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A novel anode supported $BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$ electrolyte membrane for proton-conducting solid oxide fuel cell

Lei Bi, Shangquan Zhang, Shumin Fang, Zetian Tao, Ranran Peng, Wei Liu *

Laboratory of Advanced Functional Materials and Devices, Department of Materials Science and Engineering, University of Science and Technology of China, Jinzhai Road 96, Hefei, Anhui 230026, PR China

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ABSTRACT

A novel composition of $BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$ (BCTY10) electrolyte membrane was successfully fabricated on porous NiO-BCTY10 anode substrate. The anode was prepared through a route combining a solid state reaction and a wet chemical method. After sintering at 1450 °C for 5 h, the BCTY10 membrane showed adequate chemical stability against CO_2 and H_2O. With a mixture of $La_{0.7}Sr_{0.3}FeO_{3-\delta}$ (LSF) and $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BZCY7) as cathode, a single fuel cell with 25 μm thick BCTY10 electrolyte generated maximum power densities of 195, 137, 84, 44 mW/cm^2 at 700, 650, 600 and 550 °C, respectively. The interface resistance of the cell under open circuit condition was also investigated.

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1. Introduction

The solid oxide fuel cell (SOFC) is presently the subject of intensive research activity for its significant environmental benefits and high efficiency. Up to now, considerable research efforts have been made to reduce the working temperature of SOFCs by adapting either new electrolyte with high ionic conductivity [1–3], or by reducing the electrolyte thickness [4]. Since Iwahara et al. [5,6] have found that some perovskite oxides show excellent protonic conductivity at elevated temperatures, proton conductors have become promising electrolyte candidates in the intermediate-temperature SOFC community because of their high protonic conductivity and low activation energy [7]. Besides, the proton-conducting SOFCs, in contrast to oxide-ion conductor fuel cells, form water at the cathode side, so the fuel at the anode remains pure and requires no recirculation. Therefore, doped-$BaCeO_3$ and $BaZrO_3$ have been thoroughly studied because of their potential applications as ceramic proton conductors. However, high proton conductivity and stability seem to be antagonistic, as investigated by Kreuer [8] and Norby and Larring [9]. Acceptor-doped $BaCeO_3$ shows highest protonic conductivity among the high temperature proton-conducting oxides. As a drawback, $BaCeO_3$ materials show poor chemical stability in the presence of H_2O and CO_2 containing atmosphere. Now the most widely approach to increase the chemical stability of doped $BaCeO_3$ is to partially replace Ce by Zr, at the cost of reducing protonic conductivity [10]. On the other hand, doped-$BaZrO_3$ materials show high bulk proton conductivity (10^{-2} S/cm at 400 °C) and high chemical stability but the high grain boundary resistance on $BaZrO_3$ is the main obstacle for its practical applications [11,12]. In order to improve the $BaZrO_3$ electrical properties, many investigations have been devoted to reduce the grain boundary resistance either by increasing the sintering temperatures [12], or by adding transition metal oxides such as ZnO to promote the sinterability of zirconates [13], or by partially replacing Zr by Ce to improve conduction of the grain boundary [10].

Up to now, many efforts aim to develop a new solid proton conductor which can show high protonic conductivity and adequate chemical stability against H_2O and CO_2 [14–16]. In the process of searching stable proton conductors, some ceramic oxides containing pentavalent ions show high chemical stability [17,18]. Nowick and co-workers [19,20] have found that some mixed perovskite-type oxides yield promising proton conductivity (e.g., non-stoichiometric $Ba_3CaNb_2O_9$). These research results shed light on the concept of developing new proton-conducting materials. We can make a reasonable assumption that partially replacement of Ce by pentavalent ions (such as Ta) can increase the chemical stability of doped $BaCeO_3$ materials. However, as the hard solubility of Ta_2O_5, ceramic powders containing Ta are usually prepared by the solid state reaction. These solid state reaction prepared powders have difficulty in applying in SOFC for their low sintering activity. In this study, we present a new strategy of substituting Ta for Ce to increase the chemical stability of $BaCeO_3$ against H_2O and CO_2. The half-cell SOFC with $BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$ (BCTY10)

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* Corresponding author. Tel.: +86 551 3606929; fax: +86 551 3601592.
E-mail address: wliu@ustc.edu.cn (W. Liu).

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electrolyte membrane on NiO-BCTY10 anode is prepared by an improved route combining a solid state reaction and a wet chemical method. In addition, the electrochemical properties of the BCTY10-based fuel cell are studied.

2. Experimental

$BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$ (BCTY10) powders used for anode substrate were synthesized by a route combining a Pechini method and a solid state reaction. $Ba(NO_3)_2$, $Ce(NO_3)_3 \cdot 6H_2O$ and $Y(NO_3)_3$ were dissolved at the stoichiometric ratio and citric acid was then added, which was used as complexation agent. Molar ratio of citric acid/metal set at 1.5. Then Ta_2O_5 ($\sim$17 μm) was added and the solution was heated under stirring to evaporate water until it changed into viscous gel and finally ignited to flame, resulting in a white ash. The ash was ball-milled for 24 h before calcining at 1000 °C for 3 h to form pre-BCTY10 powders. These pre-BCTY10 powders were well mixed with NiO in a weight ratio of 40:60. To form sufficient porosity in the anode, 10 wt.% starch was added as the pore former. The mixed powders were pressed under 200 MPa with 15 mm in diameter and 0.5 mm in thickness and subsequently fired at 800 °C for 3 h as anode substrates.

The BCTY10 membrane was fabricated on the anode substrate by an in situ reaction [21]. The relatively stable starting materials of $BaCO_3$, CeO_2, Y_2O_3 and Ta_2O_5 were mixed in the molar ratio of 1: 0.7: 0.1: 0.05 and dispersed into ethanol by ball-milling for 24 h to form a suspension. The suitable organic addictives (triethanolamine, benzyl butly phthalate and polyvinly butyral) were added into the suspension, which were employed to make the metal oxides and the carbonate well distribute in the ethanol. We used triethanolamine as a dispersant. The benzyl butly phthalate and polyvinly butyral were applied as a plasticizer and a binder, respectively. The solid ratio of the starting materials is 12 wt.%. The suspension was directly deposited on the anode substrate. Then the bi-layers of green electrolyte and anode were fired at 800 °C for 3 h to remove any carbon residues and subsequently co-fired at 1450 °C in the air for 5 h. Both the electrolyte layer and the anode were in situ prepared at the sintering temperature. Therefore, the half-cell SOFC with $BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$ (BCTY10) electrolyte membrane on NiO-BCTY10 anode was formed. A mixture of $La_{0.7}Sr_{0.3}FeO_{3-\delta}$ (LSF) and $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (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. Pt paste was applied on the electrode as a current collector.

Powder X-ray diffraction measurements were made using a Philips X'Pert Pro Super diffractometer with Cu Kα radiation. The single cell was tested at different temperatures with humidified hydrogen ($\sim$3%H_2O) as fuel and static air as oxidant. The flow of wet hydrogen was set at 25 mL/min. Fuel-cell performances were measured with DC Electronic Load (ITech Electronics model IT8511). Resistances of the cell under open circuit condition were measured at different temperatures by an impedance analyzer (CHI604C, Chenhua Inc., Shanghai). A 5 mV a.c. signal was applied, so that the response had to be considered linear. The frequency was swept from 100 KHz to 0.1 Hz. A scanning electron microscope (SEM, JEOL JSM-6700F) was employed to observe the fracture morphology of the tested cell.

3. Results and discussion

To study the chemical stability of the BCTY10, we treated the solid state reaction prepared BCTY10 powder in 3% CO_2 (balanced with air) at 700 °C for 24 h. The solid state reaction prepared $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ (BCY) powder was treated in the same environment for comparison. Both the samples were grinded to the same grain size (250 mesh powder) before exposing them to CO_2. Fig. 1 presents the XRD patterns of the BCTY10 and BCY powders before and after exposure to CO_2. Fig. 1a and c are the XRD patterns of the as-prepared BCTY10 and BCY powders. The Fig. 1b shows that the main phase of the BCTY10 powder remained unchanged in spite of a little formation of $BaCO_3$ after the treatment. Whereas the BCY powder, shown in Fig. 1d, decomposed completely during the exposure to CO_2. This evidence suggests that the doping of Ta can make the $BaCeO_3$ based material more stable. We also treated the BCTY10 and BCY powders in 100% CO_2 at 700 °C for 3 h, in which both these two powders decomposed completely.

Fig. 2a and b shows the XRD patterns of the anode substrate layer and the obtained electrolyte membrane after sintering at 1450 °C for 5 h. It can be seen that there are only peaks corresponding to BCTY10 in electrolyte membrane and to NiO and BCTY10 in the anode substrate, without any formation of other substances, indicating the electrolyte membrane with a pure BCTY10 phase and the anode substrate with the composition of NiO-BCTY10 have been successfully prepared through the in situ reaction. As the electrolyte membrane for SOFC, it is necessary to investigate the chemical stability of the obtained BCTY10 membrane. The BCTY10 membrane was exposed to 100% CO_2 at 900 °C for 3 h. As expected, the XRD pattern shown in Fig. 2c indicates that the structure of the BCTY10 remained unchanged after exposure to CO_2, demonstrating that the BCTY10 membrane is stable in an atmosphere containing 100% CO_2. We also tested the stability of BCTY10 membrane in boiling water. XRD examination of the BCTY10 membrane after being boiled in water for 3 h, shown in Fig. 2d, indicates that BCTY10 remained unchanged, demonstrating that BCTY10 shows adequate stability against boiling water. For comparison, the anode supported BCY membrane prepared by the same method was also treated in the same environments. Fig. 2e–g are the XRD patterns of BCY membrane before (e) and after exposure to 100% CO_2 at 900 °C (f) or being boiled in water (g), suggesting that BCY membrane decomposed during the treatment of boiling water as well as the exposure to 100% CO_2 at 900 °C. As we know that even $BaCe_{0.7}Zr_{0.2}Y_{0.1}O_{2.95}$ cannot resist the attack of boiling water as well as the treatment of 100% CO_2 at 900 °C [22], this result suggests that BCTY10 is of better chemical stability than that of $BaCe_{0.7}Zr_{0.2}Y_{0.1}O_{2.95}$. The above evidences demonstrate that the partially replacement of Ce by Ta indeed increases the chemical stability of barium cerate against CO_2 and H_2O. Because of its adequate chemical stability, BCTY10 provides an interesting electrolyte candidate that can operate in CO_2 containing atmospheres, such as hydrocarbon fuels.

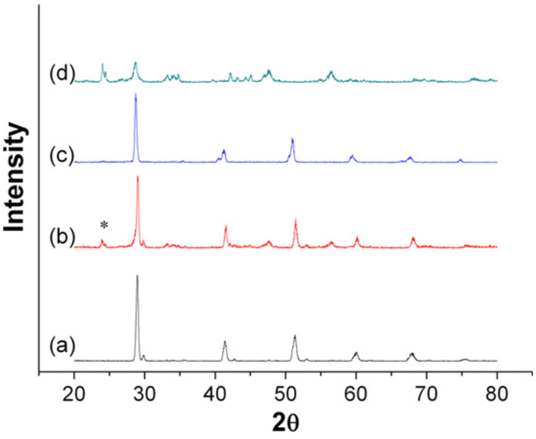

Fig. 1. XRD patterns for (a) BCTY10 powder, (b) BCTY10 powder after exposure to 3% CO_2 at 700 °C, (c) BCY powder and (d) BCY powder after exposure to 3% CO_2 at 700 °C. ∗: $BaCO_3$.

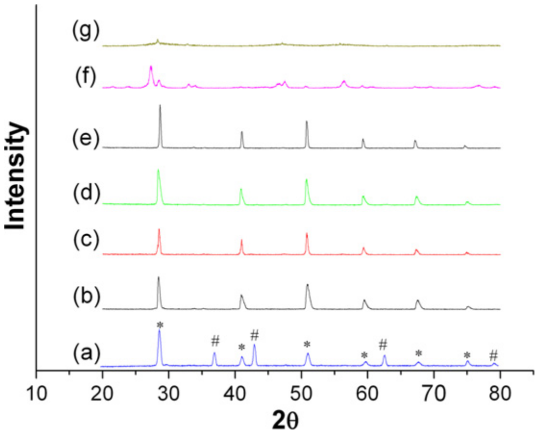

Fig. 2. XRD patterns for the bi-layers of (a) NiO-BCTY10 anode substrate, (b) BCTY10 membrane, (c) BCTY10 membrane after exposure to 100% CO_2 at 900 °C, (d) BCTY10 membrane after being boiled in water, (e) BCY membrane, (f) BCY membrane after exposure to 100% CO_2 at 900 °C, (g) BCY membrane after being boiled in water. ∗: BCTY10; #: NiO.

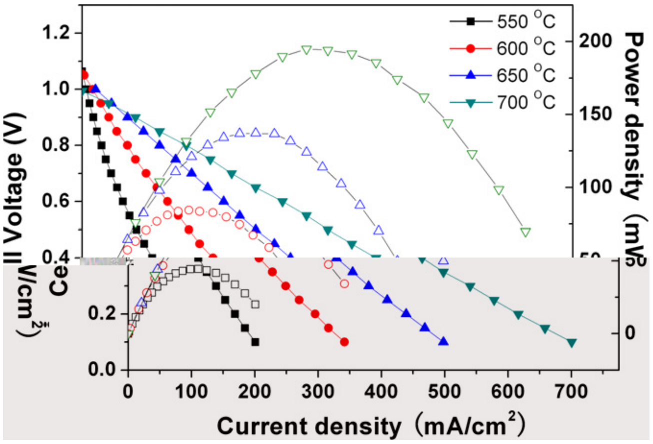

Fig. 4. Performance of a fuel cell with humidified hydrogen measured from 550 to 700 °C.

Fig. 3 shows a typical scanning electron microscopy (SEM) image of the single cell after fuel cell testing. The SEM indicates that the BCTY10 electrolyte membrane is 25 μm in thickness and quite dense, without any obvious pores and cracks. The BCTY10 electrolyte adheres very well with the layers of anode and cathode, without any cracking or delamination after testing.

Shown in Fig. 4 are the *I*–*V* and power density curves for a single cell based on a BCTY10 electrolyte membrane of 25 μm at different temperatures. The open circuit voltages (OCV) of 1.064, 1.055, 1.032 and 0.994 at 550, 600, 650 and 700 °C, respectively indicate that the BCTY10 electrolyte membrane is quite dense, as any leakage of gas will lead to severe OCV drops. The OCV of a single cell kept stable (~1.05 V) at 600 °C under the testing condition for at least 100 h. With humidified hydrogen (~3%H_2O) as fuel and static air as oxidant, maximum power densities were 195, 137, 84, 44 mW/cm^2 at 700, 650, 600 and 550 °C, respectively.

Resistances of the cell under open circuit conditions were investigated by AC impedance spectroscopy. Four typical impedance spectra, measured at 550, 600, 650 and 700 °C, respectively, are shown in Fig. 5. The intercept with the real axis at high frequency represents the ohmic resistance of the cell, which is usually taken as the overall electrolyte resistance of the cell. 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. Fig. 6 presents the total cell resistance, the overall electrolyte resistance and R_p of the cell as determined form the impedance spectra. The overall electrolyte resistances of the cell are 1.41, 1.08, 0.83 and 0.74 Ω cm^2 at 550, 600, 650 and 700 °C, respectively, which are only slightly higher but comparable with those of the traditional $BaCeO_3$-based fuel cell [3] and imply that the new strategy of partially substituting Ta for Ce reaches a good compromise between conductivity and chemical stability for $BaCeO_3$. It has to be mentioned that if we assume that the ohmic resistance of the cell mostly comes from the electrolyte, the conductivity of BCTY10 was calculated to be about 2.3×10^{-3} S/cm at 600 °C, which is several times lower than the conductivity for bulk doped-$BaCeO_3$ reported in the literature (about 10^{-2} S/cm at 600 °C) [10]. The result shows an agreement with the report that the conductivity of the supported electrolyte membrane is much smaller than the conductivity for the bulk material [23]. The difference may arise from the assumption we have made. In fact, the ohmic resistance of the cell includes the ionic resistance of the electrolyte, the electronic resistance of the electrodes and some contact resistance associated with interfaces.

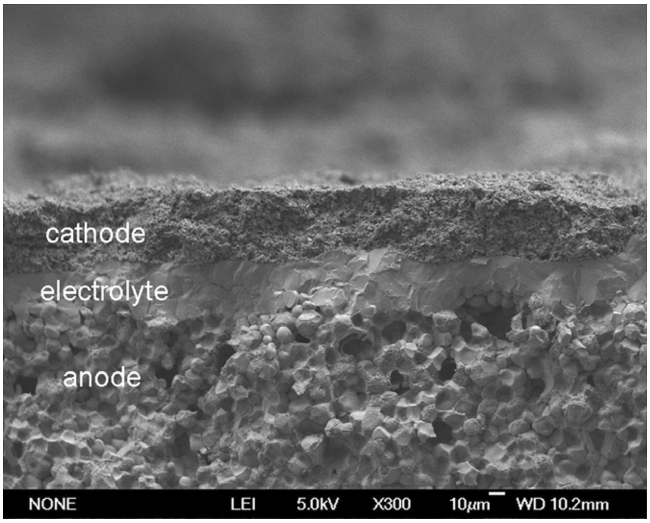

Fig. 3. SEM cross-sectional view of the single cell after testing.

Fig. 5. Impedance spectra of a single cell with a 25 μm thick BCTY10 membrane measured at different temperatures: (a) 550 and (b) 600–700 °C.