NEW CHEMICAL ROUTES FOR PREPARATION OF ULTRAFINE NiO-YSZ POWDERS FOR SOFC ANODE APPLICATIONS

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ABSTRACT

Ultra-fine NiO-YSZ composite powders with a high dispersion level of NiO (around 40% molar) have been prepared. Two different chemical routes were used to obtain nanostructured powders as starting materials promising to get high performance anode for SOFC applications. Material characteristics such as porosity, NiO particle distribution, grain size and particle to particle contact were investigated. Different morphologies were observed after calcination processes. Very small grains of each phase, NiO and YSZ, have been obtained using both preparation methods.

INTRODUCTION

Physical and chemical properties of ceramic products are highly dependent on the morphology and chemical composition of starting powders. For optimal SOFC performance, good conductivity, chemical and thermal stability and especially electrochemical activity are important factors (1). The electrochemical activity of the electrodes increases with increase in the reaction area, called triple phase boundaries (TPB), where gas, electrodes, and electrolyte are in contact. The length of the TPB depends on the morphology and the chemical composition of the electrode.

A typical SOFC system employs yttria-stabilized-zirconia (YSZ) as electrolyte and the cermet nickel-yttria-stabilized-zirconia (Ni-YSZ) as anode. The use of nickel in the anode is due to its high catalytic activity under reducing conditions while YSZ provides an anionic pathway for conveying oxygen ions from the electrolyte to the TPB (2). Therefore, it is necessary that the nickel particles be well dispersed in a continuous and open YSZ network.

In a conventional microstructure prepared by powder mixture of NiO and YSZ, grains are distributed randomly in the cermet and the sintering of NiO grains is not suppressible (3). Nanoscaled oxide powders with particles of uniform shape and narrow size distribution have been shown to possess interesting properties and have gained increasing technical importance in the development of innovative ceramic materials (4). Sol-gel and ion impregnation methods provide promising approaches to produce nanoparticles (5, 6).

The aim of this work is to synthesize ultra-fine NiO-YSZ composite powders with a high dispersion level of the NiO (about 40% molar), and control the morphology of the particles using two new chemical routes. The two methods used to obtain green bodies are: a sol-gel and a liquid mixture method. Recently, a sol-gel process, using an aqueous...
preparation of metal-YSZ was developed to obtain nanostructured material with mesoporosity (7). The same technique has been used in this work to obtain NiO-YSZ with nanoscaled grain size. A liquid mixture process is a new way to impregnate nanometric YSZ powder by using nickel acetate. Electrode activity is directly influenced by material characteristics such as porosity, NiO particles distribution, grain size and particle to particle contact. These characteristics depend on the synthesis method.

**EXPERIMENTAL**

Aqueous preparation of metal-YSZ was used by Ozin et al. to obtain nanostructured material with mesoporosity (7). The aqueous reaction method was used in this work to obtain NiO-YSZ with nano-scaled grain size of the oxides. A mixture of 10 g of Zirconium ethoxide (97% Aldrich), 100 ml of ethylene glycol (99.9% Aldrich), and 3.32 g of NaOH (anhydrous 99.99% Carlo Erba) was refluxed under stirring for 24 h at 195°C in a Pyrex® reactor to form a clear solution called zirconium glycolate (9). This thermal level was reached subtracting part of ethanol produced by the substitution of ethoxides groups from the reaction equilibrium. A small amount of glycol was distilled off at the same temperature until the solution became clear yellow. A solution of 2.4 g yttrium acetate (98% Aldrich) in 60 ml of ethylene glycol was added at the zirconium glycolate drop by drop under stirring during the cooling. All the process steps were carried out under dry nitrogen flow. The resulting thick gel, called YZ glycolate (7), was added to a solution of 7.42 g nickel acetate (tetrahydrate 99.99% Carlo Erba) dissolved in warm ethylene glycol, and then added to a mixture of 150 ml of water, 10 g of CTAB (cetyltrimethylammonium bromide, Aldrich), 4 g NaOH (anhydrous Carlo Erba) which was previously stirred at room temperature for 1 h. The resulting mixture was stirred at room temperature for 4 h and at 80°C for 5 days (10). The resulting green gel was recovered by filtration and washed with distilled water. All samples were calcined starting from the precursor at 450°C for 24 h and 600, 800, and 1000°C for 10 h in air with a heating rate of 0.75°C/min. The calcined samples were milled in agate mortar and washed again with distilled water to reduce the final sodium content of the powders.

The process called liquid mixture is an impregnation of nanometric YSZ powder by nickel acetate (tetrahydrate, Carlo Erba) which was fired forming nano sized NiO spread on the YSZ particles surface without changing the morphological and chemical bulk characteristics of the ionic conductor material. To obtain NiO-YSZ, 3.6 g of commercial nanometric 8YSZ powder (Tosoh) was added to a solution of 8.88 g of nickel acetate in 50 ml of ethyl alcohol absolute (99.999% Aldrich) in a 250 ml beaker. The liquid mixture was held in ultrasonic bath for 1 h and heated on a hot plate under vigorous stirring to evaporate the ethanol rapidly. Hence, the prepared powder was recovered, dried at 80°C and eventually, fired in a furnace at 450°C for 5 h. The as-synthesized gray-green powder was also calcined at 700 and 1350°C for 1 h in air.

Simultaneous thermogravimetric-differential thermal analysis (TG/DTA) was performed on a NETZSCH STA 409. All samples were held in a platinum sample holder under air atmosphere. The morphology and the phase composition of the NiO-YSZ composite powders were analyzed by field emission scanning electron microscopy (FE SEM LEO 1530) with an energy-dispersive analysis of X-rays device (EDAX INCA) and backscattered electrons detector (CENTAURUS).
X-rays diffraction (XRD) was performed on a Philips X'Pert MPD using CuKα radiation. The phases present in the NiO-YSZ powders at different stages of calcination were analyzed in the Bragg angle range $20^\circ \leq 2\theta \leq 85^\circ$, while a qualitative analysis for the mesoporosity of the NiO-YSZ was performed in the angle range $1^\circ \leq 2\theta \leq 10^\circ$. The FT-IR spectra were recorded on a Perkin Emer 2000 (4000-400 cm$^{-1}$) with solid samples pressed into KBr pellets.

RESULTS AND DISCUSSION

Sol-Gel Method

The precursor containing TG/DTA and FTIR analysis showed that after thermal treatment in air above 450°C the metal-YSZ glycolate with the surfactant phase was completely transformed into NiO-YSZ oxides. The weight loss was close to 80% of the total initial weight, as shown in Figure 1. The exothermic combustion between 200 and 400°C involved all the organic matter, while only a thermal treatment in air for 18-24 h can eliminate some carbon content that was detected from FTIR analysis.

![Figure 1. TG/DTA curves for the precursor synthesized by the sol-gel method.](image)

The NiO-YSZ powder prepared via sol-gel showed very small particle size as the result of the self-assembly process. FE-SEM photograph in Figure 2 displays NiO-YSZ calcined at 450°C for 24 h. The NiO particles were not distinct from the YSZ particles.

![Figure 2. FE-SEM micrography of NiO-YSZ by sol-gel calcined at 450°C for 24 h.](image)
A higher magnification (Figure 3) shows how the agglomeration of the particles leads to a non dense morphology. An evaluation of grain size from the micrographs gave particles between 4 and 30 nm. Figures 4a, c, d show respectively powders calcined at 600, 800, and 1000°C. The particle of the material calcined at 600°C is sized around 6 nm (Figure 4b). The size range increases to 20-40 nm for the material calcined at 800°C (Figure 6c) and 50-100 nm for the material calcined at 1000°C. Figure 4d shows a larger particle where sintering was started. Spherical and non spherical shaped particles mixed together were observed in both, the 800 and 1000°C calcined samples.

Figure 3. FE-SEM micrography of NiO-YSZ by sol-gel calcined at 450°C for 24 h.

Figure 4. FE-SEM micrographs for NiO-YSZ by sol-gel calcined at 600°C (a, b), 800°C (c), and 1000°C (d) for 10 h.

Both the mesoporosity and the phases of the material were investigated by XRD. In Figure 5 the diffraction pattern of the material calcined at 450°C displays the YSZ and the NiO phase. The YSZ peaks are broad with respect to the NiO peaks. A calculation of crystallite size by Scherrer equation indicated a low crystallization degree for YSZ and a mean value of 4 nm for NiO crystallite size. The peak at the small angle of Figure 6...
indicates that the sample is mesoporous at this stage of the calcination. The YSZ reflections gradually grow in intensity while the peak at small angle decreases in intensity after calcination at higher temperatures. The peak at small angle disappeared for temperature above 800°C in agreement with results of Ozin et al. (7). Figure 7 shows the diffraction pattern of the material calcined at 1000°C for 10 h. The NiO and YSZ phases are formed with mean values for the crystallite sizes of 90 nm for YZ and 90 nm for NiO, as determined by Scherrer equation.

![XRD pattern](image)

**Figure 5.** XRD pattern of the NiO-YSZ phases prepared by the sol-gel, calcined at 450°C for 24 h.

![XRD pattern](image)

**Figure 6.** XRD pattern for the mesoporous NiO-YSZ calcined at 450°C for 24 h.

![XRD pattern](image)

**Figure 7.** XRD pattern of the NiO-YSZ phases calcined at 1000°C for 10 h.

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EDX analysis performed on the sample calcined at 450°C for 24 h showed an uniform distribution of Ni and Zr elements in the sample. A map of the elements did not allow to distinguish each phase because of the small particle size of the components.

**Liquid Mixture Method**

The precursor obtained by liquid mixture method was calcined at 450°C for 5 h to eliminate the organic components form nickel acetate. At that temperature exothermic reactions were complete with a total weight loss around 25%, as shown in Figure 8. The FTIR spectra shown in Figure 9 indicate that no acetate groups are present anymore in the precursor (Figure 9 a) leaving only the bands between 500 and 600 cm\(^{-1}\) indicative of the symmetric vZr-O, vNi-O and vY-O stretching modes (7) (Figure 9 b).

![Figure 8. TG/DTA for the material obtained by the liquid mixture method.](image)

Figures 10 a and b show the XRD patterns for the precursor before and after the thermal treatment at 450°C for 5 h. The small peaks observed in Figure10 (a) are attributed to the organic compound used in the synthesis. At this stage the NiO phase was completely formed with a calculated mean crystallites size equal to 4 nm. The calculated crystallite
size of the YSZ was around 7.5-10 nm before and after the calcination. The growth of NiO crystallites resulted to be rapid for higher temperatures of calcination. Calculations using Scherrer equation indicate a mean size for the NiO phase around 70 nm at 750°C for 5 h and 120 nm at 1350°C for 5 h.

![XRD patterns for NiO-YSZ before (a) and after (b) calcination at 450°C.](image)

**Figure 10.** XRD patterns for NiO-YSZ before (a) and after (b) calcination at 450°C.

The liquid mixture preparation allowed to spread nanometric particles of NiO directly on the surface of the YSZ oxide. The morphological characteristics of a powder calcined at 700°C for 10 h are shown in Figure 11. A uniform distribution of NiO nanometric particles is the result of the acetate firing (Figure 12). The YSZ dispersed in the reaction acts like a solid support for the NiO particle formed in the firing. Qualitative evaluation of FE-SEM indicated particle size around 6-8 nm for NiO. Differences in the particle shape was detected by FE-SEM for all the samples calcined. Spherical shape particles was attributed to the YSZ commercial powder and non-spherical shape to the NiO. More details about the phase distribution were obtained from back-scattered electrons, performed on the sample calcined at higher temperatures where the particles size was bigger. Figures 11 and 12 also show that some YSZ particles are covered by NiO particles.

![FE-SEM micrograph for NiO-YSZ obtained by liquid mixture calcined at 700°C for 10 h.](image)

**Figure 11.** FE-SEM micrograph for NiO-YSZ obtained by liquid mixture calcined at 700°C for 10 h.
Figure 12. FE-SEM micrograph for NiO-YSZ obtained by liquid mixture calcined at 450°C.

Figure 13 also shows a quantitative analysis of the powder calcined at 700°C for 5 h. The first two lines arise from the of background. The content of the elements correspond to the ratio of the ZrO$_2$-Y$_2$O$_3$-NiO oxides obtained from the synthesis process. Figure 13 also shows that the oxide particles are free of impurities.

Figure 13. EDAX and micrography for NiO-YSZ by liquid mixture calcined at 700°C for 10 h.

A sintering process at 1350°C was performed for the precursor obtained using the liquid mixture process and calcined at 450°C for 5 h. The pure chemical composition and the
morphological characteristics of the NiO-YSZ material desired for anode fabrication were obtained by this method. Recently a sintering, at 1350°C, of NiO grains was performed (11). Figure 14 shows how the sintered material maintains submicrometric grain sizes with open porosity and interconnected network. The phases were investigate by back-scattered electrons and EDX analysis. NiO and YSZ phases are recognized from the elements map shown in Figure 15. The morphology of the NiO crystals is recognized (8) and the NiO grains distribution result homogeneous.

Figure 14. FE-SEM micrography for NiO-YSZ obtained by liquid mixture sintered at 1350°C.

Figure 15. EDAX and micrography for NiO-YSZ obtained by the liquid mixture sintered at 1350°C.
CONCLUSIONS

Two chemical routes were developed to synthesize nanostructured NiO-YSZ powders. The sol-gel method allows the realization of oxides particles ranged in submicrometric scale, with uniform distribution of the elements. The material from the liquid mixture was obtained with chemical purity, and uniform distribution of each phase using a simple synthesis route. Different morphologies were observed for the NiO-YSZ powders obtained by the two methods, probably due to the differences in the starting materials. Very small grains of each phase, NiO and YSZ, can be achieved using both preparation methods. Both the two chemical routes seem to be promising for the preparation of ultra-fine NiO-YSZ powders for high performance SOFC anode applications.

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