



# Highly conductive barium zirconate-based carbonate composite electrolytes for intermediate temperature-protonic ceramic fuel cells



Ka-Young Park<sup>a</sup>, Tae-Hee Lee<sup>a</sup>, Ji-Tae Kim<sup>a</sup>, Naesung Lee<sup>a</sup>, Youngho Seo<sup>a</sup>, Sun-Ju Song<sup>b</sup>, Jun-Young Park<sup>a,\*</sup>

<sup>a</sup> HMC & INAME, Green Energy Research Institute, Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 143-747, Republic of Korea

<sup>b</sup> Department of Materials Science and Engineering, Chonnam National University, Gwangju 550-749, Republic of Korea

## ARTICLE INFO

### Article history:

Received 8 August 2013

Received in revised form 13 September 2013

Accepted 19 September 2013

Available online 28 September 2013

### Keywords:

Proton conducting ceramic fuel cells

Yttrium-doped barium zirconates

Carbonates

Composite electrolytes

Proton conductivity

## ABSTRACT

Two-phase composite materials consisting of a BZY matrix phase and a binary eutectic carbonate (Li–0.5Na)<sub>2</sub>CO<sub>3</sub> phase are designed in order to promote the densification and ionic conductivity of BaZr<sub>0.85</sub>Y<sub>0.15</sub>O<sub>3–δ</sub> (BZY) proton conductors at intermediate temperature. In the presence of carbonate phase, a considerable change in microstructure for the densification of BZY electrolytes sintered at 670 °C for 4 h is clearly visible in SEM analysis. This sintering effect is due to the formation of molten phase associated with carbonates at low temperature (495 °C) by TG–DTA analysis. The conductivity of composite electrolytes is significantly higher than that of BZY over the entire temperature and atmosphere range studied by AC impedance and DC four-probe methods. In addition, the change of the carbonate content in the composite electrolyte presents a great influence on the conductivity. The composite containing 25 wt.% (Li–0.5Na)<sub>2</sub>CO<sub>3</sub> shows the highest ionic conductivity of 0.176 S cm<sup>–1</sup> at 550 °C and lowest activation energy of 0.127 eV in the temperature range of 500–650 °C.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Intermediate-temperature proton-conducting ceramic oxides (ITPCs) are promising electrolytes for the development of various electrochemical devices, such as protonic ceramic fuel cells (PCFCs), intermediate temperature-solid oxide fuel cells (IT–SOFCs), hydrogen separation membranes and electrolysis cells, because of their higher ionic conductivity compared to conventional ceramic oxygen conducting oxides in the IT range of 450–700 °C [1–5]. In particular, the application of ITPCs in PCFCs offers high efficiency with high utilization of hydrogen, because water is produced on the cathode side [6]. In addition, IT operation of PCFCs not only extends the selection of materials for individual components of high-temperature FCs with a reduction in fabrication cost, but also improves the long-term stability with respect to chemical stability and thermal expansion compatibility [7].

Among ITPCs, perovskite, based on BaCeO<sub>3</sub> and BaZrO<sub>3</sub> doped with Y<sub>2</sub>O<sub>3</sub> or lanthanide oxides has been widely investigated as an electrolyte for PCFCs [8–10]. In particular, BaZr<sub>0.85</sub>Y<sub>0.15</sub>O<sub>3–δ</sub> (BZY) is one of the most studied systems due to its high bulk proton conductivity with high chemical stability in atmospheres containing CO<sub>2</sub> and H<sub>2</sub>O [8,11–16]. Due to the refractory nature of BZY, however, this material needs extremely high sintering temperature (1700–2100 °C) with long sintering time (>24 h) to achieve full

electrolyte density, even with nanosized starting powders [5,17,18]. High sintering temperature with longer time results in a loss of barium, and deleterious secondary phases such as Y<sub>2</sub>O<sub>3</sub>, causing inferior grain boundary conductivities [19–22]. Hence, the use of sintering aids (e.g. ZnO, NiO and CuO) has required achieving a dense microstructure of BZY samples [23–26]. However, there is a disadvantage in decreasing the proton conductivity of BZY materials with increased electronic conductivity. In addition, compared to the bulk conductivity, the poor grain boundary conductivity of BZY materials suffers disadvantages due to the barium deficiency and inevitable structural distortions at the grain boundary region, leading to a decrease in protonic defects.

It has recently been discovered that two-phase composite materials consisting of a doped ceria matrix phase and a small amount of a second phase, such as carbonate, sulphate, chloride or hydroxide, have improved the transport properties of electrolytes with enhanced SOFC performance compared with doped ceria in the IT range [27–30]. In particular, rare-earth-doped ceria composites with the alkali metal carbonates as the second phase (e.g. (Li–Na)<sub>2</sub>CO<sub>3</sub> or (Li–K)<sub>2</sub>CO<sub>3</sub>) have been found to be co-ionic conductors (O<sup>2–</sup>/H<sup>+</sup>) with a high ionic conductivity of 0.1 S cm<sup>–1</sup> at 600 °C [31–33]. Using the same strategy to achieve better electrical properties, a dense BZY composite electrolyte is fabricated in this study at 670 °C by adding a Li<sub>2</sub>CO<sub>3</sub>–Na<sub>2</sub>CO<sub>3</sub> eutectic mixture. Composite BZY electrolytes with carbonate materials may show higher proton conductivity at IT due to extra defects introduced by the space charge interfaces of the dispersed particles, as demonstrated in

\* Corresponding author. Tel.: +82 2 3408 3848; fax: +82 2 3408 4342.

E-mail address: [jyoung@sejong.ac.kr](mailto:jyoung@sejong.ac.kr) (J.-Y. Park).

several recent experimental systems (notably Li-electrolyte/oxide composite systems) [32–35]. Furthermore, a high density level of BZY electrolytes can be obtained at low sintering temperature by molten-carbonate-filled intergranular pores. The electrical conductivity of  $\text{BaZr}_{0.85}\text{Y}_{0.15}\text{O}_{3-\delta}(\text{Li}-0.5\text{Na})_2\text{CO}_3$  is measured by DC and AC impedance conductivity method, and the main conduction carriers of such composite electrolytes are also discussed for different atmospheres.

## 2. Experimental

### 2.1. Electrolyte preparations

$\text{BaZr}_{0.85}\text{Y}_{0.15}\text{O}_{3-\delta}$  (BZY) powder was synthesized by the conventional solid-state reaction method. Pure powders of  $\text{BaCO}_3$  (99.8% purity, Alfa Aesar, USA),  $\text{ZrO}_2$  (99.5% purity, Alfa Aesar, USA), and  $\text{Y}_2\text{O}_3$  (99.9% purity, Alfa Aesar, USA) were mixed via ball-milling with zirconia balls for 24 h. The ball-milled powder was calcined at 1300 °C for 2 h. After calcinations, the powders were uniaxially pressed into cylindrical pellets at 20 MPa for 5 min, and then isostatically pressed at 200 MPa for 5 min. The obtained green pellets were sintered at 1670 °C for 24 h. In order to restrain the barium loss, samples were covered with BZY powder during the high-temperature sintering process. The relative densities of sintered BZY pellets were measured as 97.7% by Archimedes' principle with a density meter (MD300S, Alfa Mirage, Japan), using ethanol as the liquid medium.

The BZY/carbonate multiphase composite electrolytes were also prepared by the solid-state reaction method. A carbonate mixture of  $\text{Li}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  (purity > 99%, pure, Alfa Aesar, USA) with a molar ratio of 1:0.5 was prepared by mixing and heating at 650 °C for 1 h. BZY/carbonate composite samples were prepared by mixing the as-prepared BZY powders with various amounts of  $(\text{Li}-0.5\text{Na})_2\text{CO}_3$  (15, 25, and 35 wt.%) with zirconia balls in ethanol for 24 h. The mixtures were dried, crushed, and pelletized at a uniaxial pressure of 20 MPa for 5 min. The pellets were then sintered at 670 °C for 4 h, with heating and cooling rates of 1 °Cmin<sup>-1</sup>. The densities of the sintered BZY/carbonate composite pellets were also measured by Archimedes principle in ethanol and gradually decreased from 3.70 to 3.58 and 3.43 g cm<sup>-3</sup> with increasing carbonate content from 15 to 25 and 35 wt.%, respectively. This is because the density of the  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ , and  $(\text{Li}-\text{Na})_2\text{CO}_3$  is about 2.11, 2.54, and 2.30 g cm<sup>-3</sup> at the room temperature, whereas the density of the BZY is 5.97 g cm<sup>-3</sup> which was calculated from the XRD data.

### 2.2. Electrolyte characterizations

The phase purity and lattice parameters of the calcined powders and sintered pellets were investigated by X-ray diffraction analysis (XRD, D/MAX 2500, Rigaku, USA). The XRD analysis was carried out using Cu K $\alpha$  over a 2 $\theta$  range of 20°–80°. The microstructure of the three types of samples was inspected by field emission-scanning electron microscopy (FE-SEM, S-4700, Hitachi High tech, Japan) with an energy dispersive X-ray spectroscopy (EDX) analysis system. For the detailed analysis of the morphology and microstructure, including the interfacial boundary between two phases, high-resolution-transmission electron microscopy was used (HR-TEM, Titan, FEI, USA). HR-TEM specimens were prepared by a dual-beam focused-ion beam (FIB) instrument (Helios NanoLab™ DualBeam™, FEI, USA) with EDX to quantitatively estimate the presence of minor phases in the pellet samples. Simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) of the BZY and composites were investigated by a SDT TG-DTA equipment (Q600, TA Instruments, USA) with a heating rate of 10 °C min<sup>-1</sup> over temperature ranging from ambient temperature to 1400 °C in air atmosphere. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analyses of the composites were also carried out with a Perkin Elmer OPTIMA 8300 spectrometer to obtain the content of barium, lithium, and sodium. In order to evaluate the chemical stability of BZY/carbonate electrolytes in water-containing atmospheres, a dense pellet of composite was treated in boiling water for 5 h. The elemental analysis of the surface of the sintered BZY/carbonate pellets treated in water-containing atmospheres was examined by XRD.

The electrical conductivity of the three types of electrolytes were determined by electrochemical impedance spectroscopy (EIS) using a SP-240 Potentiostat/Galvanostat/EIS instrument (SP240, BioLogic, Claix, France). After mechanically polishing the surface of sintered pellets, Ag paste (Heraeus, USA) was coated onto both sides of the electrolyte as electrodes. The Ag ink was dried at 125 °C for 30 min and sintered at 650 °C for 1 h. Au wires were then attached to the electrodes using Ag paint, and sintered under the same conditions. Conductivity measurements were performed in wet or dry atmospheres of air and 5% hydrogen in Argon (Ar) gas. The wet gas was moisturized by bubbling through water held at room temperature. The total flow rate of the gas was set at 200 sccm. The signal amplitude was fixed at 10 mV in a frequency range of 10  $\mu\text{Hz}$  to 7 MHz and temperature range of 250–650 °C at 50 °C intervals. An equivalent circuit model was fitted to the impedance spectra using EC-Lab software (BioLogic) to separate out the components of the conductivity. Electrical measurements were also performed using a digital multimeter by DC four-point conductivity measurements (Keithley 2400 source meter).

Four-point DC conductivity measurements were performed by passing current and recording the voltage of samples as a function of temperature in wet atmospheres of air and 5% H<sub>2</sub> in Ar gas.

## 3. Results and discussion

### 3.1. Phase formation and densification

The X-ray diffraction (XRD) patterns of the sintered BZY and BZY/carbonate composites containing 15, 25, and 35 wt.%  $(\text{Li}-0.5\text{Na})_2\text{CO}_3$  are presented in Fig. 1. For all compositions, the major phase is identified as BZY materials and no secondary phases by chemical reactions occurred between the BZY and carbonates during heat treatments is detected from XRD analysis. In addition, the diffraction peaks are very sharp and the presence of peaks confirms the crystalline nature of the composites.  $\text{LiNaCO}_3$  is detected in the high-BZY/carbonate compositions, apart from the perovskite phase. The carbonates only were also prepared in the same way as composites without the addition of BZY and XRD pattern of the sintered  $(\text{Li}-0.5\text{Na})_2\text{CO}_3$  specimen is presented in Fig. 1. The

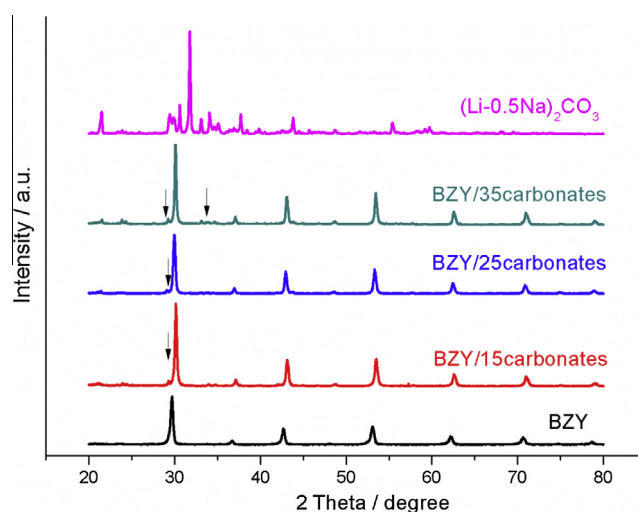


Fig. 1. XRD patterns of a series of sintered BZY and BZY/carbonate composites which contain 15, 20, and 35 wt.%  $(\text{Li}-0.5\text{Na})_2\text{CO}_3$ . Arrows denote the  $\text{LiNaCO}_3$  materials.

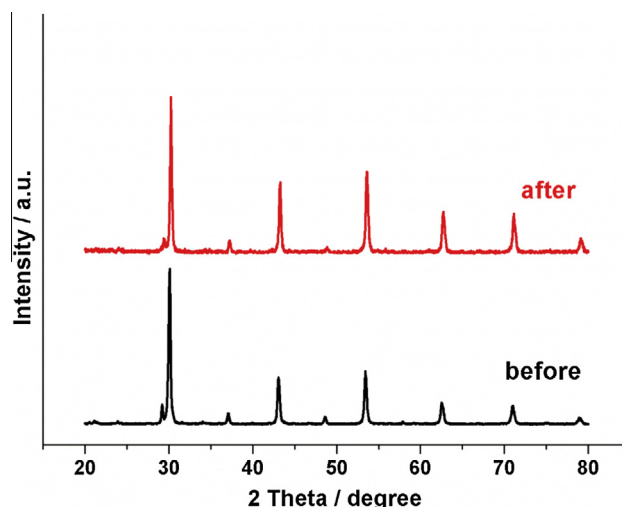


Fig. 2. XRD patterns of sintered BZY/25 wt.% carbonate sample before and after boiling water treatment.

Download English Version:

<https://daneshyari.com/en/article/1612953>

Download Persian Version:

<https://daneshyari.com/article/1612953>

[Daneshyari.com](https://daneshyari.com)