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Short communication

Electrochemical characterization of $YBaCo_3ZnO_{7+\delta}$ as a stable proton-conducting SOFCs cathode

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Abstract

$YBaCo_3ZnO_{7+\delta}$ (YBCZ) was synthesized and used as the cathode materials for proton-conducting SOFCs successfully. 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 an YBCZ cathode layer, was assembled and tested from 600 to 700 °C with humidified hydrogen (~3% H_2O) as the fuel and static air as the oxidant. An open-circuit potential of 0.98 V and a maximum power density of 307 mW cm^{-2} at 700 °C were obtained. The measured results indicated that YBCZ has the potential to be a cathode material for proton-conducting SOFCs.

Keywords: Proton-conducting SOFCs; YBCZ; Doped barium cerate; Co-pressing way

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted worldwide attention because of the demand for clean, secure, and renewable energy [1,2]. However, the costly 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 their 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) which exhibits 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 remains a challenge because the performance of low-temperature SOFCs is sensitively affected by the cathode materials. The perovskite structures (ABO3) are current performing cathodes, such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ [8], $SrCo_{0.9}Sb_{0.1}O_{3-\delta}$ [9] and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [1]. Nevertheless, the thermal expansion coefficients of these materials are mismatched with the electrolyte material BZCY7 [10]. Recently, in order to solve this problem, some new cathode materials have been applied such as $BaCe_{0.5}Bi_{0.5}O_{3-\delta}$ [11] and $BaCe_xFe_{1-x}O_{3-\delta}$ [12]. Layered cobalt oxide materials of the family $YBaCo_4O_{7+\delta}$ are also be used as electrode materials in SOFCs [13–18].

In present work, we synthesize the YBCZ by a modified Pechini method and examined the exhibition of a proton-conducting SOFC used YBCZ as cathode with BZCY7 electrolyte.

2. Experimental

YBCZ powders were synthesized by Pechini method. $Y(NO_3)_3{\cdot}6H_2O$, $Ba(NO_3)_2$, $Co(NO_3)_3{\cdot}6H_2O$ and ZnO 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

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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 YBCZ powders. The $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY7) powders were also synthesized 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, which was uniformly distributed on to the anode substrate, co-pressed at 300 MPa and sintered subsequently at 1350 °C for 5 h to denitrify the BZCY7 membrane. A mixture of BZCY7 and fine YBCZ powders were mixed thoroughly with a 10 wt% ethylcellulose–terpineol binder to prepare the cathode slurry. The cathode slurry were painted on the BZCY7 electrolyte membrane 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, 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 (IT8511). Resistances of the cell under open circuit condition were measured by CHI604B (0.1 Hz to 100 kHz). The phase of the obtained thin membrane electrolyte was examined with X-ray diffractometer (XRD) using Cu Kα 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 pattern of the YBCZ powders. The YBCZ powders which are calcined at 1000 °C for 3 h have a pure structure of hexagonal symmetry (space group *P*63*mc*) without any formation of other phases.

Fig. 2 shows the cross-sectional view of the single cell after testing. As can be seen from Fig. 2, there are four layers which are cathode, electrolyte, functional layer and anode, respectively. The thicknesses of electrolyte, cathode and functional layer are about 15 μm, 20 μm, 10 μm, respectively. From the image, we can see that the electrolyte is dense without any obvious pores which may leak the gas and lower the OCV of the measured cell.

Fig. 3 presents the *I–V* and *I–P* characteristics of the as-prepared cell measuring from 600 to 700 °C with humidified hydrogen (~3% H_2O) as the fuel. The maximum power densities of 307, 211 and 143 mW cm^{-2} with the OCV values of 0.978, 0.987 and 0.998 V were obtained at 700, 650 and 600 °C, respectively. The performance of the cell with YBCZ as the cathode material is not very high but can compare with other composite cathodes which are reported recently under almost the same condition [19,20]. The appropriate thermal expansion coefficients with the electricity performance can make YBCZ a potential cathode material for proton-conducting SOFCs.

The resistance of the cell under open circuit conditions, which was investigated by AC impedance spectroscopy, is shown in Fig. 4(a). 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 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(a), the R_p decreases with the increase of the temperature, typically

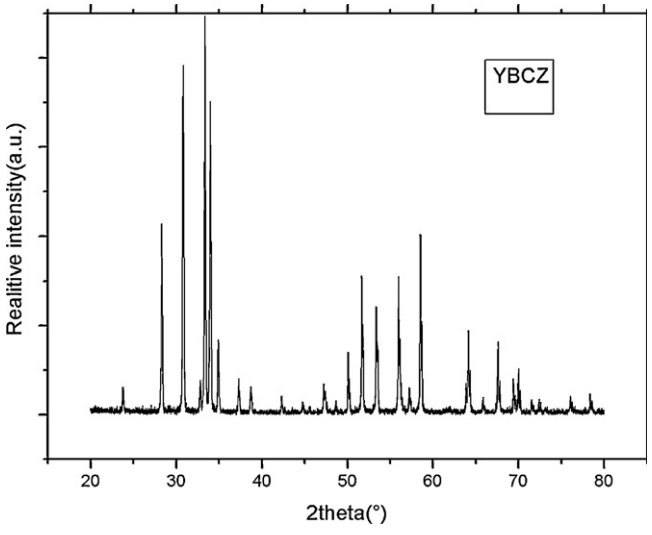

Fig. 1. X-ray diffraction patterns of $YBaCo_3ZnO_{7+\delta}$ (YBCZ) powders.

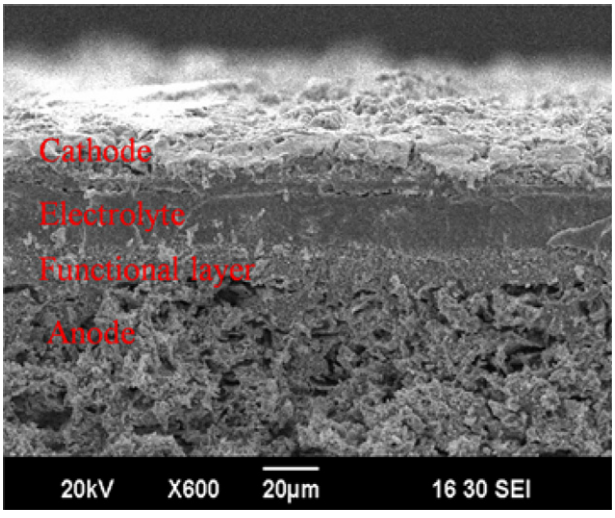

Fig. 2. Cross-section views of the cell without surface modification after fuel cell testing.

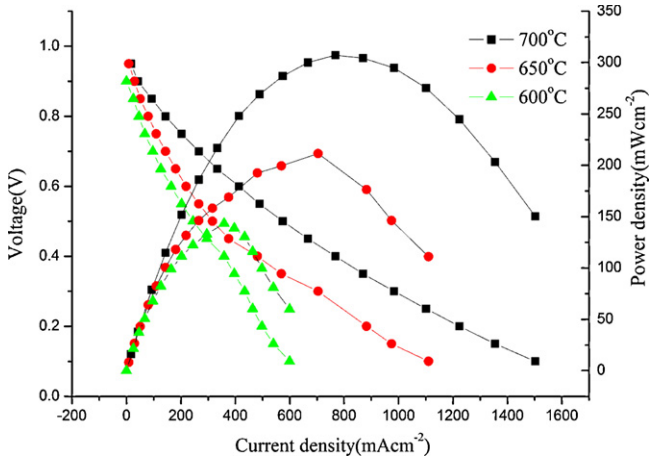

Fig. 3. Performance of a single cell under wet hydrogen atmosphere at different temperatures.

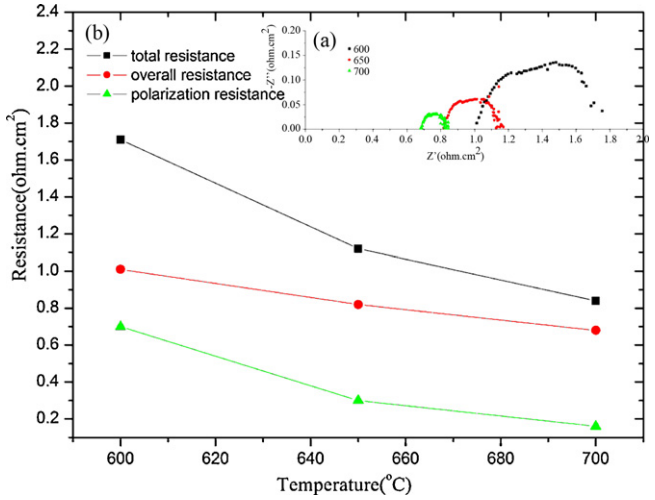

Fig. 4. (a) Impedance spectra and (b) the interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra of the as-prepared cell measured under open-circuit conditions at different temperatures.

from 0.7 Ω cm^2 at 600 °C to 0.16 Ω cm^2 at 700 °C. The R_p is lower than $BaCe_{0.5}Bi_{0.5}O_{3-\delta}$ [11] and can compare with $BaCe_xFe_{1-x}O_{3-\delta}$ [12]. The results indicate that the YBCZ can be a good candidate cathode when lower the overall resistance of the assembled cell. Further, Fig. 4(b) shows that the cell performance is determined by overall resistance but influenced by the polarization resistances, especially at temperatures below 600 °C. The overall resistances increase very little with the temperature while the R_p increase obviously.

4. Conclusions

In the present work, YBCZ powders were synthesized by Pechini method and the XRD patterns indicated that this material had a structure of hexagonal symmetry. The YBCZ was employed as the cathode material for the proton-conducting SOFCs. The cell with this cathode could reach a maximum power density of 307 mW cm^{-2} and a low polarization resistance of 0.16 Ω cm^2 at 700 °C. Considering the thermal expansion coefficient of YBCZ in the references, we thought YBCZ can be well matched with the electrolyte and may be a candidate cathode in future study.

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