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Short communication

Enhanced sinterability of $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ by addition of nickel oxide

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ABSTRACT

The effect of nickel oxide addition on the sintering behavior and electrical properties of $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) as an electrolyte for solid oxide fuel cells was systematically studied. Results suggest that the addition of a small amount (~1 wt%) of NiO to BZCYYb greatly promoted densification, achieving ~96% of the theoretical density after sintering at 1350 °C in air for 3 h (reducing the sintering temperature by ~200 °C). Further, a sample sintered at 1450 °C for 3 h showed high open circuit voltages (OCVs) when used as the electrolyte membrane to separate the two electrodes under typical SOFC operating conditions, indicating that the electrical conductivity of the electrical conductivity of the BZCYYb was not adversely affected by the addition of ~1 wt% NiO.

1. Introduction

Solid oxide fuel cells (SOFCs) represent the most cost-effective option for efficient conversion of readily available fuels (e.g., natural gas and gasified coal) directly to electricity [1,2]. As one of the most promising candidate electrolyte materials for intermediate-temperature SOFCs, proton conducting oxides have attracted more and more attention in recent years, due primarily to their low activation energy for proton conduction and good potential for high fuel utilization [3–5]. Among these candidate proton conducting electrolyte materials, the perovskite-type oxides show high proton conductivity in the intermediate temperature range under conditions for fuel cell operation [6–8] and for hydrogen separation [9–11]. One of the major challenges for tailoring the properties of these proton conductors is a proper compromise between conductivity and chemical stability. For example, doped $BaCeO_3$ has sufficiently high ionic conductivity, but the chemical stability in an atmosphere containing CO_2 and H_2O is inadequate for fuel-cell applications [12,13]. Recently, $BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZCYYb) was reported to have high ionic conductivity (~0.01 S cm^{-1} at humidified O_2 atmosphere), and adequate stability under typical fuel cell operating conditions [1]. However, it had to be sintered at high temperatures (>1550 °C) and for a long time (>10 h) to obtain dense (>96% relative density) electrolyte membranes [1].

A variety of sintering aids, such as ZnO [14], NiO [15], Al_2O_3 [16], and LiF [17] have been used for $BaZrO_3$ and $BaCeO_3$ based proton conductors to reduce the sintering temperature and soaking time. For example, Costa et al. [15] added 4 mol% of NiO as sintering aid into $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ and reduced the sintering temperature by 200 °C and promoted the densification. Tsai et al. [17] used LiF as additive, and the high density $BaZr_{0.8-x}Ce_xY_{0.2}O_{3-\delta}$ can be obtained at sintering temperature 200–300 °C lower than the usual 1700 °C with much shorter soaking time. The presence of LiF at low sintering temperatures assisted rapid densification by particle sliding and decreasing the jamming tendency. However, during the higher temperature sintering, the LiF would segregate to the grain boundaries and be entrapped as a globular phase within the fast growing grains [18], thus resulting in detrimental effect on the properties of the material. Since a cermet based on nickel is commonly used as an anode material in SOFCs, addition of NiO will not complicate the composition of the materials but could be beneficial to the sintering of the electrolyte.

Here we report our findings on the effect of adding ~1 wt% NiO on the sintering behavior and electrical properties of BZCYYb electrolytes. Results demonstrated that NiO is an effective sintering aid for BZCYYb, greatly enhancing densification and grain growth, but with minimal effect on the electrical properties of BZCYYb for SOFC applications.

2. Experimental

BZCYYb powder was prepared by a traditional solid state reaction method as described elsewhere [1]. About 1% (by weight)

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sintering aid NiO (Alfa Aesar >99% purity) was added to the BZCYYb powder. Precursors for pellet samples of blank BZCYYb and NiO-added BZCYYb were mixed by ball-milling the mixtures with Yttrium Stabilized Zirconate (YSZ) balls and ethanol for 24 h, followed by drying at 80 °C for 24 h, hydraulic dry pressing under 375 MPa pressure for 120 s. The green pellets had a diameter of 10 mm, with a typical thickness of around 1 mm. The disks were sintered at different temperatures (1250–1550 °C) with different soaking times.

X-ray diffraction (XRD) with CuKα radiation (Philips, PW-1800, tube voltage 45 kV, and tube current 40 mA) was used to analyze the crystal structure and phase composition of the sintered pellet samples. Intensities were collected in the 2θ range between 20° and 80° with a step size of 0.08° and a measure time of 20 s at each step. Relative densities of the sintered pellets were measured using the Archimedes method with water as the liquid medium. The microstructures of the sintered pellets were revealed using a scanning electron microscope (SEM; LEO 1530). The average grain sizes were determined from quantitative analysis of SEM images (by linear intercept method with multiplying a factor of 1.54) [19]. Two-probe impedance spectroscopy was used to determine the total conductivity of the sintered pellets in the ambient air at different temperatures. The sintered pellets were gold sputtered and brush painted with silver paste, and silver wire was used for electrical connection. The frequency range was from 10^5 Hz to 0.1 Hz. For the open circuit voltage (OCV) measurement, Pt pastes were used as the electrodes and silver wire for electrical connection. The test cells were affixed to the end of an alumina tube with a gas-tight ceramic paste seal. The OCV was measured under a fuel cell testing condition (humidified H_2/ambient air). The impedance spectra were collected using a Solartron 1286 electrochemical interface and a Solartron 1255 HF frequency response analyzer. We calculated the ionic transference number of each BZCYYb sample from the ratio of measured OCV to the Nernst potential of the cell using the sample as the electrolyte for the test cell.

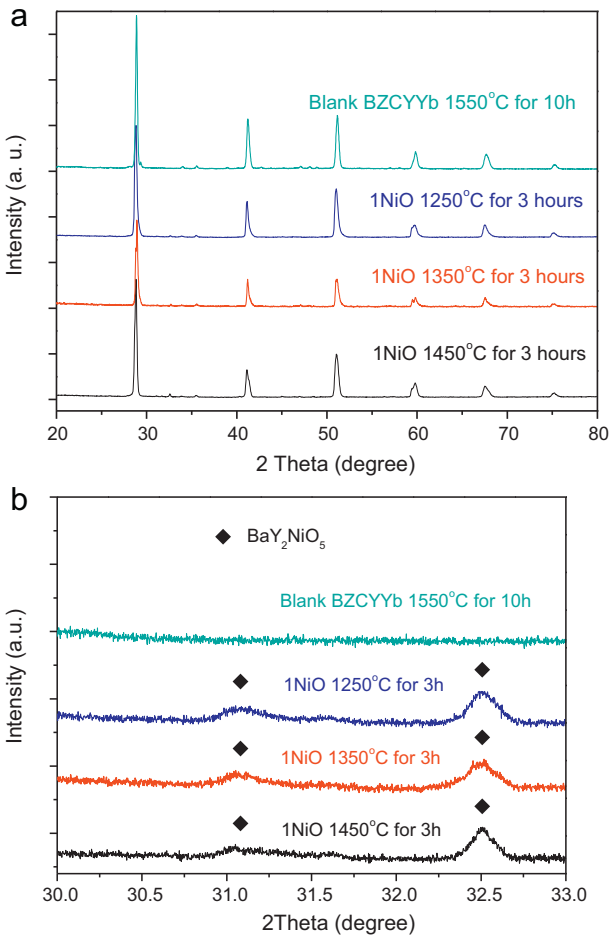

Fig. 1. X-ray diffraction patterns of sintered BZCYYb samples with and without ~1 wt% NiO presented in different 2θ range: (a) 20–80° and (b) 30–33° to show more details of the second phase(s).

3. Results and discussions

3.1. X-ray diffraction analysis

Consistent with the result reported by Tong et al. [20] for BZY20, we find that the main phase of the sintered BZCYYb with ~1 wt% NiO is still the perovskite phase, as shown in Fig. 1a, and a small amount of BaY_2NiO_5 is observable (PDF 00-041-0463) for all the NiO-modified BZCYYb samples, as seen in Fig. 1b.

3.2. Sintering behavior

To examine the effect of NiO on the sinterability of BZCYYb, relative densities and microstructures of pellets were determined using Archimedes method and SEM, respectively. Since the theoretical density of BZCYYb was not reported in the literatures, we calculated it based on the lattice parameters determined by synchrotron-based X-ray diffraction. The crystal structure of BZCYYb is orthorhombic with $a = 8.785$ Å, $b = 6.237$ Å and $c = 6.221$ Å. Thus, the theoretical density of BZCYYb is 6.211 g cm^{-3}.

Shown in Fig. 2 are some typical microstructures (SEM images) of BZCYYb and NiO-modified BZCYYb pellets sintered at 1250–1450 °C for 3 h. As expected, the grain sizes and densities of these samples increased with sintering temperature. More importantly, however, the addition of NiO to BZCYYb had significantly enhanced densification and grain growth. Fig. 3 shows the relative densities and grain sizes of BZCYYb with and without the addition of NiO sintering aid. At low sintering temperatures (e.g., 1350 °C), the BZCYYb has a lot of pores with an average grain size only 0.6–0.7 μm, reaching a relative density of ~76.5%. When the sintering temperature was increased to 1450 °C, the density increased to about 90.3% of the theoretical value, and the average grain size grew to about 2.6 μm. As shown in Fig. 2c, we could see some degree of agglomeration began to happen, however, large pores still can be seen between the grains. In stark contrast, with the addition of NiO, the densities of NiO-modified BZCYYb reached 89.9% of the theoretical value at an even lower temperature, 1250 °C. Furthermore, the densities increased to 96.5% and 98.1% when the sintering temperatures were 1350 °C and 1450 °C, respectively. Meanwhile, the grains experienced dramatic growth with sintering temperatures. For example, the average grain sizes increased approximately from 1.9 μm at 1250 °C to 3.9 μm at 1350 °C and to 16.1 μm at 1450 °C. Also, it is interesting to note that the average grain size of BZCYYb is about 7.0 μm after sintering at 1550 °C for 10 h, which is smaller than that for NiO-modified BZCYYb sintered at 1450 °C, as seen in Fig. 2e.

Similar to the observation by Tong et al. [21], the improved sintering behavior is due most likely to the formation of secondary phase BaY_2NiO_5, at the grain boundaries by the reaction between NiO and BZCYYb during the sintering process. According to the X-ray diffraction data shown in Fig. 1b, the BaY_2NiO_5 phase was detectable at temperatures as low as 1250 °C. This result is consistent with the reported BaY_2NiO_5 phase formation temperature, 1200 °C [21]. Because of the relatively low melting point of BaY_2NiO_5 (between 1450 °C and 1500 °C) [21], the presence of BaY_2NiO_5 phase at grain boundaries could promote mass transport

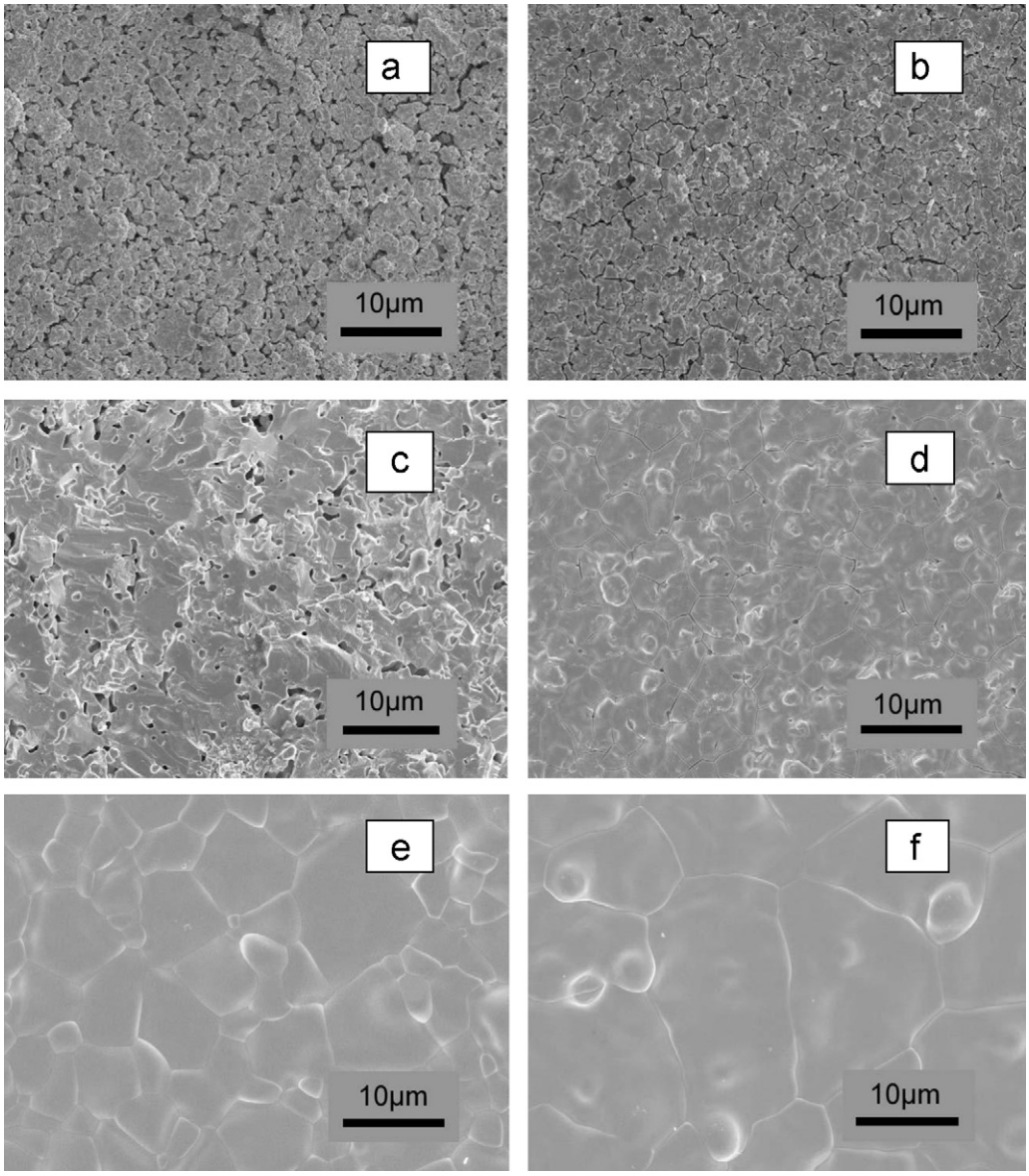

Fig. 2. SEM images for BZCYYb and NiO-modified BZCYYb pellets sintered at different temperatures for different times: (a) blank BZCYYb at 1350 °C for 3 h, (b) 1% NiO–BZCYYb at 1250 °C for 3 h, (c) blank BZCYYb at 1450 °C for 3 h, (d) 1% NiO–BZCYYb at 1350 °C for 3 h, (e) blank BZCYYb at 1550 °C for 10 h, and (f) 1% NiO–BZCYYb at 1450 °C for 3 h.

associated with grain growth and densification of BZCYYb. When the temperature was increased to 1450 °C (i.e., close to the melting point), partial liquid phase may form at the grain boundary of NiO-modified BZCYYb, which may dramatically accelerate grain growth and densification. As shown in Fig. 3, the average grain size of NiO-modified BZCYYb is about 1.9 μm, 3.9 μm, and 16.1 μm at 1250 °C, 1350 °C, and 1450 °C, respectively.

3.3. Electrical conductivity

While the addition of NiO has clearly facilitated the sintering of BZCYYb pellets, both the ionic and electronic conductivity of the NiO-modified BZCYYb should not be adversely affected. Shown in Fig. 4 are the total electrical conductivities of a BZCYYb and a NiO-modified BZCYYb sample, suggesting that the total conductivities of the NiO-modified BZCYYb (sintered at 1450 °C for 3 h) are comparable to those of the BZCYYb without the addition of NiO (sintered at 1550 °C for 10 h). It is noted, however, that the average grain size and the relative density of the NiO-modified BZCYYb sample (sintered at 1450 °C for 3 h) are greater than those of the blank BZCYYb (sintered at 1550 °C for 10 h). It is also well known that the conductivity of the grain boundary may be different from that of the grain for $BaCeO_3$-based materials [22]. The secondary phases (e.g., BaY_2NiO_5 and NiO) on the grain boundaries of NiO-modified BZCYYb, may reduce the ionic conductivity but enhance the electronic conductivity, especially under reducing conditions.

The ionic transference numbers (including the contributions from both protons and oxygen vacancies) of NiO-added BZCYYb samples were estimated from the ratio of the measured OCV to the corresponding Nernst potential under typical fuel cell testing conditions. In order to determine if the secondary phases on the grain boundaries (BaY_2NiO_5 and NiO) introduce detrimental electronic conductivity in the NiO-modified BZCYYb, we measured the open circuit voltage (OCV) across both blank BZCYYb and NiO-modified BZCYYb electrolyte membrane supported cells using Pt electrodes under typical fuel cell operating conditions: exposing one side to humidified hydrogen and other side to ambient air. As shown is Fig. 5, the OCV values for the cells based on a blank BZCYYb was higher than 1.14 V at 500 °C, which is slightly lower than the theoretical values predicted by the Nernst Equation,

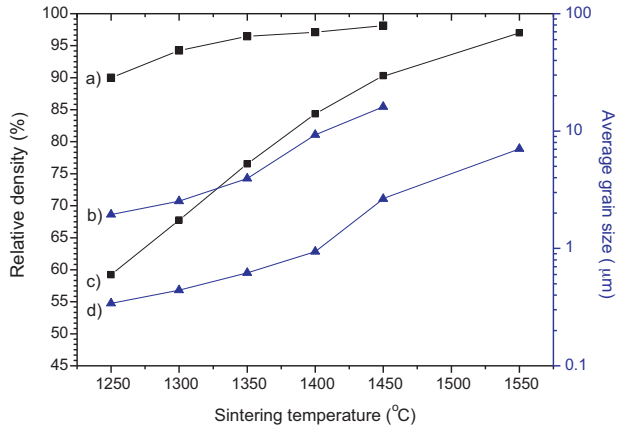

Fig. 3. The relative density and average grain sizes of NiO-modified BZCYYb (a and b) and blank BZCYYb (c and d) pellets sintered at different temperatures for 3 h.

indicating partial electronic conduction in the BZCYYb. As expected, the electronic transference number increased with temperature; varying from 0.007 at 500 °C to 0.07 at 750 °C; this is consistent with the report by Yang et al. [1]. Also shown in the figure are the OCVs for the cells based on a NiO-modified BZCYYb electrolyte. These OCVs are slightly lower than, those observed for the cells based on a pure BZCYYb, indicating that the addition of NiO to the BZCYYb introduced some small amount of additional electronic conduction. The NiO modified BZCYYb sintered at 1450 °C for 3 h is a little bit lower than the pure BZCYYb sintered at 1550 °C for 10 h, confirming that there might be some NiO remaining at the grain boundaries. Still, the NiO-modified BZCYYb has sufficiently high OCVs under fuel cell testing conditions, and it is favorable for fuel cell application [23]. At 650 °C, for example, the OCV of a cell based on the NiO-modified BZCYYb electrolyte was 1.088 V, suggesting an ion transference number of ~0.96 since the theoretical Nernst potential was ~1.127 V under the condition. The ionic transference number decreased with temperature, approaching ~0.928 at 750 °C when humidified hydrogen was used as the fuel and ambient air as the oxidant [23].

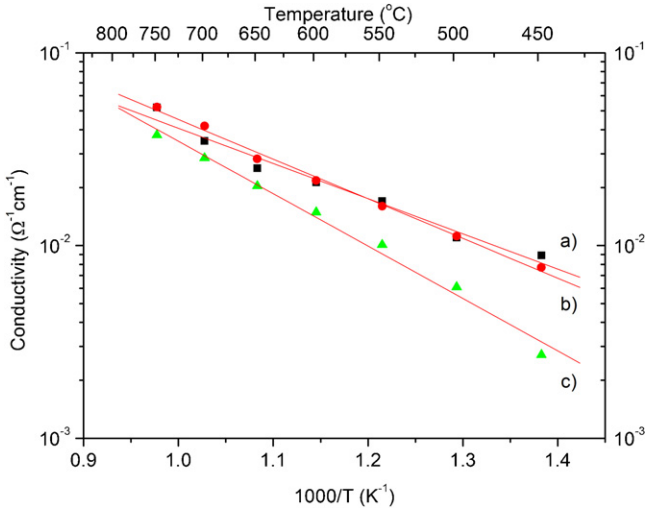

Fig. 4. Electrical conductivities of blank BZCYYb and NiO-modified BZCYYb sintered at different temperatures for different periods of time: (a) lank BZCYYb pellets sintered at 1550 °C for 10 h, (b) 1% NiO–BZCYYb pellets sintered at 1450 °C for 3 h, and (c) 1% NiO–BZCYYb pellets sintered at 1350 °C for 3 h.

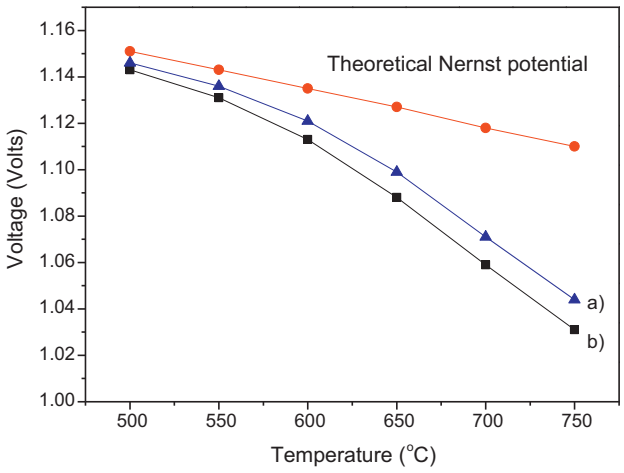

Fig. 5. Open circuit voltages (OCV) for cells with a configuration of Pt|electrolyte|Pt with wet H_2 (~3 vol% H_2O) as fuel and air as oxidant with different electrolyte membranes: (a) blank BZCYYb sintered at 1550 °C for 10 h and (b) 1% NiO–BZCYYb sintered at 1450 °C for 3 h at different temperatures.

4. Conclusion

It is shown that dense BZCYYb can be obtained at lower sintering temperatures for shorter duration with the addition of ~1 wt% of NiO as a sintering aid, achieving ~96% of theoretical density and grain size of ~4 μm after sintering at 1350 °C for 3 h. In contrast, BZCYYb pellets without NiO addition had to be sintered at 1550 °C for 10 h to achieve a similar relative density. Moreover, the total conductivities of the NiO-modified BZCYYb sintered at 1450 °C for 3 h were comparable to those of the unmodified BZCYYb sintered at 1550 °C for 10 h. The open circuit voltages of a cell based on a NiO-modified BZCYYb are sufficiently high for fuel cell applications.

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