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Properties of zirconia–magnesia solid electrolytes prepared by the citrate method

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Abstract

Reactive MgO–partially stabilized ZrO_2 (Mg-PSZ) powders have been obtained by the citrate method. X-ray diffraction, scanning electron microscopy and sedigraphic analysis have been carried out in the powders showing that they are partially stabilized (cubic and monoclinic phases) and have 1 to 4 μm average size of particle agglomerate. Pellets sintered at 1600°C for 2 h reached close to 100% of the theoretical density. Impedance spectroscopy experiments in the 5 Hz–13 MHz frequency range from 300°C to 550°C have been carried out in these pellets and in solid electrolytes of commercial oxygen sensors to compare their electrical resistivities. The main results show that the citrate route is an easy way to obtain homogeneous reactive powders yielding highly dense zirconia–magnesia solid electrolytes for oxygen sensors.

1. Introduction

Ceramic oxide solid electrolytes are widely used as electrochemical transducers in oxygen sensors. The most common oxides that behave as oxygen-ion conducting solid electrolytes are ZrO_2:Y_2O_3, ZrO_2:CaO and ZrO_2:MgO [1]. The monitoring of oxygen dissolved in molten steels can be done with disposable oxygen sensors having ZrO_2:MgO solid electrolytes as electrochemical transducers [2,3]. The addition of about 3 wt% MgO in ZrO_2 followed by sintering at temperatures higher than 1400°C produces partially stabilized zirconia (PSZ) with cubic/tetragonal and monoclinic phases. That level of stabilization was also found to give the highest value of dc ionic conductivity of ZrO_2:MgO solid electrolytes. There are several ways of preparing Mg-PSZ ceramic solid electrolytes, namely, (a) simply mixing the proper amounts of MgO to ZrO_2, pressing and sintering at high temperatures and (b) following one of a variety of chemical solution techniques. The advantages of the latter are that the powders exhibit improved chemical homogeneity and higher reactivity than the ones obtained by the conventional mixed oxide processes [4], enabling sintering to high densities at relatively lower temperatures. Amongst solution techniques, the one that yields an amorphous organic resin that can be converted to homogeneous solid solution oxides upon heating is the citrate method [5]. In this Letter, the synthesis of ZrO_2:3.4 wt% MgO powders by the citrate method is described. The powders, after characterization by X-ray diffractometry (XRD) for phase identification, sedigraphic measurements for determination of agglomerate particle distribution and scanning electron microscopy (SEM) for particle size and morphology analysis, were pressed to pellets and sintered for microstructure characterization by SEM and XRD, neutron activation analysis for determination of Mg

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content and electrical characterization by impedance spectroscopy.

2. Experimental

The raw materials used were >99% pure hydrated zirconium oxide produced at the Zirconium Pilot Plant at IPEN-Brazil, P.A. magnesium nitrate (99.5%), citric acid (99.5%) and concentrate nitric acid both from Merck, and P.A. ethylene glycol. MgO–partially stabilized ZrO_2 powders were prepared by the citrate method [5]. It consists essentially in mixing salts to citric acid and to ethylene glycol at suitable temperature baths to obtain a polymeric resin that after heating results in a reactive powder. Fig. 1 shows the experimental sequences 1 and 2 followed here. They differ in adding or not citric acid to the nitrates before the addition of ethylene glycol and citric acid to heat up to obtain the polymeric resin. Average agglomerate particle size distribution measurements have been done in a Micromeritics 5100 sedigraph analyzer. Pressed powders were sintered in a gas furnace. The densities of pressed pellets were determined by the Archimedes method. Phase identification of sintered pellets was done by X-ray diffraction using Rigaku Geigerflex and PW3710 Philips diffractometers. The magnesium content in the ZrO_2 pellets has been determined by thermal neutron activation analysis. A model JXA 6400 JEOL scanning electron microscope was used to observe particle morphology and agglomeration state in ceramic powders and grain morphology in fractured pellet surfaces. Impedance spectroscopy measurements were carried out in the 5 Hz–13 MHz frequency range with a Hewlett Packard 4192A LF impedance analyzer connected via HPIB to an HP 900 controller, in the 300–650°C temperature range. Pt electrodes were applied to the planar opposite surfaces of cylindrical pellets by sputtering under argon gas. A 1 mm section of a 4 mm diameter tubular solid electrolyte of a commercial oxygen sensor for molten steels was also used for impedance spectroscopy measurements.

3. Results and discussion

ZrO_2:3.4 wt% MgO powders have been prepared following the experimental sequences of Fig. 1.

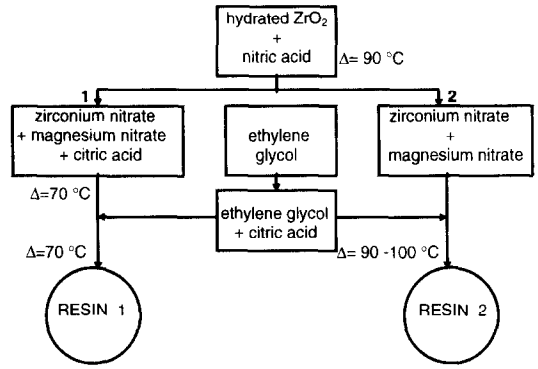

Fig. 1. Experimental sequences followed for the preparation of ZrO_2:3.4 wt% MgO polymeric resins via the citrate method; Δ = bath temperatures.

After calcining the resins resulting from sequences 1 and 2 at 450°C, grinding and calcining again at 800°C, both powders (hereafter powders 1 and 2) had their average particle size determined by sedigraphic analysis; 1.1 and 4.0 μm are the values determined for powders 1 and 2, respectively. These powders are indeed agglomerated particles and the degree of agglomeration is different for both powders as shown in the SEM micrographs of Fig. 2.

The oxide powder processed according to sequence 1 exhibits a higher degree of agglomeration in comparison to that of sequence 2 (cf. Figs. 2a and 2b). Powders obtained from sequence 1 consist of small spherical particle aggregates with few large particle agglomerates of irregular shapes. Powders from sequence 2 have aggregate particles with angular morphology with 2 to 6 μm average size. The powders have been uniaxially pressed using 14 mm diameter steel dies at 196 MPa and sintered at 1600°C/2 h in a gas furnace. The calculated amount of MgO added to zirconium nitrate, the magnesium content determined by neutron activation analysis of the sintered pellets, the average agglomerate particle size given by sedigraphic analysis of the powders, the monoclinic volume fraction of the sintered pellets determined from X-ray diffraction, and the apparent density determined by the water immersion method of the pellets are shown in Table 1.

The relative monoclinic phase content V_m has been evaluated using the Porter and Heuer equation: $V_m = 1.609 I_m[-111]/(1.609\, I_m[-111] + I_c[111])$, I_m and I_c being the peak intensities of the 100% monoclinic and cubic diffraction lines, respectively [6].

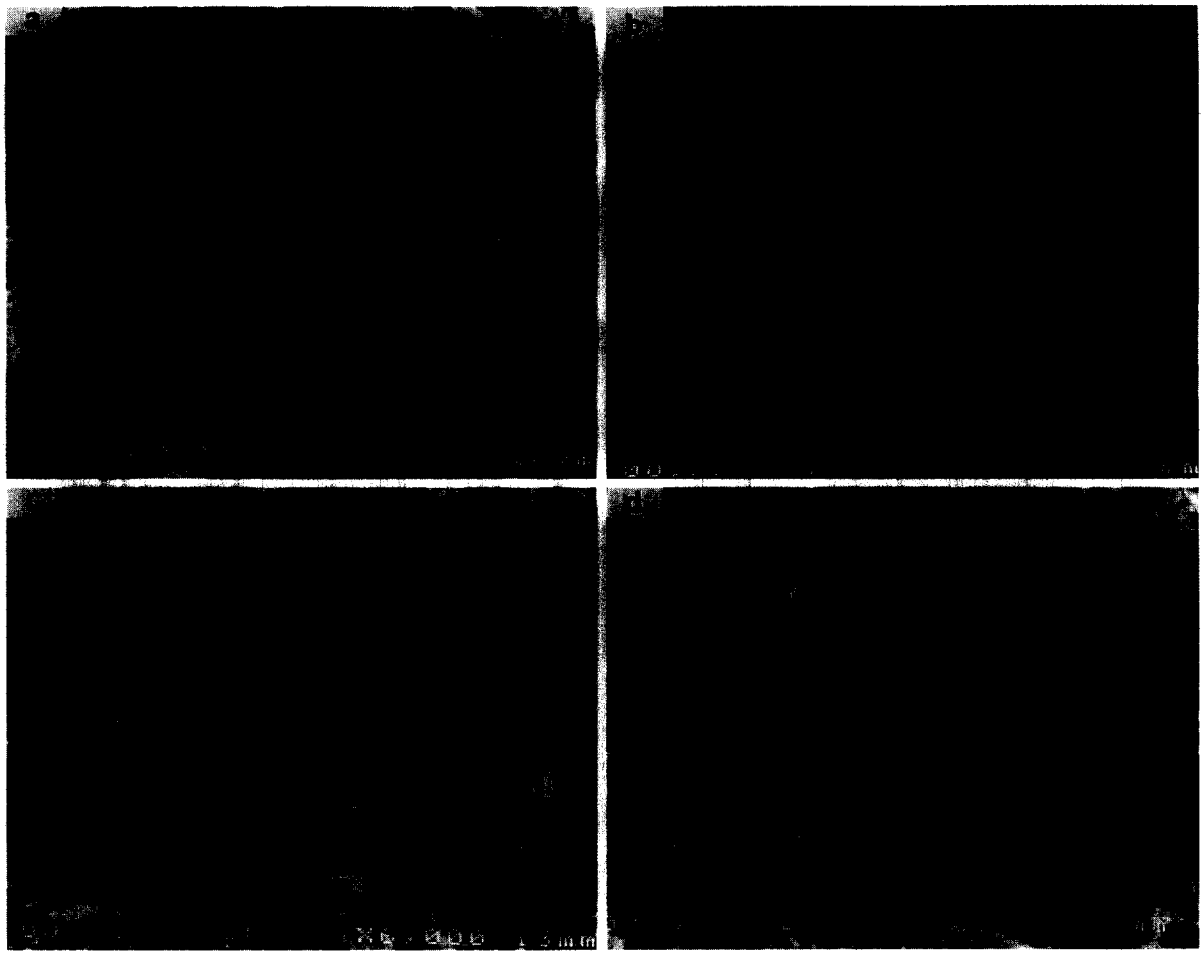

Fig. 2. Scanning electron microscopy micrographs of ZrO_2:3.4 wt% MgO powders prepared by the citrate method (a, b) and fractured sintered pellets (c, d).

Specimens prepared from powders obtained following both sequences of Fig. 1 reached high relative densities (100 and 99.5% TD). Even some degree of translucency is attained in the sintered sample from powders obtained following route 1 in Fig. 1. In this case, a cross-linked resin has been probably obtained after polymerization, resulting in a finer, more reactive and more homogeneous powder than the one obtained following route 2. The determination of the magnesium content by neutron activation analysis gives 3.7 and 3.3 wt% of MgO for specimens 1 and 2, the difference with the chemically added value (3.4) being within the

Table 1
Values of added MgO, determined magnesium content, average particle size of powders, monoclinic-to-cubic volume ratio and percentage of theoretical density (%TD) of ZrO_2:3.4 wt% MgO sintered pellets prepared from powders obtained via the citrate method

Specimen	MgO (wt%)	Magnesium content (%)	Average particle size (μm)	Monoclinic vol. fraction (%)	Hydrostatic density (%TD)
1	3.4	2.21	1.1	8	100
2	3.4	1.96	4.0	67	99.5

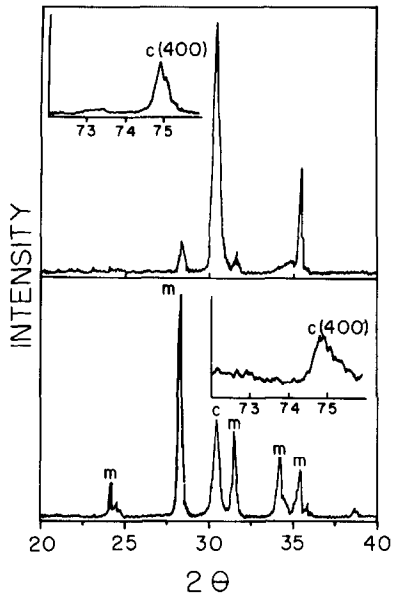

Fig. 3. X-ray diffraction patterns of ZrO_2:3.4 wt% MgO pellets sintered at 1600°C: (a) route 1 in Fig. 1; (b) route 2.

experimental error, showing that there are no magnesium losses after processing powders and pellets. In Fig. 3, X-ray diffractograms of specimens 1 and 2 with labels in the main cubic (c) and monoclinic (m) diffraction lines are shown.

The translucent specimen has a low monoclinic phase content (about 8%) whereas specimen 2 has 67% of the monoclinic phase. The inserts in Fig. 3 show X-ray diffractograms in the 72–76° 2θ range. These spectra have been measured to ascertain that the cubic and not the tetragonal phase is the major crystallographic phase along with the monoclinic phase in both specimens, within the accuracy level of X-ray diffraction phase detection. Even though both powders are from the same origin and have been pressed and annealed under the same conditions, pellets from powders with smaller average particle size sinter faster and denser due to their high surface energy, thus avoiding the cubic-to-monoclinic phase transformation during cooling after sintering. Even though the powders have different characteristics, their microstructures do not differ significantly after sintering. In Figs. 2c and 2d, SEM micrographs of fractured surfaces of pellets sintered after pressing both powders are shown. The fracture mode is mainly transgranular with large pores resulting from preferential shrinkage of agglomerates. There are few regions showing an intergranular fracture mode (zoomed in Figs. 2c and 2d) with estimated average grain size in the 1–3 μm range. These regions might be ascribed to monoclinic grains because cubic grains are usually larger [7]. It is already known that the ionic conductivity of cubic stabilized ZrO_2 ceramics is larger than that of monoclinic ZrO_2 [8].

In Fig. 4, impedance diagrams ($-Z'' \times Z'$) of specimens 1 and 2 and, for the sake of comparison, of a section of a solid electrolyte tube of a commercially disposable oxygen sensor for molten steel, are shown. Numbers in the diagrams are powers of ten of the frequency of the applied ac voltage. Curves a and b stand for specimens 1 and 2, while curve c is for the commercial solid electrolyte, all measured at 540°C. The two specimens prepared here have dissimilar impedance diagrams that can be explained in terms of their difference in monoclinic phase content. Specimens with high monoclinic-to-cubic ratio should have higher resistance to the flow of oxygen ions. The monoclinic phase can be considered an insulating phase in comparison with the cubic phase. Its contribution to the impedance diagram results in a semicircle somehow causing a deformation of the semicircle due to the bulk

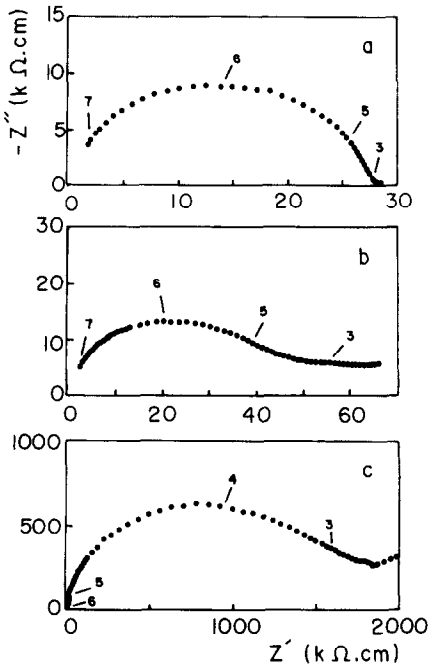

Fig. 4. Impedance spectra of ZrO_2:3.4 wt% MgO polycrystalline pellets made from powders obtained by the citrate method (a, b); of a commercial zirconia–magnesia solid electrolyte (c). Temperature of measurement: 540°C.

of the solid electrolyte [9]. The higher the monoclinic phase content, the higher the blocking of oxygen ions in the specimens. The long tail extending towards the low frequency region of the impedance diagrams in Fig. 4b and 4c might result from the grain boundary contribution to the blocking of oxygen ions. This contribution is not seen in the translucent 100% dense ZrO_2:3.4 wt% MgO specimen (cf. Fig. 4a). Impedance diagrams similar to that of Fig. 4a are found in single crystalline specimens [10]. Values of the dc resistivity of the translucent specimen have been determined dividing the value of the estimated intersection of the semicircle with the real axis in the low frequency region of the impedance diagram by the geometrical factor k ($=t/S$, t is the specimen thickness and S the electrode area). A value of 29 kΩ cm is found for the electrical resistivity of specimen 1 at 540°C. It is more than one order of magnitude lower than the value measured for the commercial solid electrolyte. Moreover, the activation enthalpies for dc conductivity in the zirconia–magnesia solid electrolytes reported here and in the specimen taken from commercial oxygen sensors have also been determined from Arrhenius plots of the dc conductivity measured in the 350–550°C range. The value determined for all specimens is 1.1 eV in agreement with previously reported values [9,11].

4. Conclusions

Solid electrolytes of 3.4 wt% MgO–partially stabilized zirconia with densities close to 100% of the theoretical density have been obtained after sintering pellets prepared from powders produced by the citrate technique. The electrical resistivity is found to be one order of magnitude lower than the one measured in solid electrolytes extracted from commercial oxygen sensors.

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