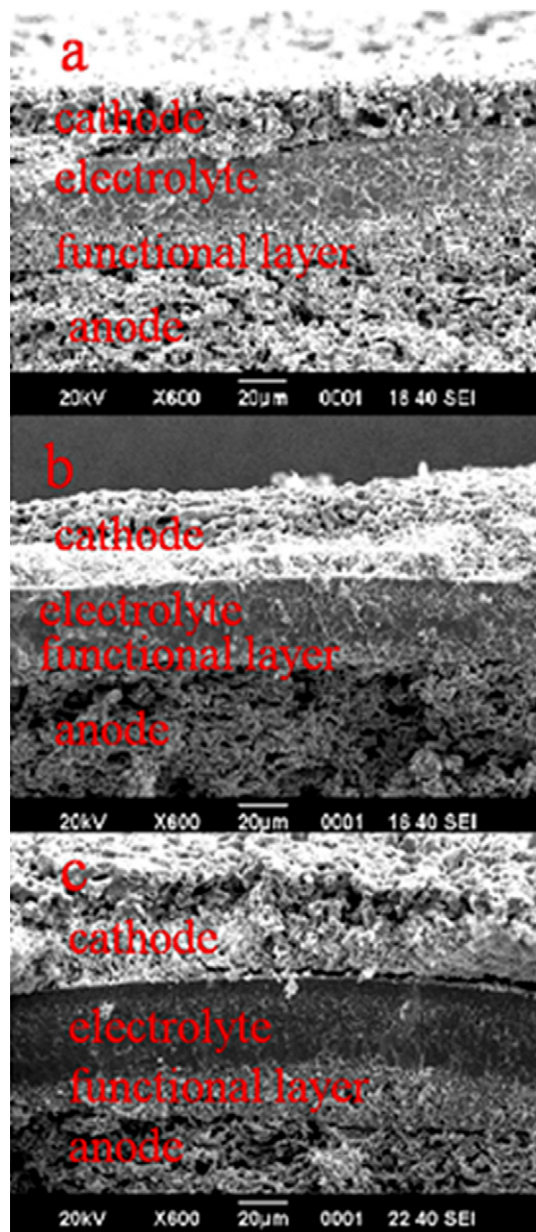

Fig. 2. Cross-section views of the different cells without surface modification after fuel cell testing (a) $BaCe_{0.15}Fe_{0.85}O_{3-\delta}$ (BCF1585), (b) $BaCe_{0.5}Fe_{0.5}O_{3-\delta}$ (BCF5050) and (c) $BaCe_{0.85}Fe_{0.15}O_{3-\delta}$ (BCF8515).

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 (∼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