



Electrical Conductivity of CeO₂ Prepared from Nanosized Powders

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Abstract. Nanosized powders of cerium dioxide with controlled physical properties were prepared by the precipitation technique using ammonium hydroxide or oxalic acid as precipitating agent. The calcined precursors were studied by nitrogen adsorption to determine the specific surface area, X-ray diffraction for phase characterization and crystallite size determination, and by laser scattering for particle size distribution. The morphology of powder particles was observed by scanning electron microscopy. It is shown that both precipitating materials may be used for the preparation of nanocrystalline powders (<10 nm) with high values of specific surface area (>90 m² · g⁻¹). The observed differences between powders prepared from hydroxides or oxalates rely on the distribution of particle sizes and in the morphology of the agglomerated particles. Impedance spectroscopy experiments were carried out in the 5 Hz–13 MHz frequency range under controlled partial pressure of oxygen from 10 ppm to 1 atm. The analysis of these results allowed for the determination of the charge carriers responsible for the electrical transport in the ceria sintered pellets.

Keywords: ceria, nanocrystalline powders, characterization techniques, electrical conductivity

1. Introduction

Cerium dioxide, CeO₂, has been extensively investigated in the past few years, because of its applications in different areas such as catalysis, high-temperature ceramics, mechanical polishing media, and solid oxide fuel cells [1–3]. Ultrafine ceria particles are required for many of these applications as they allow for obtaining a high-specific surface area material, with better sinterability and other improved properties compared to conventional microcrystalline material.

Several methods have been used for the preparation of ultrafine ceria powders including sol-gel, precipitation, hydrothermal recrystallization, combustion, salt-assisted ultrasonic aerosol decomposition and inert gas condensation [4–9]. These methods proved to be quite effective for the preparation of fine particulate materials. However, from the viewpoint of industrial

applications the precipitation method is more attractive due to its relatively low-cost, good reproducibility and high yield.

The present work was undertaken to verify the effect of the precipitating agent on physical properties of ceria powders. The electrical conductivity of sintered pellets was measured as a function of temperature and oxygen partial pressure by impedance spectroscopy.

2. Experimental Details

Cerium nitrate hexahydrate, Ce(NO₃)₃ · 6H₂O (99.9%, Aldrich), was used as cerium precursor. Ceria powders were prepared by the precipitation method using analytical grade ammonium hydroxide and oxalic acid as precipitating agent. The improved precipitation method used here was based on previous works on zirconia ceramics [10, 11]. Dried materials were thermally decomposed at 400°C for 1 h. Cylindrical specimens were prepared by uniaxial pressing at 98 MPa in a stainless steel die. Sintering experiments were performed in air

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with 1 h soaking time in the temperature range 1100 to 1500°C.

The distribution of particle/agglomerate sizes in calcined materials was determined by laser scattering (model 1064, Cilas). Specific surface area values were determined by the BET (Brunauer, Emmett and Teller) method using nitrogen adsorption (ASAP 2010, Micromeritics) measurements. Powder X-ray diffraction patterns were obtained in a diffractometer (D8 Advance, Bruker-AXS) equipped with a Ni-filtered Cu K_{α} radiation in the 20–80° 2θ range for phase characterization. The average crystallite size was estimated using Scherrer equation. The morphology of powder particles was observed by scanning electron microscopy, SEM, (XL30, Philips). The bulk density of sintered pellets was determined by the geometrical method. Platinum paste (A308, Demetron) was painted on both sides of the pellets and fired at 800°C for 1 h to act as an electrode. Resistance measurements were carried out in air and controlled oxygen pressures in the range of 1 to around 10^{-6} atm at a fixed 600°C temperature. The different oxygen pressures were achieved by gas mixtures of oxygen and argon. Isobaric resistance measurements were carried out by impedance spectroscopy using a HP 4192A LF impedance analyzer from 500 to 900°C.

3. Results and Discussion

Figure 1 shows SEM micrographs of calcined powders. The shape of ceria powder prepared from the oxalate decomposition (Fig. 1(a)) consists of platelike particles with a narrow size range. The ceria powders prepared from hydroxide decomposition (Fig. 1(b)), on the other hand, exhibit a very small spheroidal size with considerable agglomeration of particles.

The distribution of particle/agglomerate sizes of calcined ceria powders is shown in Fig. 2. A relatively sharp distribution was obtained by thermal decomposition of the oxalate precursor. In addition, the maximum diameter is considerably lower than that of the ceria powder prepared from the hydroxide precursor. Average size values are shown in Table 1. Although the hydroxide precursor leads to very small agglomerates (see Fig. 1), the average size is higher than that of ceria powder prepared from oxalate precipitation. This is an indication that microstructures observed in Fig. 1 do not represent individual particles.

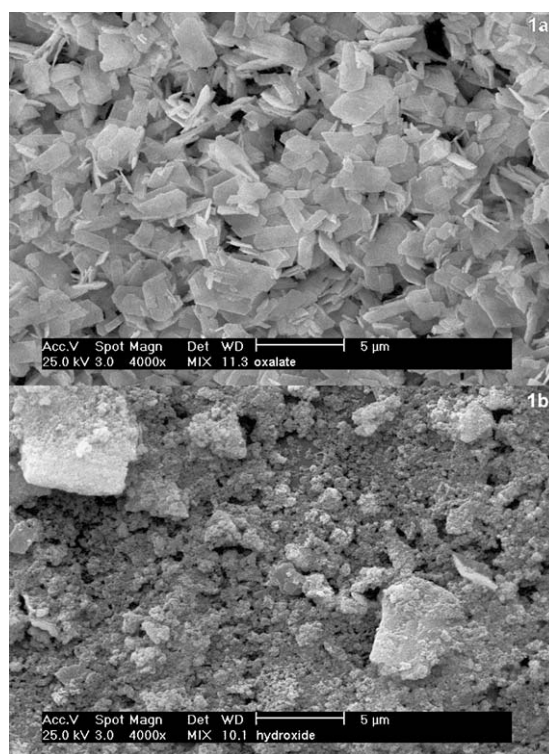


Fig. 1. SEM micrographs of calcined ceria powders.

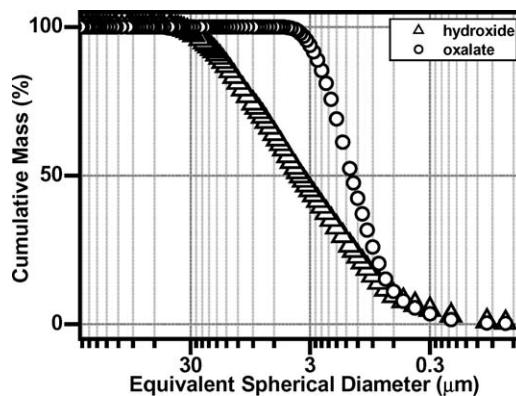


Fig. 2. Distribution of agglomerate/particle sizes of calcined ceria powders.

Values of specific surface area determined by the 5-point BET method are shown in Table 1. Relatively high values were obtained for both powders showing that reactive ceria powders may be prepared independent on the precipitating agent. However, the hydroxide precursor produced finer powders with the highest specific surface area value.

Table 1. Values of specific surface area (S), crystallite size (t_{XRD}), and agglomerate size (d_{50}) of calcined ceria powders.

Method of synthesis	S (m ² ·g ⁻¹)	t_{XRD} (nm)	d_{50} (μm)
Oxalate	91	6.7	1.35
Hydroxide	135	5.8	3.62

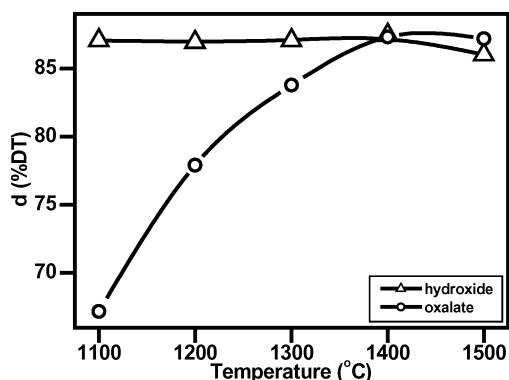


Fig. 3. Bulk density as a function of sintering temperature for ceria pellets.

Average crystallite size values determined by the Scherrer equation are also shown in Table 1. It is worth to note the similarity in these figures, besides morphological and microstructural differences of the powder materials. This result shows that powders prepared by the precipitation process are nanocrystalline in nature.

Figure 3 shows the evolution of the bulk density of powder compacts with sintering temperature. The bulk density of powder compacts prepared with the oxalate precursor increases with increasing sintering temperature up to ~1400°C, whereas for those prepared with the hydroxide precursor the density is almost constant in that temperature range, except for sintering at 1500°C, with a small decrease in the density.

Electrical resistance was measured on pellets sintered at 1400°C. Typical impedance diagrams measured at 600°C under pure argon and oxygen are shown in Fig. 4. For a ceria pellet prepared from the oxalate precursor (Fig. 4(a)) a high-frequency semicircle due to resistive and capacitive effects of the bulk, and part of a low-frequency semicircle comprising the blocking of charge carriers at grain boundaries and the electrode reactions are detected, indicating an extrinsic ionic nature of the electrical conductivity. The associated activation energy is 0.83 eV, in agreement with oxygen vacancy

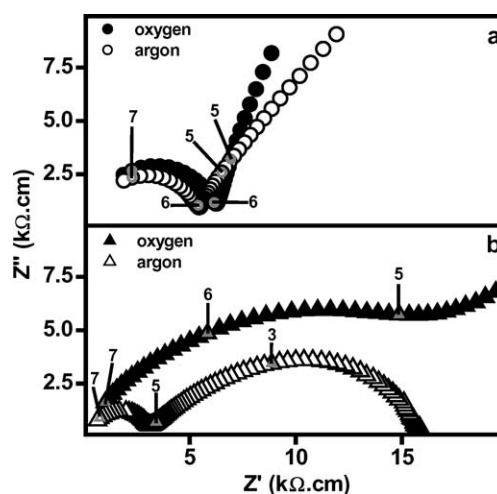


Fig. 4. Impedance diagrams of sintered pellets prepared from oxalate (a) and hydroxide (b) precursors.

migration values [12, 13]. Impedance diagrams of the pellet prepared from hydroxide precursor material (Fig. 4(b)) have a different shape when measured at different atmospheres. Under pure argon, a high-frequency semicircle is clearly resolved, whereas under oxygen this semicircle is barely resolved from the whole diagram. The electrode arc is not observed, suggesting a predominance of electronic conduction. The activation energy calculated is 0.99 eV.

The bulk electrical conductivity dependence on the oxygen partial pressure of both specimens is shown in Fig. 5. The conductivity of the pellet prepared from

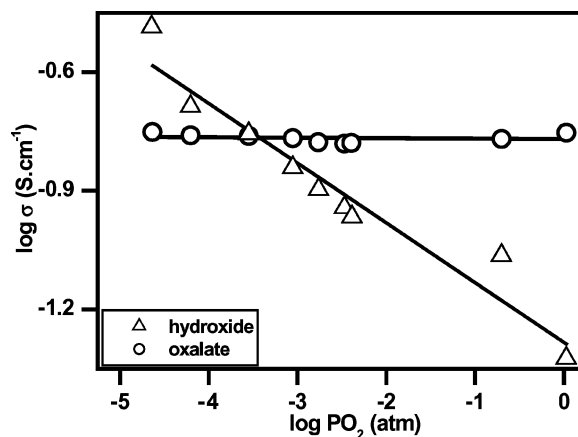


Fig. 5. Bulk conductivity versus oxygen partial pressure for both specimens.

oxalate precursor does not depend on the oxygen partial pressure, as usual for relatively low purity specimens. In contrast, the pellet prepared from hydroxide precursor shows electronic behavior. In recent studies on nanocrystalline ceria predominantly electronic conductivity was observed, under the same conditions microcrystalline cerium oxide exhibits ionic conductivity [9]. This behavior was explained as a consequence of depletion of acceptor dopants in the bulk due to their segregation at grain boundaries. In our study, both types of sintered pellets have grain sizes of 2.5–3.5 μm , and this effect is not expected. The electronic conductivity observed here is attributed to a reduction reaction of cerium ions during measurements under reducing conditions. The deviation of stoichiometry was evidenced by the blue color of the pellet.

4. Conclusions

Nanocrystalline (<10 nm) ceria powders with high (>90 $\text{m}^2 \cdot \text{g}^{-1}$) specific surface area values were prepared by the precipitation method. The electrical conductivity behavior of sintered pellets reveals different mechanisms depending on the precipitating agent used in the synthesis. The hydroxide precipitation produces a ceria powder more prone for stoichiometry deviation under reducing conditions.

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