First experimental investigation of Th⁴⁺ doped barium cerate as electrolytes for intermediate-temperature solid oxide fuel cells

Zetian Tao^{1, 2, 3}, Yaxing Wang^{1, 2}, Yanlong Wang^{1, 2}, Juan Diwu, Zhifang Chai, Shuao Wang^{1, 2*}

¹School for Radiological and interdisciplinary Sciences (RAD-X), Soochow University, 199 Renai Road, Suzhou 215123, China.

²Collaborative Innovation Center of Radiation Medicine of Jiangsu Higher Education Institutions, 199 Renai Road, Suzhou 215123, China.

³Key Laboratory for Advanced Technology in Environmental Protection of Jiangsu Province, Yancheng Institute of Technology, Yancheng 224001, Jiangsu, China

Abstract

Barium cerate doped with tetravalent Th is successfully synthesized by a traditional pechini method. The BaCe_{0.7}Th_{0.1}Y_{0.2}O_{3-δ} (BCT71) composites were applied to an anode supported coin single cell consisting of Ni-BCT71 anode/BCT71 electrolyte/ BCT71-La_{0.7}Sr_{0.3}FeO_{3-δ} cathode. The assembled cell is tested from 600 °C to 700°C with humidified hydrogen (~ 3% H₂O) as the fuel and the static air as the oxidant. An open-circuit potential of 0.93 V and a maximum power density of 104 mWcm⁻² are obtained for the single cell with an interface resistance of 0.98 Ω·cm² at 700 °C.

Key words: Ceramics; Nuclear materials ; Energy storage and conversion; Thin films

1. Introduction

ABO₃-type perovskites, particularly the rare earth doped BaCeO₃ materials are widely used as the electrolyte for the proton-conducting SOFCs for their high protonic conductivities [1-5]. However, a clear disadvantage for BaCeO₃ materials is their poor chemical stability in the presence of H₂O and CO₂ containing atmosphere, most likely due to the redox-active nature of Ce⁴⁺/Ce³⁺ couple. Alternative approach to increase the chemical stability of BaCeO₃ is to partially replace Ce with non-redox-active Zr⁴⁺ whereas protonic conductivity was dramatically reduced after the insertion of Zr⁴⁺ [6]. On the other hand, doped-BaZrO₃ materials show high bulk proton

* Corresponding author. Tel. +86 512 65882573; fax: +86 512 65884380
Email address: shuaowang@suda.edu.cn

conductivity (10^{-2} Scm^{-1} at 400°C) and relatively high chemical stability, but the high grain boundary resistance of BaZrO_3 is the main obstruction for its practical applications [7, 8]. In order to improve the BaZrO_3 electrical properties, many works concentrating on reducing the grain boundary resistance by increasing the sintering temperatures have been devoted [8], but high proton conductivity and stability seem to be antagonistic to achieve in this system.

Up to now, more and more attentions focus on finding a new doping element for BaCeO_3 which can not only improve the chemical stability but also hold a considerable conductivity [5, 9-10]. Lei Bi et al and Tao et al [19, 20] offer a new approach to solve the antagonistic between the stability and the conductivity by doping trivalent lanthanides into the host lattice of BaCeO_3 . However, the element of In has a high cost and Ga is poisonous. Alternatively, Th^{4+} is the largest tetravalent cation that can be found in the periodic table. The ionic radius of eight-coordinated Th^{4+} is $1.05 \text{ \AA}$, significantly larger than Ce^{4+} ($0.97 \text{ \AA}$) and Zr^{4+} ($0.84 \text{ \AA}$). In addition, similar with Zr^{4+} , tetravalent Th^{4+} is the only stable oxidation state for thorium. Therefore, in principle, by doping Th^{4+} into host lattice of BaCeO_3 , it is highly possible to facilitate the ion transportation with increased void space, and more importantly without sacrifice of the lattice stability. This hypothesis has been theoretically predicted by Cook et al [11], but the experimental work is scarce, likely stemming from radiation-induced operational limitation on the radioactive thorium materials. We notice that the half-life of α -decaying Th-232 is extremely long at 1.405×10^{10} year, thus, the radiation effect of this radioisotopes is low and easily controllable. In this study, we present the strategy of partially replace Ce^{4+} using Th^{4+} to obtain $\text{BaCe}_{0.7}\text{Th}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCT71) powders. The chemical stability and conductivity were investigated. In addition, the electrochemical properties of the BCT71-based fuel cell are studied.

2. Experimental

The BCT71 powders were prepared by Pechini method. $\text{Ba}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ 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 1200 °C for 3 h to form fine BCT71 powders. The phase of the obtained Powders was examined with X-ray diffractometer (XRD) using $\text{CuK}\alpha$ radiation.

The BCT71 pellets used for electrical conductivity measurement were sintered at 1550 °C for 5 h. The total electrical conductivity of the sintered BCT71 pellet in various atmospheres was studied via a two point method using an impedance analyzer (Zenium, Zahner, German) with an amplitude of 5 mV in the frequency range from 100 kHz to 0.1 Hz. Pt paste was brush-painted symmetrically on both sides of the sintered BCT71 pellet as current collectors and then fired at 950 °C for 1 h to remove the residual organics and attain good adhesion between the pellet and Pt layer. Wet gas was achieved after flowing through a bubbling bottle at a given temperature, and the saturation vapor pressure at the given temperature was just the water vapor partial pressure. The measurement was repeated several times at each temperature until the resistances became constant from one measurement to the next.

These pre-BCT71 powders were mixed with NiO in a weight ratio of 40:60. To form sufficient porosity in the anode, 20 wt. % starches 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. Then, loose BCT71 powders were uniformly distributed on to anode substrate, co-pressed at 300 MPa

and sintered subsequently at 1350 °C for 5 h to obtain dense BCT71 membrane. A mixture of $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$ (LSF) and BCT71 was printed on the electrolyte layer of the half-cell and then fired at 1000 °C for 3 h to form a porous cathode. The electrode active area was about 0.237 cm². Ag paste was applied on the cathode as a current collector. Electrochemical measurements of the fuel cell were performed in an Al₂O₃ test housing placed inside a furnace. Humidified hydrogen (~3% H₂O) 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 and impedance spectra were measured on Zahner Zennium electrochemical station with frequency range of 1 MHz to 0.1 Hz and AC signals amplitude of 10 mV at the set temperatures. 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 Figure 1, BCT71 exhibits a simple orthorhombic perovskite phase structure. XRD Rietveld refinement with the Jade 5.0 presents the parameters of the structure are $a=8.7467$ Å, $b=6.13632$ Å and $c=6.21754$ Å, respectively. The calcined temperature for BCT71 is 1200 °C which is higher than traditional BaCeO₃ electrolyte powders, likely originated from higher binding energy of Th-O compared to Ce-O.

The cell performance is well-related with the electrolyte resistance and it is critical to investigate the electrical conductivity of BCT71 to evaluate its potential application as a proton-conducting electrolyte for SOFCs. The electrical conductivity of the sintered dense BCT71 pellet was measured under various atmospheres using AC electrochemical impedance spectroscopy (EIS). Fig. 2 shows the typical conductivity calculated from EIS curves of the

BCT71 pellet measured in wet hydrogen and wet air from 300 to 650 °C. As the temperature increases, the conductivity increases under different atmospheres. A notable difference in the conductivity of the sample measured in wet (3% H₂O) hydrogen and wet air can be observed. Hydrogen molecules firstly dissociate; then, the protons can be attached to the oxygen ion sites forming hydroxide ions, as shown in following Eq (1).

Protons can also be incorporated into BCT71 via Eq. (2) after water vapor is introduced.

Consequently, proton concentration in BCT71 increases significantly with the help of hydrogen and water vapor. However, the conductivity is smaller than traditional proton-conducting electrolytes. This may be caused by the high calcined temperature which will lead to poor density at the same sintering temperature. The grain boundary resistance will be highly improved for the lower grain size.

In order to evaluate BCT71 as an electrolyte for SOFCs, anode-supported dense BCT71 electrolyte films are successfully fabricated by a dry-pressing technique followed by co-firing at 1350 °C for 5 h. Figure 3 shows the I - V and I - P characteristics of the cell, separately. The cell measuring with humidified hydrogen (~ 3% H₂O) as the fuel has a maximum power densities of 104, 67, 48 mW cm⁻² with the OCV values of 0.93, 0.993 and 1.052 V, respectively at 700, 650, and 600 °C. The cell performance is lower than the cell with un-doped electrolyte. It is necessary to observe the resistances of the cell to carry on further research.

In order to thoroughly investigate the performance of this cell, AC impedance spectroscopy is tested under open circuit conditions and shown in Figure 4(a) at elevated temperatures. **The**

resistances are fitted with the fitting model shown in figure 4(b) to observe the difference between model and experiment. 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 [12]. The overall electrolyte resistance of the cell from 600 to 700 °C is 1.44、1.08 and 0.72 $\Omega\cdot\text{cm}^2$, respectively. The total interfacial polarization resistance (R_p) significantly decreases with the increase of the temperature, typically from 3.64 $\Omega\cdot\text{cm}^2$ at 600 °C to 0.92 $\Omega\cdot\text{cm}^2$ at 700 °C. The ohm resistance is almost comparable with traditional electrolytes while the polarization resistance is much higher [13 , 14]. The cell performance can be highly improved by searching proper cathode to decrease the polarization resistance in future works.

Further, the chemical stability of BCT71 electrolyte film under fuel cell conditions is also investigated, as shown in Fig. 5. The OCV value may drop down correspondingly if the electrolyte film reacts with water vapor or CO_2 coming from the fuel gas and air. Herein, the OCV of the cell keep mostly stable after operating at 600 °C for about 48 h, suggesting that the BCT71 electrolyte film is not broken after operating for 48 h under fuel cell condition. The preliminary results demonstrate that BCT71 may be an appropriate electrolyte material for SOFCs.

4. Conclusion

In the present study, the cell consists of $\text{BaCe}_{0.7}\text{Th}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCT71) electrolyte was fabricated and tested. The total electrical conductivity of BCT71 is significantly dependent on the surrounding atmosphere, and achieves $5.4\times 10^{-3} \text{ S cm}^{-1}$ at 600 °C in wet H_2 . Lab-scale tri-layer cells of NiO-BCT71/BCT71/LSF were operated from 600 to 700 °C with humidified hydrogen ($\sim 3\% \text{ H}_2\text{O}$) as fuel and the static air as oxidant. At 700 °C, the single cell reached a relatively high

power density of 104 mW cm^{-2} with an OCV of 0.93 V. Under the open-circuit condition, the polarization resistance of the electrode was as low as $0.92 \Omega \text{ cm}^2$ at 700°C . In addition, the cell chemical stability was also evaluated through testing the OCV under fuel cell condition at 600°C for 48 h. In summary, these results indicated that Th doped BaCeO_3 was a potential electrolyte material and provided a new potential application of these low-activity isotopes besides nuclear fission.

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Figure 1. XRD patterns of $\text{BaCe}_{0.7}\text{Th}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BCT71) after co-fired at 1200 °C for 3h.

Figure 2. Electrical conductivity test of BCT71 pellets under wet air and wet hydrogen at different temperatures.

Figure 3. I-V, I-P curves of the single cells measured from 600 °C to 700 °C

Figure 4. (a)Area specific polarization resistance of the red cell measured at 600, 650 and 700°C; (b) The fitting model circuit

Figure 5. Short-term stability investigated at 600 °C.