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Preparation and characterization of anodes for intermediate temperature solid oxide fuel cells

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Abstract

This paper reports the synthesis and characterization of NiO - $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (NiO-GDC cermet) anodes for Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFC). Anode- supported and electrolyte-supported cell configurations were prepared using a commercial cermet. The effect of different carbon aggregates, addition of PVB and different synthesis temperatures were tested. The morphology and composition were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). It was found that the anodes porosity increases with the amount of carbon added. An optimum composition was determined for the anode-supported cell, being limited by the mechanical strength, which decreases with increasing carbon content. The polarization resistance of electrolyte-supported symmetric cells prepared using this optimal composition decreases more than 30% with the addition of carbon, due to the enhanced porosity.

Keywods: Anodes; Solid Oxide Fuel Cells (SOFC)

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1. Introduction

The current energy crisis revived the interest in renewable energies and solid oxide fuel cells (SOFC), operated with hydrocarbons as well as with hydrogen as fuel, are considered a good alternative within the emergent technologies. These electrochemical devices convert chemical energy into electrical energy, by oxidation of a fuel in the anode and simultaneous reduction of an oxidant in the cathode, decreasing energy losses and emissions of polluting gases. SOFC devices operated at intermediate temperatures (IT-SOFC) are particularly interesting to reduce material costs and long life performance. The optimization of an IT-SOFC first requires selecting materials and improving the simple processes that take place in a single operating cell. Posterior stacking of these optimized single cells allows increasing the device power (Larmine and Dicks, 2003).

Nomenclature	
SOFC	solid oxide fuel cell
IT-SOFC	intermediate temperature solid oxide fuel cell
GDC	Gadolinia doped Ceria ($Ce_{0.9}Gd_{0.1}O_{1.95}$)
PVB	polyvinyl butyral

Fig. 1 illustrates the operation of a SOFC, which includes two electrodes: an anode (where it is carried out the fuel oxidation) and a cathode (where the oxygen reduction occurs), separated by an electrolyte. All of them are composed of ceramic materials. The materials used as electrolytes must have a high ionic conductivity to minimize ohmic drops as well as a negligible electronic conductivity to prevent the passage of electrons through it with the consequent loss of voltage affecting the performance of the cell. Furthermore, it is desirable that electrode materials present high catalytic activity for oxygen reduction reactions (cathode) and oxidation of the fuel (anode).
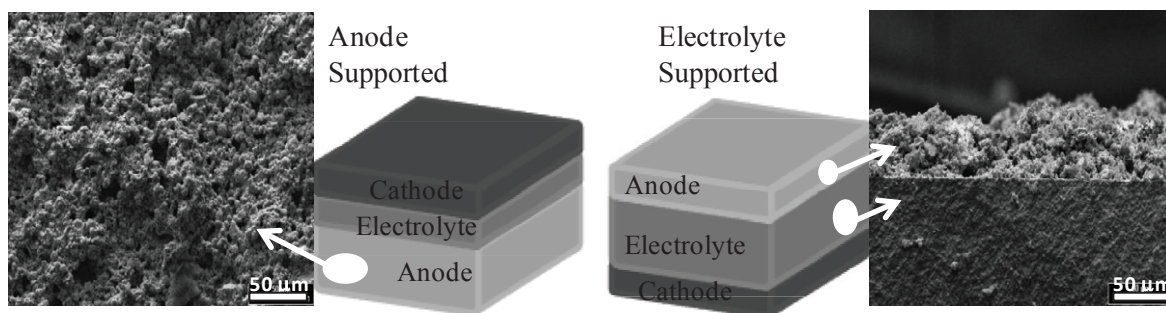

Fig. 1. Sketch of the cell arrays showing the configuration supported by the anode (a) and by the electrolyte (b). Images at the right side were obtained with a scanning electron microscope.

There are two main basic configurations for IT-SOFC cells: the anode-supported and the electrolyte-supported array. The former has a very thin electrolyte and allows obtaining high current densities and power, but are mechanically less resistant due to the porosity required for the anode. On the other side, the electrolyte-supported cells present better mechanical strength, but show less favorable electrical properties and require higher operating temperatures. The use of cells supported by the anode is one of the best strategies

to improve the IT-SOFC properties, because it opens the possibility of considerably reducing the thickness and hence the resistance, of the electrolyte (Kleinlogel and Gauckler, 2000; Wang et al., 1997). It is therefore important to optimize the microstructure for maximum porosity without affecting the mechanical properties of the material.

Because one of the most commonly used anodes is a mixture of the Gadolinia doped Ceria (GDC) electrolyte and Nickel Oxide (NiO), this paper presents a study on the synthesis and characterization of anodes prepared from a commercial NiO-GDC cermet, in the following cell configurations:

- Anode-Supported: searching the optimal composition of NiO-GDC / carbon mixtures for anodes with appropriate porosity and good mechanical properties in order to be used as support of the cell.
- Electrolyte-Supported: using a dense GDC electrolyte as support, where the anode is deposited by the spin-coating method. This configuration allowed the preparation of symmetrical cells, suitable for the electrochemical complex impedance spectroscopy study.

2. Experimental method

Different parameters were tested for the synthesis of the ceramic anodes, looking for the optimal composition. The carbon percentage was varied between 0 and 10 % and the effect of using polyvinyl butyral (PVB) as an additive was evaluated.

The anode supported cells were synthesized from a commercial cermet (Full Cell Materials) of composition 60% w / w NiO - 40% w / w $Ce_{0.9}Gd_{0.1}O_{1.95}$ (NiO-GDC) by adding different percentages of activated carbon. The mixture powder was pressed into pellets, which were sintered between 1350 ° C and 1450 ° C. Then, the samples were reduced in an Ar/H_2 (90% at-10 at %) atmosphere.

The morphology and composition of the samples were studied by X-ray diffraction (XRD) using a Philips PW1700 diffractometer with $Cu_{K\alpha}$ radiation and a graphite monochromator, by Scanning Electron Microscope (SEM) and by Energy Dispersive microanalysis (EDS) carried out with a Philips 515 equipped with an EDAX Genesis 2000 spectrometer. For the electrolyte supported cell, the anodes were prepared as inks and deposited by spin-coating method on GDC dense pellets. A rotation speed of 4000 rpm for 20 seconds was used, forming a layer of uniform thickness. Symmetrical cells (anode / electrolyte / anode) were obtained after a heat treatment to achieve good adhesion between layers. This treatment consisted in drying the deposited layer at 130 ° C for 10 min (Baqué, 2011) and posterior sintering at 1000 ° C for 12 hours. Then, samples were characterized by high resolution SEM using a field emission microscope FEI Nova NanoSEM 230, to determine the thickness of the deposited anodes, as well as the layer uniformity. Finally, using the same equipment a comparison was made between the microstructure of both anodes types.

ASR anode values were determined in the symmetrical cells from impedance spectroscopy measurements (EIS) under Ar/H_2 (95% at-5 at%) mixture, carried out heating from 500 to 700 °C (50 °C steps), and cooling down (Baqué et al., 2008).

3. Results and discussion

3.1. Anode Supported

3.1.1. Microestructural studies based on the composition (aggregated carbon and PVB)

In Fig. 3 it can be observed the surface of non-reduced (a) and (b) reduced samples. From left to right the activated carbon percentage, used to generate pores in the anodes, increases from 0% to 10%. The images

show a porosity increase with the %at C added. In addition, the porosity observed is greater after the reduction process.
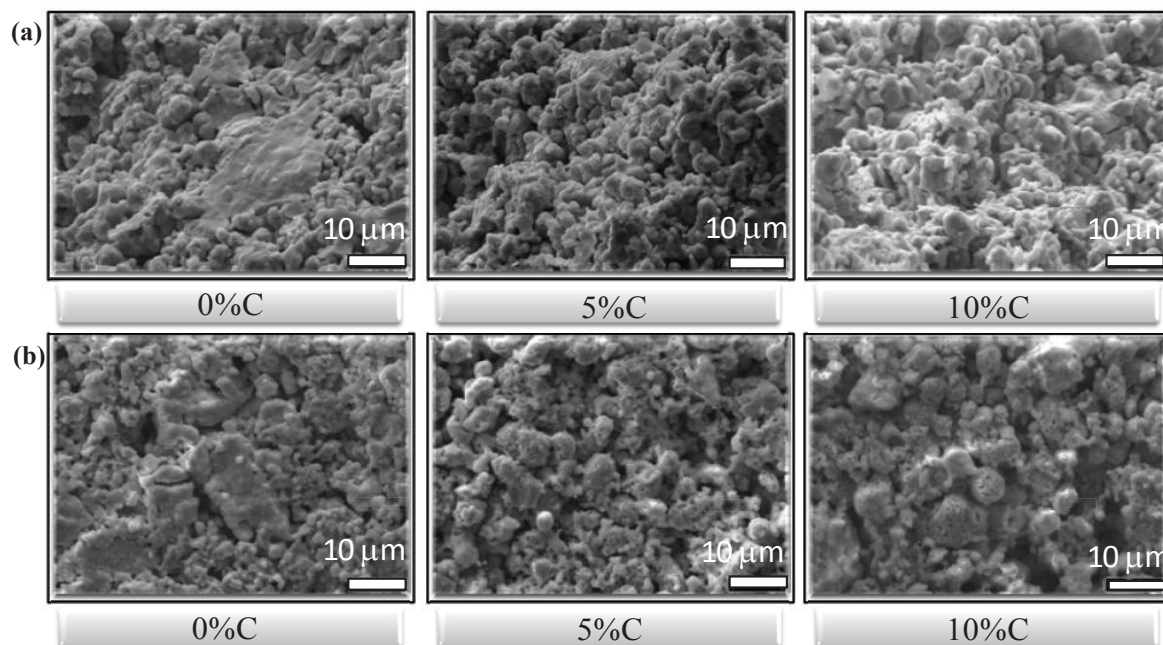

Figure 3: SEM micrographs of the anode surfaces in (a) non-reduced and (b) reduced samples.

The PVB is a material usually used as a "binder" in the synthesis of ceramic samples. Therefore it was interesting to study its effect on the anode supported samples and its possible influence on the pores generation. For that, two samples with and without PVB (A1 and A2 respectively) were prepared with 10% C at 1450 ° C. Figure 4 displays the anode´s surfaces observed at different magnifications. On sample A2 (Fig. 4b ii) a semiquantative EDS analysis shows a predominance of Cerium Gadolinium Oxide in zone A, while the area B was identified as nickel oxide. This indicates that, on one hand, both phases are separated (there is not reaction between them) and, secondly, that while the NiO retains submicron grain sizes, the GDC sinters to form larger agglomerates. Contrary, the use of PVB produced better pore distributions through the sample and less GDC agglomerates.

3.1.2. Present phases (XRD)

Fig. 5a exhibits diffraction patterns of three NiO-GDC samples. The first diffractogram (A3) shows the commercial Cermet (NiO-GDC) used as precursor. The second diffractogram (A4) shows the mixture obtained after addition of 2.5% atC and sinterization at 1450ºC. No other phases different from the precursor powder could be identified. This fact supports that the addition of Carbon only produces morphological changes (appearance of pores), but has no influence in the composition.

The third diffractogram (A4r) corresponds to sample A4 after reduction in an Ar-H_2 (90-10 at %) atmosphere. As expected from the reduction process, metallic Ni characteristic peaks appear in detriment of NiO reflections. However, no other secondary phases are observed, supporting that there is no reaction

between the NiO and the GDC during the synthesis or the reduction process. This observation is in agreement with SEM-EDS results.
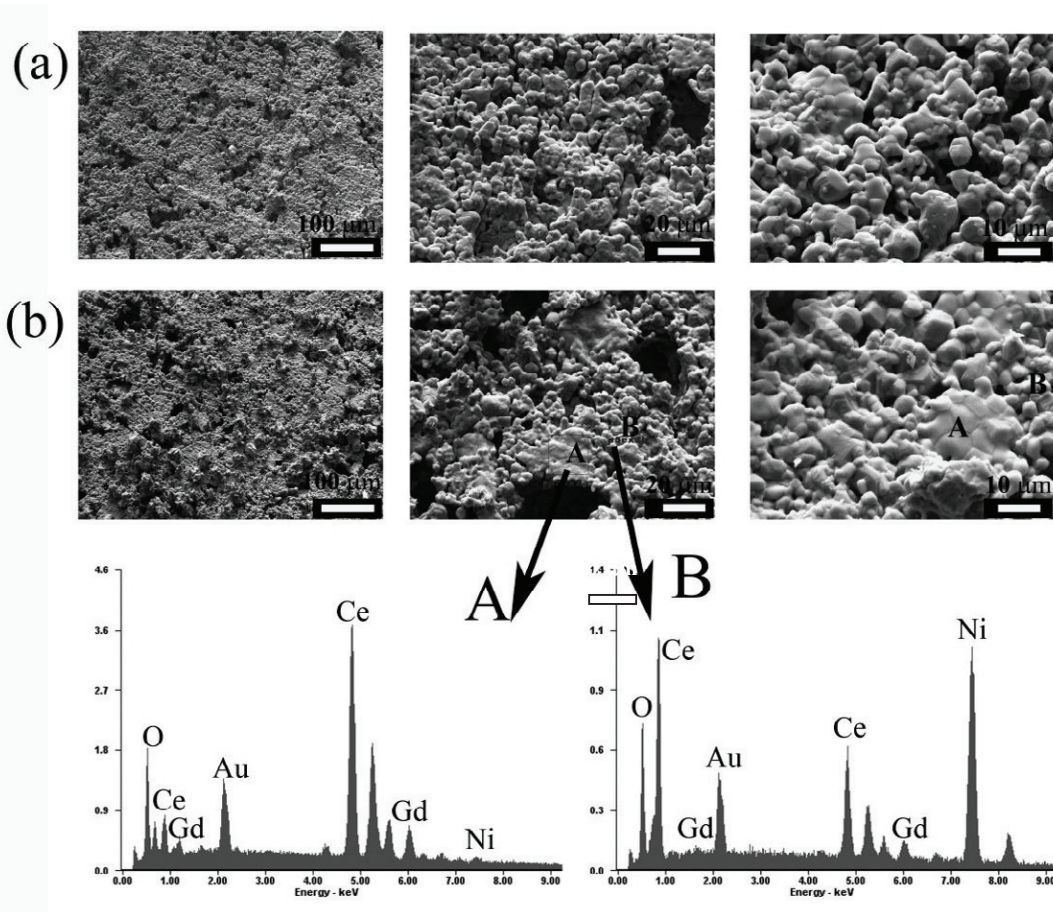

Figure 4: SEM micrographs of the sample´s surfaces prepared (a) with PVB and (b) without PVB at different magnifications. EDS spectra indicating compositions of points A and B are shown on the bottom.

3.1.3. Determination of porosity by flow porosimetry

Figure 5b shows a NiO-GDC sample, with 2.5 at% C and PVB, where the porosity was measured to determine pore size and distribution. In these tests it was found that the main pore size corresponds to diameters smaller than 1 mm. Unfortunately all samples with 10 at% C or more were too fragile for the test, and could not be evaluated.
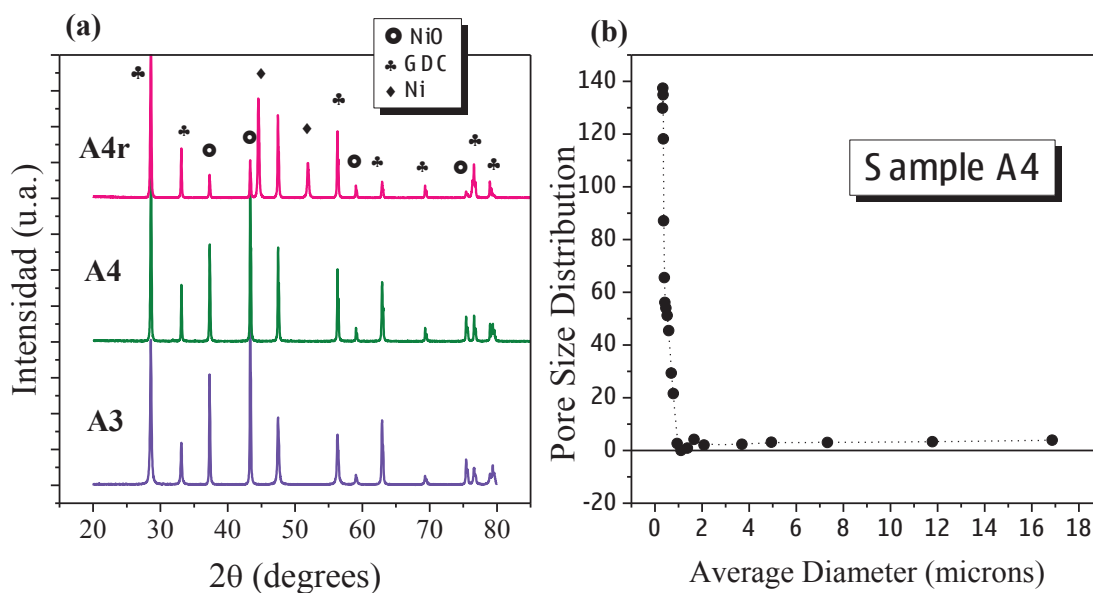

Figure 5: (a) XRD patterns of samples A3, A4 y A4r, (b) Porosity data in sample A4.

3.1.4. Evolution of the particle size with the synthesis temperature

Fig. 6 shows non-reduced samples with 10% at C and PVB sintered at increasing temperatures (1350 ° C, 1400 ° C and 1450 ° C). It can be observed that the particle size increases by increasing the synthesis temperature, reaching values greater than 10 mm for GDC grains.
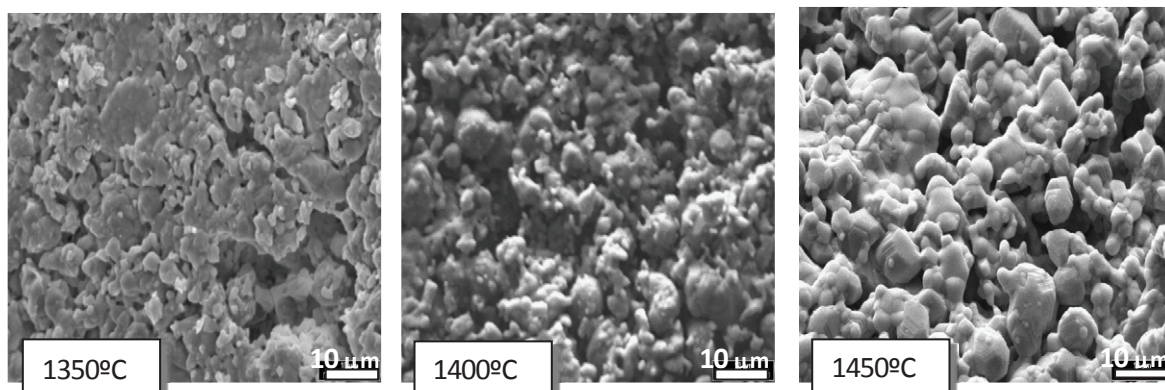
Figure 6: SEM images of samples with 10% atC sintered at different temperatures

3.2. Electrolyte Supported

The optimum composition for preparing anodes was 7.5% C. Higher amounts resulted in very fragile samples. The anodes were successfully deposited by spin coating on the GDC electrolyte. Symmetrical cells were obtained after a heat treatment at 1450°C. After the sintering treatment, these samples were reduced in an Ar-H$_2$ (90-10 at %) atmosphere at 700 ° C.
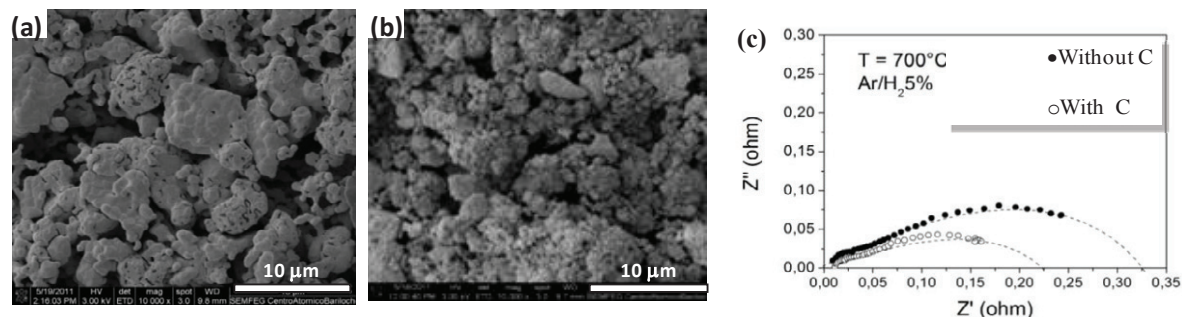

Figure 7: GDC-Ni anodes for (a) anode supported cells, and (b) electrolyte supported (c) complex impedance spectroscopy data used for the ASR calculation measured at 700 °C.

Fig. 7 displays images of two anodes, one prepared as pellet for the anode-supported cell (fig 7a) and one prepared as paint for the electrolyte-supported array (fig 7b). Although both were prepared with the same conditions, there is a noticeable difference in the microstructure. The layer deposited on GDC (7b) shows that pores and Ni (metal) particles present smaller sizes and more homogeneous distribution. Contrary, in the material prepared as bulk (fig. 7A) is possible to distinguish between the different phases: the Ni (metal) presents very small black points inside (pores), and the GDC with large grains, which are well sintered.

Complex impedance spectroscopy measurements in an Ar/H$_2$ atmosphere show better results for the electrolyte supported cells with anodes containing 7.5%at C compared to those anodes without carbon: the Area Specific Resistance (ASR) resulted: 0.089 ohm.cm^2 for the first one and 0.131 ohm.cm^2 for the later one at 700°C (see Figure 7 (c)). ASR values at 600° were 0.55 ohm.cm^2 and 1.37 ohm.cm^2 with and without

carbon, respectively. For comparison with the state of the art, Ding et al., 2010, reported ASR values of 0.63 ohm.cm^2 and 1.75 at 600 °C for anodes made from NiO- GDC nanocomposite powders, synthesized by chemical and mechanical methods, respectively. Therefore, it is possible to optimize the porosity of commercial cermet materials by adding carbon, which resulted in an excellent anode electrochemical performance.

4. Conclusions

In the anodes studied here was observed that as the amount of carbon added increases, the porosity also increases. The optimal composition was estimated to be less than 10%atC, since the mechanical strength decreases with increasing carbon content. The use of the additive PVB is favorable, because it helps the generation and distribution of pores. XRD diffractograms support that sintered anodes have no new phases, indicating that the cermets of Ni-GDC composition are chemically compatible with electrolytes based on GDC, at least until the sintering temperatures used. Furthermore, SEM micrographs of cross sections showing the interphase between co-sintered anode / electrolyte demonstrated that the junction zones are well defined, without presence of cracks. This is an optimum characteristic for proper cell operation. Using a composition of 7.5% C were prepared at symmetric cells of anodes supported by the electrolyte and found that the polarization resistance decreases more than 30% in the samples with the addition of carbon, due to increasing of the porosity. The obtained ASR values indicated an excellent anode electrochemical performance.

Acknowledgements

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