



Transport properties of $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Y}_{0.2}\text{O}_{3-\delta}$ proton conductor prepared by spark plasma sintering

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Abstract

Dense $\text{BaZr}_{0.5}\text{Ce}_{0.3}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZCY532) proton conductors were prepared by a spark plasma sintering method. Their conductivities were determined in different atmospheres: dry air, wet N_2 and wet H_2 . Moreover, the potential electronic conductivity contribution to the total conductivity was also identified by testing their total conductivities at different oxygen partial pressures ($1\text{--}10^{-24}$ atm) in combination with an XPS analysis. It is found that the prepared dense BZCY532 ceramics are good proton conductors at 600 °C. In addition, the Ce^{3+} concentration in the dense BZCY532 ceramics is around 3.5 atm% of the total Ce element, and the electronic contribution to the total conductivity can be neglected after a postheat treatment.

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1. Introduction

Barium zirconate–cerate ($\text{BaZrO}_3\text{--BaCeO}_3$) based electrolytes have been considered as the next generation of proton conductors to be used for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs). Thus, the development of these electrolytes have been studied extensively in recent years [1–6]. Normally, a high sintering temperature (≥ 1600 °C) and a long sintering time (≥ 24 h) is needed to prepare dense $\text{BaZrO}_3\text{--BaCeO}_3$ based proton conductors when using conventional sintering methods [7,8]. However, some of the Barium (Ba) can evaporate when the sintering temperature is higher than 1500 °C. Furthermore, the corresponding conductivities of these proton conductors will be lowered by 1–2 orders of magnitudes, even if the loss of Ba is only 1–2 atm% [8–10]. Therefore, a lowered sintering temperature, less than

1500 °C, is favorable for the preparation of dense $\text{BaZrO}_3\text{--BaCeO}_3$ based proton conductors.

In order to realize the goal of lowered sintering temperature, several efforts were preformed, including the sintering aids addition, importing chemical synthesis methods to prepare ultrafine powders and importing cost-effective solid-state reactive sintering (SSRS) method [11–14]. However, some controversial results emerged after the addition of sintering aids, some results showed enhanced conductivities while others showed reduced conductivities [15,16]. Though the chemical synthesis methods can improve their sintering ability and conductivity, these methods always need a complex synthesis procedure and a long synthesis time. Hence, the Spark Plasma Sintering (SPS) technique represents an alternative method to prepare dense $\text{BaZrO}_3\text{--BaCeO}_3$ based ceramics. This is due to that a lowered sintering temperature and a shortened sintering time can be achieved compared to conventional sintering methods. Moreover, the sintering aids will not be used during the SPS process, which can remove the ambiguous sintering aids effect on conductivity. However, the SPS technique is mainly used to prepare dense BaZrO_3 based ceramics. So far, no dense Ce-containing $\text{BaZr}_{0.8-x}\text{Ce}_x\text{Y}_{0.2}\text{O}_{3-\delta}$ ($0 < x \leq 0.8$) or

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BaZr_{0.9-x}Ce_xY_{0.1}O_{3-δ} ($0 < x \leq 0.9$) based proton conductors have been prepared successfully by using the SPS technique according to the authors' knowledge [17–21], except our latest achievement [22].

As one of the most promising proton conductors, BaZr_{0.5}Ce_{0.3}Y_{0.2}O_{3-δ} (BZCY532) showed good proton conductivity in the intermediate temperature range [23,24], 4.4 mS cm⁻¹ at 600 °C when tested in the wet H₂ atmosphere. Therefore, BZCY532 was selected for this study and the SPS technique was selected as the sintering method. Their electrical conductivities were investigated in different atmospheres and also at different oxygen partial pressures (P_{O2}, 1–10⁻²⁴ atm). In addition, the characterization of X-ray Photoelectron Spectroscopy (XPS) for dense BZCY532 ceramics was carried out and analyzed.

2. Experimental

2.1. Sample preparation

The BaZr_{0.5}Ce_{0.3}Y_{0.2}O_{3-δ} (BZCY532) powder was synthesized by the solid-state reaction method using water-based milling combined with a freeze drying process. The details can be found in our previous studies [25–27]. More specifically, stoichiometric amounts of raw materials were weighed and ball milled for 5 h. Then, the powder slurry was dried through a freeze-drier. After that, the dried powder mixture was calcined at 1300 °C for 5 h. Thereafter, the prepared powder was sintered by a SPS method at 1350 °C and using a holding time of 5 min. After sintering, the prepared pellets were heated to 1350 °C and kept for 2 h [22].

2.2. Characterization

A Philips X'pert X-ray diffractometer was used for X-Ray Diffraction (XRD) test. The morphologies of the sintered samples was determined by a JSM-7000F system (JEOL Ltd., Japan). Furthermore, their corresponding Energy-dispersive X-ray Spectroscopy (EDS or EDX) analysis was done by using an Oxford Instruments combined with an INCA software. The X-ray Photoelectron Spectroscopy (XPS) measurements were conducted by using an ESCALAB 250Xi X-ray Photoelectron Spectrometer System (Thermo Fisher Scientific Inc., United States). Also, a binding energy calibration was performed using C1s peak at a binding energy of 284.8 eV. The measured spectrum was analyzed by using a XPS-peak-differenating method and using a XPSPEAK 4.1 software.

2.3. Electrical and electrochemical measurements

Before each conductivity test, both surfaces of the pellet were polished. And it was made sure that the up-down surfaces were parallel. Thereafter, an Au paste was brushed on both surfaces of the pellet. And then, the Au-coated pellets were annealed at 850 °C for at least 30 min. Following that, the conductivities of the BZCY532 ceramics were determined by

using a MinisTest6000S platform (Toyo Corporation, Japan). Their conductivities in the atmospheres of dry air, wet N₂ and H₂ were tested at temperatures of 200–800 °C by using a Electrochemical Impedance Spectroscopy (EIS) method. A frequency range of 0.1–100 kHz and an excitation voltage of 100 mV were employed in an open-circuit mode. Moreover, their total conductivities at different oxygen partial pressures (P_{O2}) were also identified at temperatures of 600–800 °C, in order to determine whether there are unfavorable electronic conductivity. The settings of different P_{O2} were controlled and realized automatically by using the gas mixtures of N₂–O₂ and N₂–H₂O–H₂ to control the P_{O2} in a range of 1–10⁻² atm and 10⁻³–10⁻²⁴ atm, respectively. For the P_{O2} in the range of 1–10⁻² atm, it can be realized by simply mixed different volume ratios of N₂ and O₂. As for P_{O2} in the range of 10⁻³–10⁻²⁴ atm, the different volume ratios of gas N₂, H₂O and H₂ were calculated by a thermodynamic software, name FactSage. Firstly, the chemical reaction equilibrium constants of water decomposition reaction were calculated. Then, different volume ratios of gas H₂O and H₂ were obtained, and the N₂ was used as a balance gas. Finally, different P_{O2} can be realized automatically by setting different volume ratios of input gases via the MinisTest6000S platform. As for the specific test, the holding time at one set temperature and P_{O2} was kept at least one hour for obtaining a steady state.

3. Results and discussion

3.1. Phase and microstructure analysis

In order to confirm that no phase change had occurred in prepared BZCY532 ceramics, XRD and EDS measurements were performed. Also, Scanning Electron Microscope (SEM) studies were conducted to determine the morphology and the grain size. From Fig. 1(a), it can be seen that the synthesized powder and prepared BZCY532 pellet are pure and without other impurities. Moreover, the peaks of XRD patterns are sharp, which indicates that both of the powder and pellet are well crystallized. The small peak shift should be attributed to the smaller lattice parameter of BZCY532 at a condense state compared to its powder state. The EDS result can further confirm that there is no element loss after SPS sintering (Fig. 1(b)). The relative densities of the BZCY532 ceramics are 0.995 and the grain sizes of the BZCY532 ceramics are in the range of 400–500 nm with a narrow distribution (Fig. 1(c)) [22]. The relative densities of these samples are even higher than the results from our previous study, which included an addition of sintering aid (1 wt% NiO) [24].

3.2. Conductivities in different atmospheres

To enable a better comparison with reported results, the total conductivities of BZCY532 ceramics were determined in dry air, wet N₂ and wet H₂ atmospheres, respectively. Fig. 2 shows the typical impedance spectra of dense BZCY532 ceramics when they were tested at 600 °C. The spectrum that tested in wet H₂ showed the smallest resistance, followed by tested in

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