Densification and Electrical Conductivity of Yttria-Stabilized Zirconia Containing NiO Additions

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The role of NiO addition on sintering and electrical conductivity of 8YSZ was systematically studied in this work. Nickel carbonate was added to commercial 8YSZ to give 0.5, 1 and 5 mol% Ni. Sintering of powder compacts was carried out at several dwell temperatures and soaking times. Relative sintered density of Ni-doped pellets reached high values for short soaking times. For longer soaking times the densification of 8YSZ is higher than that of specimens containing the additive. Cubic NiO is the secondary phase formed when the additive exceeds the solubility limit, as determined by Raman spectroscopy. The grain conductivity does not change with additive up to 1 mol% independent on the soaking time. The grain boundary conductivity varies slightly in doped pellets and is lower in NiO-free samples.

Introduction

Solid electrolytes exhibiting high oxygen-ion conductivity are of special interest for applications in electrochemical devices such as oxygen sensors, oxygen separation membranes and solid oxide fuel cells, SOFCs (1,2).

In spite of many SOFC technology development efforts focused in new oxide materials exhibiting high ionic conductivity, yttria-stabilized zirconia is still the preferred solid electrolyte for SOFC devices. In recent years, one of the main concerns for SOFC commercialization is cost reduction (3). In this context, improvement of the materials processing is of great importance.

Commercially available powders of yttria-stabilized zirconia need to be sintered at temperatures higher than 1400 ºC to attain high density. Lowering of the sintering temperature by sintering aids could produce reduction in the processing cost and allow for co-sintering the solid electrolyte and the anode.

Several additives have been studied to lower the temperature and/or time to attain high density in zirconia-8 mol% yttria solid electrolyte. Addition of NiO has been previously investigated. It was shown that the solubility of NiO in yttria-doped zirconia depends on yttria content (4). In zirconia containing 5 mol% yttria the additive promoted the cubic phase stabilization (5). However, the cubic phase is only metastable and decomposes with thermal aging at 1200 ºC (6). The effect of NiO on the cubic phase decomposition of 8YSZ was studied by Raman spectroscopy. It was shown that NiO delays the cubic phase decomposition resulting from thermal aging at 1000 ºC (7). The electrical conductivity of yttria-stabilized zirconia in reducing atmospheres was changed with 2 mol% NiO (8). NiO has been shown to produce a deleterious and irreversible effect in the electrical

conductivity after 50 h at 850 ºC. However, the content of the additive was relatively higher than usual for practical purposes.

In this work, the effect of NiO addition on the densification and electrical conductivity of 8YSZ was studied. The main purpose was to verify the effect of the additive on the sintering conditions.

Experimental

Zirconia-8 mol% Y_2O_3 (99.6%, Tosoh Co.) and $Ni(CO_3)_3Ni(OH)_2.x\ H_2O$ (99.5%, Alfa Aesar) were used as starting materials. Stoichiometric proportions of 8YSZ and nickel carbonate were weighted and mixed together to result in Ni (metal basis) contents of 0, 0.5, 1 and 5 mol%. The powder mixtures were prepared in a mechanical mixer (Turbula, T2C) in alcoholic medium with zirconia balls. Cylindrical pellets were prepared by uniaxial pressing followed by sintering in air at several dwell temperatures and times.

The apparent geometrical density of the sintered pellets was determined. Phase characterization was done by X-ray diffraction (Bruker-AXS, D8 Advance) in the 20º to 80º 2θ range using Ni-filtered Cu K_α radiation with 0.05º step size and 5 s of counting time. Additional phase characterization was studied by Raman spectroscopy (Renishaw Raman Microscope 3000 system), coupled to an optical microscope (Olympus, BH-2), using a He-Ne laser (Spectra Physics, model 127) with 632.8 nm wavelength as excitation source. Electrical conductivity measurements were carried out using a LF impedance impedance analyzer (HP4192A) in the 5 Hz to 13 MHz frequency range. Silver was used as electrode material for electrical measurements.

Results and Discussion

The green density of pellets was in the range 43 to 46% of the theoretical value. The sintered density increased with increasing dwell temperature as shown in Figure 1 for soaking times of 0.1 h (a) and 5 h (b).

The sintered density of specimens containing NiO is higher than that of 8YSZ at any temperature in the 1150 to 1350 ºC range for a soaking time of 0.1 h (Figure 1a). This improvement in the density of 8YSZ has been already reported (8). It should be noted that the increase in the sintered density was similar for 0.5 and 1 mol% Ni addition. Thus, it may be concluded that very small contents of the additive and short soaking times are sufficient to enhance the 8YSZ density.

Figure 1b shows the effect of the dwell temperature on the sintered density for a soaking time of 5 h. For lower temperatures, the NiO additive promotes increase of the density. Near theoretical density was obtained at 1250 ºC for 5 h with 0.5 mol% Ni. However above 1250 ºC there is no difference in the sintered density of specimens with and without additive. This result evidences that the additive improves the sintered density only for short sintering times.

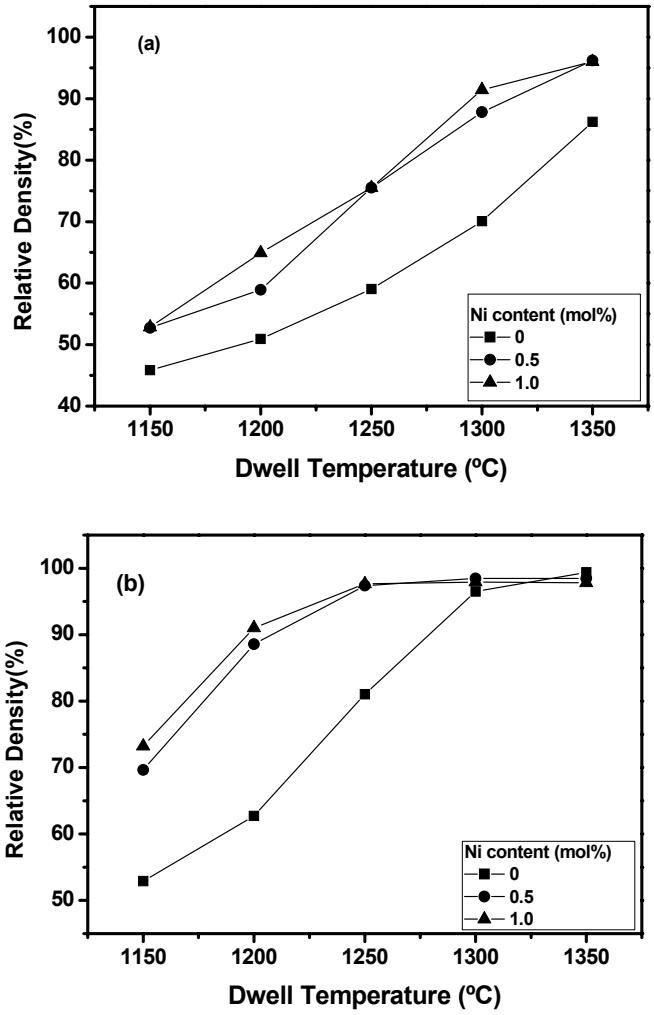


Figure 1. Values of relative sintered density for pellets sintered at several dwell temperatures for 0.1 (a) and 5 (b) h.

To obtain a better insight in the sintering process of NiO-doped 8YSZ, the densification Ψ was calculated using the relation (9):

$$\psi = \frac{V_s - V_g}{1 - V_g} \qquad [1]$$

where V_s and V_g are, respectively, the sintered and green densities normalized for the theoretical density.

Figure 2 shows the densification of specimens sintered at 1350 ºC as a function of the soaking time.

It is worth to note the increased densification of NiO-containing specimens for short soaking times. However, this benefit does hold for longer times at 1350 ºC, and the specimen without additive attains higher densification with soaking times longer than 5 h.

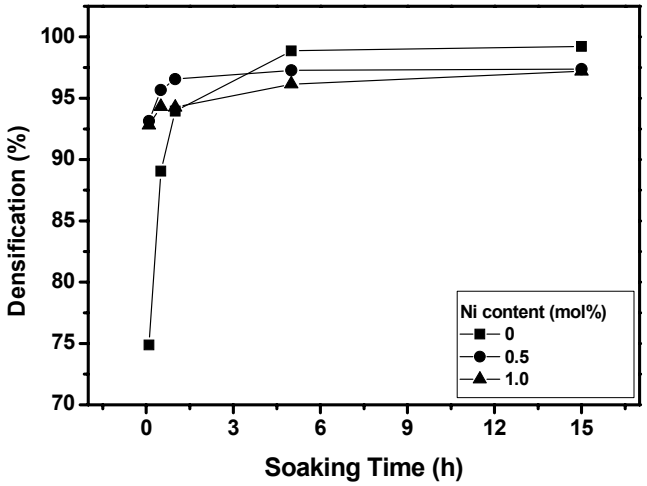


Figure 2. Densification behavior at 1350 ºC versus soaking time.

Figure 3 shows the densification versus Ni content for specimens sintered at 1250 and 1350ºC. For both dwell temperatures and 1 h soaking time, the maximum densification is achieved with 0.5 mol% Ni .

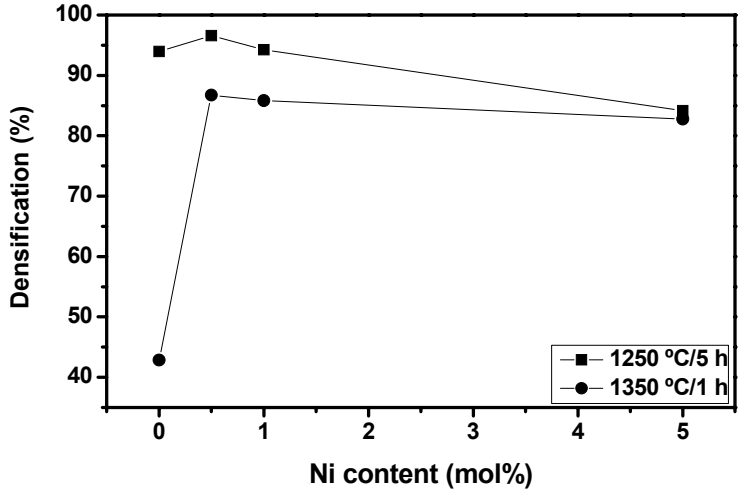
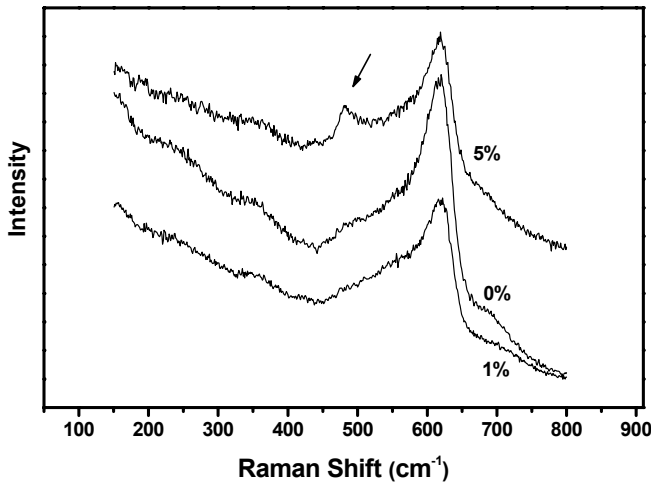


Figure 3. Densification versus Ni content for different sintering profiles.

These results on sintered density and densification show that small amounts of NiO may be useful as a sintering aid to 8YSZ once the sintering schedule involves dwell temperatures lower than 1350 ºC and a short soaking time.

Structural characterization results of sintered pellets carried out by Raman spectroscopy are shown in Figure 4a.

(a)



(b)

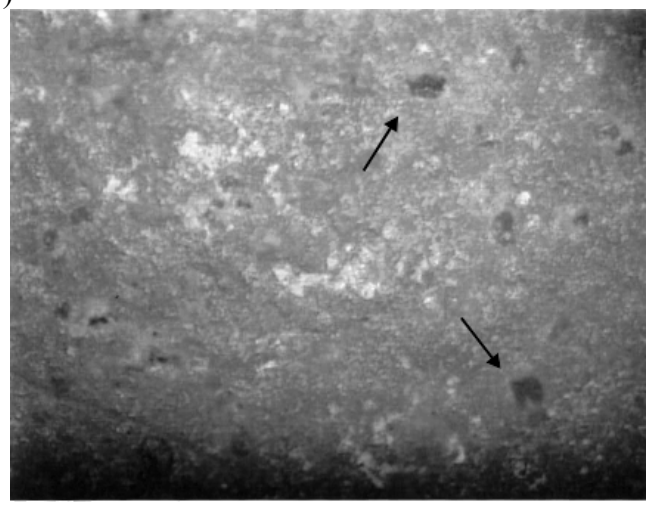


Figure 4. (a) Raman spectra of pellets with different additive contents. (b) optical micrograph of 8YSZ containing 5 mol% Ni. Magnification = 50x.

The Raman spectra of samples without and with 1 mol% Ni are similar. They exhibit a single Raman band near 616 cm^{-1} characteristic of the F_{2g} triple degenerate mode of the cubic fluorite-type structure. Some pellets show few low-intensity bands which are attributed to tetragonal zirconia. In the Raman spectrum of 5 mol% Ni-8YSZ pellet (Fig. 4a) another band centered at 481 cm^{-1} may be seen as indicated by the arrow. This band refers to the NiO cubic NaCl-type structure (10). This result shows that the solubility of nickel in 8YSZ is lower than 5 mol% when sintered at 1350 ºC.

The optical micrograph (Fig. 4b) shows that the method used to prepare the mixtures was not effective to homogenize the constituting powders. Some regions with a dark (green) contrast typical of NiO may be seen. One of this regions indicated by an arrow was the same as that where the Raman spectrum was recorded.

The structural characterization reveals that NiO was formed after sintering the powder compacts, and remained dispersed as a secondary phase in specimens with additive contents exceeding the solubility limit.

Figure 5 shows impedance spectroscopy diagrams measured at 365 ºC for 8YSZ pellets containing 0.5 and 5 mol% Ni. As usual for oxygen ion conductors the impedance diagram is composed by two off-center semicircles attributed to the grain conductivity (high-frequency) and to the blocking of charge carriers at grain boundaries (low-frequency). These diagrams were normalized for specimen dimensions allowing a comparison between the semicircle diameters, which is a direct measure of the grain and grain boundary resistivity.

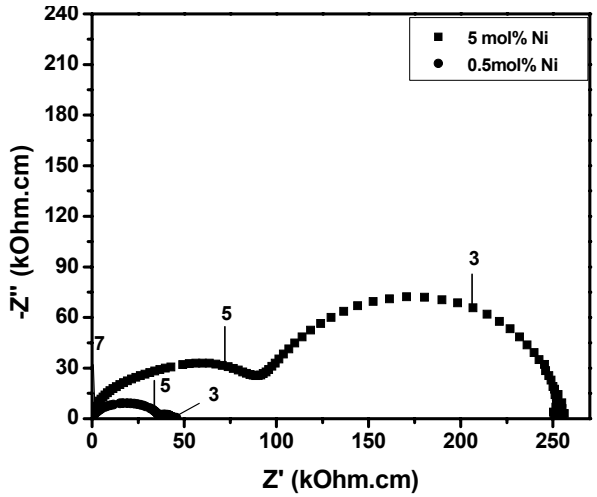
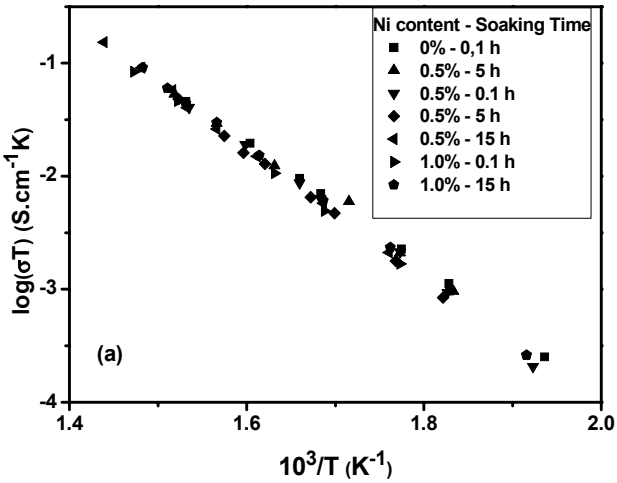


Figure 5. Impedance diagrams of NiO-containing samples sintered at 1350 ºC/1 h. Measuring temperature = 365 ºC.

These diagrams show that for relatively high additive content (exceeding the solubility limit) there is a decrease in both the grain and grain boundary conductivities.

The Arrhenius plots of the electrical conductivity for 8YSZ containing up to 1 mol% Ni are shown in Figure 6 for grain (a) and grain boundary (b) components.



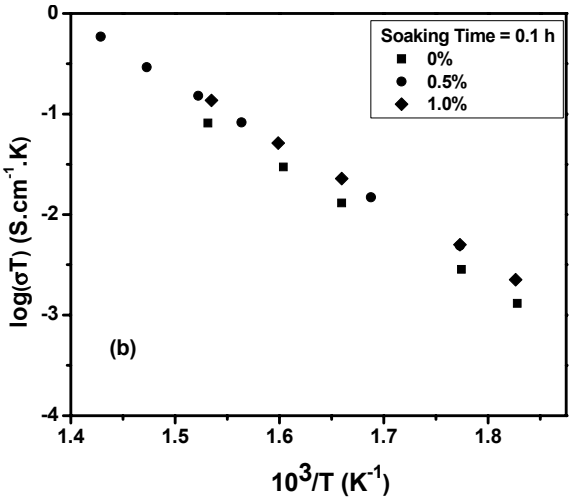


Figure 6. Arrhenius plots of grain (a) and grain boundary (b) conductivity of selected samples.

The conductivity of grains (Figure 6a) does not show any noticeable difference for soaking times ranging from 0.1 up to 15 h for a dwell temperature of … ºC when the additive is present in small concentrations (up to 1 mol%). The grain boundary conductivity exhibits a variation with NiO content. This component of the electrolyte conductivity is slightly higher in pellets with NiO additive.

Conclusions

The role of small amounts of NiO on sintering and electrical conductivity of 8YSZ was studied. NiO promotes densification at temperatures lower than usual for 8YSZ, even for small additive contents. Improvement of the sintered density may be obtained for low sintering temperatures and short soaking times. The grain conductivity of NiO-containing 8YSZ does not change in comparison to that of 8YSZ without additive, whereas the grain boundary conductivity slightly increases.

Acknowledgements

The authors acknowledge FAPESP, CNPq and CNEN for financial supports and the laboratory of molecular spectroscopy of IQ/USP for Raman spectroscopy measurements. R.M.B. acknowledges FAPESP for the scholarship.

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