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Conventional and field-assisted sintering of nanosized Gd-doped ceria synthesized by co-precipitation

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ABSTRACT

Gadolinium-doped ceria is an attractive electrolyte for potential application in SOFCs operating at intermediate temperature; for such use, the fundamental compositions typically contain 10–20 mol% Gd_2O_3. In this work, we produced nanosized 10 mol% gadolinium-doped ceria powder by co-precipitation, starting from Ce and Gd nitrate solutions and using ammonia solution as precipitating agent. The co-precipitate was characterized by DTA-TG, TEM, XRD and nitrogen adsorption analyses. We studied the behavior of the nanopowder under both conventional and Flash sintering. Very different behavior was seen: the conventional sintering cycle produced a poorly densified material, while Flash sintering allowed production of a perfectly densified material, with uniform sub-micrometric grain size.

1. Introduction

Solid Oxide Fuel Cells (SOFCs) are very promising energy-conversion devices characterized by high efficiency, modularity and noiselessness. They can use various fuels (hydrogen and methane, biogas and natural gas) at very limited emission levels [1,2].

Today the SOFCs as developed must operate at temperatures above 800 °C, due to the use of yttria-stabilized zirconia (YSZ) for the electrolyte. This leads to high costs for the materials and to limited durability. Lowering the service temperature of SOFCs is a major target for researchers operating in this field, who aim to exploit IT-SOFCs (Intermediate Temperature SOFCs), operating at temperatures between 500 and 800 °C [3,4]. One of the requirements for the success of IT-SOFCs is the availability of ceramic electrolytes characterized by ionic conductivity higher than YSZ in the specific temperature range. From this point of view, ceria-based ceramics have been identified as the fundamental candidate materials [5]. Characterized by relatively high abundance, cerium oxide (CeO_2) is a technologically important material. Applications are as catalysts, ionic conductors, oxygen sensors, oxygen permeation membranes, fuel cells, glass-polishing materials, electrochromic thin films, ultraviolet absorbents; and also in biotechnology, environmental chemistry and medicine [6].

The oxygen vacancy concentration and concomitant ionic conductivity can be increased by the substitution of cerium with a lower-valence metal ion (i.e., R^{3+} ions – R=Gd, Sm, Nd, Y, Pr etc.); the fluorite-type crystal lattice of CeO_2 lets us replace a relatively large amount of cerium cations with rare-earth cations, which can greatly influence ionic conductivity [1]. Among ceria-based ceramics, gadolinium-doped ceria (GDC) is an attractive electrolyte for potential application in SOFCs operating at intermediate temperature, typically with 10–20 mol% substitution of Ce^{+4} by Gd^{+3} [7–10]. For ionic conductivity enhancement of ceria, atoms must be used with ionic radius close to that of the cerium cation. The perfect coincidence between the host (Ce^{+4} cation) and the dopant (Gd^{+3} cation) radius in GDC accounts for high ionic conductivity and low activation energy, due to the low binding energy between oxygen vacancies and Gd^{+3} [4].

We note that in addition to the intrinsic properties of the material, ionic conductivity depends strongly on the microstructure (porosity, density, grain size, grain boundaries etc.) and is therefore influenced by materials processing. Moreover, a densified ceramic with no open porosity is essential for use as the electrolyte in SOFCs. Nevertheless, one of the main drawbacks of ceria-based materials is the high sintering temperature required to obtain full densification [2,11]. Such high sintering temperatures also lead to large grain sizes that cause poor mechanical properties [12–14]. Therefore, to improve the sintering behavior of ceria-based ceramics, a first strategy is the synthesis of more reactive

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powders, generally obtained by chemical routes, although their preparation is often too cumbersome for extensive use. Another solution is to use sintering aids (Bi_2O_3, Fe_2O_3, Co_2O_3, Li_2O etc.) [15]; but these, unfortunately, can lead to increased grain boundary resistance to ionic conduction [16].

An innovative technique called Flash Sintering has recently appeared. This technique allows the consolidation of ceramics in very short times and at relatively low temperatures, under the effect of an external electrical field [17–27]. Ceria doped with 20 mol% gadolinium was successfully densified by using flash sintering [3]. The application of an external electric field during heating allowed reduction of the sintering temperature to 545 °C. Because of the lower processing temperature, Flash Sintering represents a very attractive technique for obtaining dense and fine grained materials, with several possible applications in the SOFCs industry. Experiments on YSZ show that the application of an external DC field can strongly retard grain growth phenomena [26,27], even obtaining full densification [26].

In this work, 10 mol% gadolinium-doped ceria nanosized powder synthesized by co-precipitation was densified under conventional and Flash Sintering techniques. We aim to identify fundamental differences in the microstructure of the materials obtained, for possible application as an electrolyte in SOFCs.

2. Material and methods

Cerium (III) nitrate [$Ce(NO_3)_3 \cdot 6H_2O$, 99.0% pure, Carlo Erba, Italy] and gadolinium nitrate [$Gd(NO_3)_3 \cdot 6H_2O$, 99.0% pure, Carlo Erba, Italy] were used as starting materials for the synthesis of hydrous cerium–gadolinium oxide ($Ce_{0.9}Gd_{0.1}O_{1.95}$) by co-precipitation. The appropriate amounts of cerium and gadolinium salts were dissolved in de-ionized water, to reach a total cationic concentration of 0.1 M; the solution was then vigorously stirred for 1 h. The co-precipitation was carried out by reverse precipitation, i.e., the solution containing dissolved cerium and gadolinium nitrate was slowly added to an excess ammonia solution (~4 M) under vigorous stirring. After the precipitation, the suspension was stirred for 1 h and finally the co-precipitate was filtered and washed repeatedly with de-ionized water to remove the undesired ions. The precipitate was then dried overnight at 60 °C to produce a fine powder. The thermal behavior of the synthesized powder was analyzed by simultaneous differential scanning calorimetry and by thermogravimetric analysis (DSC and TG, Thermoanalyzer STA 409, Netzsch) in air with a heating rate of 10 °C/min up to 1200 °C, using α-Al_2O_3 as reference.

The powder obtained was also characterized by X-ray diffraction (XRD) using a Panalytical X'PERT MPD diffractometer to detect the crystalline phases. The XRD analysis was also carried out at high temperature (up to 1300 °C) in air by an Anton Paar HTK 16 high temperature stage. The heating rate was 5 °C/min with a dwell time of 10 min at each temperature before starting the X-ray analysis. The primary particle size was calculated by the Scherrer equation (X'Pert HighScore Panalytical software) [28]:

$$d = K\lambda/(B\cos\theta) \quad (1)$$

where K is the shape factor (assumed equal to 0.89), λ the X-ray wavelength (0.1541 nm for Cu Kα), θ the Bragg angle of the most intense diffraction peak and B the width at half maximum of the same peak, corrected for the instrumental broadening, given by:

$$B = B_{sample} - B_{instr} \quad (2)$$

where B_{instr} was determined using standard polycrystalline silicon.

The specific surface area of the synthesized powder was determined by nitrogen adsorption analysis (BET method) using a Micromeritics Gemini apparatus and using nitrogen as adsorbate gas; the sample was preliminary dried under vacuum at 100 °C.

The morphology of the powders was also observed by transmission electron microscopy (TEM, FEI Tecnai G2 Spirit Twin).

The powders were shaped into cylindrical pellets (diameter=8 mm) by cold isostatic pressing (ABB, CIP 32330-P2 model) at 160 MPa.

Conventional sintering was initially in air at 1500 °C for 3 h, using a heating rate of 10 °C/min and free cooling within the furnace. Then, some samples were also subjected to sintering using a lower heating rate (3 °C/min up to 300 °C, 1 °C/min between 300 °C and 350 °C and 5 °C/min from 350 °C to 1500 °C) according to previous work [7,11,29]. The low heating rate between 300 °C and 350 °C was also suggested by the DTA thermograph in Fig. 2, as in this temperature range thermal dehydration occurs and water vapor can escape slowly from the pellet.

Flash Sintering was performed in a specifically modified dilatometer (Linseis L75) using heating rate of 20 °C/min. Two platinum plates acted as electrodes, pressed against the sample with constant load of 500 mN. To improve the electrical contact between the platinum electrodes and the specimen, silver paste (Agar Scientific) was applied on the green pellet upper and lower surface. Various fields (in the range 75–150 V/cm) were applied by a DC power supply (Glassman EW series 5 kV–120 mA), which was switched on once the sample temperature reached 150 °C. A multimeter (Keitheley 2100) was used to monitor the electrical parameters (voltage and current). Once the current limit (fixed at 690 mA) was reached, the system operated under current control for 2.5 min before final shut down.

We measured the apparent density of the sintered compact pellets using a hydrostatic balance (Archimedes' principle).

The microstructure of the sintered pellets was observed by SEM (Philips XL30) after carefully polishing one of the flat surfaces and successive thermal etching.

3. Results and discussion

3.1. Gadolinium-doped ceria co-precipitate

Gadolinium-doped ceria co-precipitated powders are nanometric (~10 nm) as shown in Fig. 1. The specific surface area of the powders, measured by nitrogen adsorption analysis according to the BET method, is equal to 105 m^2/g. Under the hypothesis that all particles are spherical, we can estimate the average diameter:

$$d_p = 6/(\rho S) \quad (3)$$

where ρ is the density (supposed equal to 7.22 g/cm^3 as from crystallographic data reported in ICCD card n. 01-075-0161) and S is the specific surface area. The value obtained, very close to 8 nm, compares well with TEM observations.

The X-ray diffraction pattern, recorded on the co-precipitated powders, is shown in Fig. 2. It clearly appears that the sample is not perfectly crystallized. Similar results were obtained by Shih et al. [30], who reported that pure ceria precipitate begins to crystallize at 0 °C. All XRD peaks in Fig. 2 can be assigned to fluorite cubic gadolinium-doped ceria (ICDD card n. 01-075-0161 used as reference, related to $Gd_{0.1}Ce_{0.9}O_{1.95}$ with space group Fm-3m). The crystallite size was calculated by the Scherrer formula as 10.0 nm, further confirming previous TEM observations. In situ XRD analyses, at temperatures from ambient to 1300 °C, were carried out in static air in order to verify the thermal stability of the powders. The recorded diffraction patterns are in Fig. 3. We note the absence of any phase transformation upon heating; in addition, no peaks due to Gd_2O_3 are present, even at the highest