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Synthesis and characterization of calcia fully stabilized zirconia solid electrolytes

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Abstract

Solid solutions of zirconia containing 16 mol% CaO have been synthesized by the citrate technique. The polymeric resin produced by that technique was studied by thermogravimetric and differential thermal analyses. The ceramic powders obtained by calcination of the resin were analyzed by gas adsorption and X-ray diffraction techniques. Surface areas of powders close to 100 m²/g have been obtained. Sintered pellets reached skeletal densities close to 100% of the theoretical density. Fractured surfaces of these pellets were observed by scanning electron microscopy showing large fraction of closed porosity and coarse grains. Impedance spectroscopy measurements carried out on sintered specimens show that zirconia–calcia solid solution formation is accomplished. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Solid electrolytes based on stabilized zirconia ceramics are used in devices for determination of oxygen in gases, in liquid steel and in exhaust of combustion engines, in oxygen pumps for purifying inert gases and as electrolytes for energy conversion in solid oxide fuel cells (SOFC) [1]. They have attracted wide attention because they present suitable electrical and mechanical properties for these applications. Zirconia requires stabilization, namely solid solution formation accomplished by addition of aliovalent oxides for retaining the cubic structure at the

working temperature for the above applications (600°C for permanent oxygen sensors and 1000°C for SOFCs). The most used stabilizer oxides are Y₂O₃, CaO and MgO.

Calcia-stabilized zirconia ceramics have been prepared by several techniques, such as powder mixing [2–4], coprecipitation [5–9], thermal decomposition of metal alkoxides [10], hydrothermal [11] and rapid combustion [12]. Using the powder-mixing technique normally requires high temperatures to obtain good densification of ceramic specimens. Other techniques have been used to prepare reactive powders that after pressing, densify at temperatures relatively lower, producing sintered ceramics with more homogeneous microstructure.

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The polymeric precursor route, also known as the citrate technique, is an alternative solution technique when high chemical homogeneity is required. In this technique, an α -hydroxycarboxylic acid is used to chelate with various cation precursors by forming a polybasic acid. In the presence of a polyhydroxy alcohol, these chelates will react forming organic esters and water. Heating the mixture polyesterification occurs and with further heating a rigid resin is formed in which metal ions are uniformly distributed. Thermal decomposition of the resin gives rise to a finely divided and chemically homogeneous powder with the desired stoichiometry. This technique has been utilized for the preparation of ZrO_2 : 13 mol% CaO and the crystallization behavior has been compared with that of powders prepared by the coprecipitation technique [8]. Recently, a zirconia solid solution containing 10 mol% CaO has been prepared by the citrate technique, and the tetragonal precipitates formed by sintering have been studied by electron microscopy [13].

The aim of this work is to prepare 16 mol% CaO stabilized ZrO_2 powders by the citrate technique and verify some structural and physical properties of the sintered ceramics. The technique used in this work is a modified version of the polymeric precursor technique that was originally outlined by Pechini [14] for preparing mixed oxides. The main envisaged application of these ceramics is in the production of sensors for control of oxygen content in combustion processes. By knowing the oxygen content of the exhaust gas, adjustments can be made to improve combustion efficiency.

2. Experimental

$\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ (> 99%, produced at this Institute), CaCO_3 (99%, B. Herzog), citric acid and ethylene glycol were used as starting materials. The hydrated zirconium oxide was dissolved in hydrochloric acid to obtain a zirconyl chloride solution after determination of the value of n by gravimetry. A required amount of CaCO_3 was added to this solution under constant stirring. Citric acid and ethylene glycol were added to this solution and the temperature was increased to 100°C producing a resin after approximately 3 h. The ratio of metal ions to citric acid was

1:2 and that of citric acid to ethylene glycol was 60:40. The resulting resin was thermally decomposed at $600^\circ\text{C}/1.5$ h. Cylindrical pellets of 10-mm diameter and 15-mm thickness were prepared by cold isostatic pressing. Sintering was carried out in air at 1500°C for 2 h.

The thermal decomposition of the resin was studied by simultaneous measurements of thermogravimetry and differential thermal analyses (STA 409, Netzsch). Heating and cooling rates were $10^\circ\text{C}/\text{min}$. The thermal cycle was carried out under flowing synthetic air.

After calcination, the distribution of particle sizes was measured by laser scattering (Granulometer, Cilas 1064) using sodium pyrophosphate as dispersant. The specific surface area was determined by nitrogen gas adsorption (Quantachrome Nova). X-ray diffraction (Bruker-AXS, model D8 Advance) patterns were obtained in calcined powders and sintered pellets using Cu K_α radiation. Apparent sintered densities were determined by the Archimedes method. The true density of a sintered specimen was determined by helium pycnometry (Multivolume pycnometer 1305, Micromeritics). Microstructural observations have been carried out on fractured surfaces by scanning electron microscopy (Philips XL 30). Electrical impedance spectroscopy measurements were performed on sintered specimens using a Hewlett Packard 4192A LF Impedance Analyzer over a wide frequency range (5 Hz to 13 MHz) at various temperatures in the 300 – 550°C range. Silver electrodes were applied to the parallel surfaces of the specimens by painting and baking at 500°C .

3. Results and discussion

Fig. 1 shows thermogravimetric and differential thermal analysis curves for the resin. The major part of the mass loss, resulting from organic decomposition, occurs in the 200 – 600°C temperature range. The total mass loss is approximately 80%.

The differential thermal analysis curve shows that the most important thermal effect is the exothermic evolution of organic materials up to 600°C . A small exothermic effect between 600°C and 700°C , normally assigned to residual or intermediate carbonate decomposition, is observed.

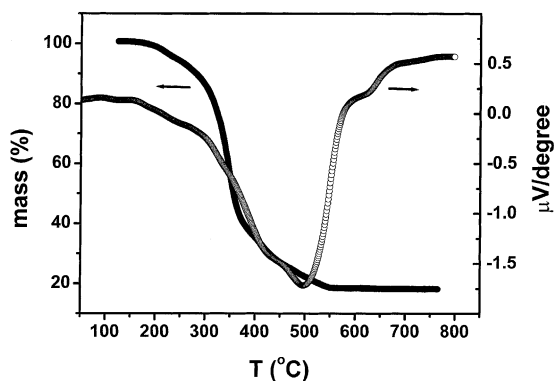


Fig. 1. Thermogravimetric and thermal differential analysis curves of zirconia-16 mol% calcia resin obtained by the citrate method.

Fig. 2 shows the particle size distribution after calcination at 600°C/1.5 h. An average particle/agglomerate size of 26 μm is estimated.

The specific surface area, determined from adsorption/desorption measurements, was 99 m^2/g . This relatively high value for the surface area ensures that the use of the citrate technique produces reactive solid solution powders that may be sintered at relatively low temperatures.

Fig. 3 shows X-ray diffraction patterns of the calcined powder (a) and sintered pellets (b). No reflections of the monoclinic phase are observed. The relative wide half-width of the peaks are due to low crystallinity achieved after calcination at 600°C. The same observation has been done for the results on specimens calcined at 400°C [8].

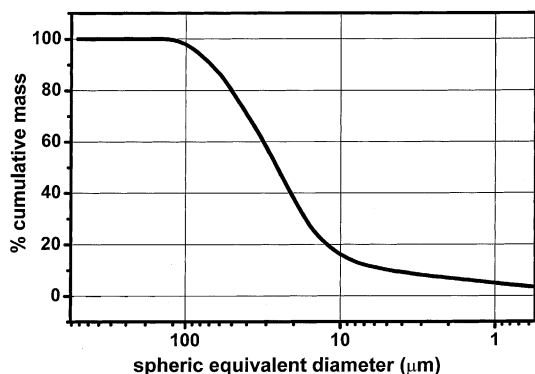


Fig. 2. Particle size distribution of zirconia-16 mol% calcia powders.

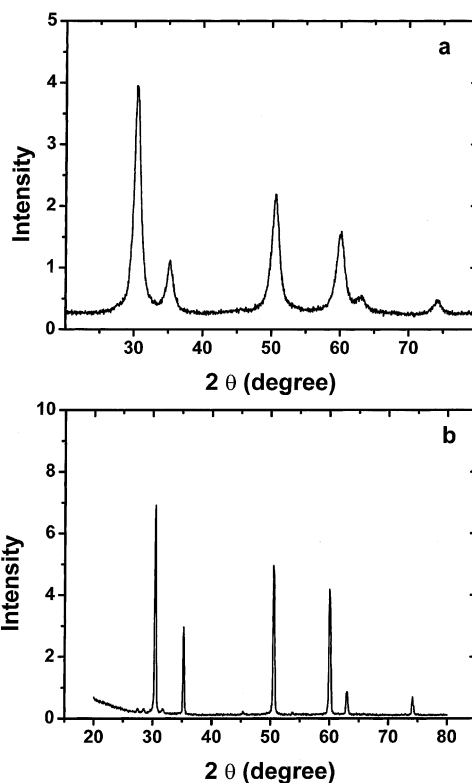


Fig. 3. X-ray diffraction patterns of zirconia-16 mol% calcia powders (a) and pellets sintered at 1500°C.

After sintering at 1500°C/2 h, the zirconia–calcia pellets are fully stabilized in the cubic structure.

The value of the apparent sintered density determined by water displacement technique was 5.12 g cm^{-3} . This value is in agreement with the microstructure analyzed by SEM (Cf. Fig. 4), where a high fraction of porosity is observed. The porosity seems to be predominantly closed and, as a consequence, coarse grains along with a low density of grain boundaries are expected.

The determined picnometric density is 5.50 g cm^{-3} . Comparing with the theoretical value (5.52 g cm^{-3}), this result shows that a well-densified skeleton containing coarse grains and closed pores predominates in the overall microstructure.

The impedance diagram measured at 466°C for the specimen sintered at 1500°C/2 h is shown in Fig. 5. Numbers over experimental points represent

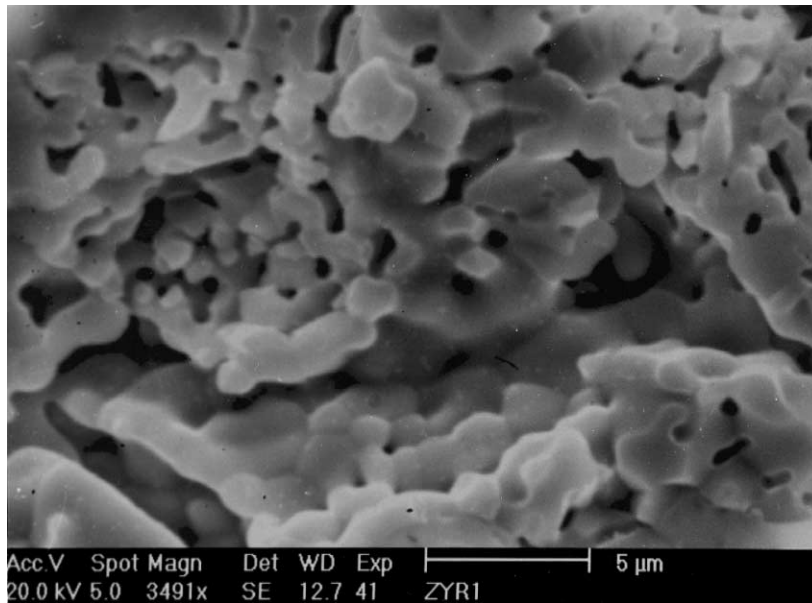


Fig. 4. Scanning electron microscopy micrograph of a fractured surface of zirconia-16 mol% sintered pellet.

the logarithm of the frequency of the applied ac voltage.

The diagram in Fig. 5 shows a semicircle relaxing in the high frequency region due to intragranular resistive and capacitive effects. The relatively small intergranular semicircle means that blocking of charge carriers at grain boundaries is negligible. This is probably due to the high purity of the powder leading to the absence of impurities segregated at the grain boundaries, and also to the low density of grain boundaries. The conduction activation energy was

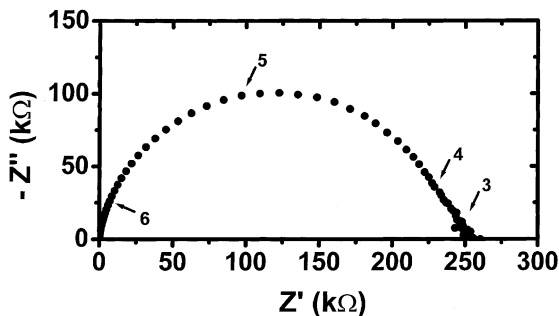


Fig. 5. Impedance spectroscopy diagram of a (10-mm diameter, 2-mm thickness) zirconia-16 mol% calcia pellet.

determined from the Arrhenius plot of the intragranular resistivity. The determined value, 1.29 eV, is in agreement with values previously reported [15].

4. Conclusions

High surface area ($99 \text{ m}^2/\text{g}$) reactive zirconia–calcia ceramic powders have been prepared by the citrate technique. Using these powders, pellets sintered at $1500^\circ\text{C}/2 \text{ h}$ achieved 99.9% of the theoretical density. Electrical resistivity determinations from impedance spectroscopy results show that solid solution has been attained. The powders produced using that technique have the properties required for producing ceramic pieces that could be used in sensor devices for analyzing oxygen content in exhaustion gases in combustion engines.

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