

Characterization of $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ proton-conducting electrolyte material synthesized by pulsed-current activated sintering

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$\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZY20) proton conductors have been investigated as electrolyte materials for intermediate temperature solid oxide fuel cells. The BZY20 powders were synthesized by both a citrate/ethylene-diamine-tetraacetic acid complexing method and a glycine nitrate process, and then sintered by pulsed-current activated sintering. Densification by pulsed-current activated sintering occurred even at 1300 °C within 5 minutes, obtaining a relative density and crystallite size of the sintered body of 95% and 190 nm, respectively.

Key words: Solid oxide fuel cell, Electrolyte, Proton conductor, BZY, Pulsed-current activated sintering.

Introduction

An advantage of solid oxide fuel cells (SOFCs) is their high operating temperature, which can increase the catalytic activity and allow the use of hydrocarbon fuels directly without external reforming. However, the high operating temperature, of around 1000 °C, leads to a limited choice of interconnect materials, thermal expansion mismatch, and chemical reactivity among the components. For this reason, intermediate temperature solid oxide fuel cells (IT-SOFCs), which operate at 500-800 °C, have been intensively investigated.

Proton-conducting oxides are appealing in this regard as they show high ionic conductivity and electrochemical properties in the intermediate temperature range of 500-700 °C [1]. Among the many proton-conducting electrolytes, $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZY20) is a promising material due to its high proton conductivity and chemical stability in a CO_2 environment. However, it is very hard to obtain dense BZY20 because of the high grain boundary resistance among the particles. In conventional sintering, BZY20 usually requires temperatures of about 1500-1700 °C and a long isothermal duration - more than 24 h. Moreover, conventional processing affords several disadvantages, such as a large grain size and an inhomogeneous chemical composition [2]. Thus, we adopted pulsed-current activated sintering [3] and attempted to densify BZY20 at a relatively lower temperature and in a short time.

Experimental

BZY20 powders were synthesized by a glycine nitrate process (GNP) [4, 5] and a citrate/ethylene-diamine-tetraacetic acid (EDTA) complexing method [6]. The stoichiometric quantity of metal nitrates of $\text{Ba}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved into deionized water. After stirring for 1 h, a calculated amount of glycine was dissolved into the nitrate solution. The ratio of glycine and nitrate (G/N) was adjusted to range of 0.25-1. After sufficient stirring (about 30 minutes), the solution was heated on a hot plate until it turned into a viscous liquid, just below 100 °C. The viscous liquid was heated to around 300 °C, where spontaneous ignition occurred.

In the case of the citrate/ethylene-diamine-tetraacetic acid complexing method, a required amount of ethylene-diamine-tetraacetic acid (EDTA) was first dissolved into aqueous NH_4OH and an appropriate amount of citric acid added to the solution; metal nitrates were then added to the citric acid/ethylene-diamine-tetraacetic acid/ NH_4OH solution and the pH adjusted to 7, using NH_4OH . The molar ratio of ethylene-diamine-tetraacetic acid/citric acid/metal ions was 1 : 1.5 : 1. The precursor was kept at 90°C with stirring to evaporate water. When transparent gels were obtained, they were dried in an oven at 130 °C for 24 h.

After completing the process, the ignited mass prepared by glycine nitrate process was calcined at 1100 °C for 10 h. The powder prepared by the citrate/ethylene-diamine-tetraacetic acid complexing method was calcined at 900 °C for 4 h and then at 1100 °C for 6 h. All calcination processes were carried out in an air atmosphere. The calcined powders were ball milled for 48 h with zirconia balls.

Phase identification of the ball milled powders was carried

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out with an X-ray diffractometer (MAX-111A, Rigaku Corporation, Japan) with a scanning speed of $4^\circ\text{minute}^{-1}$, using $\text{Cu K}\alpha$ radiation. Microstructural characterizations of the ball milled powder were carried out with a scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan).

The synthesized BZY20 powders were sintered by pulsed-current activated sintering. The powder was sintered as pellets 20 mm in diameter and 2-3 mm thick. The sintering process is summarized as follows:

- 1) the powder was placed in a graphite die;
- 2) the heating rate was $200\text{ K}\cdot\text{minute}^{-1}$ with a pressure of 80 MPa;
- 3) dwelling at 1300°C for 0-5 minutes.

The temperature was measured by a pyrometer focused on the outside surface of the graphite die. The electrical power was then switched off, the pressure released, and the sample was allowed to cool at room temperature. The sintered body was polished and then annealed in air at 1000°C for 2 h. This heat treatment removes the surface carbon contamination and relieves residual stresses caused by the pulsed-current activated sintering process or polishing.

The relative densities were checked in accordance with the isothermal dwelling time by Archimedes' method. The microstructures were observed by SEM on the fracture surface. The AC impedance and electrical conductivity were measured in a range of $500\text{--}800^\circ\text{C}$, in 100°C increments, in dry, and wet (3% H_2O) nitrogen, air, and hydrogen atmospheres.

Results and Discussion

BZY20 powders were synthesized with various glycine contents to identify the condition for forming a single phase. The molar ratios of glycine and nitrate were adjusted in a range of 0.25-1 with decrements of glycine content. X-ray diffraction patterns of BZY20, synthesized using glycine nitrate process and calcined at 1100°C for 10 h, are shown in Fig. 1. A small amount of unreacted BaCO_3 is observed in 1 : 3 and 1 : 4 G/N ratio powders. While the 1 : 1 G/N ratio BZY20 powder has only traces of BaCO_3 , the 1 : 2 G/N ratio powder is single phase.

It has been reported that the temperature of the combustion reaction is a critical factor, affecting the crystallite size of the reaction product [7]. The temperature can be controlled by adjusting the G/N ratio, and a smaller G/N value leads to a smaller crystallite size [8, 9]. Therefore, the 1 : 2 G/N ratio powder was selected and sintered by pulsed-current activated sintering. However, since the powder was sintered partially and agglomerated by high synthetic temperature during the glycine nitrate process, as shown in Fig. 2, the sintering result was not good. The sintered samples with powders synthesized by the glycine nitrate process were cracked and had a low relative density of around 86%.

The citrate/ethylene-diamine-tetraacetic acid complexing method [6] was employed to obtain much finer and less agglomerated powders. Fig. 3 shows X-ray diffraction

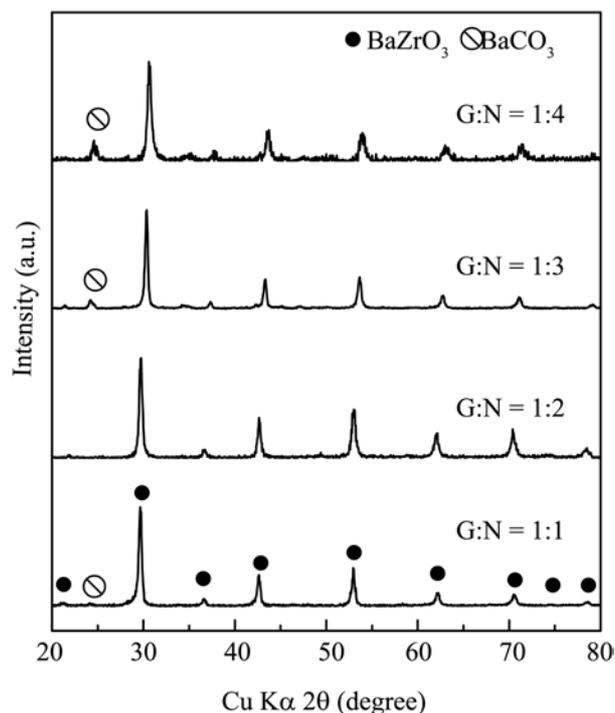


Fig. 1. X-ray diffraction pattern of BZY20 synthesized by glycine nitrate process.

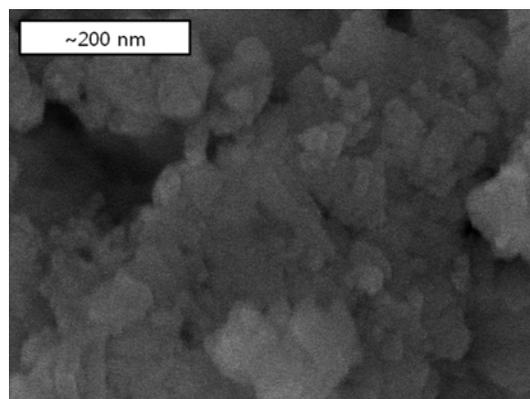


Fig. 2. SEM micrograph of the BZY20 powder synthesized by glycine nitrate process.

patterns of BZY20 powder synthesized by the citrate/ethylene-diamine-tetraacetic acid complexing method. It has been reported that the citrate/ethylene-diamine-tetraacetic acid complex finishes its reaction at around 900°C [6]; therefore, the as-synthesized powders were calcined at 900°C for 4 h. However, BaCO_3 still remains, as shown in Fig. 3. Although the calcined powders were again heated to 1100°C for 6 h, there is still a trace of BaCO_3 . It is interesting, however, that the BZY20 sample became a single phase after sintering. Meanwhile, as shown in Fig. 4, the BZY20 powder synthesized by the citrate/ethylene-diamine-tetraacetic acid complexing method was much finer and less agglomerated than the powder synthesized by the glycine nitrate process.

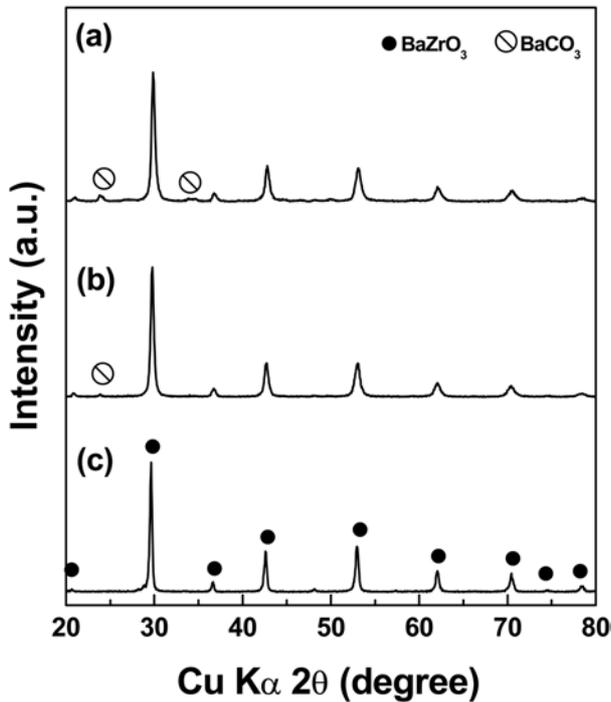


Fig. 3. XRD data of the BZY20 powders synthesized by the citrate/ethylene-diamine-tetraacetic acid complexing method firing at (a) 900°C for 4 h, (b) 900°C for 4 h and 1100°C for 6 h, and (c) the sintered body synthesized by pulsed-current activated sintering.

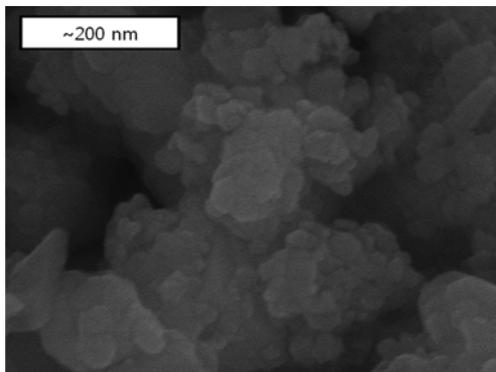


Fig. 4. SEM micrograph of the BZY20 powder synthesized by the citrate/ethylene-diamine-tetraacetic acid complexing method.

Fig. 5 shows the sintering behavior of BZY20 under a pressure of 80 MPa. The densification, which can be indicated by lowest shrinkage rate, occurs within 5 minutes. The sintering temperature is 1300 °C, indicating that the sintering time and temperature can be dramatically reduced by using pulsed-current activated sintering, compared with conventional sintering. The crystallite sizes, calculated by Stokes and Wilson's formula [10] from XRD data, are listed in Table 1.

Fig. 6 shows the dependence of the relative density on holding time at 1300 °C. The density of the sintered body was obtained by Archimedes' method. The relative density increases with an increase in the holding time. Using the powder synthesized by the citrate/ethylene-diamine-tetraacetic acid complexing method, the sintered

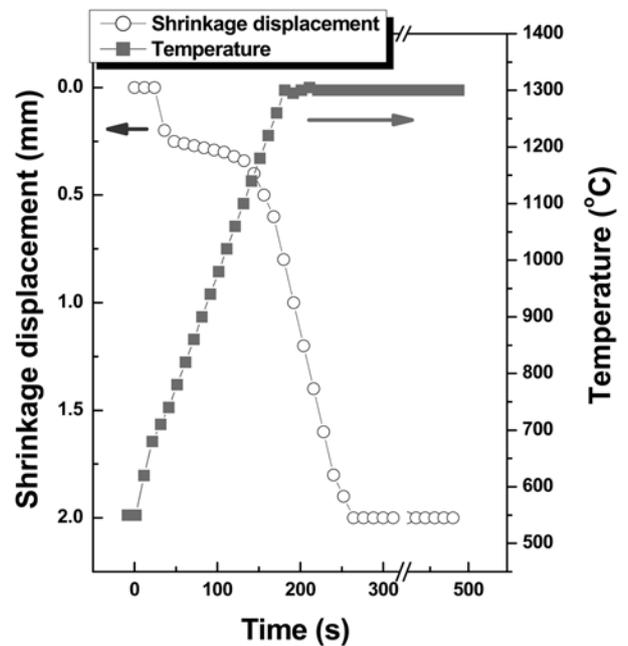


Fig. 5. Variation of temperature and shrinkage displacement of BZY20 with heating time during pulsed-current activated sintering under a pressure of 80 MPa.

Table 1. Crystallite size of BZY20 samples

Sample	Crystallite size (nm)
Powder synthesized by GNP	66
Powder synthesized by citrate/EDTA method	29
Sintered body with the powder synthesized by citrate/EDTA method (relative density of 95%)	190

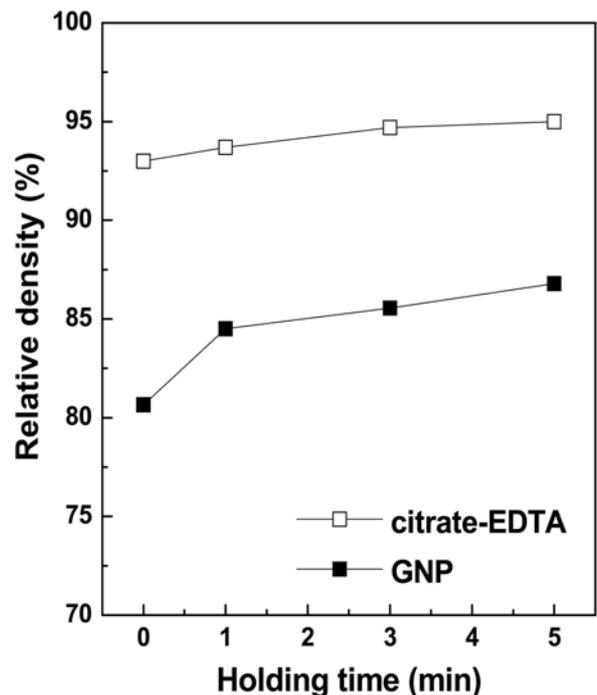


Fig. 6. Relative density dependency on holding time at 1300 °C.

body had a higher density than that using powder synthesized by the glycine nitrate process, because the powder synthesized by the citrate/ethylene-diamine-tetraacetic acid complexing method has a smaller particle size and less agglomeration. Finally, a relative density of 95%, without significant grain growth, is obtained in 5 minutes even at 1300 °C with powders synthesized by the citrate/ethylene-diamine-tetraacetic acid complexing method.

Fig. 7 shows SEM micrographs of the sintered body. There are differences between the grain sizes in the interior and at the surface of the sample. This might be due to the direct contact with the graphite die at the sample surface, which heats first.

Fig. 8 shows the AC impedance spectroscopy of BZY20 measured at 600 °C. The typical AC impedance spectra of the BZY20 electrolyte were collected under air, nitrogen, and hydrogen, in dry and wet (3% H₂O) atmospheres.

A simple equivalent circuit, consisting of an inductor (L_1), resistor (R_1), and two RQ elements was employed to fit the impedance data. The left intercept with the impedance arc on the Z' real axis at high frequencies corresponds to the ohmic resistance R_b ; the right intercept on the Z' axis indicates the total resistance R_{tot} , and the polarization resistance R_p , which is the overall size of the arcs $R_{tot}-R_b$. In a wet atmosphere, R_{tot} was less than R_{tot} in a dry atmosphere, because proton conduction occurred in the wet atmosphere.

The ionic conductivity of the BZY20 sintered by pulsed-current activated sintering as a function of temperature is shown in Fig. 9. In the high temperature region, the

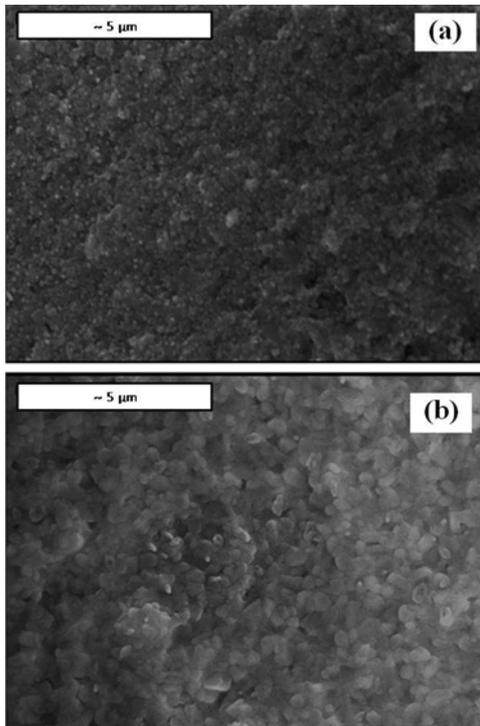


Fig. 7. SEM micrographs of the BZY20 obtained by pulsed-current activated sintering at 1300 °C for 5 minutes; (a) the interior and (b) sample surface.

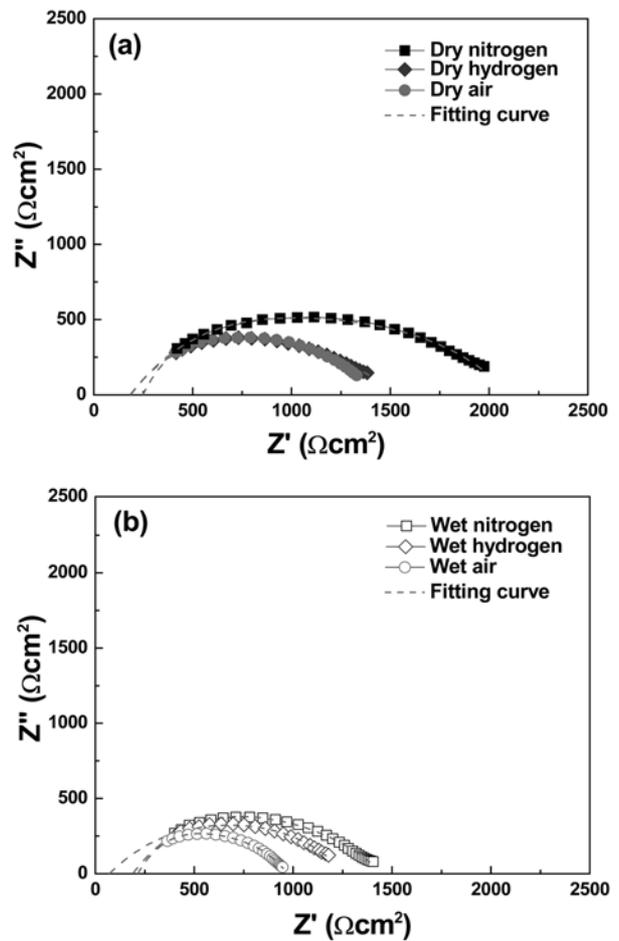


Fig. 8. Typical AC impedance spectra of BZY20 at 600 °C; (a) dry atmosphere and (b) 3% wet atmosphere.

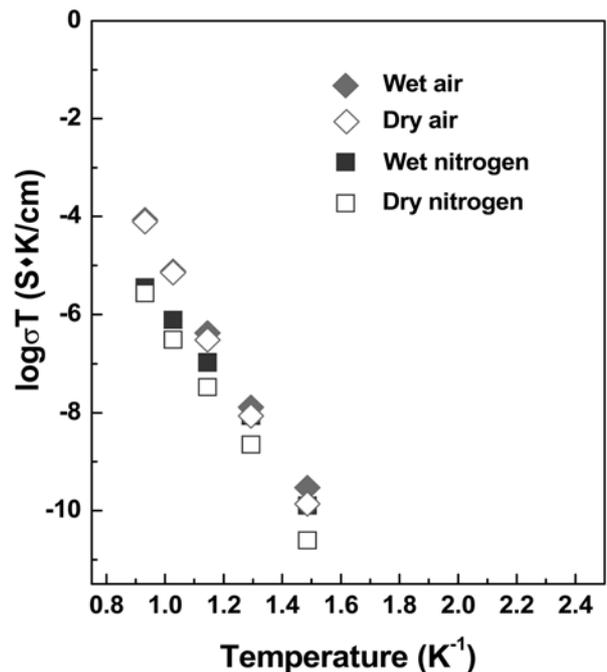


Fig. 9. Variations of the electrical conductivity of BZY20 measured in air and nitrogen atmospheres.

conductivities in wet and dry atmospheres are similar. This indicates that oxide ion conduction in BZY20 is dominant, compared with proton conduction, at higher temperatures. In contrast, in the low temperature region, the conductivity in the wet atmosphere is higher, which indicates a dominant proton conduction at a lower temperature in a wet atmosphere.

Conclusions

Fine BZY20 powders were synthesized by the glycine nitrate process and the citrate/ethylene-diamine-tetraacetic acid complexing methods, producing powder crystallite sizes of 66 and 29 nm, respectively. The powder synthesized by the glycine nitrate process was quite agglomerated because of the high synthesis temperature during the combustion reaction. In contrast, the BZY20 powder synthesized by the citrate/ethylene-diamine-tetraacetic acid complexing method could be sintered with a relatively high density by pulsed-current activated sintering at 1300 °C for 0-5 minutes. The relative density and the crystallite size of the sintered body were 95% and 190 nm, respectively. Using pulsed-current activated sintering dramatically reduced the sintering time and temperature and maintained the microstructure of the initial conditions of raw powders without significant grain growth. Electrical conductivity measurements and AC impedance spectroscopy indicate that BZY20 exhibits proton conduction, which is dominant at lower temperatures.

Acknowledgement

This work was supported by the New & Renewable Energy of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korean Ministry of Knowledge Economy (Grant number 2010T100100622).

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