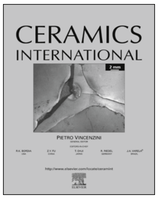
Ceramics International 42 (2016) 13689–13696

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint



Effect of synthesis atmosphere on the proton conductivity of Y-doped barium zirconate solid electrolytes

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ARTICLE INFO

Article history:
Received 11 May 2016
Received in revised form
25 May 2016
Accepted 25 May 2016
Available online 26 May 2016

Keywords:
Proton conductor
Barium zirconate
Powder synthesis
Impedance spectroscopy

ABSTRACT

Yttrium-doped barium zirconate ceramic powders were synthesized by the oxidant peroxide method in air and under controlled atmosphere of nitrogen inside a glove box. The powders were characterized by thermogravimetry, X-ray diffraction, scanning electron microscopy and transmission electron microscopy. After uniaxial cold isostatic pressing, green pellets were sintered at 1600 °C for 4 h. The electrical conductivity behavior was accessed by electrochemical impedance spectroscopy. The results show that specimens synthesized under controlled atmosphere achieved higher electrical conductivity, two orders of magnitude higher than specimens prepared in laboratory air. The enhancement in electrochemical properties and increase in sintering ability is attributed to the less carbonate contamination as a result lower grain boundary density in the samples prepared under controlled atmosphere.

1. Introduction

Solid oxide fuel cells (SOFCs) have attracted increased attention due to their high conversion efficiency of chemical energy into electricity with low environmental impact, compared to fuel combustion [1–5]. SOFCs are also a sustainable alternative to energy production over other hydrogen-based technologies. Even though hydrogen does not contribute to the greenhouse effect, this element is not available in the environment in the sense that expensive methods must be employed for its synthesis, separation and purification. In addition, hydrogen handling and storage have to be carefully addressed because of safety issues. This is the main reason for continuing research to find new solutions for hydrogen production, which could be achieved under solid oxide fuel cell operation, fueling the cell with hydrogen containing species (internal reform). Since cell operation occurs at high temperatures (800–1000 °C), methane and hydrocarbons can be directly injected into the cell for in situ production of hydrogen, which is then consumed for electricity production. The most developed and commercially available SOFCs are based on oxygen ion conducting solid electrolytes and the operating temperature is in the 600–1000 °C range [5]. Yttria-stabilized zirconia (ZrO_2: 8 mol% Y_2O_3) is considered the state-of-the-art solid electrolyte for high temperature SOFCs. This electrolyte has predominant ionic conduction reaching 0.1 S/cm at 1000 °C. However, there are several problems associated with the high temperature, including thermal expansion mismatch of components, cell poisoning and degradation due to CO and CO_2 formation leading to carbon deposition (coking), decreasing cell performance and lifetime [6–8]. Therefore, efforts continue to reduce SOFC working temperature to an intermediate range (650–850 °C, ITSOFC) [9,10] and even a lower range (400–650 °C. LTSOFC [11].

Oxides with perovskite structure based on barium cerate and barium zirconate, and a combination of both (BCX, BZX e BCZX, X=trivalent cation – Y^{3+}, Gd^{3+}) are proposed for application as solid electrolytes in ITSOFCs. In addition, yttrium-doped barium zirconate (BYZ) has also been proposed as the best choice due to its high chemical stability under CO_2-rich atmospheres and high mechanical resistance, and high proton conductivity at intermediate temperatures [12–15]. Indeed, the bulk conductivity at 500 °C of barium zirconate containing 20 mol% Y^{3+} in solid solution (BZY20) is comparable to the conductivity of gadolinium-doped ceria ($Ce_{0.9}Gd_{0.1}O_{2-\delta}$), which is one of the best oxygen-ion conductors [12]. However, the major concern is on the total proton conductivity, i.e., bulk and grain boundary conductivities. Due to the refractory nature of BZY, it has limited grain growth during sintering, which leads to a high density of grain boundaries and a high electrical resistivity. BZY powders are usually synthesized by solid state reaction of the precursor oxides, which generally leads to nonstoichiometric compounds. Moreover, the specimens must be exposed to aggressive sintering conditions to obtain pellets with density high enough for use as solid electrolytes in ITSOFCs. The conditions involving very high temperatures and long dwell

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http://dx.doi.org/10.1016/j.ceramint.2016.05.167
0272-8842/

times for synthesis and sintering (>1700 °C, >24 h) lead to barium loss, resulting in electrical conductivity decrease [16]. This is the major drawback when developing electrochemical devices based on barium zirconate. Therefore, the main challenge is to achieve dense ceramic bodies, while applying sintering conditions that could inhibit barium loss with lower grain boundary electrical resistivity [14,16–18].

Many synthesis and processing techniques have been applied for making better quality solid electrolytes: wet-chemical synthesis, co-doping, and sintering aids, among others. Very recently, BZY protonic ceramic fuel cells with high power output have been reported using BZY solid electrolytes sintered with CuO sintering aid [19]. Wet-chemical routes have already been used to produce powder particles with higher sinterability to obtain pellets sintered at relatively low temperatures [16,18,20–24]. A total proton conductivity of ~0.01 S/cm at 450 °C in a polycrystalline BZY20 sample produced by a sol-gel route was reported. The high proton conductivity was achieved in large-grain samples produced from a nanocrystalline precursor and reactive sintering (in presence of $BaCO_3$) [25]. The decrease of proton conductivity in BZY compounds containing higher than 20 mol% yttrium is related to the reduced symmetry due to lattice distortions, increased oxygen basicity (Y^{3+} is less electronegative than Zr^{4+}) and proton trapping effects due to the formation of dopant-defect associates which reduce the mobility of charge carriers [26–32].

Among the synthetic routes, the oxidant peroxide method (OPM) is also very promising since it is free from common contaminants such as carbon or halides [33]. Besides, this method allows the formation of stoichiometric powders with reactive nanoparticles [33–38]. In the present work, experiments were carried out on the synthesis by the oxidant peroxide method of $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ following two approaches: i) under usual laboratory air and ii) under controlled nitrogen atmosphere inside a glove box. The main idea was to compare sintered ceramic pellets prepared with powders subjected to these two atmosphere conditions, aiming to avoid the formation of aggregates of the powder particles, known to be due to the presence of chemical species attached to the as precipitated precursor particles [39]. It is expected that powders with cleaner particle surfaces should produce better sintering conditions for obtaining pellets with improved electrical properties. Morphological and electrical characterizations were performed on the sintered pellets.

2. Material and methods

Ceramic powders of composition $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY10) were synthesized by the oxidant peroxide method (OPM) by two different approaches: (i) in laboratory air, referred hereafter as AIR, and (ii) inside a glove box under nitrogen atmosphere, referred as N_2. The starting materials and the synthesis procedure have been described elsewhere [31,38].

2.1. AIR powders

The precursor powders obtained by the synthesis in air were calcined at 900 °C/4 h and 1200 °C/2 h with 10 °C/min heating and cooling rates. Thermogravimetric analyses of the precursor powder were performed in a Netzsch STA 409E thermal analyzer. About 60 mg of sample was heat treated from 25 to 1200 °C with heating rate of 10 °C/min under nitrogen. Buoyancy corrections were made by recording baselines with empty crucibles. X-ray fluorescence analyses were carried out in Shimadzu EDX-720 equipment.

2.2. N_2 powders

The N_2 samples were calcined at 900 °C/4 h and 1200 °C/24 h, with 10 °C/min heating and cooling rates.

The thermal profile of the precursor powder was monitored by thermogravimetric analysis in a Netzsch STA 449 analyzer with ~ 20 mg of sample, heating under argon from 25 to 1200 °C with 10 °C/min heating rate. Buoyancy corrections were made by recording baselines with empty crucibles. The chemical composition was evaluated by quantitative chemical analysis in a WDS Cameca SX-100 electron microprobe, with 15 kV accelerating voltage, probe current 20 nA and beam size 1 μm. For the analysis, the calcined powders were pressed into 5 mm diameter pellets and sintered at 1200 °C for 24 h; the surface was polished and carbon-coated. The composition of the sample was determined using an average of 6–10 points. Both powder samples synthesized in air or under N_2 were subjected to powder X-ray diffraction in a D8 Advance Bruker-AXS diffractometer equipped with Cuk_α radiation in 2θ range from 20 to 80° with a step size 0.02°/s. Jade 6.1 software (Materials Data Inc.) was employed for phase identification of the X-ray data. The lattice parameters were evaluated with the Unit Cell software.

2.3. BZY10 compacts

The calcined BZY10 powders were uniaxially cold pressed at 18 MPa to cylindrical pellets with 5 mm diameter and 2 mm thickness. The pellets were embedded in 10 mol% Ba-excess BZY10 powder, to avoid barium volatilization, inside zirconia crucibles with lids, and sintered in air in a Zircar Hot Spot 110 Furnace at 1600 °C/4 h with 3 °C/min heating and cooling rates.

The investigation of the morphology of calcined powders and their fracture surfaces was carried out in a FEI Inspect F50 scanning electron microscope. The complementary morphological characterization of all calcined samples, produced either in laboratory air or under nitrogen atmosphere, was performed in a FEI Tecnai TF20 field emission gun high-resolution transmission electron microscope.

The electrical conductivity of the sintered pellets was evaluated by impedance spectroscopy with a Hewlett Packard 4192 A analyzer connected to a Hewlett Packard series 360 Controller. Silver electrodes were applied onto the parallel sample surfaces. The measurements were performed in laboratory air (65% R.H.) from 200 to 600 °C in the 5 Hz to 1.3×10^7 Hz frequency range under 200 mV voltage. Special software was used to collect the $[-Z''(f)\times Z'(f)]$ impedance spectroscopy data and also for deconvolution of the impedance diagrams [40] for the evaluation of bulk and grain boundary electrical resistance. The impedance spectroscopy diagrams were normalized by the geometrical factor of the pellets (S/L, S=electrode area, L=pellet thickness).

3. Results and discussion

Fig. 1 shows the thermal behavior of both BZY10 samples produced by the OPM under laboratory air (AIR) and under controlled nitrogen atmosphere (N_2). The mass loss of the AIR sample reached 27.5%, which is 5.5% higher than the value found for the N_2 sample. The thermal event related with the water loss that takes place up to 250 °C is similar in both samples. The mass loss corresponding to the complete degas/bulk dehydration, which is known to occur between 600 and 700 °C in protonic conductors, starts at a temperature at least 40 °C lower in the N_2 sample than the AIR sample. Another important observation is the decarbonation events that usually start at approximately 800 °C. A possible carbonate phase in the AIR sample continues to