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Short communication

High performance of proton-conducting solid oxide fuel cell with a layered $\text{PrBaCo}_2\text{O}_{5+\delta}$ cathode

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ARTICLE INFO

Article history:

Received 14 May 2009

Received in revised form 28 May 2009

Accepted 3 June 2009

Available online 11 June 2009

Keywords:

Proton-conducting solid oxide fuel cell

High performance

Cathode

ABSTRACT

A dense $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) electrolyte is fabricated on a porous anode by in situ drop-coating method which can lead to extremely thin electrolyte membrane ($\sim 10\ \mu\text{m}$ in thickness). The layered perovskite structure oxide $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) is synthesized by auto ignition process and initially examined as a cathode for proton-conducting IT-SOFCs. The electrical conductivity of $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) reaches the general required value for the electrical conductivity of cathode absolutely. The single cell, consisting of $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO)/ $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY)/ $\text{NiO-BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) structure, is assembled and tested from 600 to 700 °C with humidified hydrogen ($\sim 3\% \text{H}_2\text{O}$) as the fuel and air as the oxidant. An open-circuit potential of 1.01 V and a maximum power density of $545\ \text{mW cm}^{-2}$ at 700 °C are obtained for the single cell, and a low polarization resistance of the electrodes of $0.15\ \Omega\ \text{cm}^2$ is achieved at 700 °C.

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1. Introduction

Solid oxide fuel cells (SOFCs) have received tremendous attention recently due to their high energy conversion efficiency, low emissions and excellent fuel flexibility [1]. Considerable research efforts have been made to reduce the SOFC working temperature from high temperature ($\sim 1000\ ^\circ\text{C}$) to intermediate-temperature (500–700 °C) for plenty of benefits such as versatile cell materials, prolonged lifetime, and reduced fabrication cost [2]. Unfortunately, the performance of these intermediate-temperature solid oxide fuel cells (IT-SOFCs), especially proton-conducting IT-SOFCs, is strongly dependent on the property of the cathode–electrolyte interface, since the polarization resistance increases rapidly as the temperature decreases [3].

Therefore, one key to improve the cell performance is reducing the polarization resistance of cathode–electrolyte interface. Recently, Zhang et al. [4] have reported that among the various layered $\text{LnBaCo}_2\text{O}_{5+\delta}$ oxides $\text{PrBaCo}_2\text{O}_{5+\delta}$ has the highest bulk diffusion coefficient and surface exchange coefficient, suggesting it may perform better than others as cathodes for proton-conductor IT-SOFCs. Nevertheless, up to now, cathode material for proton-conductor IT-SOFCs is still lack in the literature regarding $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) electrode.

In addition, another key to improve the cell performance is reducing the thickness of electrolyte for lessening the total ohmage

of the cell. So far, many techniques have been tried for producing thin electrolyte membrane $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) reported by Zuo et al. [5] on porous anode support. However, the majorities have been suitable for laboratory demonstration instead of commercialization and electrolyte membranes are somewhat thick. Thus, it is necessary to develop a simple and effective route to fabricate thin electrolyte membrane for proton-conductor IT-SOFCs.

In the present study, we employed in situ drop-coating technology to fabricate thin dense $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) electrolyte membranes on porous anode support. With $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) as a new cathode for proton-conductor IT-SOFCs, the performances of the full cells were studied.

2. Experimental

2.1. Cell fabrication

$\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) powders were prepared by auto ignition process. $\text{Pr}(\text{NO}_3)_3$, $\text{Ba}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_3$, 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 then heated till self-combustion occurred. The as-synthesized powders were subsequently calcined at 900 °C for 2 h to obtain fine $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) powders. The $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) powders were also synthesized by auto ignition process with the raw materials $\text{Ba}(\text{NO}_3)_2$, $\text{Zr}(\text{NO}_3)_4$, $\text{Ce}(\text{NO}_3)_3$ and $\text{Y}(\text{NO}_3)_3$ at a proper molar ratio and then calcined at 1000 °C for 2 h.

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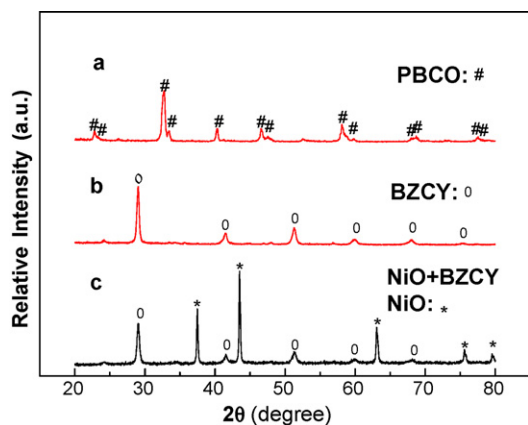


Fig. 1. XRD diffraction patterns of (a) $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO), (b) $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) membrane and (c) NiO-BZCY anode substrate (*NiO).

To make a single cell, a mixed powder of NiO + $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) + corn starch (with a weight ratio of 60:40:20) was pressed at 200 MPa and then sintered at 800 °C for 2 h to form an anode substrate. The anode active layer consisting of NiO and $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) (with a weight ratio of 60:40) was dispersed into ethanol by ball-milling for 24 h to form a suspension with 10 wt.% of the mixed powder and then was drop-coated [6] on the porous anode substrate. The $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) layer was coated subsequently by the same process on the anode active layer after it being dried in air at room temperature. Changing the volume of the suspension can control the thickness of membranes. The bi-layer and anode support were then co-fired at 1400 °C for 5 h. After that, fine $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) powders were mixed thoroughly with a 10 wt.% ethylcellulose–terpineol binder to prepare the cathode slurry, which was painted on the $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) electrolyte membrane, and fired at 900 °C for 2 h in air to form a single cell.

2.2. Cell testing and microstructure characterisation

The cell components were selected as follows: $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO)/ $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY)/NiO- $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) measured by X-ray diffraction technique (XRD, Philips X'pert PROS diffractometer). Morphology and microstructure were observed by scanning electron microscopy (SEM, FEI XL30). Electrical conductivity of $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) was studied using the standard DC four-probe technique on H.P. multimeter (Model 34401) from 400 to 800 °C. Single cells were tested from 600 to 700 °C in a home-developed-cell-testing system with humidified hydrogen (~3% H_2O) as fuel and air as oxidant, respectively. An Electrochemical Workstation (IM6e, Zahner) was used to characterize single cells. The current–voltage curve was obtained by using a galvanostat mode and the electrochemical impedance spectra were measured at open-circuit conditions in the frequency range from 0.1 Hz to 1 MHz (10 mV as AC amplitude).

3. Results and discussion

As shown in Fig. 1(a), it can be seen that the as-prepared powder of $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) exhibits a layered perovskite phase structure which is consistent with the data reported by Zhang et al. [4]. Fig. 1 also represents the XRD spectra of anode and electrolyte sintered at 1400 °C for 5 h. It is obvious that there are only peaks corresponding to $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) in electrolyte membrane (Fig. 1(b)) and to NiO and $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) in the anode substrate (Fig. 1(c)) with no peaks attributable to impurities detected.

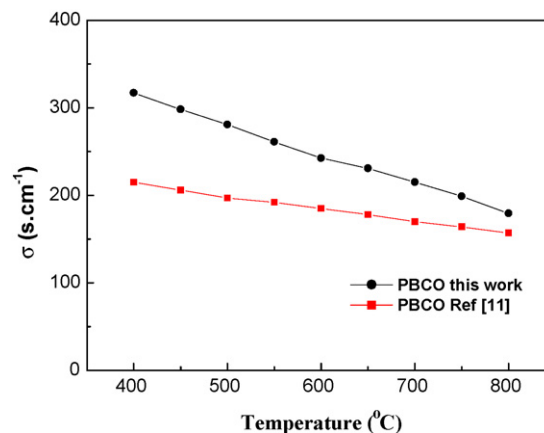


Fig. 2. Temperature dependence of the conductivity for $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) sample at 400–800 °C in air.

Fig. 2 shows the electrical conductivity behaviors of the $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) sample versus the temperature when exposed to an air atmosphere. Within the 400–800 °C temperature range, the electrical conductivity of $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) gradually decreases with increasing temperature from 317 to 179 S cm^{-1} , which presents metallic-like behavior. A similar behavior with lower conductivity value has been reported. Electronic conduction within $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) is believed to occur via electron hopping along Co–O–Co bonds. Generally, increasing the operating temperature decreases the materials' electrical conductivities due to the creation of oxygen vacancies. Such lattice defects broke the Co–O–Co bonds and resulted in obvious decreases in electronic conductivity [4]. For cathode materials of SOFC, the general required value for the electrical conductivity is about 100 S cm^{-1} at the operating temperature [7]. Therefore, the electrical conductivity of $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) as a cathode is acceptable for application in proton-conductor IT-SOFCs.

Micrograph of cross-sectional view of the single cell after electrochemical tests is provided in Fig. 3. It is evident that the $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) cathode has a fine porous microstructure. Moreover, the dense $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) membrane which is about 10 μm in thickness indicates distinctly that the in situ reaction-sintering drop-coating technology is successful. As compared to other technologies such as co-pressing (thickness of membrane: ~25 μm) [8] and screen-printing (thickness of membrane: ~25 μm) [9] applied to producing electrolyte membranes,

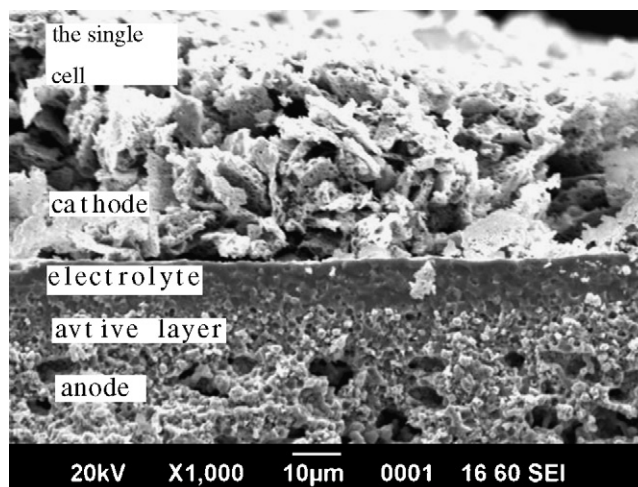


Fig. 3. Cross-section views of the cell after fuel cell testing.

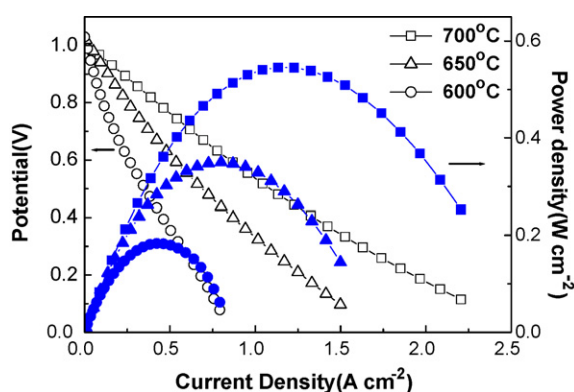


Fig. 4. Cell performance of a single cell (PBCO/BZCY/NiO-BZCY) measured at 600–700 °C under wet hydrogen atmosphere.

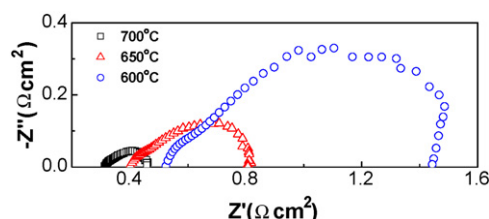


Fig. 5. Impedance spectra of the single cell measured under open-circuit condition.

the drop-coating technology could obtain extraordinarily thinner electrolyte membrane simply and effectively. In addition, the anode active layer ($\sim 10 \mu\text{m}$ in thickness) applied between the electrolyte and the anode support has finer and less porous microstructures than the anode substrate, which could increase the TPB length [10].

Fig. 4 presents the I – V and I – P characteristics of the cell measuring from 600 to 700 °C with humidified hydrogen ($\sim 3\% \text{H}_2\text{O}$) as the fuel. The maximum power densities of, 545, 349, and 183 mW cm^{-2} with the OCV values of 1.01, 1.02, and 1.03 V are obtained at 700, 650, and 600 °C, respectively, hinting that the electrolyte membrane is sufficiently dense. It is unambiguously pointed out that the cell with $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) cathode has higher power density than the values (270 and 148 mW cm^{-2} at 700 and 600 °C) [5], which might due to the thinner electrolyte and the relatively lower interfacial resistance shown in Fig. 5.

To intensively evaluate the performance of layered $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) working as a cathode for proton-conductor IT-SOFCs, resistances of the cells under open-circuit conditions surveyed by AC impedance spectroscopy are shown in Fig. 5. The high frequency intercept corresponds to the ohmic resistance of the cell (R_b), while the low frequency intercept corresponds to the total resistance of the cell (R_{total}). 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 [11], including the cathode–electrolyte interface resistance and the anode–electrolyte interface resistance. As expected, the increase of the measuring temperature resulted in a significant reduction of the interfacial resistances, typically from $0.92 \Omega \text{ cm}^2$ at 600 °C to $0.15 \Omega \text{ cm}^2$ at 700 °C. As compared to the fuel cell with uniform

anode and electrolyte but other layered perovskite structure cathode materials such as: $\text{SmBaCo}_2\text{O}_{5+\delta}$ [9] and $\text{GdBaCo}_2\text{O}_{5+\delta}$ [12], the interfacial resistance of $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) is somewhat lower at or below 700 °C, which might due to the highest bulk diffusion coefficient and surface exchange coefficient among $\text{LnBaCo}_2\text{O}_{5+\delta}$ oxides. Moreover, the interfacial resistance of the cell with $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) is lower than the fuel cell with uniform anode and electrolyte but simple perovskite structure cathode materials such as: $\text{BaCe}_{0.4}\text{Pr}_{0.4}\text{Y}_{0.2}\text{O}_3$ [13] and $\text{SrCo}_{0.9}\text{Sb}_{0.1}\text{O}_3$ [14]. The above results confirm that $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) may be relatively suitable for intermediate-temperature operation.

4. Conclusions

A dense $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) electrolyte membrane was fabricated on a porous anode by in situ drop-coating in order to fabricate proton-conductor IT-SOFCs. As compared to other technologies such as co-pressing and screen-printing, the drop-coating technology could obtain extremely thinner electrolyte membrane simply and effectively. Further, the layered perovskite structure oxide $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) was synthesized by auto ignition process and initially examined as a cathode for proton-conductor IT-SOFCs. The electrical conductivity of $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) attained 317 and 179 S cm^{-1} in the temperature range of 400–800 °C, respectively. The maximum power density of the $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO)/ $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY)/NiO– $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY) cell with about $10 \mu\text{m}$ thick electrolyte was 545 mW cm^{-2} at 700 °C. A relatively low interfacial polarization resistance of $0.15 \Omega \text{ cm}^2$ at 700 °C indicated that the $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) could be a good candidates as SOFC cathode materials.

Acknowledgments

The authors gratefully acknowledge the support of this research by National Natural Science Foundation of China under contract (No. 50572099 and No. 50730002) and National High-tech R&D Program of China (Grant No.: AA2060140001).

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