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MW-Assisted Polyol Mediated Synthesis of Gadolinium-Doped Ceria Nanopowders

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Abstract

Gadolinia-doped ceria (GDC) is one of the most promising electrolyte for intermediate temperature solid oxide fuel cells (SOFCs). In particular, the production of GDC as nanopowders leads to an higher reactivity that allows better performances, milder sintering conditions and lower production costs. However, nanopowders can be produced only by carefully tailoring their production process. The choice and optimization of the synthesis process is therefore a key step for the production of powders suitable for efficient SOFC components.

In this work nanocrystalline GDC ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$) particles were successfully obtained by one-step microwave-assisted synthesis from a diethylene glycol solution of metal nitrates under mild conditions (170°C, 1 atm). The as-prepared powder showed good crystallinity with specific surface area of 50 m²/g. The sintering and electrochemical properties were compared with a nanometric commercial powder. The MW-produced powder showed an improved sintering behaviour and a uniform sub-micronic microstructure. Electrochemical tests for the MW-produced GDC showed at 600°C twice the conductivity of the corresponding commercial sample.

Introduction

In the recent years, gadolinia-doped ceria (GDC) has attracted a lot of interesting as material for intermediate temperature SOFC [1]. Unfortunately, CeO₂-based ceramics reach a suitable density at temperatures well above 1300°C [2], involving therefore high production costs. Moreover, the high sintering temperature induces the reduction of Ce^{IV} to Ce^{III} with the consequent creation of an electronic leakage that decreases the system effectiveness and leads to poor mechanical stability [3].

To overcome these problems the research is recently considering nano-scale row materials. Nano-powders in fact due to their high reactivity allow milder sintering conditions

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and as a consequence, better performances and lower production costs. Different chemical techniques have been proposed for the synthesis of GDC including combustion [4], cation complexation [5], nano-blast [6], carbonate co-precipitation [7], self-propagating room temperature [8], polymeric precursor [9], hydrothermal [10] synthesis, homogeneous precipitation [11], spray pyrolysis [12], co-precipitation [13], gel casting [14]. In most cases however the procedure needs long dwelling time and/or the application of a pressure. Moreover the powders obtained require an additional calcination step to transform the initial amorphous precursors into a crystalline phase. This process can cause severe aggregation and consequently the loss of nanometric nature of the powders.

Conversely, the "polyol route" allows the direct precipitation of oxides in a high-boiling alcohol [15] that hinders the formation of hydroxide as intermediate phase, preventing at the same time particle agglomeration as a consequence of its surface capping action [16]. Due to its high dipole moment, the polyol can also serve as an excellent solvent for microwave heating. Compared to conventional procedure, microwave dielectric heating has some unique advantages in nanostructured materials synthesis, such as rapid volumetric heating (that can lead to fast homogeneous nucleation) and the possibility of forming novel nanostructures.

In this study, a novel method for the preparation of nanocrystalline GDC is reported. $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ powders were successfully prepared by microwave irradiation (MW) under mild conditions. The ceramics obtained showed enhanced electrochemical properties for SOFC applications.

Experimental

GDC powders were prepared following the procedure reported in Figure 1. $\text{Gd}(\text{NO}_3)_3 \cdot 7\text{H}_2\text{O}$ (99.9%, Alfa Aesar) and $\text{Ce}(\text{NO}_3)_3 \cdot 7\text{H}_2\text{O}$ (99.5%, Alfa Aesar) were used as starting materials. The stoichiometric mixtures of reagents were dispersed in diethylene glycol (DEG) to have a final metal concentration of 0.1M. The solution was heated under reflux in a commercial microwave oven designed for chemical synthesis (MicroSYNTH Plus, Milestone, USA) at 170°C for 2h. To improve the salts hydrolysis, a water excess (1:10 = [M]:[H₂O]) was added to the DEG solution at 140°C. The precipitated powders were separated by centrifugation, washed in ethanol and characterized by X-ray diffraction. XRD measurements were carried out at room temperature with a Bragg/Brentano diffractometer (X'pertPro Panalytical) equipped with a fast X'Celerator detector, using Cu anode as X-ray source ($K\alpha = 1.5418 \text{ \AA}$). The chemical composition of the as-synthesized powders was determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (Liberty 200, Varian, Clayton South, Australia). The powder morphology was investigated by scanning electron microscopy (SEM, Leica Cambridge Stereoscan 360). The specific surface area of the powders was measured by BET method (Sorptly 1750, Carlo Erba, Italy). The sintering behaviour was compared to commercial GDC powder by dilatometer analysis (Netzsch Dilatometer 402E, Germany). The GDC powders were uniaxially (700 MPa) pressed in bars and sintered at 1400°C for 6h. Conductivity measurements were made in O₂ atmosphere in the 250-900 °C temperature range (50 °C step) by a.c. impedance spectroscopy (IS). Impedance spectra were collected using a frequency response analyser Autolab PGSTAT100, applying 100mV amplitude signal in the frequency range 1MHz to 1Hz (10 points per decade). Measurements were carried out on pellets using a two-electrode cell configuration and under symmetrical cell conditions with Pt deposition on 2 opposite faces (about 200 nm of Pt via DC magnetron sputtering), mounting them on a ProboStat (NorECs) test-rig.

Impedance spectra consisted of a higher frequency arc related to phenomena occurring in the electrolyte bulk and of a lower frequency arc representing the grain boundary

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response, aside from the contribution at low frequency ascribed to electrode/electrolyte interface phenomena. Total ionic conductivities were determined with the lower frequency intercept of grain boundary arc for each temperature.

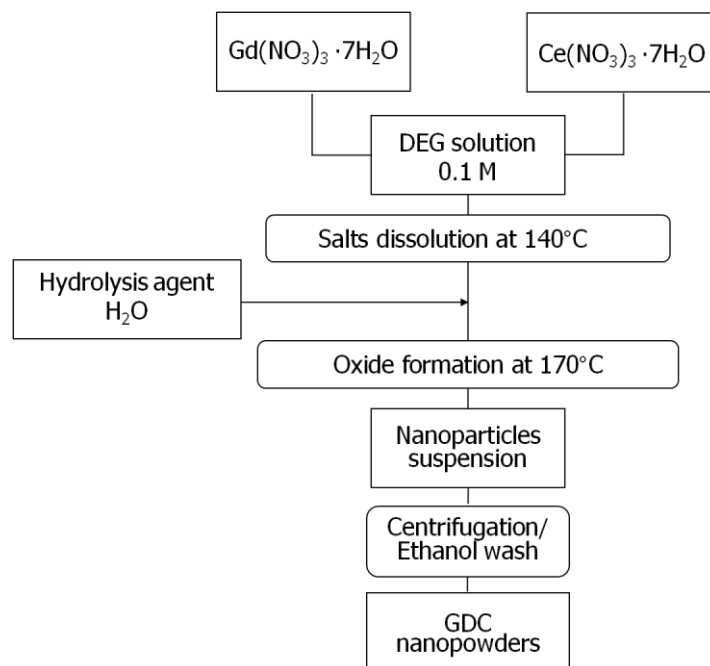


Figure 1 Scheme of the synthesis of the GDC powders.

Results and Discussion

Nanocrystalline ceria doped particles were produced by one-step microwave-assisted synthesis from a diethylene glycol solution of cerium nitrate and gadolinium nitrate by adjusting the synthesis conditions. 170°C for 2h were the reaction conditions able to give crystalline nanometric powders with sufficient reaction yield. Under these mild conditions the powders show a well-defined fluoritic structure (Figure 2) with the stoichiometric composition of $\text{Ce}_{0.795 \pm 0.005} \text{Gd}_{0.205 \pm 0.002} \text{O}_{1.95}$ determined by ICP analysis. The as-synthesized powders show an average crystallite size of about 5 nm, estimated by the XRD pattern using the Debye-Scherrer equation.

The morphology of the powders synthesized is reported in Figure 3. Sub-micrometric, round shape, soft-agglomerated uniform powders with a specific surface area of 50 m²/g were obtained.

The sintering behaviour of Gd-doped ceria powders was studied by dilatometry in the range between 25 and 1500°C and compared with the one of a commercial GDC nanopowders (Fuel Cell Materials, USA) (Figure 4). The GDC obtained via the polyol method show a sintering behaviour that is very similar to the one of the commercial powders. However, the maximum shrinkage for the MW-polyol powders occurs in the range 300 - 900°C. This temperatures range is decisively lower than the one needed to densify commercial powders (600-1200°C). The improvement of the sintering behaviour is related to the higher specific surface area of the MW-polyol-GDC powders respect to the commercial ones that promotes the densification at lower temperatures.

The as-synthesized powders and commercial nanometric GDC were uniaxially pressed and sintered at 1400°C for 6 hours. Archimede's densities of both sintered samples are over 95%, suggesting a good densification.

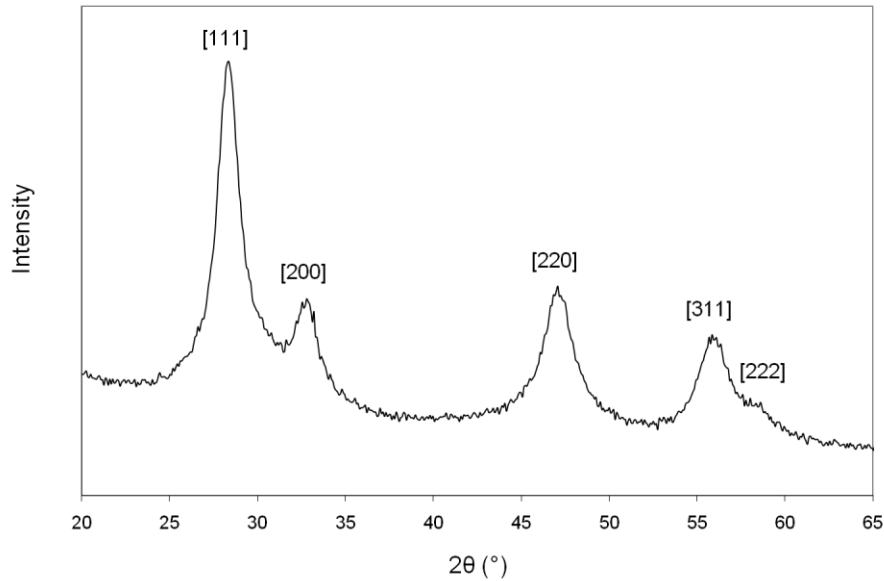


Figure 2 XRD diffractogram of as-obtained powders at 170°C, 2h.

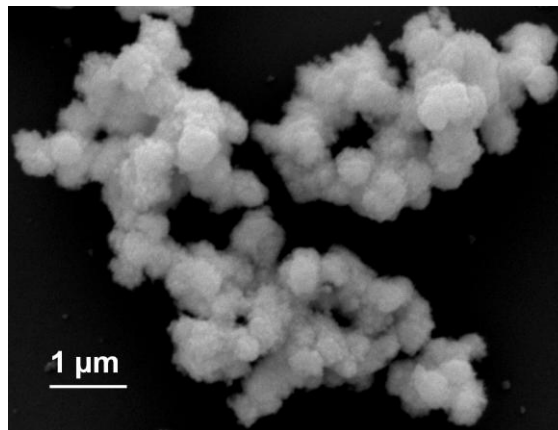


Figure 3 SEM micrographs of the as-prepared GDC powders.

The microstructures of the sintered ceramics are shown in Figure 5. The micrographs confirm that a uniform sub-micronic microstructure is obtained at 1400°C starting from either commercial and MW-polyol GDC powders. The mean grain size decreases from 1.3 to 0.8 μm starting from the commercial or MW-polyol GDC respectively, as a consequence of the lower particles size of the latter.

Finally the GDC obtained through the optimization of the MW-polyol synthesis process exhibited values of ionic conductivity systematically higher than those showed by commercial produced nano-powders of the same composition by a solid state synthesis (Figure 6). In particular at 600°C a conductivity of 0.01 S·cm⁻¹ was recorded, twice the values of the corresponding commercial sample.

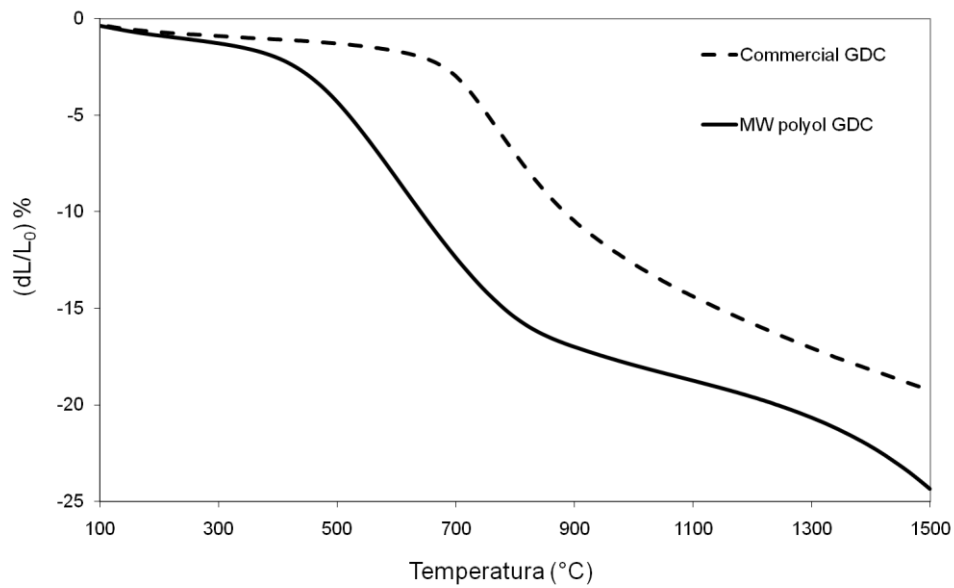


Figure 4 Sintering curves for the commercial and MW-polyol GDC powders.

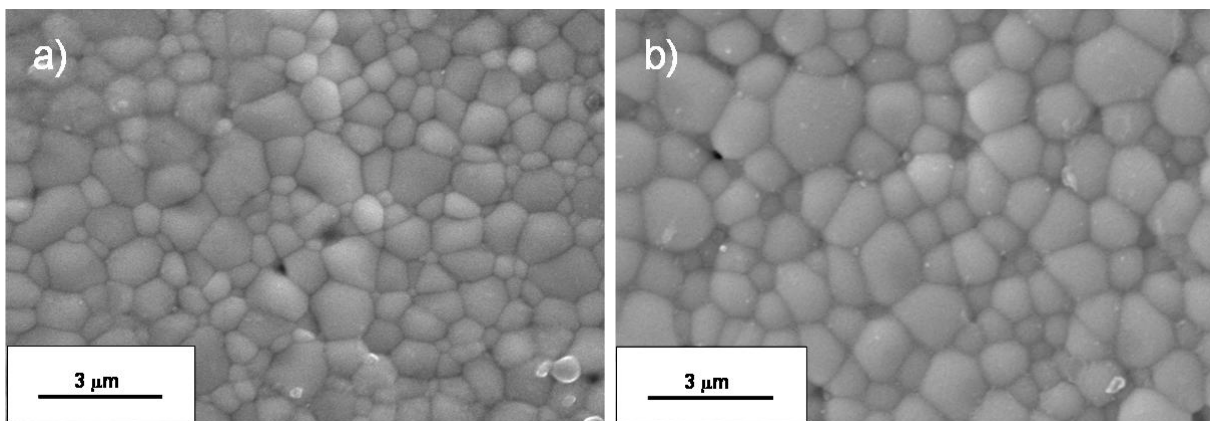


Figure 5 SEM micrographs of polished and etched surfaces of the sintered pellets at 1400 for 6 h: a) MW-polyol GDC and b) Commercial GDC.

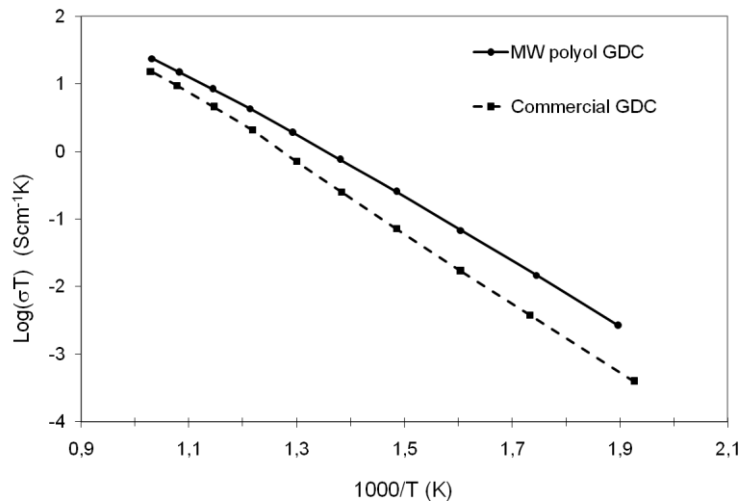


Figure 6 Arrhenius plots of total conductivity for MW-polyol and commercial GDC ceramics.

Conclusions

Applying the polyol process combined with microwave heating, nanocrystalline with a uniform size distribution $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (GDC) particles were successfully produced under very mild conditions (170°C, 1 atm). This one-step method allows the direct formation of the fluoritic phase without the intermediate decomposition and/or calcination steps required by the other chemical synthesis routes. The powders obtained show an improved sintering behavior and better ionic conductivity than the other commercial nanometric powders.

This is a very promising method to easily produce ultrafine GDC powders for SOFC applications with enhanced electrochemical properties.

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