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A stable $BaCe_{0.7}Ta_{0.1}In_{0.2}O_{3-\delta}$ electrolyte membrane for proton-conducting solid oxide fuel cells

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Abstract

In and Ta co-doping $BaCeO_{3-\delta}$ ($BaCe_{0.7}Ta_{0.1}In_{0.2}O_{3-\delta}$) powders were synthesized by an improved route combining solid state reaction and wet chemical method. Green $BaCe_{0.7}Ta_{0.1}In_{0.2}O_{3-\delta}$ (BCTI) $|NiO+BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BZCY) half cells were successfully fabricated by co-pressing BCTI powders on NiO–BZCY substrate, which were sintered at a relatively low temperature of 1300 °C for 5 h and then produced dense BCTI membrane. The stability testing showed that BCTI membrane is excellently stable against carbon dioxide and boiling water. A single fuel cell with 44 μm-thick BCTI electrolyte was assembled by brushing $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SSC–SDC) composite cathode on dense electrolyte membrane, which generated maximum power densities of 59, 49, 34 mW/cm^2 at 650, 600 and 550 °C, respectively. Meanwhile, the resistances of the cell were measured by electrochemical impedance spectroscopy under open circuit condition. Moreover, the long-term test of the cell showed stable power output and open circuit voltages. The above described performance indicates that BCTI is stable electrolyte material for intermediate-temperature solid oxide fuel cells. Besides, the super stable electrolyte material can be used as online high-temperature hydrogen sensor.
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Keywords: Proton-conducting SOFC; Chemical stability; X-ray diffraction; Electrochemical properties

1. Introduction

With the ever-increasing energy demand and increasingly serious environmental problems, high-efficiency and environment-friendly technologies for energy supply are expanding for sustainable development. In this scenario, solid oxide fuel cells (SOFCs), which is able to convert chemical energy of fuels to electrical energy, has attracted great attention due to their unique benefits, such as high-energy conversion efficiency, clean emissions, quiet operations, reliability and fuel flexibility [1,2]. Compared with the oxygen ion conductors (SDC, YSZ, LSGM), proton-conducting solid oxide fuel cells (H-SOFCs) have several advantages. The lower activation energy for proton than oxygen ion transport implies that the H-SOFCs can operate at intermediate or lower temperatures. Furthermore, water is produced in the cathode side, thus the fuel gas will not be diluted during fuel cell operation [3,4]. The electrolyte material of H-SOFCs should meet the intrinsic high ion conductivity and chemical stability under fuel cells operating conditions. Doped-$BaCeO_3$ and $BaZrO_3$ have been thoroughly studied because of their potential applications as ceramic proton conductors. Although the doped-$BaCeO_3$ shows high proton conductivity, the poor chemical stability in the H_2O and CO_2 atmosphere is a fatal flaw. Doped-$BaZrO_3$ possesses the high chemical stability, but the high grain boundary resistance and the high sintering temperature limit its practical application [5–7].

In this work, In and Ta co-doped $BaCeO_3$ electrolyte were synthesized and investigated. As far as we know, $BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$ (BCTY10) shows adequate chemical stability against CO_2 and H_2O, but has a high sintering temperature [7]. However, In-doped $BaCeO_3$ has good chemical stability and good sinterability [8]. Combining the above, BCTI not only exhibits the more excellent chemical stability, but also has the lower sintering temperature.

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2. Experimental

The $BaCe_{0.7}Ta_{0.1}In_{0.2}O_{3-\delta}$ (BCTI) powders were prepared through a route combining solid state reaction and Pechini method [7]. Stoichiometric quantities of $BaCO_3$, $Ce(NO_3)_3$ and $In(NO_3)_3$ were dissolved in an aqueous solution of nitric acid. Citrate was used as complexation agent and molar ratio of citric acid/metal ions set at 3/2, followed by adjust pH value to 7. The solution was heated under stirring at 70 °C to evaporate water until it changed into gel and then Ta_2O_5 was added. After uniformly mixed under stirring, the mixture was ignited by heating, resulting in a white ash. The as-prepared powders were then calcined at 1000 °C for 3 h in air. $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC), $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ (SDC) and $BaCe_{0.7}Zr_{0.1}Y_{0.2}O_{3-\delta}$ (BZCY) were synthesized via Pechini method. The as-prepared SSC, SDC and BZCY powders were calcined at 950, 600 and 1000 °C for 3 h, respectively. The phase structure of all powders was shown in Fig. 1.

The anode powders were obtained by ball-milling the mixture of NiO, BZCY and starch (weight ratio of 3:2:1), which were pre-pressed under 200 Mpa to form substrate. After that, the BCTI powders were uniformly distributed on anode substrate and then co-pressed at 400 Mpa, obtaining green half cells. The green half cells were sintered at 1300 °C in the air for 5 h to obtain the half-cells with dense BCTI electrolyte. The SSC–SDC cathode slurry was prepared by mixing SSC and SDC in weight ratio of 7:3 using 10% ethylcellulose–terpineol binder. The SSC–SDC was printed on the electrolyte membrane and fired at 1000 °C for 3 h to form a single cell. Single cells were tested from 550 to 650 °C with humidified hydrogen ($\sim$3% H_2O) as fuel and static air as oxidant. The flow rate of the fuel gas was controlled at 25 mL/min.

Furthermore, the chemical stability of the dense electrolyte membrane was researched. BCTI membrane was exposed to humid CO_2 ($\sim$3% H_2O) and stayed at 600 °C for 3 h. The stability against H_2O was investigated by keeping it in the boiling water for 3 h. The phase structures of samples after treatment were checked by XRD. Raman spectroscopy (514.5 nm, labRamHR) was used to detect the occurrence of carbonates after CO_2 tested membrane.

The phase structures of electrolyte membrane and powders were identified by X-ray diffraction (XRD) analysis on a Philips PW1730 diffractometer using CuK_α radiation. Fuel cell performance was measured with DC Electronic Load (IT8511). Resistances of the cell under open circuit condition were measured at different temperatures by CHI604B (100 kHz–0.1 Hz). Scanning electron microscope (SEM, JEOL JSM-6700F) was employed to observe the surface and cross-section morphology of the tested cells.

3. Results and discussion

Barium cerate can indeed react both with carbon dioxide and water vapor according to the following reactions [9]:

$$BaCeO_3 + H_2O \rightarrow Ba(OH)_2 + CeO_2$$

$$BaCeO_3 + CO_2 \rightarrow BaCO_3 + CeO_2$$

Usually, the Ce-site doping of elements with high electronegativity could favorably improve the chemical stability. The doping of Ta can reduces the basicity of the ceramic oxide because of the relatively high electronegativity of Ta, which makes the oxide less easily react with acidic gases. Therefore, the chemical stability of the oxide in the CO_2 and H_2O containing atmosphere is improved [7]. Meanwhile, In-doped $BaCeO_3$ material improves the chemical stability [8]. Therefore, In and Ta co-doped $BaCeO_3$ should have the better stability than In-doped $BaCeO_3$ and Ta-doped $BaCeO_3$.

The poor chemical stability of the electrolyte material will decline the cell performance sharply. Therefore, it is

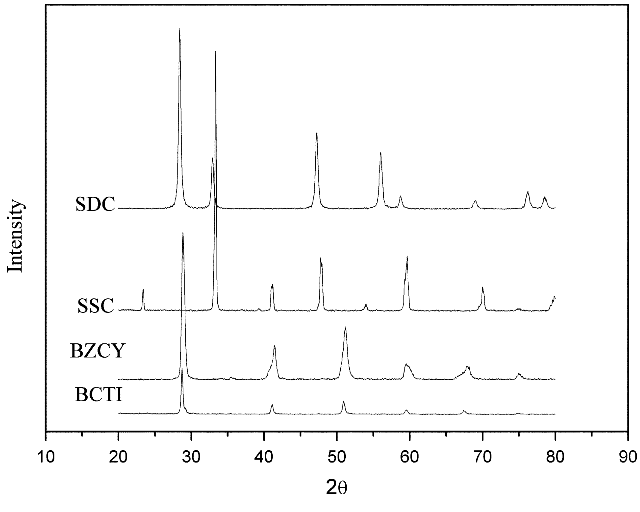

Fig. 1. The powder X-ray diffraction patterns of (a) BCTI, (b) BZCY, (c) SSC, (d) SDC.

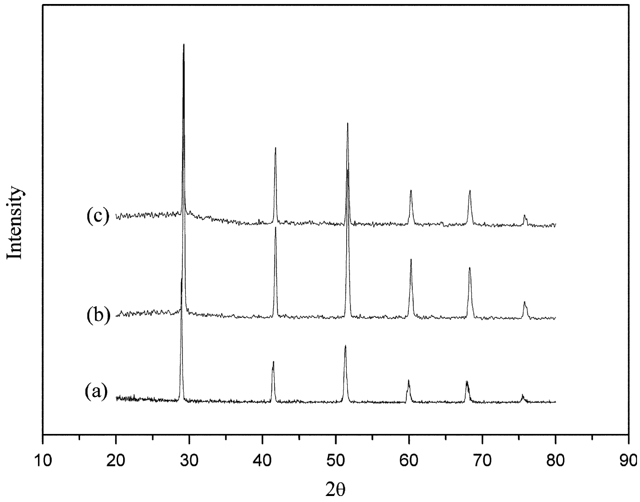

Fig. 2. XRD patterns for (a) BCTI membrane, (b) BCTI membrane after exposure to 100% CO_2 at 600 °C, (c) BCTI membrane after being boiled in water.

necessary to investigate the chemical stability of the obtained BCTI membrane. Fig. 2a shows the phase structure of the BCTI membrane sintered at 1300 °C for 5 h. It is easy to find that the phase structure of the BCTI after exposure to 100% CO_2 at 600 °C (Fig. 2b) remained unchanged, demonstrating that the BCTI is stable in a harsh CO_2-atmosphere. As shown in Fig. 2c, the peaks of BCTI after dealing with the boiling water also remained unchanged, illustrating that BCTI possesses adequate stability against boiling water. 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 for 3 h [10,11], the above results suggest that BCTI is of better chemical stability than that of $BaCe_{0.7}Zr_{0.2}Y_{0.1}O_{2.95}$.

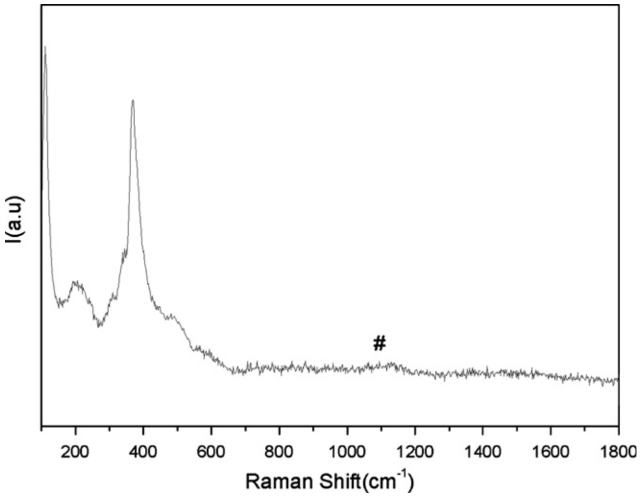

Fig. 3. The Raman spectra of BCTI membrane after exposure to 100% CO_2 at 600 °C.

In order to get further evidence about the chemical stability of electrolyte material, we checked the occurrence of carbonates on electrolyte membrane surface using Raman spectra. From Fig. 3, it can be seen that $BaCO_3$ was not formed after the CO_2 treatment [12]. The typical brand at 1059 cm^{-1}(due to the symmetric stretching vibrations) are not present in the Raman spectra [13].

Fig. 4a shows the SEM image of the surface morphology of the BCTI electrolyte before testing. From this image, we can see that the electrolyte membrane is dense and the grain size is about 5 μm. It illustrates that In-dopant reduces the sintering temperature, therefore, In element is a good sintering aid. Fig. 4b shows the cross-section image of electrolyte, confirming that the electrolyte is dense without any connected pores after testing. It can be seen from Fig. 4c that the BCTI electrolyte with 44 μm in thickness might have affected the power output of the cell as one of the factors. From Fig. 4d, it can be observed that the adhesion of the SSC–SDC cathode to the BCTI electrolyte seems to be excellent and the cathode layer is porous, but the porosity is not very high. Also, the interface appears not characterized by proper bonding between electrolyte and electrodes. Therefore, as a new stable electrolyte material, a suitable electrode material is needed to obtain superior cell performance.

Shown in Fig. 5 are the *I–V* and *I–P* curves for a single cell based on a BCTI electrolyte membrane at different

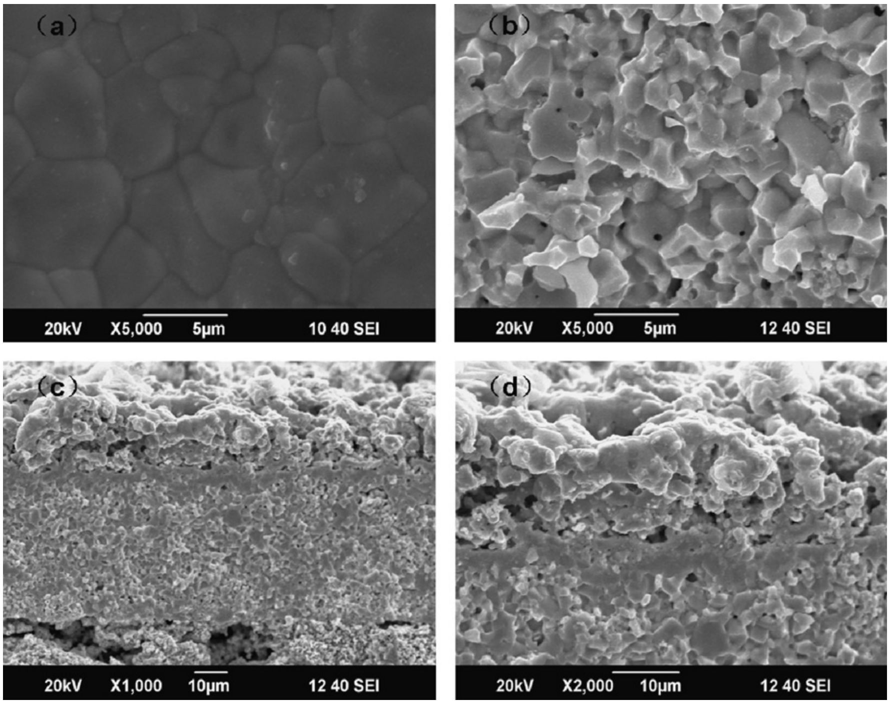

Fig. 4. SEM images of surface morphology of BCTI electrolyte before testing (a), and the cross-section of the tested cell electrolyte (b), a single cell (c and d) cathode–electrolyte interface.

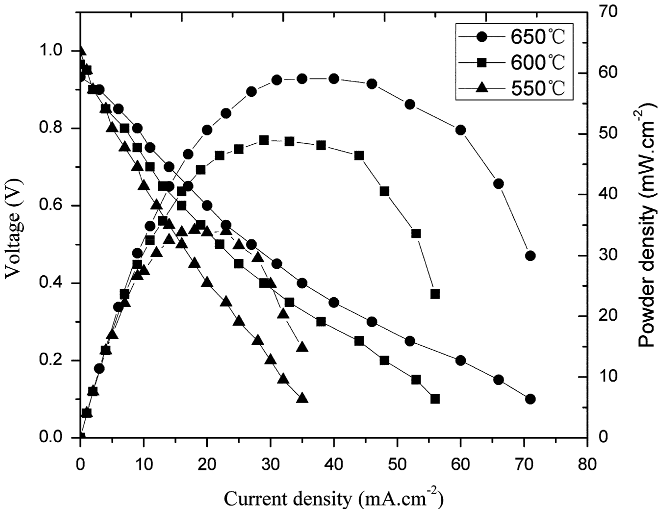

Fig. 5. Performance of a fuel cell with humidified hydrogen measured from 550 to 650 °C.

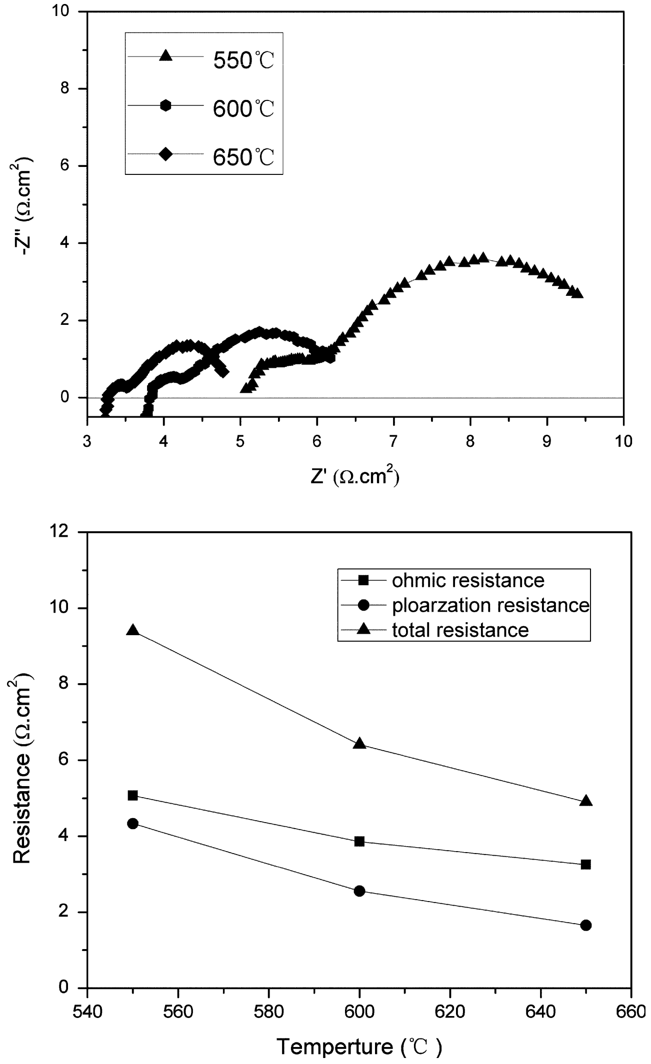

Fig. 6. (a) Impedance spectra of a single cell with 44 μm-thick BCTI membrane measured at different temperatures. (b). The estimated resistances of the tested cell as the function of the temperature.

temperatures. The open circuit voltages (OCV) were 0.933, 0.965 and 0.998 V at 650, 600 and 550 °C, respectively. Compared with those $BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$ electrolyte prepared by solid state reaction (0.96 V at 600 °C [14]), the OCV illustrates that the electrolyte membrane is dense, which is identify with the SEM result. The maximum power densities were 59, 49 and 34 mW/cm^2 at 650, 600 and 550 °C, respectively. Compared with the power densities reported for several $BaCeO_3$-based fuel cells [2,7,14], the BCTI shows weak power density. We think that the low power densities primarily derive from the high ohmic resistance, namely, low ionic conductivity. It has been proved that the co-existing between high conductivity and good chemical stability is difficult for $BaCeO_3$ material system. In others words, the BCTI has the excellent chemical stability at the expense of the proton conductivity. Meanwhile, the electrode material is not suitable for this electrolyte membrane, which makes the low power density.

To investigate the origin of power loss, the AC impedance spectroscopy at different temperatures were used to investigate the different contributions to the total resistance under the open circuit condition, as shown in Fig. 6a. In these spectra, the low frequency intercept and the high frequency intercept with the real axis, respectively represent the total resistance (R_{total}) and the ohmic resistance (R_{ohm}) of the cell, while the different of the two values corresponds to the sum of the resistance of the two interfaces: the cathode–electrolyte interface and the anode–electrolyte interface [15]. In Fig. 6a, it can be seen that the R_{ohm} and the polarization resistance (R_p) decrease with the increasing of the temperature. Fig. 6b shows the resistances (R_{total}, R_{ohm} and R_p) obtained from the impedance spectra. The R_{ohm} reach 3.25 Ω cm^2 at 650 °C, 3.86 Ω cm^2 at 600 °C, and 5.07 Ω cm^2 at 550 °C, respectively, while R_p increases from 1.65 Ω cm^2 (650 °C) to 4.33 Ω cm^2 (550°C). R_p was far larger than the values reported in the literature what studies the optimization of cathode materials for H-SOFCs [4,16]. The low porosity of cathode will lead to the high R_p value. The high R_{ohm} can be interpreted as the following: Ta-doped $BaCeO_3$ and In-doped $BaCeO_3$ improve the excellent chemical stability greatly [7,8,17,18]. However, excellent chemical stability and the high proton conductivity seem to be antagonistic. The oxide basicity favors the formation of the protonic defects, as mentioned by Kreuer [19]. The relatively high electronegativity of Ta and In can reduce the basicity of the ceramic oxide. Therefore, the reduced oxide basicity is disadvantageous for the formation of protonic charge carriers, which cause some conductivity performance losses [7]. Furthermore, the 44 μm-thick BCTI electrolyte may be the second factor.

The proton conductor of electrolyte is calculated by the $\sigma = L/R \times S$, $L = 44\ \mu m$ $S = 0.237\ cm^2$. Thereby, we get the conductivity value, 1.35×10^{-3} $S\,cm^{-1}$, 1.13×10^{-3} $S\,cm^{-1}$, 0.87×10^{-3} $S\,cm^{-1}$ at 650, 600 and 550 °C, respectively.

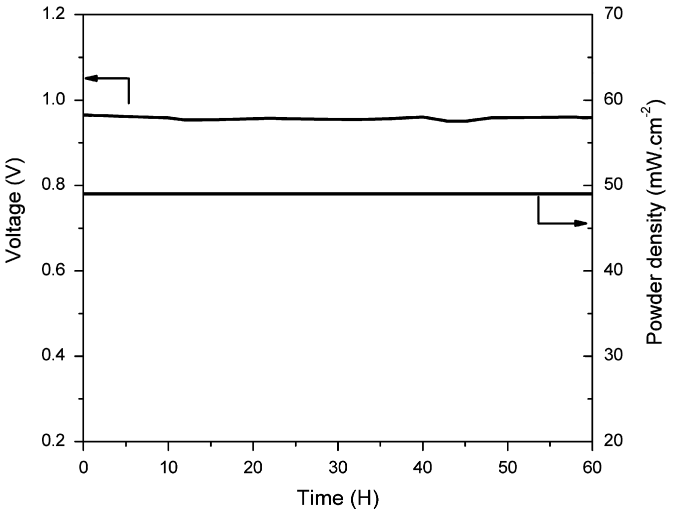

Fig. 7. The long-term stability of the Ni–BZCY|BCTI|SSC–SDC single cell.

The cell exhibits an excellent stable performance (OCV, maximum power density) for 60 h at 600 °C under open circuit condition, as shown in Fig. 7. Stable OCV shows that BCTI membrane owns excellent chemical stability against carbon dioxide and water. The current stabilized density indicates that resistance value remains unchanged within the 60 h operating time. In literature reports, the long-term stability tests for $BaCeO_3$-based fuel cell only last 1000 min [20]. The long-term stable performance confirms that the BCTI should be the candidate material for the practical application of H-SOFCs.

The high temperature proton conductor electrolyte is the most promising high temperature sensor, especially, in the petrochemical industry. The long-time stability and reproducibility were still insufficient for a practical application of sensor material [21]. From the above results, the BCTI has superior chemical stability, which should be used as the high-temperature hydrogen sensor.

4. Conclusions

In this study, a new composition of BCTI prepared by solid-state reaction and wet chemical method was successfully developed as an electrolyte for H-SOFCs. The stability test shows that BCTI membrane owns the adequate chemical stability against CO_2 and H_2O. An anode-supported H-SOFCs using BCTI as the electrolyte was fabricated by co-pressing and co-firing process at 1300 °C. Moreover, the single cell exhibits an extreme long-term stability at 600 °C. These results indicate that the BCTI is a stable promising electrolyte material for H-SOFCs and can be used as the high-temperature hydrogen sensor.

Acknowledgements

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