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Microwave-assisted synthesis of gadolinia-doped ceria powders for solid oxide fuel cells

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Abstract

Gadolinia doped ceria (GDC) is an attractive electrolyte material for intermediate temperature solid oxide fuel cells (IT-SOFCs) for its high ionic conductivity at low temperature (500–700 °C). A number of different methods are currently used to prepare nano-sized doped-ceria powder. Among the others, precipitation in solution remains the best method to obtain well-dispersed particles of controlled properties. In this work, nanocrystalline $Ce_{1-x}Gd_xO_{2-\delta}$ (GDC) particles were produced by polyol microwave assisted method in very mild conditions (170 °C, 2 h, 1 atm). The as-synthesized powder showed good sinterability and ionic conductivity comparable to the ones of the corresponding nanometric commercial GDC.

Keywords: GDC; Microwave heating; Polyol method; IT-SOFC

1. Introduction

Ceria and rare earth-doped ceria powders have important applications in catalysis [1], for gas sensors [2], and in electronics [3]. In recent years, it has received considerable attention as an alternative to yttria stabilized zirconia (YSZ) as electrolyte for solid oxide fuel cell (SOFC). Among the others, gadolinium doped ceria (GDC) with its high ionic conductivity at $T = 600$ °C, is attractive as electrolyte material for solid oxide fuel cells operating at intermediate temperatures (IT-SOFCs) [4].

Several methods are currently used to prepare nano-sized doped-ceria including hydrothermal [5], microemulsion [6], precipitation [7], and sol–gel [8]. In most of these cases, however, an additional calcination step (at 400–600 °C) is generally required to transform the initial amorphous powder into a crystalline phase. During this process severe aggregation and sintering often occur. Precipitation in solution remains the best method to obtain well-dispersed particles of controlled properties [9]. With this technique, it is possible to produce crystalline doped-ceria powder without a calcination step at temperature near 100 °C but with very long precipitation time (more than 12 h) [10,11]. Polyol mediated method has been recently used [12] to synthesize dispersion of different metals [13] and high purity mixed oxides [14,15]. In this method fine particles are formed by heating their precursor salts in high boiling alcohols (e.g. ethylene glycol, diethylene glycol, etc.). The polyol acts as stabilizer for its chelating behaviour hindering the particles agglomeration during synthesis [16], while its high-boiling point allows to obtain nanocrystalline powders straight after synthesis. Furthermore, as a consequence of its high dipole moment, the polyol can be used as microwave absorbing solvent. Microwave irradiation has in fact some unique advantages: among them a rapid volumetric heating that induces a fast homogeneous nucleation of the particles [17,18].

In this study, a new method for the preparation of nanocrystalline GDC by microwave assisted polyol method under mild conditions (170 °C, 2 h) is reported. The as-synthesized powders were pressed, sintered and electrically characterized. A comparison with a commercial nanometric powder is also reported.

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2. Experimental

2.1. Synthesis

$Ce_{0.8}Gd_{0.2}O_{1.95}$ powder was synthesized using cerium nitrate hexahydrate (99.5%, Aldrich, Italy) and gadolinium nitrate hexahydrate (99.9%, Aldrich, Italy) as starting materials.

The precursor solution was prepared by mixing the precursor salts with molar ratio Ce:Gd = 0.8:0.2 in 200 mL of diethylene glycol (DEG, 99%, Alfa Aesar, Germany), to have a final metals concentration of 0.1 M ($[Ce^{3+}] + [Gd^{3+}] = 0.1$ M). The solution was heated under reflux in a commercial microwave oven for chemical synthesis (MicroSYNTH Plus, Milestone, USA) at the final temperature of 170 °C for 2 h. During the reaction a water excess (1:10 = $[M^{3+}]$:$[H_2O]$) was added to the DEG solution at 140 °C to induce the hydrolysis of the precursor salts. The precipitated powder was separated by centrifugation, washed in ethanol and dried at 105 °C for 2 h. The as-synthesized powders and commercial nanometric GDC (GDC20, Praxair, USA) were uniaxially pressed in pellets (700 MPa) and sintered at 1400 °C for 6 h.

2.2. Powder characterizations

The crystalline phase purity of the dried powder was assessed with a Bruker D-8 Advance X-ray diffractometer (Germany) at room temperature using Cu anode as X-ray source (Ka = 1.5418 Å). The powder morphology was investigated by scanning electron microscopy (SEM, Leica Cambridge Stereoscan 360). The size distribution of the powders was determined using a dynamic light scattering analyzer (DLS Nano S, Malvern, UK) whereas for the chemical composition an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Liberty 200, Varian, Clayton, South Australia) was used. The ICP samples were prepared dissolving the powder in an acidic mixture of H_2SO_4 and HCl 1:1 (w/w%). The conductivity of the sintered pellets with sputtered Pt electrodes was measured by a.c. impedance spectroscopy (IS) in the 1–10^6 Hz frequency range (10 points per decade) with a 100 mV applied voltage, using an Autolab PGSTAT100 potentiostat/galvanostat and a ProboStat (NorECs) test rig. Conductivity measurements were done between 250 and 900 °C (50 °C step) in O_2 atmosphere.

3. Results and discussion

3.1. Powder synthesis

Nanocrystalline $Ce_{0.8}Gd_{0.2}O_{1.95}$ (GDC) powders were produced by one-step microwave-assisted synthesis from a diethylene glycol solution of precursor salts at 170 °C for 2 h. Fig. 1 shows the XRD pattern of as-synthesized GDC powder (GDC 1). The typical CeO_2 fluoritic phase (JCPDF 34-394) was obtained in the mild conditions of synthesis used (170 °C for 2 h).

SEM micrograph (Fig. 2) shows as-obtained powder formed by sub-micrometric agglomerates of nano-spherical particles. Dynamic light-scattering (DLS) experiments performed after re-dispersion of the washed powder in diethylene glycol, confirm an agglomerates size ranging from 300 to 900 nm (inset of Fig. 2) with a monomodal distribution centered at 450 nm.

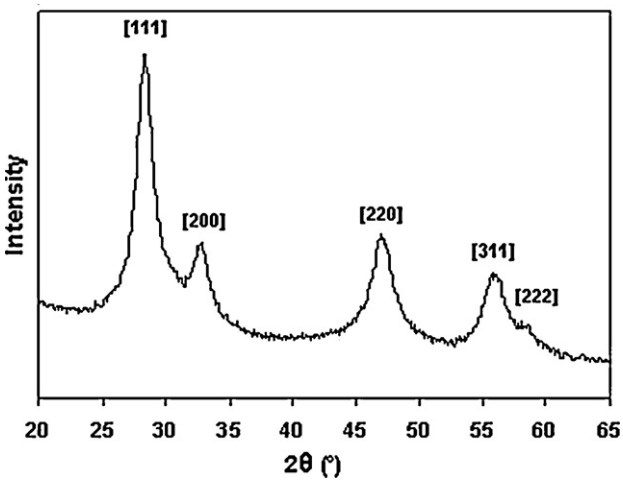

Fig. 1. X-ray diffraction pattern of the as-synthesized powder.

The crystallite's size calculated from the XRD patterns using Debye–Scherrer equation was estimated to be around 4 nm.

ICP analysis revealed powder of composition equal to $Ce_{0.83\pm0.02}Gd_{0.167\pm0.005}O_{1.95}$ that is, a compound with a gadolinium amount lower than expected. The low stoichiometry of the system was thought to be due to the low temperature used. For this reason the synthesis temperature was increased up to 240 °C (maximum temperature at which the teflon used for the thermocouple sheath can stand). Even at this temperature, the synthesized GDC retains the stoichiometry already seen in milder conditions (i.e. $Ce_{0.83\pm0.02}Gd_{0.167\pm0.005}O_{1.95}$).

A possible explanation is that the low amount of Gd in the GDC powder was therefore linked to the formation of stable gadolinium complexes in the reaction environment. During

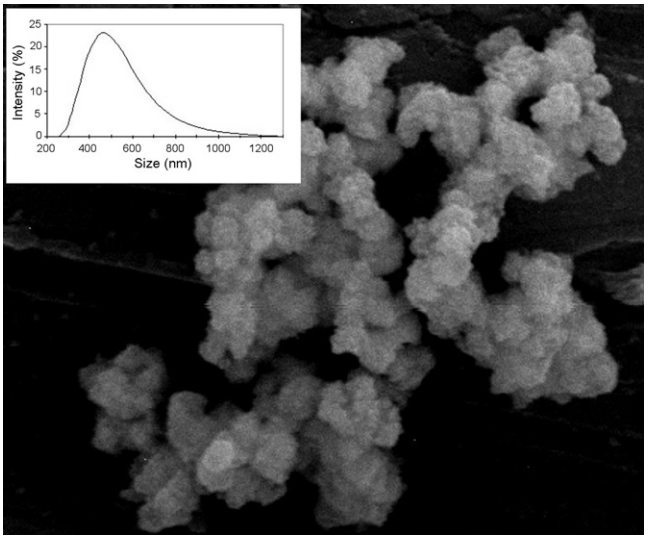

Fig. 2. SEM micrograph of the as-synthesized powder. The inset shows the results of dynamic light-scattering (DLS) after re-dispersion of the as-synthesized powder in diethylene glycol.

synthesis, some of the products of DEG oxidation could be able to complex some of gadolinium ions of the precursors, making them not available for the subsequent reaction. Gd^{3+} is in fact well known to have strong affinity with complexing agents especially the ones containing bidentate carboxilate groups [19].

These compounds are formed in the reaction solution as a consequence of the diethylene glycol oxidation during synthesis. Shen et al. and Svetlakov et al. have shown in fact that diethylene glycol can react with nitric compounds to form diglycolic acid [20].

$$HOCH_2CH_2OCH_2CH_2OH \xrightarrow{NO_3} OOCCH_2OCH_2COOH$$

Thus, diglycolic acid can strongly coordinate gadolinium [19] and therefore make it unavailable.

To verify this hypothesis and obtain stoichiometric GDC, the gadolinium amount subtracted for the formation of complexes was restored adding a surplus of gadolinium precursor in the starting solution. This amount was calculated on the basis of the DEG oxidation reaction during synthesis. As previously shown, the nitrates introduced into the mixture reaction with the precursor salt are able to oxidize the solvent producing the chelating agent. It is reasonable to assume the complex concentration equal to the lack in Gd detected in the GDC powders after synthesis, that is $0.200 - 0.167 = 0.033$ (16.5%). Therefore to obtain the exact stoichiometry it is necessary to add an excess of $[Gd^{3+}]$ equal to 16.5%. In this way both Gd amount and nitrate concentration are increased. However, Gd is added as nitrate salt: increasing the moles of Gd means to also increase the nitric part and, as a consequence the diglycolic acid. It is therefore necessary to take in account this additional chelating agent in the calculation of the Gd excess need. Total gadolinium excess to add to the starting solution was then calculated considering also the proportional increase of chelating agent introduced with the precursor. For doing so, it is necessary to add to the previously considered 16.5% of [Gd] a further 16.5% of this latter amount to balance the introduction of additional oxidizing part (NO_3^-) that is a total 19.2% of gadolinium salt. A new batch of powder (GDC 2) was therefore produced adding a 19.2% mole excess of Gd salt to restore the gadolinium concentration in the starting solution keeping the final temperature and time equal to 170 °C and 2 h. Doing so, powders with the desired stoichiometry were obtained. The as-synthesized powder (GDC 2) shows a pure fluoritic phase, with same morphology and size distribution of the previous sample (GDC 1).

3.2. Electrical characterization

Archimedes' densities of the sintered samples are shown in Table 1. In particular commercial GDC shows the highest density value.

All the sintered samples exhibit a homogeneous microstructure with grain size in the range of 0.5–2 μm. Fig. 3 present typical SEM micrographs obtained for various GDC samples.

Table 1
Experimental and relative density of the $Ce_{1-x}Gd_xO_{2-\delta}$ samples after sintering at 1400 °C for 6 h. Relative density was calculated considering GDC theoretical density equal to 7.34 g/cm^3.

Sample	x (dopant concentration)	Archimedes density (g/cm^3)	Density (%)
GDC 1	0.167	6.80	92.6
GDC 2	0.205	6.89	93.9
Commercial GDC	0.197	6.95	94.7

The Arrhenius plots of the total conductivity of the GDC samples are shown in Fig. 4.

Both samples chemically produced (GDC 1 and GDC 2) show an ionic conductivity at low temperature (<600 °C)

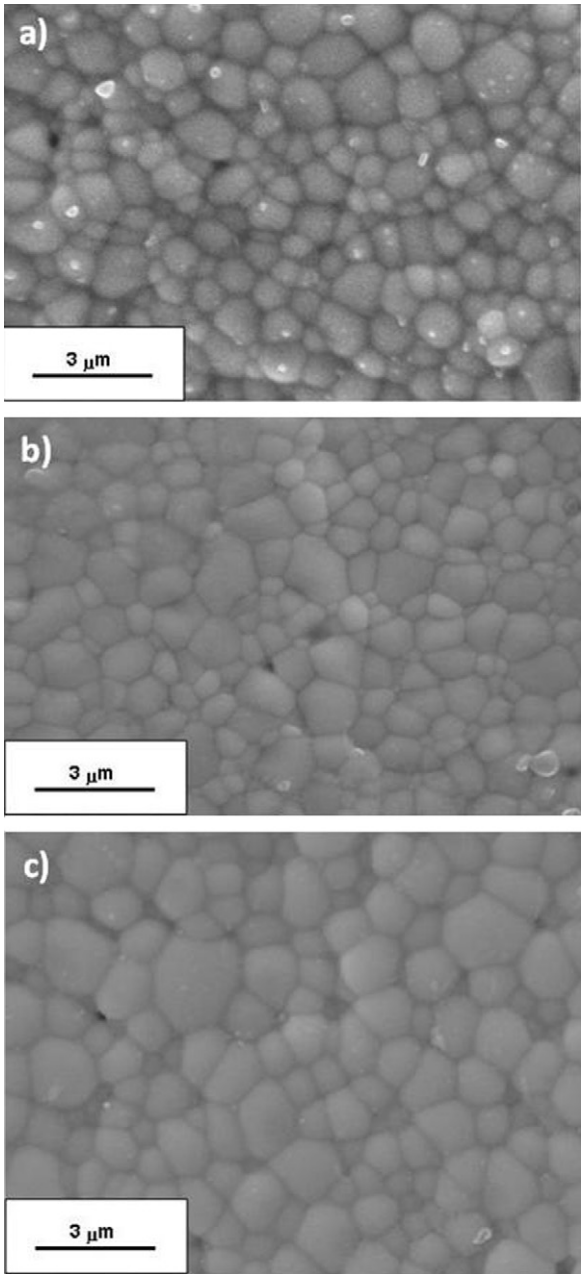

Fig. 3. SEM micrographs of polished and etched surfaces of the sintered pellets at 1400 for 6 h: (a) GDC 1, (b) GDC 2 and (c) commercial GDC.

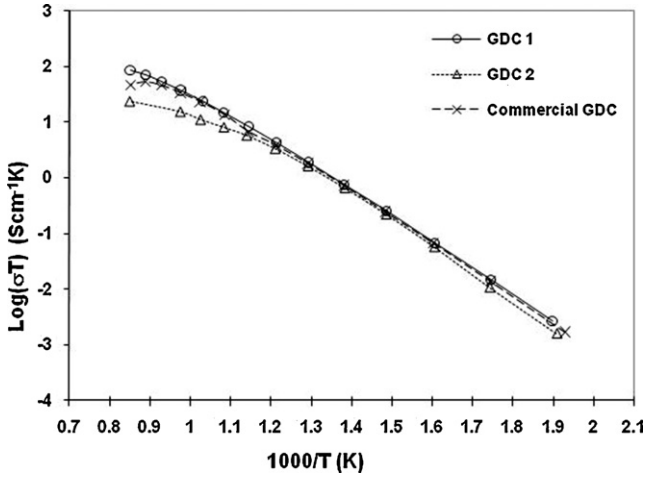

Fig. 4. Arrhenius plots for electrical conductivities of GDC 1, GDC 2 and commercial GDC.

comparable with the one of the pellet produced with commercial GDC. Kudo and Obayashi [21] observed for Gd doped ceria electrolytes the maximum in electrical conductivity at a dopant concentration of $x = 0.20$. On the other hand Zha et al. [22] found the highest conductivity for Gd doped ceria at 15 mol% of Gd. GDC 1 stands between these two values of gadolinium concentration, indicating a peak value of conductivity between the two abovementioned values.

4. Conclusion

The polyol microwave assisted method was used to synthesize nanocrystalline $Ce_{1-x}Gd_xO_{2-\delta}$ (GDC) particles in very mild conditions (170 °C, 2 h, 1 atm). This method allows to obtain nanocrystalline powder straight after synthesis without the need of an additional calcination step as generally required by the other chemical synthesis methods. The as-synthesized powder contains a lower gadolinium amount than what expected. This gadolinium lacking is probably due to the formation of stable gadolinium diglycolate complexes in the reaction environment. To obtain stoichiometric GDC it was necessary to add a surplus of gadolinium precursor in the starting solution.

Powders synthesized by this method show good densification and ionic conductivity similar to the corresponding nanometric commercial GDC in spite of a slightly lower final density. The highest ionic conductivity for the as-synthesized powder was observed at dopant concentration of 0.167. GDC synthesized by polyol microwave assisted method is a very promising material for IT-SOFC electrolyte applications thanks to its high conductivity at low temperature (600 °C) and its good sinterability.

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