A novel single phase cathode material for a proton-conducting SOFC

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A B S T R A C T
A novel single phase BaCe0.5Bi0.5O3-δ (BCB) was employed as a cathode material for a proton-conducting solid oxide fuel cell (SOFC). The single cell, consisting of a BaZr0.1Ce0.7Y0.2O3-δ (BZCY7)-NiO anode substrate, a BZCY7 anode functional layer, a BZCY7 electrolyte membrane and a BCB cathode layer, was assembled and tested from 600 to 700 °C with humidified hydrogen (~3% H2O) as the fuel and the static air as the oxidant. An open-circuit potential of 0.96 V and a maximum power density of 321 mW cm−2 were obtained for the single cell. A relatively low interfacial polarization resistance of 0.28Ω cm2 at 700 °C indicated that the BCB was a promising cathode material 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, BaZr0.1Ce0.7Y0.2O3-δ (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 simple perovskite-type mixed ionic (oxygen ion)- electronic conductors such as Ba0.5Pr0.5CoO3, Ba0.5Sr0.5Co0.8Fe0.2O3 [8,9], have been extensively studied as possible cathode materials. Nevertheless, the practical applications of the proton-conducting SOFCs are limited while using these materials as cathode, most likely because of the limited active sites for oxygen reduction at the interface between the proton-conducting electrolyte and the oxygen ion conducting cathodes. In order to mitigate the effect, composite cathode consisting the cathode and electrolyte material is developed [10]. The composite cathode 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. Recently, electrochemical performances of Pr and Gd doped barium cerate and Ba(Ce1-xBix)O3(x = 0.0–0.5) have been reported [11–15]. These mixed-conducting doped barium cerates exhibit good chemically compatibility with the barium cerate-based electrolytes, showing great potential to be cathode materials for proton-conducting SOFCs. In this work, the single phase perovskite sample of BaCe0.5Bi0.5O3-δ, synthesized by a modified Pechini method was examined as a new cathode for a proton-conducting SOFC based on a BZCY7 electrolyte.

2. Experimental
BaCe0.5Bi0.5O3-δ (BCB) powders were synthesized by Pechini method. Ba(NO3)2, Ce(NO3)3·6H2O and Bi(NO3)3·5H2O 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 BCB powders. The BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_3$ (BZCY7) powders were also synthesized by Pechini method with the raw material Ba(NO$_3$)$_2$·9H$_2$O, Ce(NO$_3$)$_3$·6H$_2$O, Zr(NO$_3$)$_4$·4H$_2$O 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, calcined at 1000 °C for 3 h to form a pure perovskite oxide, was uniformly distributed on to anode substrate, co-pressed at 300 MPa and sintered subsequently at 1350 °C for 5 h to densify the BZCY7 membrane. Fine BCB powder was mixed thoroughly with a 10 wt% ethylcellulose–terpineol binder to prepare cathode slurry, which was painted on the BZCY7 electrolyte membrane, and fired at 1000 °C for 3 h in air to form a single cell. The electrode active area was 0.237 cm$^2$. Ag paste was applied as a current collector for both anode and cathode. Electrochemical measurements of the fuel cell were performed in an Al$_2$O$_3$ test housing placed inside a furnace. Humidified hydrogen (≈3% H$_2$O) 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 fuel. Cell performance was measured with DC Electronic Load (IT8511). Resistances of the cell under open-circuit condition were measured by CHI604C (0.1 Hz–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

As shown in Fig. 1a, the as-prepared powder of BCB exhibits a simple perovskite phase structure, without the formation of other phases. Fig. 1 also presents the XRD spectra of anode/electrolyte bi-layer sintered at 1350 °C for 5 h. It could be clearly seen that there were only peaks corresponding to BaZr$_{0.1}$Ce$_{0.7}$Y$_{0.2}$O$_3$ (BZCY7) in the electrolyte membrane (Fig. 1b) and to NiO and BZCY7 in the anode substrate (Fig. 1c), which give no evidence for the formation of other substance.

Fig. 2a shows the cross-sectional view of the single cell after testing. As can be seen, the BZCY7 electrolyte is about 25 μm in thickness, and adhered 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. 2b shows a morphology of the electrolyte. It can be seen that the electrolyte is quite dense and the size of the crystal is about 1–2 μm.

Fig. 3 presents the $I$–$V$ and $I$–$P$ characteristics of the as-prepared cell measuring from 600–700 °C with humidified hydrogen (≈3% H$_2$O) as the fuel. The maximum power densities of 321, 218 and 127 mW cm$^{-2}$ with the OCV values of 0.956, 0.971 and 0.989 V are obtained at 700, 650 and 600 °C, respectively. It can be seen that the performance of the cell with the single phase proton-conducting cathode can compare with other composite cathodes.
which are reported recently under almost the same condition [16,17]. The resistance of the cell under open-circuit conditions, which was investigated by AC impedance spectroscopy, is shown in Fig. 4a. 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 [18]. 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 the Fig. 4a, the $R_p$ significantly decreases with the increase of the temperature, typically from 1.60 $\Omega \text{cm}^2$ at 600 °C to 0.28 $\Omega \text{cm}^2$ at 700 °C. More important, the BCB was a protonic material with the substitution of Bi for Ce in the BaCeO$_3$, which can be chemically and thermally compatible to the BaCeO$_3$-based electrolyte for the proton-conducting SOFCs. These results indicated that the cathode BCB was a good cathode material candidate for proton-conducting SOFCs operating at or below 700 °C.

### 4. Conclusions

In this study, a single phase BCB, instead of the traditional dual phase composite material, was employed as a cathode for a proton-conducting SOFC with a structure of NiO–BZCY7/BZCY7/BCB. Without an addition of the electrolyte powder for the cathode, a single cell generated a maximum power density of 321 mW cm$^{-2}$ at 700 °C, which can compare with the proton-conducting SOFCs with composite cathode materials. The polarization resistance of the electrode was as low as 0.28 $\Omega \text{cm}^2$ at 700 °C. More important, the BCB was a protonic material with the substitution of Bi for Ce in the BaCeO$_3$, which can be chemically and thermally compatible to the BaCeO$_3$-based electrolyte for the proton-conducting SOFCs. These results indicated that the cathode BCB was a good cathode material candidate for proton-conducting SOFCs operating at or below 700 °C.

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