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Electrical Conductivity of Y\(^{3+}\)-doped Ba(Ce,Zr)O\(_3\) in Wet Nitrogen Atmosphere

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Abstract. Proton conducting ceramics such as barium cerate-zirconate oxide, Ba(Ce,Zr)O\(_3\) is one of promising candidates to be used as an electrolyte material in intermediate temperature solid oxide fuel cell (IT-SOFC). In this work, single-phase of BaCe\(_0.54\)Zr\(_0.36\)Y\(_{0.1}\)O\(_{2.95}\) (BCZY) powder was successfully prepared using a sol-gel method. The powder was pressed into a pellet with diameter, \(d=13\) mm and thickness, \(t=\sim1\sim2\) mm using an uniaxial pressing technique with pressure of 369 MPa for 5 minutes. The pellet with relative density of 92% was obtained after underwent two-step sintering (TSS) method at \(T_1=1500\)°C and \(T_2=1450\)°C with holding time 1 minute and 12 hours respectively. Impedance data of the sample with grain in sub-micron size (as measured by SEM) was collected using an impedance spectroscopy (IS) in wet nitrogen atmosphere at temperature ranging from 500 to 800°C. All responses in the impedance spectrum were separated and fitted accordingly to an equivalent circuit based on a brick-layer model (BLM) with equivalent circuit of \(R_1|Q_1‒R_2|Q_2\). Analysis of the impedance spectrum showed the sub-micron grain resulted in high grain boundary resistance with conductivity of \(10\sim4\) S cm\(^{-1}\) at 500 °C to 700 °C. The conductivity of the sample was thermally activated and obeyed Arrhenius behavior with activation energy (\(E_\text{a}\)) of 0.76 eV.

1. Introduction
Proton conductor fuel cell (PCFC) is a device that converts chemical energy into electrical energy which hold benefit over oxide-ion conductor fuel cell in terms of operating temperatures. It has been widely studied due to its benefits in intermediate temperature SOFC (IT-SOFC). Among all of the components in a single cell, electrolyte materials have been extensively investigated owing to its major contribution to the cell performance. Currently, BaCeO\(_3\) and BaZrO\(_3\) are the most investigated pair which is considered as the state of the art in proton-conducting oxide ceramic materials. BaCeO\(_3\) alone had shown many advantages in term of conductivity, however, it lack in terms of stability. It has relatively low chemical stability in water and CO\(_2\) atmospheres. Whereas BaZrO\(_3\) shows good chemical stability but low total conductivity [1]. A work by Baral et al. [2] revealed that in CO\(_2\) or wet operating conditions, barium cerates are unstable but conversely for barium zirconates which show good stability. Yet, it lack in terms of conductivity due to very high grain boundary resistance.
Hence, researchers focused to one type of ceramic material in perovskite-oxide family, Y-doped Ba(Ce,Zr)O$_3$ which has been proposed as a good candidate for electrolyte component in intermediate temperature proton conductor fuel cell (PCFC). The material shows promising results at intermediate operating temperatures based on electrochemical and microstructure analysis [3-5]. Among all composition of BaCe$_{1-x-y}$Zr$_x$Y$_y$O$_{3-δ}$, the Ba(Ce$_{0.6}$Zr$_{0.4}$)$_{0.9}$Y$_{0.1}$O$_{3-δ}$ (BCZY) was chosen in this work due to its composition almost similar to that reported by J. F. Basbus et al [6]. They investigated the conductivity of BaCe$_{0.4}$Zr$_{0.4}$Y$_{0.1}$ which was 1x10$^{-3}$ S cm$^{-1}$ at temperature of 300 °C in wet 20% O$_2$/Ar atmosphere. However, no details impedance analysis was performed under wet N$_2$ condition on the mentioned BCZY composition, which would be the focus of this paper.

2. Experimental

Raw materials of Ba(NO$_3$)$_2$ (99%, ACROS), Ce(NO$_3$)$_3$ (99.5%, ACROS), Zr(NO$_3$)$_4$O.xH$_2$O (99.5%, ACROS) and Y(NO$_3$)$_3$.5H$_2$O (99.9%, ACROS) were used to prepare BCZY powders. The starting materials of BCZY powder are weighed in stoichiometric amount accordingly and synthesised using a sol-gel process. A detailed preparation of the single-phase BCZY powder has been reported elsewhere [7]. The powder was pressed into a pellet of 13 mm in diameter and thickness about 1–2 mm using uniaxial pressing technique at 369 MPa for 5 minutes. The pellet was subjected to two-step sintering (TSS) process at 1500 °C for 1 minute and 1450 °C for 12 hours with respective heating rates of 5 °C min$^{-1}$ and 30 °C min$^{-1}$.

Geometrical method was used to measure density for each of the sintered pellet. The grain morphology of the pellet was observed using Benchtop SEM (Phenom XL) with 9000x magnification at 15kV. Pt paste was manually painted onto both side of the pellet and heated at 950°C for 2 hours to get a good contact between the Pt metal and BCZY electrolyte. Electrical measurement of the sample was completed using AC impedance spectroscopy in the frequency range between 42 Hz-1 MHz with an amplitude voltage of 500 mV. Impedance data was collected in wet N$_2$ atmosphere by using HIOKI 3532-50 LCR HiTESTER impedance analyser. Prior to the measurement, the pellet was stabilized for 24 hours in wet N$_2$ flow at 700 °C before going up to 800 °C and gradually step down for 50 °C for each temperature measurement. The impedance spectra obtained were analysed to extract the possible electrical responses produced by the sample using ZMAN software.

3. Result and Discussion

Figure 1 shows the micrographs of (a) polished surface area and (b) cross-section for BCZY pellet. The SEM image confirmed the dense microstructure of pellet at density of 92% and the grain was a mixture between small and large grains with average grain size of 274 nm as measured by ImageJ software. TSS method as reported by N. W. Othman et al. [8] proved to help the sample to achieve high density with small grain size. Furthermore, according to Abdullah S. S. C et al. [9] grain growth was controllable while the density of the pellet can be increased by executing TSS method. Therefore, it is important to attain high density which subsequently hardness is greatly dependent on the density of the pellet.
Figure 1. SEM micrographs of a) surface area of a polished Ba(Ce0.6Zr0.4)0.9Y0.1O3-δ pellet and b) cross section of a fractured BCZY pellet after TSS method.

Comparative Nyquist plot impedance data of the sample at 500 °C, 600 °C and 700 °C in wet N2 atmospheres is shown in Figure 2. For all temperatures, there two arcs were observed. The first arc can be attributed to grain boundary (R2) resistance in mid-frequency range while the second arc represent the interfacial resistance (R3) in low-frequency range. The intercept value at Z’ axis was taken as the grain resistance (R1). The obtained results were aligned from those previously reported [10].

Figure 2. Typical Nyquist plot for Ba(Ce0.6Zr0.4)0.9Y0.1O3-δ pellet at different measurement temperatures

Equivalent circuit fitting was done to stimulate the resistance, capacitive, and inductive element components associated with the ac impedance responses [11]. The impedance spectrum circuit comprise of resistance with two parallel pair of resistance-constant phase element connected in series as shown in Figure 3. From the equivalent circuit and fitting procedures, the capacitance values can be calculated using equation 1:

$$ C = Y_n^1 \times R_n^{1-1} $$

(1)
Where C is the capacitance value (F), Y and n refers to the parameter associated with the constant phase element (CPE) while R represents as the resistance [12].

![Figure 3](image)

**Figure 3.** Impedance spectrum of experimental and simulation data were well fitted. (Insert is an equivalent circuit representing the responses in the spectrum of BCZY at 500 °C)

Table 1 shows the geometrical capacitance values for the total resistance response of Ba(Ce0.6Zr0.4)0.9Y0.1O3-δ at 500, 600 and 700 °C. The obtained capacitance values correlate with the usual range of grain boundary in order of 10⁻⁹ to 10⁻¹⁰ Farad at mid-frequency region [13].

| Temperature (°C) | Capacitance, (F) |
|-----------------|-----------------|
| 500             | 1.82 x 10⁻⁹     |
| 600             | 2.06 x 10⁻⁹     |
| 700             | 1.05 x 10⁻⁹     |

The overall conductivity was calculated since the grain response was no longer possible at temperature above 300 °C due to incapability of impedance technique to measure the response as stated by Barison S. et al. [14]. The obtained conductivity was found to be 1.28 x 10⁻⁴ Scm⁻¹ at 500 °C, 5.58 x 10⁻⁴ Scm⁻¹ at 600 °C and 1.18 x 10⁻⁴ Scm⁻¹ at 700 °C. The sample exhibit low conductivity values which can be explained by the small grain size owned by the BCZY sample, considering the grain boundary area were large and hence contributes to high total resistivity of the sample.

The Arrhenius graph of the total conductivity were plotted as shown in Figure 4. Activation energy, Eₐ that is the combination of energy of defect formation and energy of defect migration can be observed from the slop of Arrhenius plot [15] and was calculated to be 0.77 eV. Comparing to typical value of Eₐ for similar materials (0.78 eV) [16], that may be concluded it was due the occupied Zr⁴⁺ and Ce⁴⁺ ions in the perovskite B site has difference in electronegativity site and a higher repulsive interactions between Ce-H than Zr-H.
4. Conclusion

The Ba(Ce₀.₆Zr₀.₄)₀.₉Y₀.₁O₃-δ pellet with density of 92% and its grain in the sub-micron size was prepared via TSS method. Analysis of the impedance spectrum showed the sub-micron grain resulted in high grain boundary resistance. In wet N₂ atmosphere, the conductivity of the sample was found to be in the range of 10⁻⁴ S cm⁻¹ at 500 °C to 700 °C with activation energy (Eₐ) of 0.76 eV.

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References

[1] Fabbri E, Epifanio A D, Bartolomeo E D, Licoccia S and Traversa E 2008 179 558–64.
[2] Baral A K, Choi S K, Byung K L and Jong-Ho L J. Renew. Sustain. Energy 1–9.
[3] Sawant P, Varma S, Wani B N and Bharadwaj S R 2012 Int. J. Hydrog. Energy 37(4) 3848–56.
[4] Nasani N, Ramasamy D, Mikhailov S, Kovalevsky A V and Fagg D P 2015 J. Power Sources 278 582–9.
[5] Hakim M, Joo J H, Yoo C Y, Kim B K and Yu J H 2015 J. Eur. Ceram. Soc. 35(6) 1855–63.
[6] Basbus J F, Arce M D, Prado F D, Caneiro A and Mogni L V 2016 J. Power Sources 329 262-7.
[7] Othman N W, Ramli A, Osman N, Abdullah S S C and Rahman M E A 2015 819(3) 129–33.
[8] Othman N W, Ramli A, Osman N, Abdullah S S C and Rahman M E A 2015 819(3) 129–33.
[9] Abdullah S S C, Abdullah R and Osman N 2014 962–6.
[10] Baral A K, Choi S K, Byung K L and Jong-Ho L 2014 J. Renew. Sustain. Energy 1–9.
[11] Li J, Luo J, Chuang K T and Sanger A R 2008 Electrochimica Acta 53 3701–7.
[12] Ismail I, Osman N and Jani A M M 2017(Malaysia: iMIT-SIC Vol 2) pp 177- 8
[13] Nasani N, Dias P A N, Saraiva J A and Fagg D P 2013 Int. J. Hydrog. Energy 38(20) 8461–70.
[14] Mortalo C, Barison S and Battaglini M 2008 J. Mater. Chem. 5120–5128.
[15] Baral A K, Choi S K, Byung K L and Jong-Ho L 2014 Mater Renew Sustain Energy 1–9.
[16] Sawant P, Varma S, Wani B N and Bharadwaj S R 2012 37(4) 3848–56.