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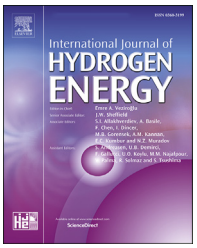

Effects of co-doped barium cerate additive on morphology, conductivity and electrochemical properties of samarium doped ceria electrolyte for intermediate temperature solid oxide fuel cells

Meng Xia [a], *Lichao Jia* [a], *Jin Li* [a], *Yongpeng Liu* [b], *Xin Wang* [a,*], *Bo Chi* [a], *Jian Pu* [a], *Li Jian* [a]

[a] *Center for Fuel Cell Innovation, State Key Laboratory of Material Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science & Technology, Wuhan, 430074, China*

[b] *Laboratory for Molecular Engineering of Optoelectronic Nanomaterials (LIMNO), École Polytechnique Fédérale de Lausanne (EPFL), Station 6, CH-1015, Lausanne, Switzerland*

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ABSTRACT

The composite of samarium doped ceria ($Sm_{0.2}Ce_{0.8}O_{2-\delta}$, SDC) and co-doped barium cerate ($BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$, BZCYYb) is prepared by mechanical mixing and investigated as electrolyte for intermediate temperature solid oxide fuel cells (IT-SOFCs). Coexistence of SDC and BZCYYb are observed for composite electrolyte by X-ray diffraction after sintering at 1500 °C for 5 h, while the slight deviation of the diffraction peak indicating the element diffusion between two phases. The scanning electron microscope and electron probe micro-analyzer results demonstrate that small BZCYYb grains disperse uniformly around the grains of SDC, limiting the growth of SDC grains and decreasing the average grain size of composite electrolyte. Impedance spectroscopy measurement reveals that the grain boundary resistance can be significantly reduced by about an order of magnitude through adding 15–30 wt. % BZCYYb to SDC. Single cells based on the composite electrolyte are fabricated using nickel cermet (Ni-SDC) anode and perovskite ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, LSCF) cathode.

Relatively high open circuit voltage (OCV), much lower polarization resistance and encouraging high power density are obtained for cells with composite electrolyte compared to those with single SDC electrolyte. Among all of the samples, single cell based on 15 wt. % BZCYYb-85 wt. % SDC composite electrolyte exhibits the lowest total resistances of 0.641 $\Omega \cdot cm^2$ and the highest peak power densities of 0.56 $W \cdot cm^{-2}$ at 600 °C.

Introduction

Reducing the operating temperature of solid oxide fuel cells (SOFCs) from near 1000 °C to the intermediate temperature (IT) range between 500 and 800 °C can reduce the costs by using cheaper alternative materials and increasing their working expectancy [1,2]. However, the performance of crucial component of SOFCs will drop rapidly with the decrease of operating temperature, especially for the

* *Corresponding author.*
E-mail address: xinw@hust.edu.cn (X. Wang).

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electrolyte material. Yttria stabilized zirconia (YSZ) is the most widely used electrolyte material in traditional high temperature SOFCs, but it exhibits poor ionic conductivity below 700 °C, which will degrade the overall cell performance [3,4]. Therefore, research on materials for electrolyte with higher ionic conductivity is of practical significance and great urgency for the development of IT-SOFCs.

Alternative electrolyte materials such as doped ceria [5,6], perovskite protonic conductors [7], doped bismuth vanadium oxide [8], strontium and magnesium doped lanthanum gallate [9] have been explored to obtain higher conductivity in intermediate temperature. Among them, doped ceria is one of the most promising materials for IT-SOFCs electrolyte due to its distinct advantages, such as high oxygen ionic conductivity, excellent chemical and thermal compatibility with cathode, well-controlled morphology, and relatively low cost [10–12]. Taking for example samarium doped ceria (SDC), a total conductivity of 1.81×10^{-2} S cm^{-1} was reached for $Sm_{0.2}Ce_{0.8}O_{1.9}$ in air at 600 °C, compared to 5.01×10^{-3} S cm^{-1} of YSZ under identical conditions [13–15]. However, the major drawback inherent to doped ceria electrolytes is the partial reduction of ceria ($Ce^{4+} \rightarrow Ce^{3+}$) occurring at low oxygen partial pressure (P_{O_2}) and elevated temperature, as shown by the Kröger-Vink notation,

$$2Ce_{Ce}^{x} + O_{O}^{x} \rightarrow \frac{1}{2}O_2 + V_{\ddot{O}} + 2Ce'_{Ce} \quad (1)$$

Accordingly, the open circuit voltage (OCV) and output power density of the cells will be significantly decreased by the generated electronic conductivity of doped ceria electrolyte. Also, the accompanied lattice expansion from Ce^{4+} (0.096 nm) [16] to Ce^{3+} (0.114 nm) [17] will adversely affect its mechanical stability [18].

Substantial efforts have been made to suppress the electronic conductivity and promote the application of ceria-based electrolytes. It was found that adding some co-dopants such as calcium or alkali element into the single doping GDC or SDC can increase their resistance towards reduction [19–21]. Coating a thin electronic conductivity blocking layer (ECB) such as YSZ on the surface of doped ceria electrolytes also helps prevent electronic conduction and improve mechanical stability [22–24]. For example, the OCV of single cells with SDC/YSZ (22μm/2 μm) bilayer electrolyte increases from 0.779 V (SDC, 22 μm) to 0.918 V at 650 °C [24]. However, the effect of co-dopants is limited due to their low solubility in fluorite structure, while the adoption of ECB layer can increase the ohmic resistance at lower temperatures and the overall cost of manufacturing. Another approach to overcome this drawback is by adding other electrolyte material to doped ceria to form a two-phase composite electrolyte. Perovskite protonic conductors (including $BaCeO_3/BaZrO_3$ based materials) have the potential to be applied, because they have high ionic conductivity at lower temperature, negligible electronic conductivity under low oxygen partial pressure (P_{O_2}), good chemical and thermal compatibility with doped ceria [25–27]. Various composite electrolyte materials such as $Gd_{0.2}Ce_{0.8}O_{1.9}$-$BaCe_{0.8}Y_{0.2}O_{3-\delta}$ (GDC-BCY) [27], $Sm_{0.2}Ce_{0.8}O_{1.9}$-$BaCe_{0.8}Y_{0.2}O_{3-\delta}$ (SDC-BCY) [28], $Nd_{0.1}Ce_{0.9}O_{2-\delta}$-$BaZr_{0.85}Y_{0.15}O_{3-\delta}$ (NDC-BZY) [29], $Gd_{0.1}Ce_{0.9}O_{2-\delta}$-$BaCe_{0.7}In_{0.3}O_{3-\delta}$ (GDC-BCI) [30] and $Sm_{0.2}Ce_{0.8}O_{2-\delta}$-$BaCe_{0.8}Sm_{0.2}O_{3-\delta}$ (SDC-BCS) [31] have been studied and higher ionic conduction or peak power density of single cells have been achieved. For instance, the OCV of cells with GDC-BCY (molar ratio 1:1, ~40 μm) electrolyte reached 0.93 V at 650 °C [27], while the OCV of cells with SDC-BCS composite electrolyte (SDC: BCS = 80:20 wt%, ~30 μm) was improved to 0.81 V compared to 0.76 V of the cells with SDC electrolyte (~30 μm) at 650 °C [31]. Although these studies demonstrated the feasibility of this method to obtain improved electrolyte performances, available research is still limited and the function principle of the dual phase composite systems has not been clearly explained.

As a co-doped perovskite protonic conductor, $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) has higher conductivity and better stability than single doping barium cerate under typical operation conditions of IT-SOFCs [32]. Moreover, previous research found that when BZCYYb was adopted as anode material, OCV of the SOFCs with SDC electrolyte was significantly improved by forming an electron blocking interface between the anode and electrolyte [12]. Therefore, we speculated that SDC-BZCYYb composite was a potential electrolyte candidate for IT-SOFCs, to address the drawback of single doped ceria and result in a better electrochemical performance. In this work, SDC as well as two composite samples by mixing BZCYYb additive with SDC matrix were prepared and their phase composition, microstructure, electrical conductivity and single cell performances were examined. These investigation results will help to reveal their composite effects.

Experimental

Powders synthesis and electrolyte preparation

$BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) and $Sm_{0.2}Ce_{0.8}O_{2-\delta}$ (SDC) powders were both synthesized by conventional sol-gel method. All the raw materials were purchased from Sinopharm Chemical Reagent Co., Ltd. For BZCYYb, stoichiometric amounts of the raw materials of $Ba(NO_3)_2$ (99.5%), $Zr(NO_3)_4 \cdot 5H_2O$ (AR), $Ce(NO_3)_3 \cdot 6H_2O$ (AR, 99%), $Y(NO_3)_3 \cdot 6H_2O$ (AR, 99%), $Yb(NO_3)_3 \cdot 5H_2O$ (99.9%) were dissolved into deionized water. Then EDTA (dissolved by ammonia to prevent flocculation) and citric acid were added successively to the solution, with a molar ratio of the metal ions: EDTA: citric acid = 1: 1: 2. Adding ammonia to adjust its pH value to 7–8, then kept the solution in oil bath at 80 °C under agitation until viscous gel was formed. Dried the gel at 300 °C for 3 h to obtain loose precursor. Grounded and calcined the precursor at 1100 °C for 5 h to form BZCYYb powders. For SDC, added appropriate amounts of $Sm(NO_3)_3 \cdot 6H_2O$ (99.9%), $Ce(NO_3)_3 \cdot 6H_2O$ (AR, 99%) and citric acid as chelant agent into deionized water. Stirred the solution for 9 h in oil bath at 80 °C to form a viscous gel. Then dried the gel at 200 °C and grounded it. SDC powders were obtained after calcining the precursor powders at 800 °C for 5 h.

Electrolyte pallets with different compositions were prepared, including pure SDC, 15 wt% BZCYYb-85 wt% SDC (B15S85) and 30 wt% BZCYYb-70 wt% SDC (B30S70). Powders in the mentioned proportions were weighed and ball milled separately with zirconia balls in ethanol at 350 rpm for 5 h. Afterwards, they were respectively die-pressed under 10 MPa and sintered at 1500 °C for 5 h to form dense pallets (φ22 × 1.2 mm).

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