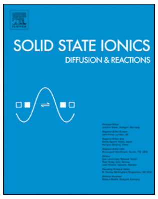
Solid State Ionics 323 (2018) 25–31

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi



High performance In, Ta and Y-doped $BaCeO_3$ electrolyte membrane for proton-conducting solid oxide fuel cells

Zongzhen Zhang, Leihang Chen, Qihua Li, Tengfei Song, Jinrui Su, Bin Cai*, Hao He*

School of Physics and Engineering, Zhengzhou University, Zhengzhou 450001, China
Key Laboratory of Material Physics of Ministry of Education, Zhengzhou University, Zhengzhou 450052, China

ARTICLE INFO

Keywords:
Proton-conducting SOFC
Chemical stability
In, Ta, and Y-doped $BaCeO_3$
Sintering activity
Electrochemical properties

ABSTRACT

A novel $BaCe_{0.7}In_{0.15}Ta_{0.05}Y_{0.1}O_{3\text{-}\delta}$ (BCITY) electrolyte membrane was fabricated on a NiO-BCITY (mass ratio: 6:4) composite anode by combing solid state reaction and Pechini method. The BCITY membrane exhibits high sintering activity, conductivity and apparently improved chemical stability in boiled water or 100% CO_2 at 600 °C. Using the mixture of $La_{0.7}Sr_{0.3}FeO_{3\text{-}\delta}$ (LSF) and $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3\text{-}\delta}$ (BZCY) with mass ratio of 7:3 as the composite cathode, a single cell with BCITY electrolyte generated the maximum power densities of 315, 303, 274, 200, and 116 mW/cm^2 at 750, 700, 650, 600, and 550 °C, respectively. No detectable variations of open circuit voltage and power density were observed for the cell worked at 600 °C for 100 h. The interface resistance of the cell was also studied under open circuit condition.

1. Introduction

As the representative of the solid proton conductors for solid oxide fuel cells (H-SOFCs), the $BaCeO_3$-based oxides have attracted the most wide and intensive attention over the last few decades [1–9]. At present, the $BaCeO_3$-based materials are still among the best proton-conducting oxides although the highest proton mobility was found for Y doped $BaZrO_3$ [10–12]. Unfortunately, the highly conductive $BaCeO_3$ shows poor thermodynamic stability in the presence of H_2O [2] and CO_2 [3] resulted from the hydrocarbon fuel due to the following reactions:

$$BaCeO_3 + CO_2 \rightarrow BaCO_3 + CeO_2 \tag{1}$$

$$BaCeO_3 + H_2O \rightarrow Ba(OH)_2 + CeO_2 \tag{2}$$

Accordingly, the investigation on the improvement of thermodynamic stability of $BaCeO_3$ with less loss of conductivity becomes very important [2–8,11–15].

To improve the comprehensive performance of $BaCeO_3$-based materials, some researchers thought up an idea of partially replaced Ce by single element, such as Zr [5], Nb [6], Ti [7], and In [8] etc. Among these studies, the Zr-doped $BaCeO_3$ electrolyte owned the best comprehensive performance of conductivity and chemical stability. However, the stability improvement of $BaCeO_3$ doped with Zr was limited; furthermore, the sintering characteristics for $BaZrO_3$ materials should be a more serious problem [5]. Bi et al. found that the In doping can improve the sintering performance and stability of $BaCeO_3$-based materials while it has little effect on the conductivity [8]. In addition, the Y doping can improve the electrical conductivity of $BaCeO_3$-based materials although the chemical stability was still poor [2,3,9].

In 2016, Medvedev et al. [15] gave a good summary on the main strategies for the development of highly conductive and stable solid oxide proton electrolytes: (1) double cation doping (co-doping) of $BaCeO_3$ by two kinds of metallic elements, (2) co-doping of $BaCeO_3$ by metallic and nonmetallic elements, and (3) composites development by the addition of a phases with high stability to the $BaCeO_3$-based material. The co-doping method is the most common strategy. During co-doping, one element enables high ionic conductivity (acceptor element) while the other element enhances the stability of perovskite structure (acceptor, isovalent and donor dopant). E.g., the $BaCe_{0.7}Ta_{0.1}In_{0.2}O_{3\text{-}\delta}$ [16], $BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3\text{-}\delta}$ [17], and $BaIn_{0.3-x}Y_xCe_{0.7}O_{3-\delta}$ (x = 0, 0.1, 0.2, and 0.3) [18] electrolyte membranes showed well performance in chemical stability against CO_2 and H_2O. However, both In, Ta [16] and Ta, Y [17] co-doped $BaCeO_3$ showed some lower proton conductivity, which were 1.13×10^{-3} and 2.3×10^{-3} S/cm at 600 °C, respectively. In addition, the sintering temperature (> 1450 °C) of Ta co-doped $BaCeO_3$ was also some high.

As aforementioned, the double doping of $BaCeO_3$ by two kinds of metallic elements may be not the best way to improve the comprehensive performance of $BaCeO_3$ based electrolytes. Accordingly, the triple doping of $BaCeO_3$ by three kinds of metallic elements was also employed, such as $BaCe_{0.4}Zr_{0.3}Sn_{0.1}Y_{0.2}O_{3\text{-}\delta}$ [19]. Although the

---

* Corresponding authors.
E-mail addresses: bcai@zzu.edu.cn (B. Cai), hehao@zzu.edu.cn (H. He).

https://doi.org/10.1016/j.ssi.2018.04.021
Received 14 February 2018; Received in revised form 26 April 2018; Accepted 27 April 2018

Table 1
Effects of the co-doping with two or three kinds of metallic elements M^{v+} on the total conductivity σ_t, sintering temperature T_s and stability of $BaCeO_3$-based electrolyte membranes.

Electrolytes membrane	M^{v+}	σ_t in wet H_2 (10^{-3} S·cm^{-1})	T_s (°C)	Thermal stability		Ref
				Environment	Phenomena	
$BaCe_{0.7}Ta_{0.1}In_{0.2}O_{3-\delta}$	In^{3+} Ta^{5+}	1.13 at 600 °C	1350	100% CO_2 at 600 °C 100% boiled H_2O for 6 h	No impurity phases observed	16
$BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$	Ta^{5+} Y^{3+}	2.3 at 600 °C	1450	100% CO_2 at 900 °C 100% boiled H_2O for 6 h	No impurity phases observed	17
$BaIn_{0.3-x}Y_xCe_{0.7}O_{3-\delta}$ (x = 0, 0.1, 0.2, 0.3)	In^{3+} Y^{3+}	8.7 at 800 °C for x = 0.2	1100 (x = 0)	Wet 3% CO_2 at 700 °C for 24 h	x from 0 to 0.3, CeO_2 and $BaCO_3$ phases decreased	18
$BaCe_{0.4}Zr_{0.3}Sn_{0.1}Y_{0.2}O_{3-\delta}$	Zr^{4+} Sn^{4+} Y^{3+}	9 at 700 °C	1450	(3% CO_2 + 3% H_2O + 94% Ar) at 700 °C for 24 h	No impurity phases observed	19
$BaZr_{0.3}Ce_{0.5}Y_{0.2-x}Yb_xO_{3-\delta}$ (x = 0, 0.05, 0.1, 0.15, 0.2)	Zr^{4+} Y^{3+} Yb^{3+}	10, 9.4, 8.5, 7, 6.5 for x = 0, 0.05, 0.1, 0.15, 0.2 at 700 °C	> 1550	Not studied	–	20

chemical stability and conductivity can be some improved, the sintering temperature (1450 °C) of Zr, Sn and Y-doped was still some higher, which kept almost the same as that of Zr, Y co-doped $BaCeO_3$. In 2014, Shi et al. found the $BaZr_{0.3}Ce_{0.5}Y_{0.2-x}Yb_xO_{3-\delta}$ electrolyte has high conductivity and better sintering activity compared to Zr, Y co-doped $BaCeO_3$ materials [20]. In short, the triple doping of $BaCeO_3$ by three kinds of metallic element becomes increasing important for the further improvement of the comprehensive performance of $BaCeO_3$ electrolytes. For comparison, the effects of co-doping with above mentioned metallic elements on the total conductivity, sintering temperature and stability of $BaCeO_3$-based electrolytes were shown in Table 1.

In this study, the In, Ta and Y-doped $BaCeO_3$ electrolyte membranes were investigated by the measurements of chemical stability and electrochemical performance. In addition, a practical method by measuring the shrinkage of sample diameter during sintering was proposed to characterize the sintering activity. It was found that the $BaCe_{0.7}In_{0.15}Ta_{0.05}Y_{0.1}O_{3-\delta}$ (BCITY) electrolyte membrane exhibited apparently improved chemical stability in boiled water and 100% CO_2 atmosphere at 600 °C; furthermore, higher power density was also observed for the NiO-BCITY|BCITY|LSF-BZCY ($La_{0.7}Sr_{0.3}FeO_{3-\delta}$-$BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$) H-SOFCs. At last, all components of the single cell are Co-free, which can effectively lowered the production costs.

2. Experimental

The $BaCe_{0.7}In_{0.15}Ta_{0.05}Y_{0.1}O_{3-\delta}$ (BCITY) powder was prepared by combing solid state reaction and Pechini method to ensure homogeneity of mixed oxides [12,16–18]. Firstly, the $Ba(NO_3)_2$, $Ce(NO_3)_3{\cdot}6H_2O$, $In(NO_3)_3{\cdot}4.5H_2O$, and $Y(NO_3)_3{\cdot}6H_2O$ with the stoichiometric amounts were dissolved in deionized water. Secondly, the citric acid, as a complexation agent, was added with the molar ratio (3:2) of citric acid to metal ions. After the pH value of the solution was adjusted to be 7 by adding appropriate ammonia water, the stoichiometric amount of Ta_2O_5 was added. Thirdly, the solution added with Ta_2O_5 was stirred continuously during heating to evaporate water until it was changed into viscous gel and finally ignited to flame, which resulted in the formation of some white ashes. Finally, the BCITY powder was obtained by calcining the white ashes at 1000 °C for 5 h in air. In addition, the $BaCe_{0.7}Y_{0.3}O_{3-\delta}$ (BCY) powder was also prepared by Pechini method [16–18] and calcined at 1000 °C for 5 h in air.

The NiO-BCITY anode powder with mass ratio 6:4 of NiO to BCITY was prepared by a modified auto-combustion of nitrate-citrate gel method [21]. As the support layer of single cells, the NiO-BCITY anode substrate was formed by pressing the corresponding powder under 200 MPa. To obtain green half cells, the BCITY powder was uniformly distributed on the NiO-BCITY anode substrate and co-pressed at 400 MPa. The green half cells were sintered at 1350 °C for 5 h in air to obtain the half-cells. The $La_{0.7}Sr_{0.3}FeO_{3-\delta}$ (LSF) powder prepared by the glycine method was calcined at 850 °C for 3 h in air [22] while the $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) prepared by the citrate method was calcined at 1000 °C for 5 h in air [23]. The LSF-BZCY cathode slurry with mass ratio 7:3 of LSF to BZCY was printed on the electrolyte membrane and fired at 950 °C for 3 h to form a single cell. For all single cells, the electrode active area was 23.7 mm^2.

For comparison, two kinds of reported electrolytes $BaCe_{0.7}In_{0.2}Ta_{0.1}O_{3-\delta}$ (BCIT) [16], $BaCe_{0.7}Ta_{0.1}Y_{0.2}O_{3-\delta}$ (BCTY) [17] and another $BaCe_{0.7}In_{0.1}Ta_{0.1}Y_{0.1}O_{3-\delta}$ (BCITY-R) designed in this work were also prepared with the same method. For all single cells with different electrolytes were prepared by the above method with the same condition. In addition, the thickness of cathode, electrolyte, and anode for all single cells are about 20, 25, and 600 μm, respectively. It is to be mentioned that the Al_2O_3 crucible was used in the preparation of the electrode and electrolyte powders.

For stability study, as-sintered BCY and BCITY electrolyte membranes were soaked in boiled water or exposed in 100% CO_2 at 600 °C for 6 h, and then grounded to powders for X-ray diffraction (XRD)