

Electrical conductivity of yttria-stabilized zirconia with cobalt addition

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ARTICLE INFO

Article history:

Received 19 September 2008

Received in revised form 8 January 2009

Accepted 1 February 2009

Keywords:

Electrical conductivity

Microstructure

Densification

Additives

ABSTRACT

Yttria-stabilized zirconia is the most developed solid electrolyte for use in high-temperature solid oxide fuel cells. Commercial yttria-stabilized zirconia powders reach high densification at temperatures higher than that of the usual anode materials. Reduction of the sintering temperature of the solid electrolyte could allow for co-firing of both ceramic components, thereby reducing production costs. The main purpose of this work was to study the effect of small cobalt additions on densification and on electrical conductivity of 8 mol% yttria-stabilized zirconia. Linear shrinkage results show that the onset temperature for shrinkage decreases with increasing cobalt content. Impedance spectroscopy measurements reveal that the electrical conductivity depends on the sintering profile. For specimens sintered at 1400 °C for 0.1 h the electrical conductivity of grains and grain boundaries are almost unchanged with that of 8YSZ. In contrast, for specimens sintered at the same temperature but for 0.5 h of soaking time, the electrical conductivity is higher in 0.025 mol% samples and is lower for 1 mol% Co doped 8YSZ. Degradation of the microstructure by increased porosity was obtained for high additive contents.

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1. Introduction

Yttria-stabilized zirconia ceramic is the preferred solid electrolyte for application in high temperature solid oxide fuel cells (SOFC) due to the combination of its electrical, mechanical and chemical properties [1,2]. One important requirement for SOFC commercialization is cost reduction, which is primarily associated with device fabrication. In this context, optimization of fabrication steps may contribute to accomplish this requirement. Reduction of the solid electrolyte sintering temperature, for example, could allow for the co-firing with the anode material [3].

In this case, the use of sintering aids has been recognized as a suitable approach. The benefits produced by the use of transition metals as sintering aids are controversial as they are known to reduce the sintering temperature, but they are also prone to introduce an additional electronic component to the total electrical conductivity. In this aspect, the role of cobalt addition to yttria-stabilized zirconia is not fully understood.

Stochniol et al. [4] observed an increase in the electrical conductivity of 8 mol% yttria-stabilized zirconia (8YSZ) with 5 mol% Co addition, which was attributed to the electronic conductivity component. Hartmanová et al. [5] reported an improvement in the densification of 12 mol% yttria-stabilized zirconia (12YSZ) for Co₂O₃ additions up to 0.5 wt.%. These authors observed an increase in the electrical con-

ductivity with small cobalt contents with maximum at 0.1 wt.%. This result was explained as a consequence of simultaneous substitutional and interstitial solid solutions formation. Recently, Lewis et al. [6] obtained improved densification along with lowering of the electrical conductivity in 8YSZ containing Co additions. In a previous study [7] it was found that the electrical conductivity of 8YSZ is higher than that of samples containing 0.05 or 0.5 mol% Co sintered at 1300 °C. At this sintering temperature the solubility limit of Co in 8YSZ is lower than 5 mol%, and the predominant phase above the solubility limit was found to be Co₃O₄ by Raman spectroscopy. However, separation of grain and grain boundary contributions to the total electrical conductivity was not carried out, because of the overall superposition of these components for specimens sintered at that temperature.

In this work, the effect of Co addition on densification and on electrical conductivity of grain and grain boundaries in 8YSZ was investigated. Special attention was given to varying low additive contents and soaking time.

2. Experimental

Commercial 8 mol% yttria-stabilized zirconia (Tosoh Co., Japan) and cobalt carbonate (99%, Alfa Aesar) were used as starting materials. Green compacts (diameter = 10 mm and thickness = 2 mm) consisting of mixtures of 8YSZ and x mol% Co with $0 \leq x \leq 1$ were sintered at 1400 °C for 0.1 and 0.5 h.

The linear shrinkage of powder compacts (diameter = 5 mm and thickness = 7 mm) was evaluated by dilatometry (Setaram, model Labsys) heating at a rate of 10 °C min⁻¹ up to 1400 °C. Apparent sintered density was determined by the water immersion method. For

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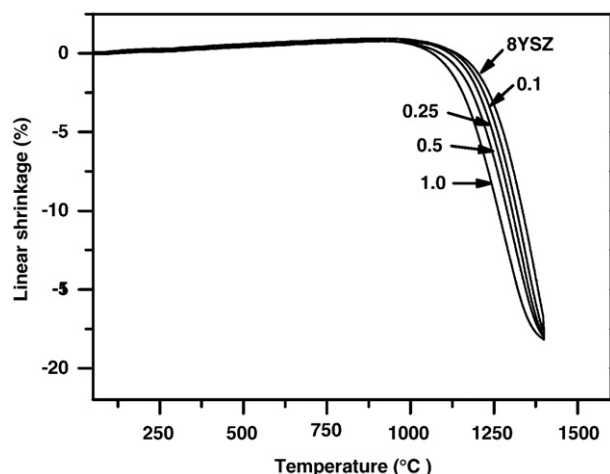


Fig. 1. Linear shrinkage curves for 8YSZ and Co-containing 8YSZ.

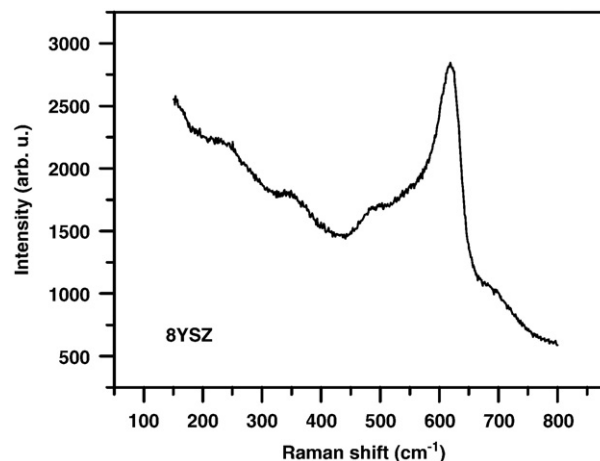


Fig. 2. Room-temperature Raman spectrum of 8YSZ.

the theoretical density value it was assumed that of the producer's specification (5.90 g cm^{-3}). Phase characterization was carried out by Raman spectroscopy (Renishaw Raman microscope 3000 system) using a He–Ne laser with 632.8 nm as excitation source. The morphology of sintered samples was studied by scanning electron microscopy, SEM (Philips, model XL30) on polished and thermally etched (100°C below the sintering temperature) surfaces. Average grain size values were determined by the intercept method [8]. The electrical conductivity of sintered samples was calculated from resistances measured by impedance spectroscopy using an impedance analyzer (LF 4192 A, HP) in the 5 Hz–13 MHz frequency range with 100 mV of applied signal. Resistance measurements were recorded in the $250\text{--}450^\circ\text{C}$ range, which allows for differentiating the grain and the grain boundary contributions. Silver (silver paste PO2008, Cerdec) was used as electrode material for these measurements. Impedance data were analyzed using special software [9].

3. Results and discussion

3.1. Densification and crystalline structure

All sintered samples reached high apparent density values ($>5.7 \text{ g cm}^{-3}$ or $>96.5\%$ of the theoretical value) independent on the soaking time.

Fig. 1 shows linear shrinkage curves for 8YSZ and 8YSZ + x mol% Co with $x = 0.1, 0.25, 0.5$ and 1 . All samples have an onset temperature for shrinkage (T_{onset}) higher than 1000°C . Total shrinkage at 1400°C is approximately 18%. It is worth to note that even with 1 mol% Co the shrinkage at 1400°C , which is the uppermost limit of the equipment, was not complete.

Table 1 summarizes the onset temperature for shrinkage and the temperature at which the maximum rate of shrinkage (T_{max}) occurred as the additive content was increased. These data were obtained from linear shrinkage curves. The commercial 8YSZ has an onset temperature of 1208°C and a maximum shrinkage rate at approximately

1377°C . As the Co content increases up to 1 mol% the values of T_{onset} and T_{max} decreased to 1115 and 1272°C , respectively.

These figures are slightly lower than those obtained by Lewis et al. [6] probably because these authors used a different starting cobalt precursor material and different processing steps to prepare the powder compacts.

After sintering, all samples exhibited a crystalline structure similar to that of 8YSZ without additive. The Raman spectrum shown in Fig. 2 evidences a prominent and asymmetric band at $\sim 616 \text{ cm}^{-1}$ characteristics of the cubic structure. The peak position shifts towards higher wavenumber in Co-containing samples, but no additional bands were detected up to the solubility limit of Co in the zirconia matrix. Additional low intensity bands may be seen in this spectrum, which are clearly associated to tetragonal zirconia. The tetragonal phase content is below the limits of detection by X-ray diffraction (not shown here) and may be regarded as a surface minor impurity.

3.2. Electrical conductivity and microstructural characterization

Typical impedance spectroscopy diagrams of some studied samples are shown in Fig. 3. These diagrams were normalized for sample dimensions. The temperature of measurement is indicated in

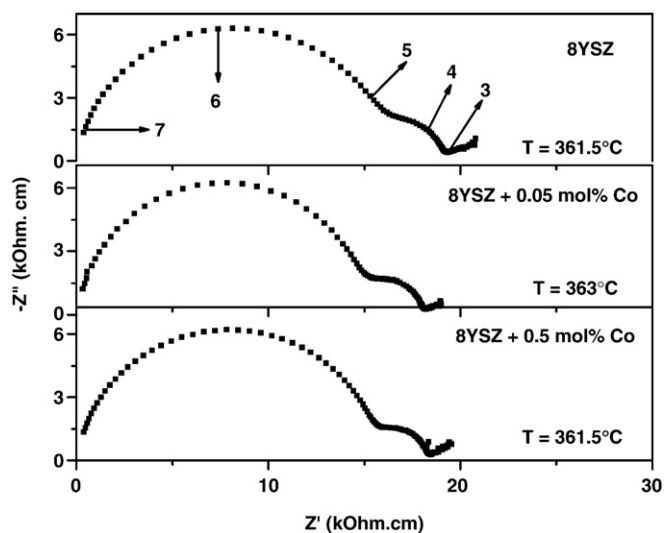


Fig. 3. Impedance spectroscopy diagrams of 8YSZ and Co-containing 8YSZ samples sintered at $1400^\circ\text{C}/0.5 \text{ h}$.

Table 1

Onset temperature for shrinkage, T_{onset} , and temperature of maximum shrinkage rate, T_{max} , for 8YSZ with and without Co additions.

Co content (mol%)	$T_{\text{onset}} (^\circ\text{C})$	$T_{\text{max}} (^\circ\text{C})$
0	1208	1377
0.1	1201	1345
0.25	1186	1333
0.5	1157	1309
1.0	1115	1272

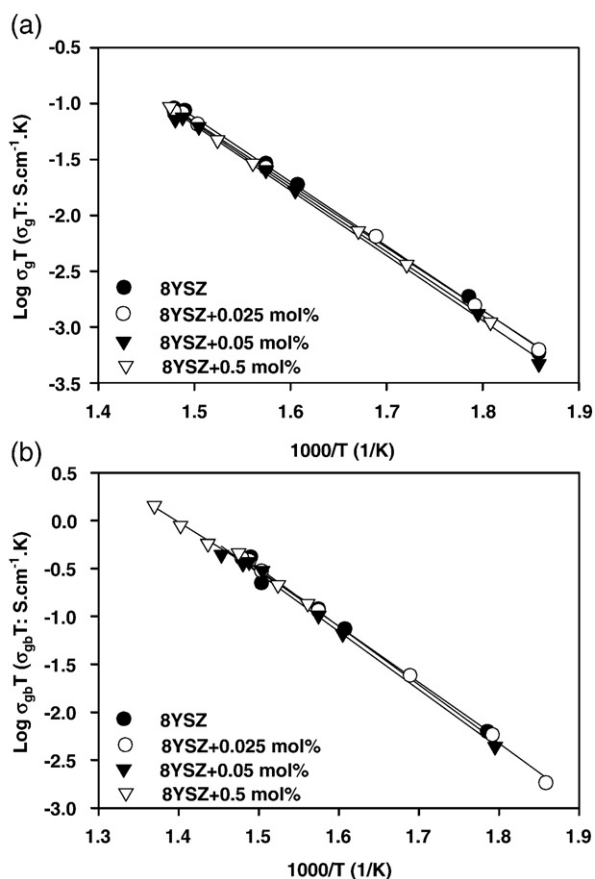


Fig. 4. Arrhenius plots for grains (a) and grain boundaries (b) of samples sintered at 1400 °C/0.1 h.

these plots, and numbers over experimental points are the logarithm of frequency (in Hz). All diagrams are composed by two semicircles and a spike at low frequencies which is related to the reactions occurring at the electrolyte/electrode interface. In the order of decreasing frequency, the two semicircles correspond to the impedance response of grains and grain boundaries. In the 250 to 450 °C temperature range of measurements, impedance diagrams are similar in shape.

The Arrhenius plots of the electrical conductivity for samples sintered at 1400 °C for 0.1 and 0.5 h are shown in Figs. 4 and 5, respectively. Fig. 4a shows the electrical conductivity of grains which are essentially similar to that of undoped 8YSZ. The same occurs for the electrical conductivity of grain boundaries (Fig. 4b). The activation energy for conduction is, as usual, slightly lower for grains than for grain boundaries, and the total activation energy is 1.13 ± 0.05 eV. No change in the activation energy for conduction was observed in Co-containing samples. Then, at this sintering condition the additive may enhance densification with negligible influence on the electrical conductivity.

Increasing the soaking time to 0.5 h produces a diverse effect on both grains (Fig. 5a) and grain boundaries (Fig. 5b). In this case, there is a slight increase in the electrical conductivity for samples containing 0.025 mol% Co. A similar effect was reported previously [5] and was attributed to changes in the crystallographic ordering of the oxygen sublattice due to simultaneous formation of substitutional and interstitial solid solutions. Taking into account the relatively low level of the additive, the increase of the electrical conductivity is probably due to ionic contribution. In fact, substitution of Zr^{4+} ($r^{VIII} = 0.84$ Å) for Co^{2+} ($r^{VIII} = 0.90$ Å) instead of Y^{3+} ($r^{VIII} = 1.010$ Å) into the zirconia lattice is expected to reduce the elastic strain due to cation radius mismatch. The total activation energy value for

conduction is 1.10 ± 0.05 eV and did not show any specific trend with Co additions. In samples containing 1 mol% Co the electrical conductivity of grain and grain boundaries decreased, as shown in Fig. 5a and b, respectively. This effect may be a consequence of the solubility limit of cobalt oxide at the sintering conditions used in this work resulting in Co_3O_4 segregation at grain boundaries.

Fig. 6 shows SEM micrographs of (a) 8YSZ and (b) 8YSZ + 1.0 mol% Co samples sintered at 1400 °C for 0.5 h, and (c) 8YSZ + 1.0 and (d) 10 mol% Co sintered at 1300 °C for 0.5 h for comparison purposes.

The morphology of grains is similar for all samples and porosity is mostly confined at grain boundaries or at triple grain junctions. Increase of the grain size may be observed in these micrographs with increasing Co content. The average grain size values (in μm) determined by the intercept method over a large population of grains were 1.40 ± 0.14 (8YSZ – 1400 °C/0.5 h), 2.98 ± 0.16 (8YSZ + 1.0 mol% Co – 1400 °C/0.5 h), 0.86 ± 0.19 (8YSZ + 1.0 mol% Co – 1300 °C/0.5 h) and 2.76 ± 0.48 (8YSZ + 10.0 mol% Co – 1300 °C/0.5 h). The sample containing 1 mol% Co sintered at 1300 °C has a much smaller average grain size than that sintered at 1400 °C, because the dwell temperature is near that of maximum shrinkage rate (Fig. 1), where densification predominates over grain growth.

In the literature reports may be found on yttria-stabilized zirconia, where the effect of other transition metals was related to suppression of grain growth [10,11]. Although no abnormal grain growth is observed in this case, the opposite effect occurs with Co as revealed in these micrographs.

In Co-containing samples, bubbles randomly distributed seem to be formed. It is worth to mention that the outer surface of samples did exhibit neither bubbles nor excessive porosity. The microstructures

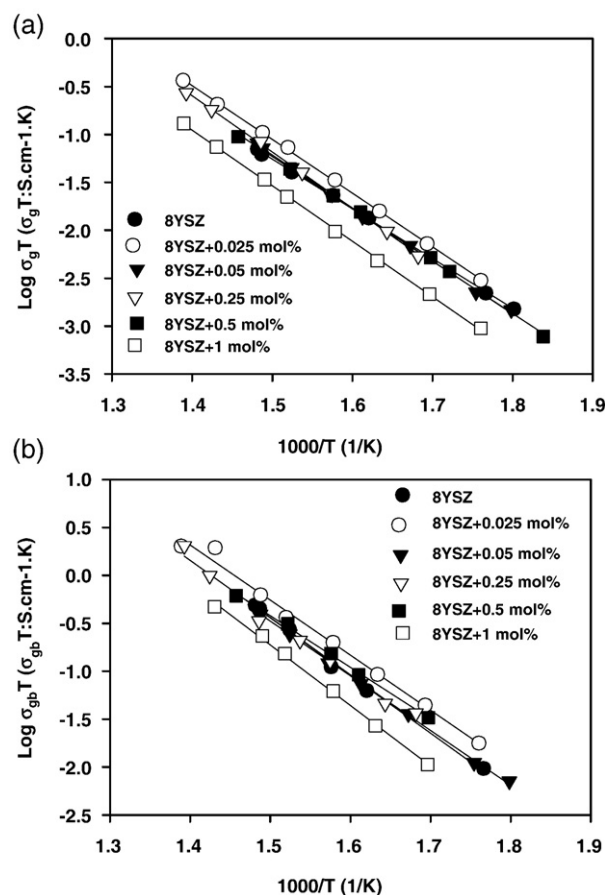


Fig. 5. Arrhenius plots for grains (a) and grain boundaries (b) of samples sintered at 1400 °C/0.5 h.

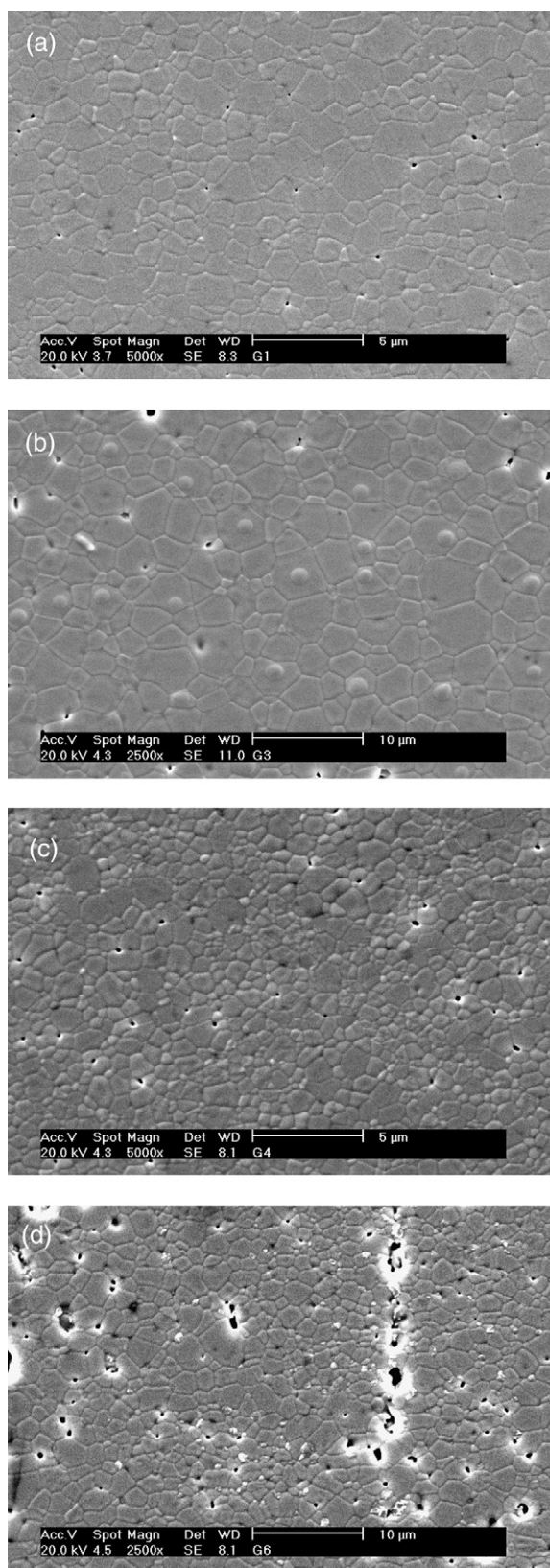


Fig. 6. SEM micrographs of 8YSZ (a), 1 mol% (b) Co samples sintered at 1400 °C/0.5 h, and 1 mol% (c) and 10 mol% (d) Co samples sintered at 1300 °C/0.5 h. Bar size: (a) and (b) 5 µm; (c) 10 µm.

shown in Fig. 6 correspond to the inner surface of the samples. SEM results obtained for specimens with high cobalt contents (Fig. 6d) evidenced also an increased porosity. It is known that Co_3O_4 has high

thermal expansion for temperatures above ~300 °C [12]. Hence, these effects may be related to Co_3O_4 , which can be formed due to incomplete solid solution formation during sintering.

The overall results show that small additions of Co to YSZ exert a minor beneficial effect on densification and electrical conductivity. However, the sintering profile should be suitably chosen to avoid formation of Co_3O_4 which introduces a deleterious effect in the microstructure of 8YSZ and in the microstructure-related properties.

4. Conclusions

Small amounts of Co promote grain growth and limited densification in 8YSZ, which are not suitable for co-firing SOFC solid electrolyte and electrode. The electrical conductivity increases slightly in 0.025 mol% Co samples and decreases for 1 mol% or higher additive contents. The sintering profile plays a key role in the microstructural development and in the electrical conductivity.

Acknowledgements

The authors are thankful to FAPESP, CNEN and CNPq (#504562/2004-5) for sponsoring the facilities used in this work. One of the authors (G.C.T.Silva) acknowledges CNPq for the scholarship.

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