



Short communication

A stable BaCeO₃-based proton conductor for intermediate-temperature solid oxide fuel cells

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ABSTRACT

BaCe_{1-x}Ga_xO_{3-δ} ($x = 0.1, 0.2$) and BaCe_{0.8}Y_{0.2}O₃ (BCY) powders are successfully synthesized by a solid-state reaction method. According to thermal gravity analysis in the atmosphere of CO₂, BaCe_{0.9}Ga_{0.1}O_{3-δ} (BCG10) and BaCe_{0.8}Ga_{0.2}O_{3-δ} (BCG20) are quite stable while BaCeO₃ shows obvious reaction and decomposes into CeO₂ and BaCO₃. A fuel cell with electrolyte of BaCe_{0.8}Ga_{0.2}O_{3-δ} is prepared by a suspension spray combining with in situ sintering method 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 0.99 V and a maximum power density of 236 mW cm⁻² are obtained for the single cell with an interface resistance 0.32 Ω cm² at 700 °C.

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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 [3,4]. Since the proton-conducting SOFCs are found by Iwahara et al. [5,6], the advantages of the proton-conducting SOFCs such as low activation energy [7] and high energy efficiency [8] have attracted more and more attention.

Many ABO₃-type perovskites, particularly the rare earth doped BaCeO₃ materials which exhibit the highest protonic conductivities are used as the electrolyte for the proton-conducting SOFCs [9–13]. However, high proton conductivity and stability seem to be antagonistic, as investigated by Kreuer [14] and Norby and Larring [15]. Acceptor-doped BaCeO₃ shows highest protonic conductivity among the high temperature proton-conducting oxides. As a drawback, BaCeO₃ materials show poor chemical stability in the presence of H₂O and CO₂ containing atmosphere. Now the most wide approach to increase the chemical stability of doped BaCeO₃ is to partially replace Ce by Zr, at the cost of reducing protonic conductivity [16]. On the other hand, doped-BaZrO₃ materials show high

bulk proton conductivity (10⁻² S cm⁻¹ at 400 °C) and high chemical stability, but the high grain boundary resistance of BaZrO₃ is the main obstruction for its practical applications [17,18]. In order to improve the BaZrO₃ electrical properties, reducing the grain boundary resistance by increasing the sintering temperatures have been devoted many investigations [18].

Up to now, more and more attention focus on finding a new doped element for BaCeO₃ which can not only improve the chemical stability but also hold a considerable conductivity [13,19]. Lei Bi et al. [19] offer a new approach to solve the antagonistic between the stability and the conductivity which can be improved by high doping level by using the trivalent element indium which possesses high electronegativity to dope BaCeO₃. In this study, we present a strategy of substituting Ga whose electronegativity is even higher for In to increase the chemical stability of BaCeO₃ against H₂O and CO₂. BaCe_{1-x}Ga_xO_{3-δ} ($x = 0.1, 0.2$) powders were synthesized by a solid-state reaction method. The chemical stability and conductivity were investigated. A suspension spray combining with in situ sintering method is utilized to prepare a fuel cell with BaCe_{0.8}Ga_{0.2}O_{3-δ} electrolyte [20]. In addition, the electrochemical properties of the BCTY10-based fuel cell are studied.

2. Experimental

The BaCe_{1-x}Ga_xO_{3-δ} ($x = 0.1, 0.2$) powders were prepared by a solid-state reaction method with the raw materials BaCO₃, CeO₂ and Ga₂O₃. The materials above in the stoichiometric ratios of

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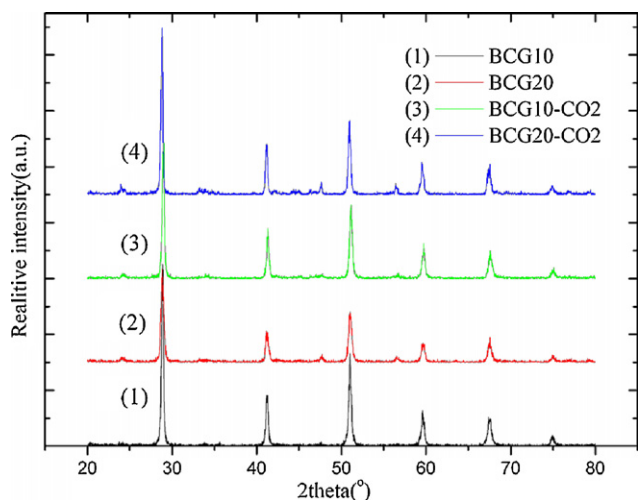


Fig. 1. X-ray diffraction patterns of $\text{BaCe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ($x=0.1, 0.2$) and the powders disposed by the 3% CO_2 at 700°C for 3 h.

$\text{BaCe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ($x=0.1, 0.2$) were ball-milled in ethanol for 24 h. The resultant mixtures were then dried and fired at 1300°C for 5 h. The phase of the obtained thin membrane electrolyte was examined with X-ray diffractometer (XRD) using $\text{CuK}\alpha$ radiation. Thermal gravity analysis (TGA) tested the chemical stability of the powders prepared above in the CO_2 (3%) which were carried out on a thermal gravity analyzer (PCI-III) from 400 to 700°C . At 400°C , the temperature was held until the gravity of the sample did not change and the temperature at 700°C was held for 3 h. The flow rate of CO_2 was 20 ml min^{-1} . XRD tests were used to detect the phase changes of the powder samples after TGA tests.

These pre-BCG20 powders were well mixed with NiO in a weight ratio of 40:60. To form sufficient porosity in the anode, 20 wt.% starch was added as the pore former. The mixed powders were pressed under 250 MPa with 15 mm in diameter and 0.5 mm in thickness and subsequently fired at 700°C for 3 h as anode substrates. The BCG20 membrane was fabricated on the anode substrate by an in situ reaction [20]. The relatively stable starting materials of BaCO_3 , CeO_2 and Ga_2O_3 were mixed in the stoichiometric ratio and dispersed into ethanol by ball-milling for 24 h to form a suspension. The suitable organic additives (triethanolamine, benzyl butyl phthalate and polyvinyl butyral) were added into the suspension, which were employed to make the metal oxides and

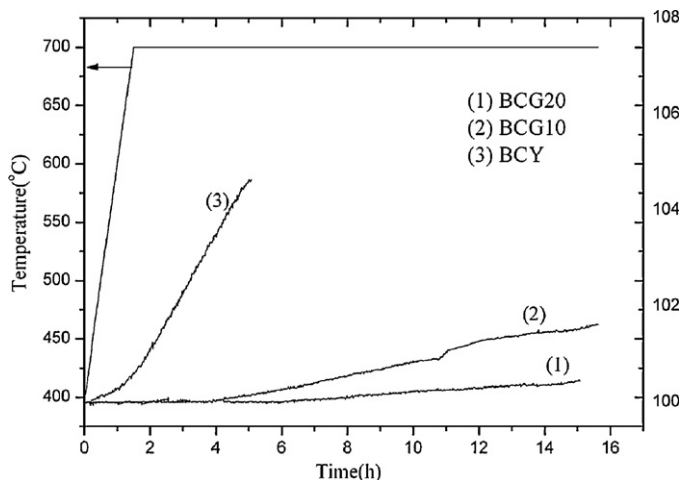


Fig. 2. TGA spectra of $\text{BaCe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ($x=0.1, 0.2$) and $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ powders in CO_2 .

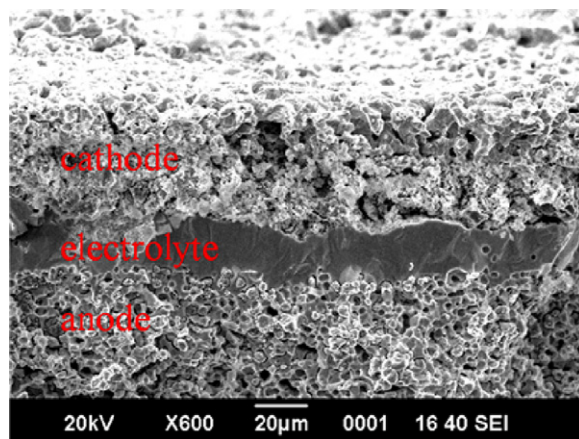


Fig. 3. Cross-section views of the cell without surface modification after fuel cell testing.

the carbonate well distribute in the ethanol. The solid ratio of the starting materials is 5 wt.%. The suspension was directly deposited on the anode substrate. Then the bi-layers of green electrolyte and anode were co-fired at 1450°C in the air for 5 h. A mixture of $\text{LaSr}_3\text{Co}_{1.5}\text{Fe}_{1.5}\text{O}_{10-\delta}$ (LSCF) and $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY7) was printed on the electrolyte of the half-cell and then fired at 1000°C for 3 h to form a porous cathode. The electrode active area was 0.237 cm^2 . Ag paste was applied on the electrode as a current collector. 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 (IT8511). Resistances of the cell under open-circuit condition were measured by CHI604B (0.1 Hz to 100 KHz). 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. 1, BCG10 and BCG20 both exhibit a simple perovskite phase structure, without the formation of other phases. In order to investigate the chemical stability, the powders are exposed to 3% CO_2 at 700°C for 3 h. As expected, the XRD patterns in Fig. 1 remain unchanged after exposure to CO_2 , demonstrating that the

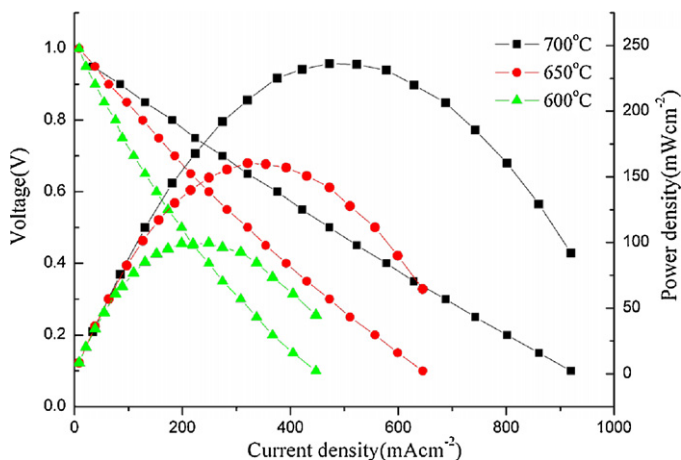


Fig. 4. Performance of a single cell under wet hydrogen atmosphere at different temperatures.

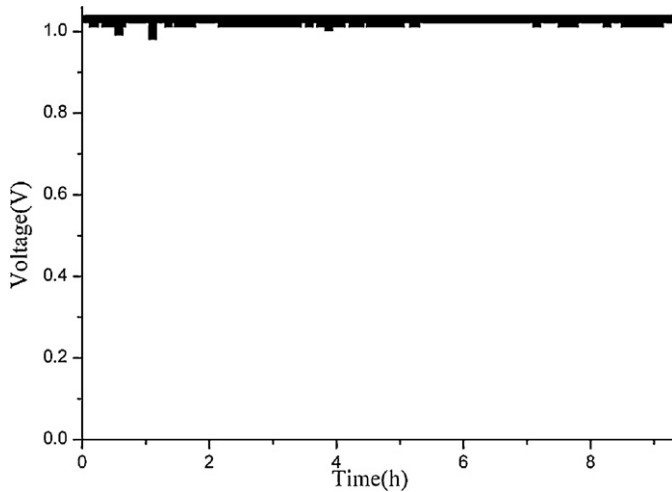
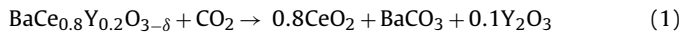


Fig. 5. Short-term performance of the cell.

BCG10 and BCG20 powders are stable in an atmosphere containing 3% CO₂.

Fig. 2 shows TGA spectra of the powder samples prepared above. As shown in the figure, the weight of BCG10 and BCG20 powders in 3% CO₂ increase less than 2% at the measuring temperature for more than 10 h while the weight of BCY powders increases rapidly with the increase of temperature. This implies that the BCY is unstable in the CO₂ atmosphere which can react into BaCO₃, CeO₂, and Y₂O₃ [13].



In comparison, BCG10 and BCG20 are very stable with a little increase in the weight. The essence may be that a more electronegative element Ga could increase the acidity of doped BaCeO₃ and suppress reaction (1).

Fig. 3 shows the cross-sectional view of the single cell after testing. As can be seen, the BCG20 electrolyte is about 20 μm in thickness, and adhered very well to the anode functional layer and the cathode.

Fig. 4 presents the *I*–*V* and *I*–*P* characteristics of the as-prepared cell measuring from 600 to 700 °C with humidified hydrogen (~3% H₂O) as the fuel. The maximum power densities of 236, 160, 99 mW cm⁻² with the OCV values of 0.995, 1.019 and 1.035 V are obtained at 700, 650 and 600 °C, respectively. The single cell kept stable at the testing condition of 600 °C and shown in Fig. 5. The doping of Ga can reduce the oxygen vacancy concentration and increase the interstitial proton concentration of the ceramic oxide for the relatively high electronegativity of Ga, which make the oxide less easily react with acidic gases. Therefore, the chemical stability of the oxide in the CO₂ and H₂O containing atmosphere is improved. The oxygen vacancy concentration favors the formation of the protonic defects, as mentioned by Kreuer [14]. Therefore, the reduced oxygen vacancy concentration of the ceramic oxide is an obstacle for the formation of protonic charge carriers, which will decrease some conductivity performance. So the cell performance is a little lower than the traditional BaCeO₃-based fuel cell (~132 mW cm⁻² at 600 °C) [21]. The resistance of the cell under open-circuit conditions, was investigated by AC impedance spectroscopy, as shown in Fig. 6(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 [22]. 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. 6(b), the *R*_p significantly decreases with the increase of the temperature, typically from 2.09 Ω cm² at 600 °C to 0.32 Ω cm² at 700 °C, which is far greater than those of other well-known cathode materials for SOFCs [23] and restricted the performance of the cell. The results indicate that the development

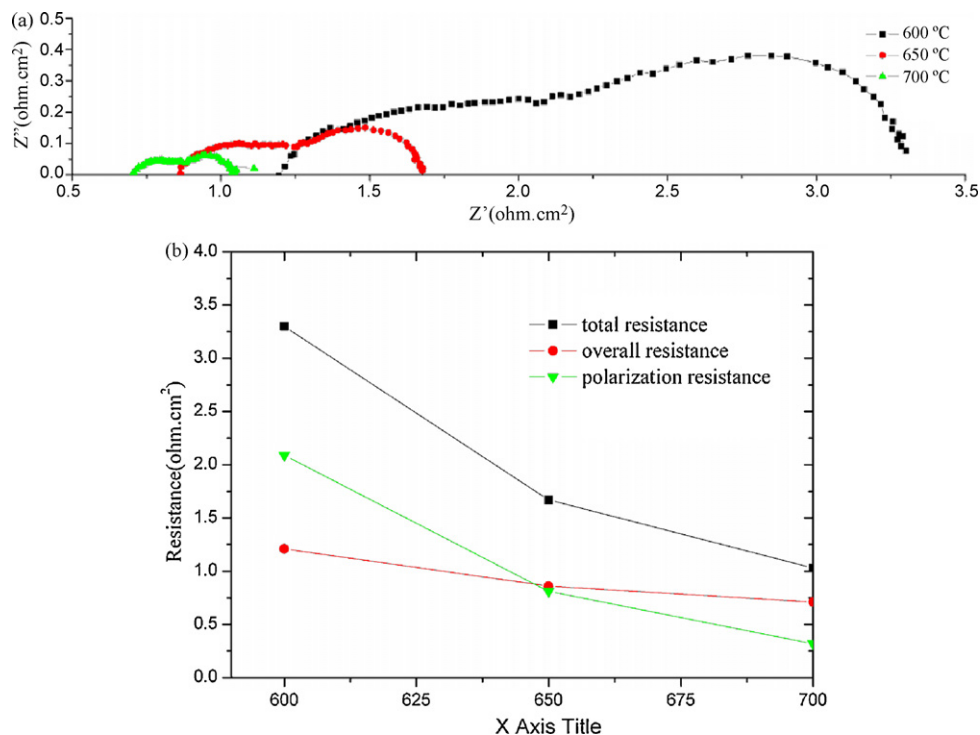


Fig. 6. (a) Impedance spectra and (b) the interfacial polarization resistances, electrolyte resistances, and total resistances determined from the impedance spectra of the as-prepared cell measured under open-circuit conditions at different temperatures.

of a suitable cathode for the BCG20 electrolyte remains a big challenge.

4. Conclusion

In this study, we synthesized $\text{BaCe}_{1-x}\text{Ga}_x\text{O}_{3-\delta}$ ($x = 0.1, 0.2$) powders by a solid-state reaction method and sintered at 1300°C for 5 h. The compounds containing Ga showed desired chemical stability in 3% CO_2 during thermal gravity analysis test from 400 to 700°C . With a mixture of LSCF and BZCY7 as cathode and a wet suspension approach, a single cell was assembled and tested. The cell generated a maximum power density of 236 mW cm^{-2} at 700°C . The overall resistance is $0.71\ \Omega\text{ cm}^2$ and the polarization resistance of the electrode was $0.32\ \Omega\text{ cm}^2$ at 700°C . The impedance study showed that the BCG20 electrolyte resistance can be comparable with that of the traditional BaCeO_3 -based electrolyte, and the short-term performance test demonstrates that the fuel cell has good stability as well as desired compatibility between electrolyte and electrodes. Therefore, the doping of Ga in BaCeO_3 provided an effective strategy comprising high proton conductivity and adequate chemical stability for BaCeO_3 -based materials.

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