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Exploring the role of NiO as a sintering aid in $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ electrolyte for proton-conducting solid oxide fuel cells

Bin Wang[a], Lei Bi[a,*], X.S. Zhao[a,b]

[a] *Institute of Materials for Energy and Environment, and College of Materials Science and Engineering, Qingdao University, Ningxia Road No.308, Qingdao, 266071, China*
[b] *School of Chemical Engineering, The University of Queensland, St Lucia, QLD, 4072, Australia*

HIGHLIGHTS

- NiO was used as the dopant for $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ proton-conducting oxide.
- High sinterability with improved conductivity was achieved.
- The doping strategy showed advantages over the traditional approach of using NiO.
- The cell with $BaZr_{0.1}Ce_{0.66}Ni_{0.04}Y_{0.2}O_{3-\delta}$ electrolyte showed a high performance.

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ABSTRACT

NiO is used as a sintering aid to modify $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ by an external addition method and by an internal doping strategy to improve the sinterability of $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$. In both cases, the modified $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ materials show an improved sinterability compared with the original $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$. However, doping $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ with NiO to form $BaZr_{0.1}Ce_{0.66}Ni_{0.04}Y_{0.2}O_{3-\delta}$ is found to be an effective strategy to significantly improve the electrolyte properties. The $BaZr_{0.1}Ce_{0.66}Ni_{0.04}Y_{0.2}O_{3-\delta}$ sample shows a high density and large grain size after sintering at a relatively low temperature (1400 °C). Electrochemical studies reveal that the doping strategy offers a high proton conductivity in both the bulk and across grain boundaries. The conductivity of $BaZr_{0.1}Ce_{0.66}Ni_{0.04}Y_{0.2}O_{3-\delta}$ sintered at 1400 °C is observed to be higher than that of $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ sintered at 1600 °C. With $BaZr_{0.1}Ce_{0.66}Ni_{0.04}Y_{0.2}O_{3-\delta}$ as the electrolyte, a proton-conducting solid oxide fuel cell displays a large peak power density of 477 $mW\,cm^{-2}$ at 600 °C and a high electrolyte membrane conductivity of $6.3 \times 10^{-3}\,S\,cm^{-1}$.

1. Introduction

Solid oxide fuel cells (SOFCs) are gaining more and more attention in the past decade due to their all solid structures and flexibility in fuels [1–5]. In order to improve the life-time of SOFCs, lowering the operation temperature of SOFCs is one of the keys for the development of SOFCs [6,7]. Proton-conducting oxides are regarded as promosing electrolyte candidates for achieving intermediate-temperature SOFCs as they can offer good proton conductivity, lowering the electroyte resistance of the cell and thus allowing the operation of the cells at the intermediate temperature range [8–11].

Amongst all proton-conducting oxides, barium-based perovskite-structured materials such as $BaZrO_3$ and $BaCeO_3$ are the most popular ones because of their higher proton conductivity than other proton-conducting oxides [12–15]. Yttrium (Y) is usually used as dopant for furthering enhancing the proton conductivity of $BaCeO_3$ [16]. One of the drawbacks of $BaCeO_3$ is its poor stability against H_2O or CO_2. It has been reported that partial substitution of Ce by Zr can improve the chemical stability of the material [17,18]. For example, a proton conductor $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) has been shown to exhibit an adequate chemical stability under mild conditions [19]. In addition, this BZCY material has also been found to display a higher proton conductivity than most of oxygen-ion conducting oxides at intermediate temperatures [19].

Although different preparation and processing methods have been proposed to prepare BZCY materials, the fabrication of dense BZCY electrolyte membranes for SOFCs usually requires a high-temperature sintering step [20–22]. The high-temperature sintering leads to some critical problems, such as severe thermal treatment conditions, difficulties in choosing compatible materials and the possible change of

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* Corresponding author.
E-mail addresses: bilei@qdu.edu.cn, bilei81@gmail.com (L. Bi).

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chemical compositions of the electrolyte [23]. Therefore, it is desirable to lower the sintering temperature for fabricating BZCY electrolyte membranes and still maintain its high conductivity. Although different sintering aids have been proposed to promote the sinterability for $BaCeO_3$-based materials [24–27], most sintering aids were used added to proton conducting oxides [28–31]. Actually, sintering aids can be used as the internal dopant by controlling the stoichiometry of the sample. Although the work of using internal dopant specifically for BZCY is less reported, this strategy has been found to use for other proton-conducting oxides. Gorbova et al. [32] have screened a series of transition metals and investigated their impact on the sinterability of $BaCe_{0.9}Gd_{0.1}O_3$(BCG) proton conductor, finding a suitable selection of internal dopant can enhance the sinterability of BCG. Ricote and Bonanos [33] have studied cobalt and nickel doped $BaZr_{0.9}Y_{0.1}O_3$ (BZY) at a low concentration of 1–2 mol.%, revealing the internal doping Co or Ni can greatly enhance the sinterability of BZY but also introduce some p-type conduction. Similar results are also obtained with In or Ga internally doped samples [34]. Liu et al. [35,36] have screened Pr, Nd, Sm and Gd as the internal dopants for BZY and found Nd can greatly improve the sinterability of BZY with a doping concentration of 20 mol.%, leading an improved processability for the proton conductor. These studies indicate that the internal doping strategy, which only receive increasing attentions in recently years, is also an effective way for improving the properties of proton conductors. However, direct comparisons of different strategies of using sintering aids which includes the external addition and internal doping methods are scarcely reported, making a less insight understanding of the influence of sintering aid on the properties of BZCY materials. The exploration of the role of the sintering aids would be important to understand the optimal approach to use the sintering aids, leading to a rational design and optimization of proton conducting oxides.

In this study, NiO was used in different strategies to improve the sinterability of BZCY. The influence of using NiO sintering aid in different strategies on the phase structure, sintering activity and electrical performance of the materials were investigated, and a further comparison was also made between the pure BZCY and the NiO modified BZCY. A fuel cell with the NiO modified BZCY was fabricated and tested, demonstrating the advantages and feasibility of using this material for proton-conducting SOFCs.

2. Experimental

The $BaZr_{0.1}Ce_{0.66}Ni_{0.04}Y_{0.2}O_{3-\delta}$ (BZCNY) powder was synthesized via a wet chemistry route. Briefly, the required amounts of analytic grades metal nitrates of 5.23 g $Ba(NO_3)_2$, 0.86 g $Zr(NO)_4{\cdot}5H_2O$, 5.73 g $Ce(NO_3)_3{\cdot}6H_2O$, 1.53 g $Y(NO_3)_3{\cdot}6H_2O$ and 0.23 g $Ni(NO_3)_2{\cdot}6H_2O$ were dissolved in an aqueous solution, followed by the addition of citric acid. The molar ratio between citric acid and total metal ions was 2:1. The pH value of the mixed solution was adjusted in the range of 7–8 b y slowly adding ammonium hydroxide solution. This solution was heated under stirring to evaporate water, and the gel was acquired. The gel finally ignited with a flame, producing ash. Then the ash was fired at 1000 °C for 5 h to obtain the pure phase BZCNY powder. For this BZCNY powder, NiO was used as a dopant for $BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (BZCY) and it can be considered as use the sintering aid NiO internally. Modification-free BZCY powder was also synthesized as a reference by using the same route using $Ba(NO_3)_2$, $Zr(NO_3)_4{\cdot}5H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, $Y(NO_3)_3{\cdot}6H_2O$ as the starting materials. For comparison, traditional BZCY-4 mol.%NiO (BZCYNi4) powder was synthesized by using the wet chemical route as mentioned above and BZCYNi4 was to use NiO as the sintering aid externally. Phase structures of the powders were identified by X-ray diffraction (XRD, Rigaku Ultima IV). The nanostructure information of the as-prepared powders was recorded by using a transmission electron microscope (TEM, JEOL JEM2100).

BZCNY, BZCYNi4 and BZCY powders were pressed into pellets and sintered at 1400 °C for 5 h, and another BZCY pellet was also sintered at 1600 °C for 5 h to enhance the densification of the pellet. The pellets were protected with powder bath to prevent the evaporation of elements at high sintering temperatures. The morphologies of the sintered samples were observed by a field-emission scanning electron microscope (FESEM, JSM-7800 F) and the elemental distribution of the sintered membranes was analyzed by energy dispersive X-ray spectroscopy (EDS). The conductivity measurements were performed on the dense pellets with AC impedance technique using an electrochemical workstation (CHI 760 E, CH Instruments).

The anode supported single cells were fabricated by a co-pressing and co-firing procedure. BZCNY powder was mechanically mixed with NiO to form the anode powder in a mass ratio of BZCNY (40): NiO (60). 20 wt.% of starch was added and used as the pore former in the anode. The BZCNY film was deposited on the NiO- BZCNY composite anode substrate by a co-pressing method, followed by a co-firing at 1400 °C for 5 h. Then the half-cell consisted of NiO-BZCNY composite anode and BZCNY electrolyte was obtained. The composite $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC)-BZCY material in a weight ratio of 1:1 was used as the cathode, and the impregnation method was applied to fabricate the cathode and the preparation details can be found elsewhere. The BZCY backbone was fired at 1200 °C, while the SSC phase was formed by heating the SSC nitrate precursors at 800 °C for 2 h. The single cells were tested with humidified hydrogen (~3% H_2O) as the fuel. The fuel cell outputs were recorded with an electrochemical workstation (CHI 1110C). The morphology of the cell was observed with FESEM.

3. Results and discussion

Fig. 1(a) shows the X-ray diffraction (XRD) patterns of the BZCNY, BZCYNi4 and BZCY powders after firing at 1000 °C. One can see that pure perovskite phase was formed in the samples without any impurities. The pure phase BZCNY powder suggests that the doping of NiO in BZCY does not change the structure of the material and the material still possesses the perovskite structure. However, it is interesting to note that BZCYNi4 powder is also a pure perovskite phase without any detectable secondary phases. In the powder synthesis procedure, the Ni source was added externally and the target material was the composite

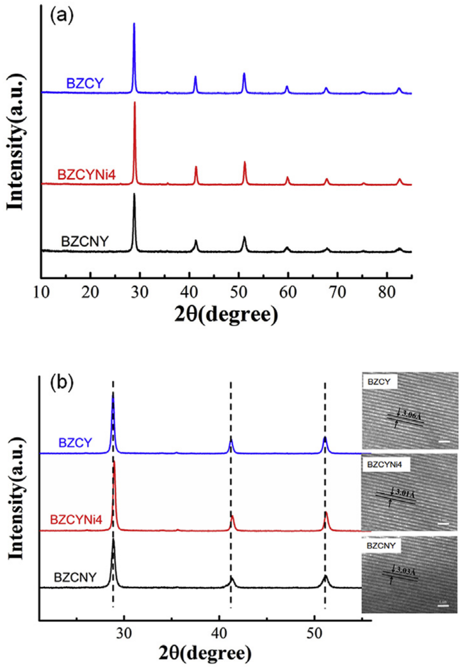

Fig. 1. (A) XRD patterns for BZCY, BZCYNi4 and BZCNY powders; (b) Enlarged region of the XRD patterns for BZCY, BZCYNi4 and BZCNY powders with corresponding HRTEM images.