A novel $\text{BaCe}_{0.5}\text{Fe}_{0.3}\text{Bi}_{0.2}\text{O}_{3-\delta}$ perovskite-type cathode for proton-conducting solid oxide fuel cells

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Abstract

A perovskite-type $\text{BaCe}_{0.5}\text{Fe}_{0.3}\text{Bi}_{0.2}\text{O}_{3-\delta}$ (BCFB) was employed as a novel cathode material for proton-conducting solid oxide fuel cells (SOFCs). The single cells with the structure of $\text{NiO-BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY7) anode substrate| NiO-BZCY7 anode functional layer|BZCY7 electrolyte membrane|BCFB cathode layer were fabricated by a dry-pressing method and investigated from 550 to 700°C with humidified hydrogen (~3% H_2O) as the fuel and the static air as the oxidant. The low interfacial polarization resistance of $0.098\ \Omega\text{cm}^2$ and the maximum power density of $736\ \text{mWcm}^{-2}$ are achieved at 700 °C. The excellent electrochemical performance indicates that BCFB may be a promising cathode material for proton-conducting SOFCs.

Keywords: Proton-conducting SOFCs, Doped barium cerate, Solid oxide fuel cells, Perovskite structure

1. Introduction

During the past several years, solid oxide fuel cells (SOFCs) have been paid great attention due to the relatively high efficiency and the demand for clean energy [1, 2]. Unfortunately, there are still certain limitations when it comes to the commercial applications such as expensive system, high operating temperature, poor stability and easily sulfur-poisoned in the long time run [3, 4]. Reducing the working temperature to intermediate/lower temperatures is the urgent demand for board commercialization, which can benefit both fabrication and stability [5]. Proton-conducting SOFCs show lower activation energy compared with oxide-ion conductors, which were considered to have the potential for outputting high performance in the reducing temperatures [6-8]. Among developed proton-conducting materials, $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY7) [9] that exhibits both sufficient proton conductivity and good stability under the condition of the SOFCs operation is one of the most popular electrolyte material.

It is generally recognized that the cathode materials are of great importance for proton-conducting SOFCs since they sensitively affect the performance of fuel cells. Many cobalt-containing perovskite materials have been used as the cathodes to optimize the SOFCs, such as $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{2-\delta}$ [10-12], $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ [13-15] and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ [16]. Even though some of them have achieved high power density in the operating SOFCs, the apparent problems such as high thermal expansion coefficients (TECs) and high cost remain unsolved [17, 18]. Clearly, developing high-performance cobalt-free cathodes are significant for

SOFCs. Substituting the cobalt by iron can improve the compatibility between the cathode and the electrolyte as well as the cathode stability, even though it might lead to low oxygen reduction reaction (ORR) [19, 20]. Bismuth is introduced as another element to improve the conductivity and ORR [21-23]. As we know, BaCeO_3 based materials are practicable electrolytes for SOFCs [15, 24]. Considering the mixed conducting properties of doped BaCeO_3 materials, they can also be used as cathodes at intermediate temperature [22, 25]. Some single element doped materials based on the BaCeO_3 have been applied. For instance, Tao et al. [22, 26] have reported bismuth-doped BaCeO_3 and iron-doped BaCeO_3 cathodes, which achieves a peak density of 321 mWcm^{-2} and 395 mWcm^{-2} at 700°C , respectively. Also, Tao et al. reported a Pr-doped barium cerate- $\text{BaCe}_{0.6}\text{Pr}_{0.4}\text{O}_{3-\delta}$, which obtained an open-circuit potential of 0.99 V and a maximum power density of 378 mWcm^{-2} at 700°C [27]. Besides, Zuo et al. introduced Pr and Y co-doped BaCeO_3 ($\text{BaCe}_{0.4}\text{Pr}_{0.4}\text{Y}_{0.2}\text{O}_{3-\delta}$) as the cathode material for low-temperature solid oxide fuel cells with a peak power density of 270 mWcm^{-2} at 700°C [9]. However, the performance of the above cathode materials is difficult to meet the demands for a wide range of applications, so further investigation on the property of double elements co-doped BaCeO_3 is needed.

In this work, we report a BaCeO_3 -based cathode co-doped by iron and bismuth ($\text{BaCe}_{0.5}\text{Fe}_{0.3}\text{Bi}_{0.2}\text{O}_{3-\delta}$) for the first time, which was synthesized by the citric acid-nitrate gel combustion method. Phase structure, microstructure, electrochemical performance and short-term stability were characterized and investigated.

2. Experimental

2.1 Material preparation and powder synthesis

BaCe_{0.5}Fe_{0.3}Bi_{0.2}O_{3-δ} (BCFB) powders were synthesized by a citric acid-nitrate gel combustion method. Ba(NO₃)₂, Ce(NO₃)₃·6H₂O, Bi(NO₃)₃·5H₂O and Fe(NO₃)₃·9H₂O were dissolved at the stoichiometric ratio and citric acid was then added as the complexation agent. Molar ratio of citric acid/metal ion was set at 1.5. The solution was heated under stirring to flame, resulting in ash which was calcined at 1000°C for 3 h to form BCFB powders. The BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} (BZCY7) powders used as the electrolyte and the NiO-BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-δ} (NiO-BZCY7) composite powders used as both anode substrate and anode functional layer were also synthesized by the citric acid-nitrate gel combustion method. Ba(NO₃)₂, Ce(NO₃)₃·6H₂O, Y₂O₃, Zr(NO₃)₄·5H₂O and Ni(NO₃)₂·6(H₂O) were used as the raw materials. The as-prepared powders were calcined at 1000°C for 3 h to form BZCY7 and NiO-BZCY7. To get sufficient porosity for the anode layer, 20% starch was added to the NiO-BZCY7 powders. The anode supported half cells consisting of NiO-BZCY7 anode, NiO-BZCY7 functional layer, and the BZCY7 electrolyte were fabricated by die-pressing and co-fired at 1400 °C for 5 h. The BCFB powders were grinded thoroughly with the 6 wt.% ethylcellulose-terpineol binder to form the cathode slurry, which was painted on the electrolyte membrane and co-fired at 1000°C for 3h to form a single cell with the effective cathode area of 0.195 cm².

2.2 Characterization and electrochemical measurements

The phase of the obtained powders were examined by X-ray diffractometer (XRD) with Cu K α radiation. The microstructure of the assembled cell was investigated by

Scanning electron microscope (SEM; JEOL JSM-6700F). Single cell was tested in the home-made testing system from 550 to 700°C with humidified H₂ (~3% H₂O) as the fuel at a flow rate of 30 mL min⁻¹ and the cathode was exposed to ambient air. The I-V experimental data of the cells were measured by DC Electronic Load (IT8511), and an impedance analyzer (CHI604B) was used to measure the electrochemical impedance spectra of the cell under open circuit conditions.

3. Result and Discussion

Fig.1 shows the XRD patterns of BCFB, BZCY7 and NiO-BZCY7. Both of BZCY7 and NiO-BZCY7 exhibit a pure orthorhombic perovskite structure. As for BCFB, except for the peaks corresponding to the doped BaCeO₃, some minor peaks like (110), (200) and (211) were also found which belong to the BaFeO₃-based cubic phase and it is not detrimental to the cathode performance [28].

The cross-sectional view of single cell after testing is shown in Fig 2a-c, as can be seen, the electrolyte is about 25 μm in thickness, and adhered very well to the anode functional layer and the cathode with no cracks or delamination, which is helpful to output high performance of single cell. Fig 2d shows the surface of the electrolyte. It can be seen that the electrolyte is quite dense without pores or cracks.

The I-V and I-P curves of the as-prepared single cell measured from 550 to 700 °C with humidified hydrogen as the fuel are presented in the Fig. 3. The open-circuit voltages (OCVs) of the cell achieved 0.988, 1.014, 1.034 and 1.052 V at 700, 650, 600 and 550°C, respectively, which indicates that the electrolyte is quite

dense and it consists with the SEM figures. The corresponding maximum power densities are 736, 551, 362 and 203 mWcm^{-2} , respectively. The cell performance is superior to the cells with $\text{BaCe}_{0.5}\text{Bi}_{0.5}\text{O}_{3-\delta}$ (321mWcm^{-2} at 700°C) [22], $\text{BaCe}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ (395mWcm^{-2} at 700°C) [26] and $\text{BaCe}_{0.6}\text{Pr}_{0.4}\text{O}_{3-\delta}$ (378mWcm^{-2} at 700°C) [27], and even slightly higher than the cells with cobalt-containing cathodes, such as, SSC-SDC (665mWcm^{-2} at 700°C) [29] and SSC-BZCY (725mWcm^{-2} at 700°C) [30], showing $\text{BaCe}_{0.5}\text{Fe}_{0.3}\text{Bi}_{0.2}\text{O}_{3-\delta}$ is a good cathode material candidate for proton-conducting SOFCs.

Fig.4a shows the typical electrochemical impedance spectra (EIS) curves of the single cell with BCFB cathode fired at 1000°C . The intercept with the real axis at high frequencies represents the resistance of electrolyte, whereas the difference between the high-frequency and low-frequency intercepts with the real axis represents the sum of the electrode polarization resistances of the cell. The total cell resistances together with the polarization resistances and the electrolyte resistance as a function of the temperature were shown in Fig.4b. As the temperature decreases, both the polarization and electrolyte resistances increase, while the polarization resistances increase more rapidly, typically from $0.098\Omega\text{cm}^2$ at 700°C to $1.190\Omega\text{cm}^2$ at 550°C . It should be noted that the polarization resistances are extremely lower than that using $\text{BaCe}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ ($0.25\Omega\text{cm}^2$ at 700°C) for proton-conducting SOFCs [22], demonstrated that introducing Bi into $\text{BaCe}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ can effectively enhance the ORR which is consistent with previously reported works. Also we can see that the electrolyte resistance dominates the total cell resistance at 650°C and 700°C , whereas

the polarization resistances determine the cell performance below 600°C within the range of temperatures under investigation.

To clarify the stability of the as-fabricated fuel cell, the short-term stability of the single cell power output was also tested at 600°C under the cell voltage of 0.7 V. Fig.5 shows the correlation curve between the power density and time. As can be seen, the power density is around 300 mWcm⁻² and no obvious degradation was observed during the period of testing, indicating that BCFB cathode materials is chemically stable against water vapor in ambient air and it may be an alternative cathode material for IT-SOFCs.

4. Conclusions

In this work, a new cobalt-free cathode material BCFB was developed for SOFCs with proton-conducting electrolyte. With a structure of NiO-BZCY7|BZCY7|BCFB, the single cell generated a maximum power density of 736, 551, 362 and 203 mWcm⁻² at 700, 650, 600 and 550°C, respectively. The polarization resistance of the electrodes was as low as 0.098Ωcm² at 700 °C. Short-term stability of the cell has been evaluated, which shows that the cell is quite stable at 600°C. These results indicate that the BCFB may be a good cathode material candidate for proton-conducting SOFCs.

Acknowledgments

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Captions:

Figure 1 XRD patterns of NiO-BZCY7, BZCY7, $\text{BaCe}_{0.5}\text{Fe}_{0.3}\text{Bi}_{0.2}\text{O}_{3-\delta}$ power fired at

1000 °C for 3 h.

Figure 2 The cross-sectional morphology of the cells and the surface of the electrolyte after testing.(a)(b)(c) cross-sectional view of the cells (d) surface of the electrolyte

Figure 3 I-V and I-P curves of single cell measured under wet hydrogen atmosphere at different temperatures.

Figure 4 (a)EIS of the cells measured under open circuit conditions at different temperatures.(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.

Figure5 Short-term stability of the single cell with BCFB as the cathode, and $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ as the electrolyte tested under cell voltage of 0.7 V at 600°C.

Fig. 1

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