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Influence of the autocombustion synthesis conditions and the calcination temperature on the microstructure and electrochemical properties of $BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ electrolyte material

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A B S T R A C T

This study focuses on the influence of the microstructure on the conductivity of the $BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ compound, prepared by nitrate-glycine autocombustion, with a special attention to the influence of less studied parameters, i.e. the nature of the precursors and the ratio between the nitrate precursors and the glycine, and the temperature of the calcination step. It has been shown that the nature of the precursors and the ratio between the nitrate precursors and the glycine impact strongly both the microstructure of the powders after autocombustion and of the pellets calcined at 1000 °C and sintered at 1400 °C. The highest total conductivity in dry air (above 10^{-2} S/cm from 700 °C) was obtained for a sample without secondary phase. The impact of the calcination temperature was subsequently studied between 700 °C and 1000 °C on this latter sample. EIS measurements make possible the differentiation of the grain and grain boundary contributions to the total conductivity, in accordance with the change of the microstructure visible on SEM images after sintering of pellets calcined at different temperatures. It has been shown that the grain boundaries play a key role on the evolution of the total conductivity of $BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$, which is, at high temperatures, mainly anionic.

1. Introduction

The increasing energy consumption and the dwindling of oil and gas resources require the development of renewable sources of energy. Nevertheless wind and solar generated energies are intermittent and fuel cells associated with electrolyzers are a promising solution to balance the energy network [1]. Among the fuel cells technologies, the advantages of the solid oxides fuel cells (SOFCs) are their high fuel flexibility, low contamination and efficiency [2]. However, SOFCs operate at high temperature which leads to other issues such as the premature aging of the cell and the use of high temperature resistant materials to shape the entire fuel cell [3]. The output of a fuel cell is often limited by the electrochemical behavior of the electrolyte material. The prospect of electrolyte efficient in the intermediate temperature (temperature range of 600–700 °C) led to the development of various electrolyte materials from anionic conductors such as rare earth doped ceria (GDC, SDC) or strontium and magnesium doped lanthanum gallate (LSGM) to alkali metal carbonate composites and protonic conductors. The first protonic conductor was reported in 1981 by Iwahara [4] based on doped and undoped $BaCeO_3$ and $BaZrO_3$ [2,5]. Indeed, protons having a lower activation energy than oxygen ions [2], the use of a proton conducting electrolyte for SOFC instead of the conventional anion conducting electrolyte would reduce the operating temperature of the fuel cell.

This study focuses on the extensively studied proton conducting electrolyte material BCZY which is a solid solution of yttrium-barium zirconate (BZY) and yttrium-barium cerate (BCY). BCY exhibits one of the best total protonic conductivity level around 10^{-2} S/cm at 600 °C [6–7,8] but is not stable in the operating conditions of SOFC, especially in wet carbon dioxide atmosphere [9–10,11]. On the contrary, BZY is chemically stable but shows lower conductivity level compared to that of BCY due to a large blocking grain boundary effect. Moreover yttrium-barium zirconate requires a very high sintering temperature to obtain a dense electrolyte material with large grain size reducing the grain boundary resistance [12]. BCZY solid solution shows properties which are a compromise between the high proton conductivity of BCY and the stability of BZY [13,14]. Most of the studies from the literature on BCZY focus on the tuning of the conductivity properties by varying the proportion of $BaCeO_3$ and $BaZrO_3$ within BCZY solid solution [7,15–20], concluding to a concomitant increase of the stability and decrease of the conductivity of the solid solution when the ratio Zr/Ce increases. The stoichiometry of 80% of $BaCeO_3$ and 10% of $BaZrO_3$

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doped with 10% of Y seems to be a good compromise.

Nevertheless, the composition is not the only pertinent parameter, and the link between microstructure and electrochemical properties of SOFC materials have been widely studied: tuning of the microstructure, and more precisely of the grains size, has been reported, either by changing the calcination temperature for LSCF perovskite anodes [21] and LSF cathodes [22] for instance, or by changing the pressure and temperature of sintering by spark plasma sintering for LSZO electrolyte material [23]. It has been shown that the microstructure of BCZY derivatives can be controlled by varying synthesis routes [24–31], tuning the composition including additional elements [32,33] or adding sintering aids [27,34–40], with a balance between grain and grain boundary contributions which have been in some cases separated by using electrochemical impedance spectroscopy (EIS) [15,41].

Nevertheless, as claimed in recent work [42], obtaining good conductivity values still requires the use of high sintering temperatures. The addition of ZnO as sintering aid is also reported, but the amount of this aid must also remain limited in order to avoid too important conductivity decrease [42]. Indeed, BCZY powders can be synthesized by glycine-nitrate auto combustion which leads to nano-sized powders [43–45]. This technique in liquid phase enables the mixing of the precursors at the molecular level and the lowering of the sintering temperature [16,46]. After synthesis, the powder undergoes a calcination treatment to remove the organic materials and complete the crystallization of BCZY powder and a sintering treatment at higher temperature to densify pellets of BCZY powders. If it is largely reported that the sintering temperature influence the morphology and the conductivity of the product, the influence of the removal of the organic materials, which depends both of the nature of the organic species and of the calcination treatment, has not been studied, and is the objective of this study. Indeed the first part of the study deals with the influence of the auto combustion conditions on the microstructure and conductivity with a fixed calcination temperature of 1000 °C and an optimized sintering treatment to obtain a relative density above 90% in the different cases. The second part of the study focuses on the influence of the calcination temperature with fixed conditions of the synthesis and a sintering temperature of 1400 °C, with a special attention given to the respective contribution of the bulk and of the grain boundary to the total conductivity.

2. Experimental

2.1. Powder syntheses

$BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ powders were synthesized by glycine-nitrate auto-combustion [47]. Typically, 15 g of BZCY were prepared for each synthesis. Metal nitrate precursors of $BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{3-\delta}$ were dissolved in the minimum amount of de-ionized water. When Yttrium oxide Y_2O_3 is used, it is prior mixed with nitric acid HNO_3 to form yttrium nitrate $Y(NO_3)_3$. Glycine ($C_2H_5NO_2$) is the fuel of the combustion. It is used as a chelating agent for the metallic cations. 2 mol% ZnO, used as sintering aid, was also added to this solution. In order to avoid entrance of Zn into the structure, this sintering aid is introduced as ZnO and not as Zn nitrates. An ammonia solution was used to neutralize the pH of the solution in order to maximize the efficiency of glycine as a chelating agent [48].The solution is heated at 80 °C and stirred to evaporate water. A brown viscous gel is obtained at the end of dehydration. Further heating to temperatures about 300 °C during a few minutes leads to the ebullition of the gel and a self-propagating combustion. Yellow nano-sized powders are obtained after combustion.

The two syntheses are expressed with Eqs. (1) and (2), in which z is the coefficient that controls the proportion of glycine introduced in the reaction.

$$
\begin{aligned}
&Ba(NO_3)_2 + 0.8Ce(NO_3)_3 + 0.1ZrO(NO_3)_2 + 0.1Y(NO_3)_3 + zNC_2H_5O_2 \\
&\quad \rightarrow BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{2.95} + 2zCO_2 + 2.5zH_2O + (0.5z + 2.45)N_2 \\
&\qquad + (5.925 - 2.25z)O_2
\end{aligned} \tag{1}
$$

$$
\begin{aligned}
&0.05Y_2O_3 + 0.3HNO_3 \rightarrow 0.1Y(NO_3)_3 + 0.15H_2O \\
&Ba(NO_3)_2 + 0.8Ce(NO_3)_3 + 0.1ZrOCl_2 + 0.1Y(NO_3)_3 + zNC_2H_5O_2 \\
&\rightarrow BaCe_{0.8}Zr_{0.1}Y_{0.1}O_{2.95} + 2zCO_2 + (2.5z - 0.1)H_2O + 0.2HCl \\
&\quad + (0.5z + 2.35)N_2 + \\
&(5.675 - 2.25z)O_2
\end{aligned} \tag{2}
$$

Then the powders undergo a calcination in order to remove the organic materials from the powders. Pellets of the powders were subsequently shaped using a uniaxial press (150 MPa) and sintered in air at around 1400 °C. As shown for instance by Civera et al. for the perovskite $LaMnO_3$ [49] electrode or by Mumtaz et al. for the Sr and Zr co-doped $BaCeO_3$ electrolyte [50], the outcome of the autocombustion synthesis is very sensitive to the operating conditions. In this study, two parameters have been changed, the type of the precursors and the glycine to metal nitrate precursors ratio z. The results from four different syntheses are presented in the following. Two syntheses started with only metal nitrates precursors: $Ba(NO_3)_2$ (SIGMA-ALDRICH, 99.9%), $Ce(NO_3)_3.6H_2O$ (ACROS Organics, 99.5%), $ZrO(NO_3)_2{\cdot}6H_2O$ (ACROS Organics, 99.5%) and $Y(NO_3)_3{\cdot}6H_2O$ (ACROS Organics, 99.9%) in stoichiometric amounts (z_s = 5.925/2.25) or a glycine-rich synthesis (Alfa Aesar,99.5%) with a glycine coefficient equal to $z_s \times 1.5$. In order to evaluate the effect of the presence of another counter-anion, two other syntheses started with mixed type precursors: $Ba(NO_3)_2$, $Ce(NO_3)_3{\cdot}6H_2O$, $ZrOCl_2{\cdot}8H_2O$ (pro-analyst, 99%) and Y_2O_3 (Alfa Aesar, 99.99%) dissolved in nitric acid for the synthesis in stoichiometric conditions (z_s = 5.675/2.25) or a glycine-rich synthesis with a glycine coefficient equal to $z_s \times 2.5$. Chloride ions were introduced by replacing $ZrO(NO_3)_2$ by $ZrOCl_2$, which is more soluble than the three other chloride precursors $BaCl_2$, $CeCl_3$ or YCl_3.

In the first part of the study, except for the synthesis carried out with mixed type precursors in fuel-rich conditions (see explanation in Section 3.1) all powders were calcined at T_{calc} according to the following treatment:

$$T_{amb} \rightarrow 5^{\circ}C/min \rightarrow T_{calc}{}^{\circ}C\,(10h) \rightarrow 5^{\circ}C/min \rightarrow T_{amb},$$

with T_{calc} = 1000 °C. In the second part of the study, different values of T_{calc}, in the 800 °C–1000 °C range, were used.

In order to present the requested density, samples are sintered at T_{sint} according to the following treatment:

$$T_{amb} \rightarrow 1^{\circ}C/min \rightarrow T_{sint}(12h) \rightarrow 1^{\circ}C/min \rightarrow T_{amb},$$

with T_{sint} = 1400 °C, except for powder issued from the synthesis carried out with mixed type precursors in fuel-rich conditions (see explanation in Section 3.1).

2.2. Powder and pellets characterization

The powders obtained by autocombustion were characterized with a particle characterization tool with a laser-based technology (Beckman coulter ls 230) in liquid phase (absolute ethanol) and the specific surface areas were determined by the BET method (Micromeritics 3flex). Before sintering, the powders were uniaxially pressed into pellets (10 mm in diameter and 1.2 mm in thickness). The density of the sintered pellets was determined by measurements of the sample dimensions and weight. For instance, for a density values of 92%, the diameter of the pellet is 7.87 mm, its thickness is 0.88 mm, and it weigh is 0.247 g.

X-ray diffraction (XRD) patterns were recorded on the powders and the pellets at room temperature using a Bruker D8 Advance diffractometer in Bragg-Brentano geometry with a Cu anode X-ray source ($\lambda_{Cu\ K\alpha1}$ = 1.5406 Å) in the 5–80° 2θ range with a step size of 0.018°