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Journal of the European Ceramic Society 25 (2005) 2637–2641
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Electrical properties of YSZ/NiO composites prepared by a liquid mixture technique

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Abstract

We report the preparation and characterization of yttria-stabilized zirconia/nickel oxide composites (YSZ/NiO). This composite is the precursor material of the cermet YSZ/Ni, which is used as solid oxide fuel cell anode material. The performance of the anode is strongly dependent on the microstructural properties of the cermet. Therefore, the control of the microstructure of the YSZ/NiO composite is a key step for the fabrication of high-performance anodes. In this study, the composites were prepared by a modified liquid mixture technique. Scanning electron microscopy analysis evidenced the good dispersion of the phases and that NiO nanoparticles are spread over the YSZ surface. Sintered pellets were studied by X-ray diffraction and impedance spectroscopy. The main results show that the composite is comprised of a well-dispersed mixture of the two phases. The electrical conductivity data show that there is a strong dependence of the transport mechanism on the relative composition of phases.

Keywords: Mixed conductor; Composite; Electrical properties; Solid oxide fuel cells (SOFC)

1. Introduction

There has been a considerable interest on the electrical behavior of composite media due to both the intriguing observed properties and the technological applications.[1] The possibility of tailoring the properties by controlling the relative volume fraction of phases for specific applications is an important aspect regarding composite materials. In addition to the electrical properties of each phase, the properties of composites are strongly influenced by the microstructural features such as grain size, distribution, and morphology.[2] In fact, some unusual electrical properties of composites formed by the mixture of two phases with different charge carrier species have been reported. An example is the decrease of the electrical conductivity (σ) by the addition of Ni in the NiO matrix.[3] Some models like percolation, effective media, and space-charge layers have been applied to account for the observed electrical behavior of composites.[2,4] Moreover, the nature of the charge carriers and the dependence of σ on the microstructure, temperature, and oxygen partial pressure can be considered as important parameters for electrochemical applications.

Several applications such as fuel cell electrodes, sensors, electrocatalytic reactors, and gas separation membranes, have attracted the attention to mixed ionic-electronic conductors.[1] These materials exhibit both electronic and ionic charge carriers and can be either single-phase or composites. For example, in a solid oxide fuel cell (SOFC) the electrode materials are mixed conductors. Usually, in the SOFC anode, the desired mixed conductivity and electrocatalytic activity are achieved by mixing an ionic conductor (yttria-stabilized zirconia, YSZ) and a metal (nickel).[5] The use of nickel is due to its low cost and good electrochemical properties, such as the high electrical conductivity and catalytic activity under reducing conditions. The YSZ provides an ionic pathway for O^{2-}, enhances the match of the thermal expansion coefficients, and inhibits the sintering of the metallic particles.[5] The electrochemical activity of the electrodes increases with in-

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doi:10.1016/j.jeurceramsoc.2005.03.116

creasing reaction area, called triple phase boundaries (TPB). Therefore, the length of the TPB depends on both the chemical composition and the microstructure of the electrode. In addition, it is necessary to have well-dispersed nickel particles in a continuous network to provide electronic transport to the external circuit. The anode composite is usually fabricated by a heat treatment of the yttria-stabilized zirconia/nickel oxide composite (YSZ/NiO) precursor in a reducing atmosphere. The stoichiometric NiO is an insulator, however, due to composition deviations it assumes a p-type semiconductor behavior, where the electron holes are created by Ni vacancies.[6]

Thus, in order to obtain high-performance anode materials it is important to control the parameters during the synthesis of the precursor composite. In the present work, we have investigated the precursor material for SOFC anodes prepared by a modified liquid mixture technique in a wide relative concentration range of the phases.[7] The electrical conductivity of the YSZ/NiO composite was studied by means of impedance spectroscopy measurements. The main results indicate that the electric properties are strongly influenced by the relative composition and three different transport mechanisms were found through the analysis of the electrical conductivity data.

2. Experimental

Composite samples of $(1-m)(\mathrm{ZrO_2}{:}8\,\mathrm{mol.\%}\ \mathrm{Y_2O_3})/m$ NiO (YSZ/*m* NiO), with *m* ranging from 0 to 84 vol.%, were prepared by a modified liquid mixture technique. This process consists in the evaporation of a dispersion of YSZ (Tosoh) powder in a solution of nickel acetate (tetrahydrate, Carlo Erba) and ethanol.[7] The liquid mixture was held in ultrasonic bath for 1 h and heated on a hot plate under vigorous stirring to evaporate the ethanol. The prepared powders were dried at 80 °C and calcined in air at 450 °C for 5 h. This is the optimal temperature for the removal of organic material, as inferred by simultaneous thermogravimetric and differential thermal analyzes. This method results in nanosized NiO particles homogenously spread on the YSZ surface, as revealed by scanning electron microscopy analysis.[7] Cylindrical pellets were fabricated by uniaxial pressing and sintering at 1350 °C for 1 h. The sintered samples were analyzed by X-ray diffraction (XRD) in a Bruker-AXS D8 Advance diffractometer at room temperature using Cu Kα radiation in the $20 \leq 2\theta\,(^\circ) \leq 85$ range. The electrical properties of the composite samples were studied by means of impedance spectroscopy $Z(\omega,T)$ measurements carried out from 100 to 800 °C in the 5 Hz–13 MHz frequency range with an applied excitation signal of 200 mV. In all $Z(\omega,T)$ measurements, Ag contact pads were painted on the parallel surface of samples and cured at 400 °C.

3. Results and discussion

The relative densities of the specimens were determined by the Arquimedes method. The theoretical densities (TD) were calculated by the rule of mixtures considering the nominal volume fraction and reported densities of the two oxides. The results show that sintering at 1350 °C for 1 h resulted in samples with high relative density (∼96% of the TD). An exception is the specimen *m* = 84 vol.% NiO, with ∼80% TD.

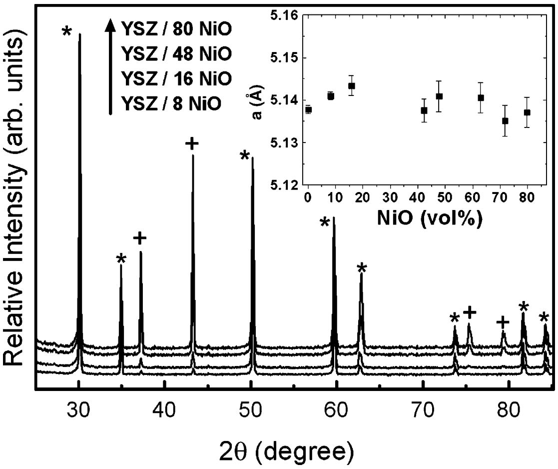

Fig. 1. X-ray diffraction patterns of $(1-m)$ $(\mathrm{ZrO_2}{:}8\,\mathrm{mol.\%}\ \mathrm{Y_2O_3})/m$ NiO samples. The (*) and (+) symbols indicate the YSZ and NiO diffraction peaks, respectively. The inset shows the calculated lattice parameter of cubic YSZ.

The XRD analyzes of the YSZ/*m* NiO samples revealed that all the observed peaks belong to the cubic phases of yttria-stabilized zirconia and nickel oxide, as shown in Fig. 1. Increasing the NiO content *m*, increases the intensity of the corresponding diffraction peaks, which can be identified even for the lowest concentration *m* = 8 vol.%. In addition, the XRD patterns revealed the absence of extra reflections belonging to any additional phase in samples. The calculated YSZ lattice parameters were found to be in agreement with previously reported data and no significant dependence on the NiO content was observed, as shown in the inset of Fig. 1.[8] The formation of solid solution between YSZ and NiO would significantly decrease the cubic zirconia lattice parameter due to the smaller ionic radius of $\mathrm{Ni^{2+}}$ in comparison to both the $\mathrm{Zr^{4+}}$ and $\mathrm{Y^{3+}}$.[9] These results suggest that the samples are comprised of a mixture of the two oxides and no appreciable solubilization of $\mathrm{Ni^{2+}}$ into the cubic zirconia was detected within the resolution of the XRD technique. It was already reported that the NiO solubility limit in the cubic zirconia structure is ≤5 mol.% (∼8 vol.%) for samples sintered at 1600 °C for 4 h.[10] In the present work, the lower sintering temperature and time are believed to inhibit the solid solution formation between the two phases.

The $Z(\omega,T)$ diagrams exhibit at least two semicircles in the whole frequency and temperature ranges studied, as displayed in Fig. 2. However, in this study we focus on the total electrical resistance of the YSZ/*m* NiO composite, which was obtained by fitting the low-frequency end of the impedance diagrams.

The NiO content dependence of the total electrical conductivity $\sigma(T)$, shown in Fig. 3, reveals that increasing the

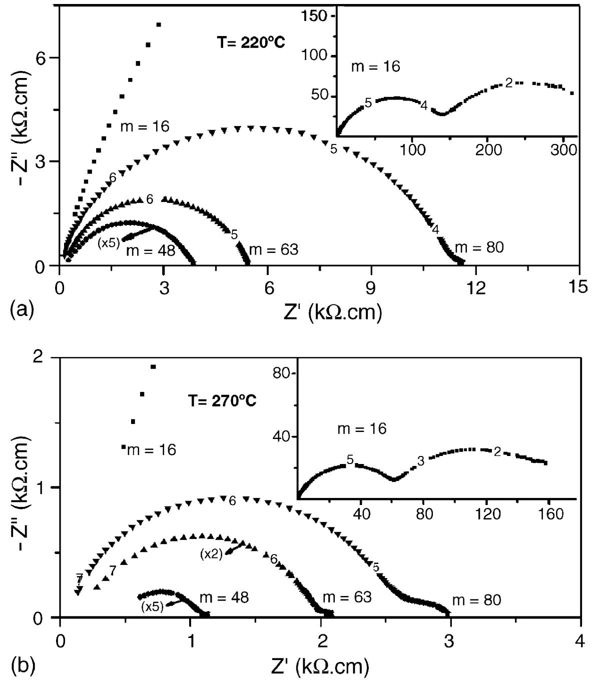

Fig. 2. Impedance diagrams of $(1-m)$ (ZrO_2:8 mol.% Y_2O_3)/m NiO composites for m = 16, 48, 63, and 80 vol.%, measured at 220 °C (a) and 270 °C (b). The numbers replacing the data points are the logarithm of the measuring frequency.

semiconductor content has a strong effect on the transport properties of the composite. For low m values ($m \leq 16$ vol.%), a slight increase of $\sigma(T)$ is observed at low measuring temperatures. Such a feature is a further indication that no Ni^{2+} is dissolved into the cubic zirconia structure. The formation of solid solution would be expected to decrease the electrical conductivity (σ) of the YSZ due to defect interactions, since the 8 mol.% YSZ is within the optimal stabilizer content range for maximum σ.[11] The $\sigma(T)$ data also reveal that increasing m results in larger magnitudes of $\sigma(T)$ and that such a feature is much more pronounced at low temperatures ($T < 500$ °C). It was already reported that even small additions of NiO to YSZ generates appreciable electronic transport.[12] In fact, at $T \sim 190$ °C, a three orders of magnitude increase of σ is observed for intermediary m values, changing from $\sim 10^{-7}$ $(\Omega\,\mathrm{cm})^{-1}$ for the YSZ to $\sim 5 \times 10^{-3}$ $(\Omega\,\mathrm{cm})^{-1}$ for $m = 58$ vol.%. This pronounced increase of σ(T) is related to the increasing electronic charge carriers with increasing NiO content and indicates that the percolation threshold is achieved at m ~30 vol.%. This value is consistent with the expected critical volume fraction for the percolation of a metallic phase in an insulating matrix.[2] However, further increasing the NiO content results in a slight downturn of the $\sigma(T)$ ($m > 58$ vol.%) and for $m = 84$ vol.% $\sigma(190\,°\mathrm{C}) \sim 10^{-6}$ $(\Omega\,\mathrm{cm})^{-1}$. The latter value is expected due to the high porosity of the sample. Thus, three different NiO concentration regions can be identified: (1) $m < 30$ vol.%; (2) $30 \leq m < 60$; and (3) $m > 60$ vol.%. These regions indicate that distinct transport mechanisms take place depending on the NiO content. In region (1) the main charge carriers are the oxygen ions, further increasing the NiO content (region 2) a mixed conduction process is more likely to occur, and in region (3) the main charge carriers may be the electron holes of NiO and YSZ grains act as insulating scattering centers. Similar NiO concentration ranges were defined for the ionic (region 1), mixed (region 2) and electronic (region 3) transport in a previously reported work.[12] However, in that study, the higher sintering temperature promoted the solubilization of NiO into the YSZ, and both the mixed and electronic conduction regions are attained at slightly higher NiO concentrations. This is probably related to microstructural differences arising from the fabrication methods. As a result of the liquid mixture method, our samples have a better homogeneity than the ones prepared by the solid state reaction. Such a feature allows for the interconnection of NiO particles at lower concentrations and results in considerably higher σ values at low temperatures. With increasing temperature, the dependence of the $\sigma(T)$ on the NiO content is less pronounced, and $\sigma(T)$ values have the same order of magnitude in the investigated composition range, as observed in Fig. 3.[12] The $\sigma(T)$ data of the YSZ/m NiO composites reflect the higher electrical conductivity of NiO at lower temperatures ($T < 500$ °C). In addition, due to the higher activation energy of the ionic conductor phase, the YSZ/m NiO σ values are comparable at higher temperatures. This is an indication that the activation process of the electrical conduction is also modified by the NiO addition.

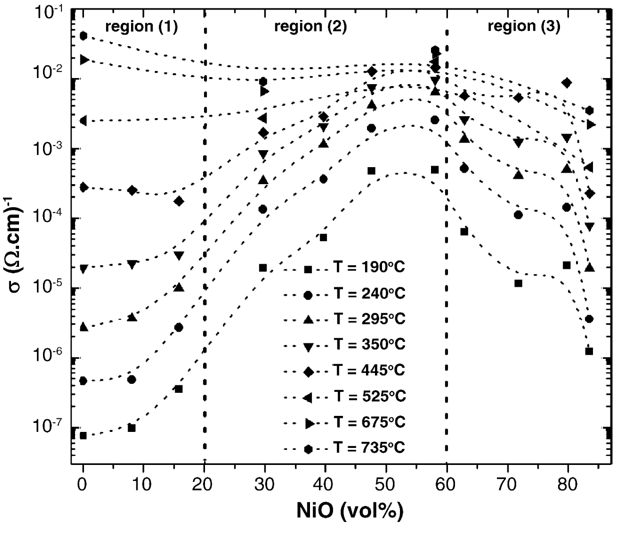

Fig. 3. NiO content dependence of the electrical conductivity of $(1-m)$ (ZrO_2:8 mol.% Y_2O_3)/m NiO composite measured at different temperatures. The lines are guide for the eye.

In fact, the electrical resistivity $\rho(T)$ behavior was found to follow Arrhenius-type activated process, as shown in Fig. 4. For YSZ/m NiO specimens with $m < 30$ vol.% (region 1), a thermally activated process is observed with activation energy ΔE close to the YSZ ($\Delta E \sim 1$ eV). For intermediary NiO compositions (region 2), a clear discontinuity of the Arrhenius behavior is observed at $T \sim 250$ °C, a temperature found

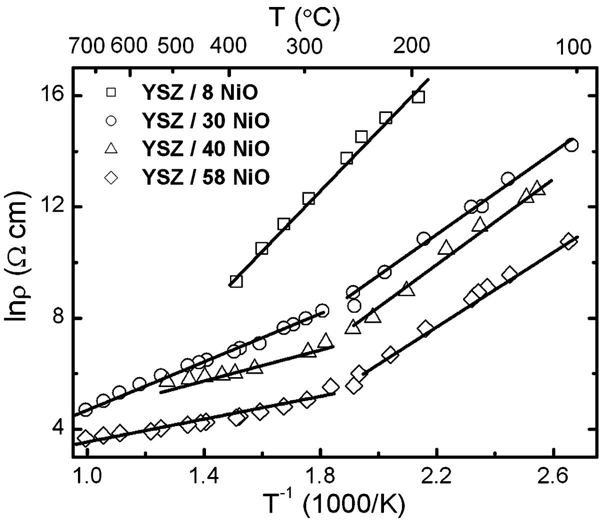

Fig. 4. Arrhenius plots of the $(1-m)$ (ZrO_2:8 mol.% Y_2O_3)/m NiO composites.

to be NiO-concentration independent and close to the Néel temperature of NiO.[13] In order to describe the $\rho(T)$ curves of the NiO compositions $m > 20$ curves, two Arrhenius processes were used.

Assuming thermally activated processes, the ΔE for both temperature ranges were determined for the YSZ/m NiO specimens, as displayed in Fig. 5. In the composition region (1), even a small amount of the semiconductor phase significantly decreases the ΔE of the pure YSZ (0.98 ± 0.02 eV) to $\Delta E = 0.65 \pm 0.01$ eV for the $m = 16$ vol.% specimen.[14] This constitutes a further evidence that the NiO addition enhances electronic transport in YSZ/NiO composites. With increasing NiO content (region 2), two ΔE are found. For $T < 250$ °C, the obtained values are close to $\Delta E \sim 0.7$ eV, and for $T > 250$ °C the $\Delta E \sim 0.3$ eV. Specimens with higher concentrations of NiO (region 3) have slightly higher ΔE values, possibly due to the YSZ scattering of the charge carriers. These results are consistent with previous reported ΔE values for the electric conduction of the NiO. This oxide is known to have $\Delta E \sim 0.7$ eV for $120 \leq T$ (°C) ≤ 250 °C and $\Delta E \sim 0.3$ eV for $250 \leq T$ (°C) ≤ 900.[12,13] Thus, the estimated ΔE dependence on the NiO content provides further evidence that the transport mechanisms in the NiO concentration regions (1), (2), and (3) are due to ionic, mixed, and electronic charge carriers, respectively.

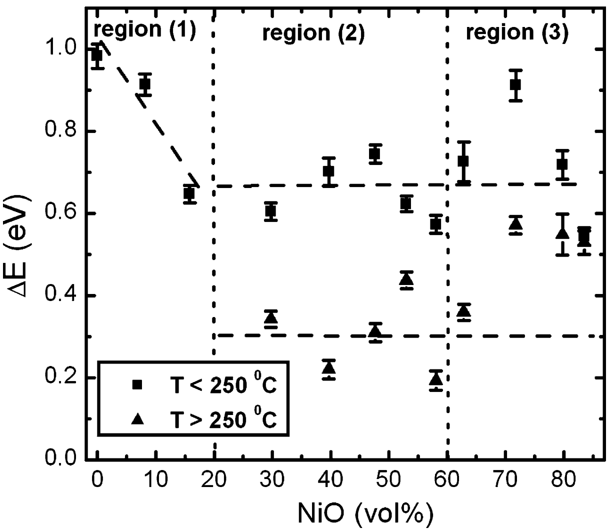

Fig. 5. Activation energy dependence on the NiO content of $(1-m)$ (ZrO_2:8 mol.% Y_2O_3)/m NiO composites.

In summary, we have fabricated YSZ/NiO composites by a liquid mixture method, which resulted in homogenous powders with good sinterability. The relatively low sintering temperature inhibited the solid solution formation between the two oxides. Specimens with different NiO content exhibited different electrical conductivity behavior and thermal activation energies. The NiO concentration ranges where the main charge carriers are ionic, mixed, and electronic were estimated. The effectiveness of the described preparation method is evidenced by the high measured values of both the relative density and the electrical conductivity of the composites, indicating that this is a suitable method for the fabrication of precursors for SOFC anodes.

Acknowledgments

This work was partially supported by the Brazilian agencies FAPESP (98/14324-0, 99/10798-0 and 03/08793-8) and CNPq (306496/88-7, 300934/94-7 and 301661/04-9); and by the Italian Ministry of Education, University and Research (MIUR).

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