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Preparation and Characterization of $Ce_{0.8}Gd_{0.2}O_{1.9}$ Solid Electrolyte by Polymeric Precursor Techniques

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ABSTRACT: $Ce_{0.8}Gd_{0.2}O_{1.9}$ solid ionic conductors have been prepared by techniques involving polymeric precursors: the Pechini and the amorphous citrate techniques. The aim of this work is to determine among these techniques the most suitable to obtain solid solutions with high chemical homogeneity and high sinterability. The main results show different paths for decomposition of the polymeric precursors. Calcined powders presented similar particle size distribution curves although they are related with the distribution of agglomerated particles. This result explains the difference in average particle size values calculated from results obtained by laser scattering and gas adsorption analysis. X-ray diffraction patterns show the main peaks of the cubic phase for calcinations at 600 °C. Agglomerate morphology is also quite different as observed by scanning electron microscopy.

INTRODUCTION

Solid ionic conductors with the fluorite-type structure have been extensively studied due to their excellent electrical properties. For applications requiring high ionic conductivity such as oxygen sensors and solid oxide fuel cells (SOFC´s), systematic studies have been carried out on zirconia- and ceria-based solid solutions [1,2]. Yttria-stabilized zirconia (YSZ) which is a purely ionic conductor at 1000 °C, is the most developed solid electrolyte for SOFC applications. Doped ceria exhibits a similar ionic conductivity as YSZ but at a lower temperature (800 °C). However, at high temperatures and low oxygen partial pressures the loss of oxygen induces a reduction of Ce^{4+} to Ce^{3+} introducing some electronic conduction [3,4]. Recent experiments have shown that doped ceria may be used as a solid electrolyte for SOFC´s in the temperature range of 500 to 700 °C [5,6].

Alkaline earth and rare-earth oxides have high solubility in cerium oxide. They form substitutional solid solutions where the introduction of aliovalent cations gives rise to oxygen vacancies as charge compensating defects. These anion vacancies are responsible for the ionic conduction observed in these solid solutions. Higher values for conduction have been obtained with Sm, Gd, and Y as dopants in ceria ceramics [2].

Doped ceria solid electrolytes have been prepared by several methods like conventional powder mixing [7,8], coprecipitaton [9-13], and hydrothermal recrystallization [14]. In general, chemical techniques have the advantage over conventional techniques that the precursor presents high reactivity allowing a reduction in the sintering temperature and/or time. Although polymeric precursor techniques have also been used to prepare ceria-based solid solutions these studies have focus on microstructural and electrical properties of sintered ceramics [11,15,16]. A

mixture of ethylene glycol and tartaric acid has been used to form the resin starting from the precipitated hydroxides of cerium and yttrium. For a sintering temperature of 1520 °C and sintering times ranging from 8 h to 18 h, ceramic specimens with relative densities between 92% to 98% were obtained [11]. For ceramic specimens prepared with a mixture of ethylene glycol and citric acid and using nitrates of Ce and Gd as starting materials, a relative density close to 90% was obtained for sintering at 1600 °C/2 h [15]. More recently it was obtained sintered ceramics of gadolinia-doped ceria containing co-dopants with relative densities greater than 97% by sintering at 1400 °C/2 h. In that case, the calcined powders were wet milled for 20 h.

In this work $Ce_{0.8}Gd_{02}O_{1.9}$ solid solution was prepared by two polymeric precursor techniques. Some physical and microstructural properties of powders prepared by these techniques are compared. The main purpose is to determine among these techniques the most suitable to obtain solid solutions with high chemical homogeneity and high sinterability.

EXPERIMENTAL

Cerium nitrate hexahydrate (99.99%, Aldrich) and gadolinium oxide (99.9%, Aldrich) were used as starting materials. All other reagents were of analytical grade. A gadolinium nitrate solution was prepared by dissolution of the corresponding oxide in hot nitric acid.

$Ce_{0.8}Gd_{0.2}O_{1.9}$ solid solutions were prepared by two polymeric precursor techniques. Fig. 1 shows the flow charts of the synthesis techniques. In the citrate technique originally developed by Pechini [17] the required amounts of cation solutions were mixed under stirring. Citric acid was added to form metal citrates. Ethylene glycol was introduced in the resulting solution after the homogenization of metal-citrate complexes. The molar ratio metal:citric acid was 1:2 and the ratio citric acid:ethylene glycol was 60:40. In the amorphous citrate technique [18] a citric acid solution is added to the cation solution. The molar ratio metal:citric acid was 1:2. Increasing the bath temperature, evolution of water and NO_x vapors occurs increasing the solution viscosity, and thus forming a gel. Further increase in the bath temperature induces a complete elimination of NO_x vapor with the resulting formation of a resin.

Thermal decomposition of resins was carried out in two steps. A partial decomposition was performed at 250 °C / 1 h, and a final calcination was done at 600 °C / 1 h. Cylindrical specimens with 12 mm in diameter were prepared by uniaxial pressing at 96 MPa. Sintering of pellets was performed in air at 1500 °C / 3 h.

The weight loss of resins was followed by thermogravimetric analysis with a heating rate of 5 °C.min^{-1} up to 1200 °C in air. X-ray diffraction experiments were carried out in a Bruker AXS D8 Advance diffractometer from 20° to 90° 2θ interval. The distribution of particle size was obtained in water dispersed calcined powders using sodium pyrophosphate as dispersing agent. The specific surface area was determined by the BET method (ASAP 2010, Micromeritics) after drying the calcined powders at 300 °C. The morphology of calcined powders was observed by scanning electron microscopy (XL 30, Philips). Apparent sintered densities were determined by the immersion technique.

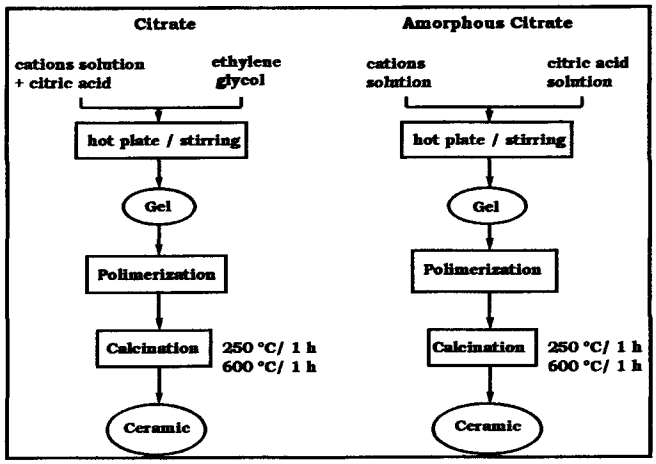

Fig. 1: Experimental procedures used in the preparation of gadolinia-doped ceria powders.

RESULTS AND DISCUSSION

Fig. 2 shows the weight loss of the precursor resins prepared by the citrate and amorphous citrate techniques. In the citrate technique the total weight loss is 66.5% up to 512 °C and for higher temperatures it is negligible. The weight change is continuous and resulted from the evaporation of water and evolution of organic material. In the amorphous citrate technique the total weight loss up to 430 °C is 58.1%. It was observed [19] that the main pyrolysis products are CO, CO_2, H_2O and NO_x in the presence of nitrate ions. The weight loss up to ~150 °C is attributed to the decomposition of free citric acid in the resin. This step of weight loss due to free citric acid is not observed in the precursor prepared by the citrate technique. The presence of free citric acid and metal nitrates was observed to be responsible for the hygroscopic nature of the precursor prepared by the amorphous citrate technique [20,21].

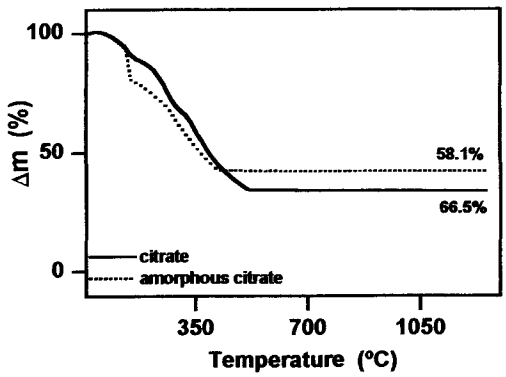

Fig.2: Thermogravimetric curves of resins prepared by polymeric precursor techniques.

Fig. 3 shows X-ray diffraction patterns for precursors calcined at 600 °C/1 h. These X-ray diffraction patterns are similar of that of the crystallized cubic ceria (JCPDS 34-394) except for slight shifts in diffraction angles due to solid solution formation. However, line broadening shows that the crystallite sizes of the decomposed precursors remain small.

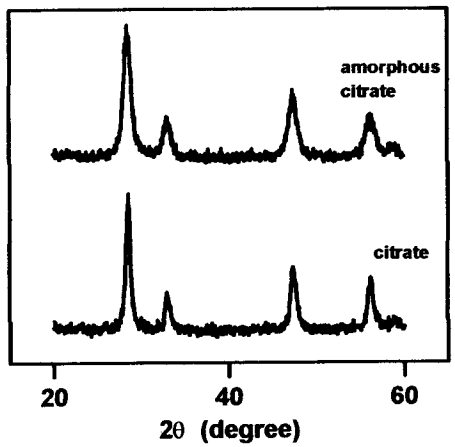

Fig.3: X-ray diffraction patterns of calcined ceria-gadolinia powders.

Because powders prepared by chemical techniques have particle diameters in the nanometer size, they tend to form agglomerates. It was shown earlier [12] that in coprecipitated ceria powders the particle size has a strong influence on the sinterability of the compacted ceramic. In that case, it was observed an increased sinterability for powder with smaller particle size. Fig. 4 shows the particle size distribution for ceria-gadolinia powders obtained by the citrate and amorphous citrate techniques using laser scattering. A similar behavior is observed for both powders. However, the solid solution prepared by the amorphous citrate technique presents a comparatively narrow distribution. Values of average particle size (d_{50}) obtained at 50% cumulative mass are shown in Table 1. From these results, the particle size obtained for the solid solution prepared by the citrate technique is 5 times greater than that obtained by the amorphous citrate technique.

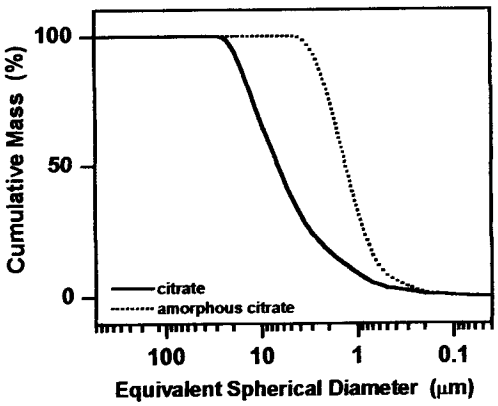

Fig 4. Particle size distribution curves of calcined ceria-gadolinia powders.

Table 1: Values of average particle size and specific surface for the ceria-gadolinia powders, and apparent density values for sintered specimens.

TECHNIQUE	d_{50} (μm)	S ($m^2.g^{-1}$)	d_{BET} (μm)	d_h (%TD)
Citrate	6.74	23.9	0.034	79.5
Amorphous Citrate	1.33	44.4	0.018	99.2

Specific surface values determined by nitrogen adsorption are shown in Table 1. The difference in powders prepared by polymeric precursor techniques is considerable. Assuming a spherical shape for particles and that they are non-porous, a particle size (d_{BET}) can be calculated from the specific surface area value. Calculated values are also shown in Table 1. These results show that particle sizes are in the nanometer range in contrast with values calculated from particle size distribution curves. This discrepancy can be understood considering that the distribution curves do not represent the particle size but the distribution of agglomerate/particle in each powder.

Fig. 5 shows scanning electron micrographs of the calcined powders. The morphology of particle/agglomerates are quite different for powders prepared by the two polymeric precursor techniques. Smaller particles/agglomerates are clearly seen in the powder prepared by the amorphous citrate technique. The powder prepared by the citrate technique exhibits a morphology that suggests that an initial sintering of particles have already started.

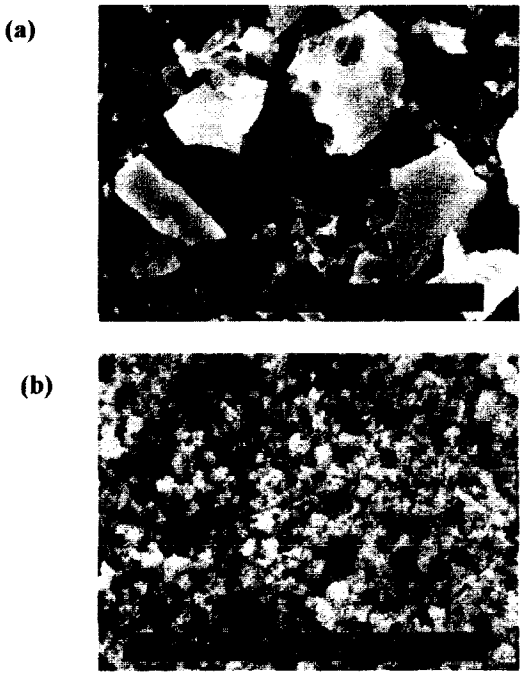

Fig. 5: Scanning electron microscope micrographs of the calcined ceria-gadolinia powders.(a) citrate; (b) amorphous citrate.

In general, rare-earth doped ceria solid solutions present low densification even for powders prepared by chemical methods. As a consequence, long soaking times (> 5 h) and high temperatures (> 1500 °C) are usually used. Powder compacts were prepared by pressing and sintering at 1500 °C/3 h. Results on apparent densities (Table 1) show that the ceramic prepared by the amorphous citrate technique reached a high densification compared with that obtained for the specimen prepared by the citrate technique. This result shows that similar techniques may present quite different behavior and properties.

CONCLUSIONS

Nanosized particles of gadolinia-doped ceria solid solutions have been prepared by polymeric precursors techniques. Total decomposition of the precursors were obtained at temperatures lower than 600 °C. The morphology of calcined powders is characterized by nanosized agglomerated particles. X-ray diffraction patterns are consistent with the cubic fluorite type phase. Agglomerate morphology of calcined powders is quite different. The main advantages of these synthesis techniques in comparison with coprecipitation or conventional routes are the relative simplicity, low cost, and effectiveness for obtaining reactive ceramic powders. High densification was obtained with powders prepared by the amorphous citrate technique.

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