



Influence of Bi₂O₃ additive on the electrical conductivity of calcia stabilized zirconia solid electrolyte

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Abstract

A few compositions of Bi₂O₃-doped calcia stabilized zirconia (Zr_{0.88-x}Bi_xCa_{0.12}O_{2-δ}; $x = 0.0, 0.02, 0.05, 0.10$) were prepared via solid state reaction route. Addition of Bi₂O₃ decreased the sintering temperature of calcia stabilized zirconia (CSZ) and also augmented the growth of zirconia grains. Dense ceramic systems were formed in a temperature range of 1200–1300 °C. X-ray Rietveld refinement analysis of the system revealed the formation of cubic zirconia phase at room temperature. Microstructural studies of the sintered pellet depicted highly dense grain morphology. XPS spectra of the compositions confirmed the elemental confinements and various characteristic valence states of the constituents. Thermal expansion coefficient of the Bi₂O₃ doped CSZ system was found to be compatible with the other components of solid oxide fuel cells (SOFC). Furthermore, conductivity analysis evidenced an Arrhenius type thermally activated ionic conduction above 300 °C. The electrical conductivity of the system was found to increase with bismuth content up to $x = 0.05$, thereafter decreased due to less solubility of Bi³⁺ into zirconia matrix. A high conductivity $\sim 0.019 \text{ S cm}^{-1}$ was achieved for 5 mol% Bi₂O₃ calcia-codoped cubic zirconia system at 760 °C. Thus, cost effective bismuth codoped calcia stabilized zirconia might be a possible alternative to yttria stabilized zirconia (YSZ), due to its ionic conductivity comparable to that of the YSZ.

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1. Introduction

Solid oxide fuel cell (SOFC) is one of the most promising clean-energy conversion technologies for a new generation power system due to its high efficiency, high waste-heat utilization, greater fuel flexibility and very less pollution.¹ The present challenge of SOFC technology is to develop practical set-up with its operation in intermediate temperature range, i.e., in the range of 500–800 °C, formally known as Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFC).² The high-temperature operation has several disadvantages, as it requires high cost materials for long term operation. Development of low-cost materials with high durability at cell operating temperature is one of the major challenges. The prime

objective for the commercialization of SOFC, is to reduce the temperature of operation using new cost-effective solid electrolytes, which exhibits high oxide ion conductivity in the intermediate or low temperature range.^{3–5} Among the components of SOFC, electrolyte, sandwiched between cathode and anode, plays a key role in the successful operation of the device. Moreover, electrolytes with improved ionic conductivity at low or moderate temperatures SOFC along with co-firing process of the component materials (i.e., air electrode, electrolyte, and fuel electrode) at low sintering temperature (1000–1200 °C), are highly desirable.⁵ Currently, cubic stabilized zirconia is being widely used as a solid electrolyte. Its ionic conductivity is sufficient for the use as a solid electrolyte only at higher temperatures (800–1000 °C).^{6–8} Pure zirconia possesses monoclinic structure at room temperature which shows quite a low conductivity. The improved conductivity in zirconia is obtained only when it has cubic phase. To change the monoclinic phase of zirconia into cubic phase, suitable doping of a few rare-earth elements

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or alkaline earth metal cations is needed. Generally, tri-valent substituents like Y^{3+} , Sc^{3+} , Dy^{3+} , etc., and a few divalent substituents like Ca^{2+} , Mg^{2+} , etc., are implanted in zirconia matrix to establish cubic phase at room temperature.^{6–14} A few other prominent materials are also investigated for SOFC electrolytes but the mixed conduction, reducibility (in case of Gd/Sm doped CeO_2 and Bi_2O_3) and phase instability (in case of Sr and Mg doped $LaGaO_3$, LSGM) are the major constraints for these kinds of materials.^{15–21} Reducing the cost of SOFC is also one of the key goals currently pursued by the researchers and industry people. Currently, many efforts are being made to reduce the operating temperature (500–700 °C) and simultaneously to reduce the cost of other components of the cell.^{4,5} Calcia (CaO) is one of the cheapest and suitable stabilizers of the zirconia that stabilizes its cubic phase at room temperature.¹⁴ Therefore, in search of cheap and widely stable materials, fluorite structured calcia stabilized zirconia (CSZ) has also been proposed as an alternative electrolyte material for SOFC. This material offers not only high ionic conductivity but also very less cost compare to other solid electrolytes.²² Nakamura and Wagner²³ reported that the ionic conductivity of calcia stabilized zirconia initially increases with oxygen vacancy concentration and reaches a maximum for 12–13 mol% of CaO content. CSZ electrolytes with excellent crack resistance and good electrical conductivity have been fabricated by normal sintering.²⁴ In search of fluorite based solid electrolytes, stabilized Bi_2O_3 was also reported as a fast oxide ion conductor.²⁵ The incorporation of small amount of trivalent Bi^{3+} into the stabilized zirconia produces vacant sites.^{8,11,12} Gil et al.²⁶ reported a low-temperature densification and grain growth of Bi_2O_3 -doped-ceria gadolinia ceramics. They estimated the solubility limit of Bi_2O_3 in sintered $Ce_{0.9}Gd_{0.1}O_{1.95}$ ceramics as ≤ 0.8 wt.% of Bi_2O_3 . Hirano et al.²⁷ fabricated the stable cubic scandia stabilized zirconia that showed, on the addition of Bi_2O_3 , excellent ionic conductivity without appearance of rhombohedral phase. Bai et al.²⁸ also investigated the physical and electrochemical properties of Bi_2O_3 -doped scandia stabilized zirconia and found that a trace amount of Bi_2O_3 acts as sintering aid for zirconia systems. The addition of more than 1.0 mol% Bi_2O_3 resulted in suppression of the rhombohedral to cubic phase transformation to 600 °C and cubic phase stabilization at room temperature. The ionic conductivity of 10 mol% Sc stabilized zirconia was also found to be improved on Bi_2O_3 additions. Yeh et al.²⁹ studied the effect of bismuth doping on the sintering process of YSZ and found that a small amount of Bi_2O_3 addition is effective in reducing the sintering temperature and promoting the densification rate of the ceramics. Winnubst et al.³⁰ reported the variations of the ionic conductivity in YSZ doped with different amount of Bi_2O_3 . They observed that the bulk conductivity at 800 °C is increased from 0.0028 S cm^{-1} for undoped YSZ to 0.0162 S cm^{-1} for 0.5 mol% of Bi_2O_3 added YSZ. The results of ionic conductivity in YSZ and Bi_2O_3 -doped YSZ specimens reported by Winnubst et al. are very low, even though enhancement of conductivity is almost one order higher than that of the YSZ. Therefore, in the scope of our investigations for cost-effective electrolyte materials with improved ionic conductivity in intermediate temperature

range, we prepared calcia stabilized zirconia (CSZ) powders (containing 12 mol% CaO) and tried to investigate the effect of Bi_2O_3 doping on CSZ.

The present study was concerned with the study of influence of the addition of Bi_2O_3 in CSZ on sintering properties, crystalline phase, grain growth, elemental confinement, thermal expansion and electrical conductivity. In the present investigation, these properties were investigated employing X-ray Rietveld analysis, scanning electron microscopy, X-ray photoelectron spectroscopy, BET surface area measurement, dilatometry and impedance spectroscopy techniques, respectively.

2. Experimental

A few compositions of the system $Zr_{0.88-x}Bi_xCa_{0.12}O_{2-\delta}$ with $x = 0.00, 0.02, 0.05$ and 0.10 were synthesized via solid state reaction route. An appropriate amount of constituent oxides, having purity greater than 99.5% were mixed in a planetary ball mill. CaO-doped zirconia and Bi_2O_3 -CaO-codoped zirconia powders were prepared applying 12 h continuous ball milling at 150 rpm using acetone as mixing media in zirconia jars. The ball milled powders were calcined at 1100 °C for 6 h. After calcination, calcined powders were crushed and reground using mortar–pestle for 1 h before sintering and then uniaxially pressed at 100 kg cm^{-2} to form green compact pellets. The green compact pellets were sintered at 1300 °C for 6 h in air. The bulk density of the sintered samples was measured using the Archimedes principle. The crystal phases of the sintered powders were examined using X-ray diffractometry (XRD) with $Cu-K\alpha_1$ radiation (Rigaku Miniflex II desktop) using Rietveld refinement technique. Microstructural morphology of the polished surface of the sintered pellet was examined by scanning electron microscopy (MIRERO Inc. AIS2100 instrument) technique. The average grain size of each sample was measured by the interception method on the SEM images. X-ray photoelectron spectra (XPS) of the system were recorded employing KRATOS (Amicus model) high-performance analytical instrument using Mg target under the pressure of 1.0×10^{-6} Pa. The specific surface area of calcined powders was estimated by BET method through Micromeritics (ASAP 2020) Accelerated Surface Area and Porosimetry System using adsorption–desorption isotherms of nitrogen. Dilatometry of the sample was performed in air using a dilatometer DIL 402 PC (NETZSCH, UK) from room temperature to 1000 °C. The electrical conductivity of the samples was measured in a temperature range of 300–800 °C by AC impedance spectroscopy technique using a Wayne Kerr 6500 P impedance analyser in the frequency range 20 Hz to 1 MHz.

3. Results and discussion

3.1. XRD study

In the present study, the system $Zr_{0.88-x}Bi_xCa_{0.12}O_{2-\delta}$ is designated as CSZB and the compositions with $x = 0.00, 0.02, 0.05,$ and 0.10 of this system are assigned as CSZB00, CSZB02, CSZB05 and CSZB10, respectively. For example, CSZB05

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