

## Synthesis of nickel oxide - zirconia composites by coprecipitation route followed by hydrothermal treatment

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**Abstract.** Nickel oxide-yttria stabilized zirconia (NiO-YSZ) for use as solid oxide fuel cell anode were synthesized by coprecipitation to obtain amorphous zirconia and crystallized  $\beta$ -nickel gels of the corresponding metal hydroxides. Hydrothermal treatment at 200°C and 220 psi from 2 up to 16 hours, under stirring, was performed to produce nanocrystalline powder. The as-synthesized powders were uniaxially pressed and sintered in air. Powders were characterized by X-ray diffraction, laser scattering, scanning and transmission electron microscopy (SEM/TEM), gas adsorption technique (BET) and TG-DTA thermal analysis. Ceramic samples were characterized by dilatometric analysis and density measurements by Archimedes method. The characteristics of hydrothermally synthesized powders and compacts were compared to those produced without temperature and pressure application. Crystalline powders were obtained after hydrothermal process, excluding the calcination step from this route. The specific surface area of powders decreases with increasing time of hydrothermal treatment while the agglomerate mean size is not affected by this parameter.

### Introduction

Solid oxide fuel cells (SOFCs) is a promising device to generate electricity electrochemically with high conversion efficiency and low pollutant emission [1]. Transition metals are the best candidates for the SOFC anode materials because of their high catalytic activity and high stability in reducing atmospheres. Taking into account the volatility, chemical stability, catalytic activity for hydrogen reduction and cost, nickel appears to be the best candidate as a metallic anode [2]. However, the addition of ionic conducting electrolyte is necessary due to the differences between the thermal expansion coefficients of the electrolyte and the metal. It also assures a major improvement to oxygen ions migration from the electrolyte to the triple-phase boundary (TPB) [3,4]. Considering the above mentioned requirements, the most common anode material used in solid oxide fuel cells is Ni-YSZ ceramic-metallic composite. This material also has good electrochemical performance in the intermediate temperature fuel cells when used as supporting anode [5,6]. There are several methods for preparation of the Ni-YSZ composite such as mechanical alloying [7], gel precipitation [8], combustion [9] and coprecipitation synthesis [10,11]. Among these, the coprecipitation is a great alternative for anode manufacture, because it allows a mixture of precursors already in the solution, resulting in a gel with a high degree of chemical homogeneity that ensures a uniform distribution of nickel particles in the ceramics matrix [11]. However, when coprecipitation is employed for powder synthesis, gel treatments are necessary to reduce formation of hard agglomerates after drying and calcination. Submitting the gel to ethanol washing step, ethoxide groups attached to powder surface contribute to

the formation of the intra-agglomerate porosity which reduces bond strength between particles. Milling of calcined powders is another alternative to eliminate hard agglomerates. Several investigations suggest that the formation of strong interparticle bonds under hydrothermal conditions is greatly diminished or even avoided. This behaviour is due to the reduction of operation temperature (100 to 350°C) for oxide crystallization when high pressures are applied (few to 3000 psig) [12]. In this paper NiO-YSZ powders prepared by coprecipitation and submitted crystallization under hydrothermal conditions were evaluated. Powder properties, green compact structure and sinterability were compared with those obtained by coprecipitation followed by calcination and milling.

## Experimental Procedure

Zirconium oxychloride (IPEN, Brazil), yttrium chloride (prepared by hydrochloric acid dissolution of 99.99%  $Y_2O_3$  – Aldrich Chemical Co, USA) and nickel chloride (obtained by aqueous dissolution of 98% nickel chloride hexahydrate – Merck) solutions were the precursors used in this investigation for synthesis of a composite containing a mixture of 56wt% of nickel oxide and 44wt% of 8.5 mol% yttria stabilized zirconia. After coprecipitation [11], the resulting precipitate was divided into two parts. The first one was dried, calcined at 800°C for 1 hour and submitted to ball milling for 15 hours in ethanol media. In the second set of experiments gel portions were transferred to an autoclave (Parr Instruments, 4566 Mini Reactor) where hydrothermal ageing was performed at 200°C and 220 psi. Time of isothermal hydrothermal treatment was varied from 2 to 16 h under water medium and without additives. After autoclave cooling to room temperature, the product was separated by filtration and was dried at 80°C for 16 h. The resulting powders were ground in an agate mortar. All resulting experimental powders were uniaxial pressed under 25MPa to obtain green compacts of 5mm diameter and about 5 mm height. The samples were sintered at 1350°C for 1 h. with 10°C.min<sup>-1</sup> temperature rate. Powders were characterized by X-ray diffraction for phase identification, scanning electron microscopy (XL30, Phillips) for observation of agglomerate morphology, transmission electron microscopy (Jeol Jem 2100) for particle size measurement, laser scattering (granulometer 1064, Cilas) for agglomerate size distribution determination and gas adsorption (Nova 1200, Quantachrome) for surface area measurements. Thermogravimetric-differential thermal analysis (TG-DTA) of the composite was carried out using Setaram Labsys –TG/DTA, under dynamic air and heating rate of 10 C.min<sup>-1</sup>. Ceramic sinterability was evaluated by dilatometric analysis (Setaram Labsys –TMA) and apparent density measurements by the Archimedes method.

## Results and discussion

X-ray diffraction patterns of synthesized powders by coprecipitation followed by hydrothermal treatment (Fig. 1.A) show that the relative intensity of each phase has no significant change with time of ageing in autoclave and confirms the formation of  $\beta$ -Ni(OH)<sub>2</sub> polymorphic form that crystallizes in hexagonal system with brucite type structure and cubic yttria stabilized zirconia [13, 14]. On the other hand, as dried coprecipitated powders (Fig. 1.B.a) show the formation of a mixture of amorphous zirconia and crystallized  $\beta$ -Ni(OH)<sub>2</sub>. The calcined and milled coprecipitation powders (Fig. 1.B.c) show the formation of a mixture of rhombohedral nickel oxide and cubic yttria stabilized zirconia.

Fig. 2.A shows that agglomerate mean size of NiO-YSZ precursor powders is not influenced by hydrothermal treatment time in the range of 2-8 hours. NiO-YSZ powders calcined and milled presents the greater agglomerate mean size. The results of specific surface area are presented in Fig. 2.B which shows the decrease tendency of this property as time of hydrothermal ageing increases. Calcined and milled powders showed the lowest specific surface area (23.2 m<sup>2</sup>.g<sup>-1</sup>).

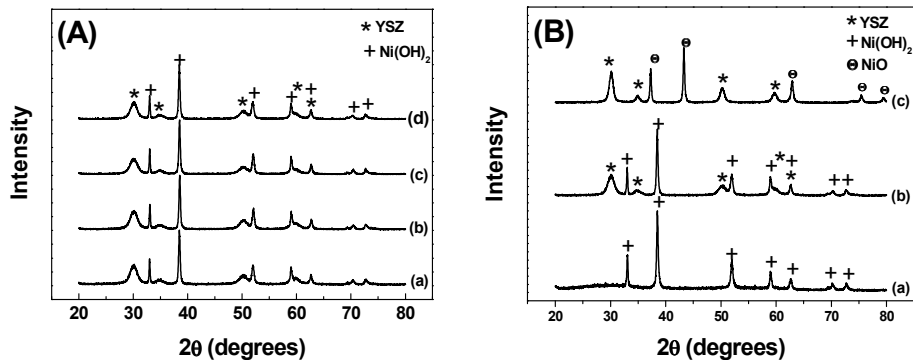


Fig. 1 - (A) XRD pattern of NiO:YSZ precursor powders as a function of hydrothermal treatment time: (a) 02, (b) 04, (c) 08 and (d) 16 hours. (B) - XRD pattern of as dried coprecipitated NiO:YSZ precursor powders (a), after hydrothermal treatment (b), and calcination and milling(c).

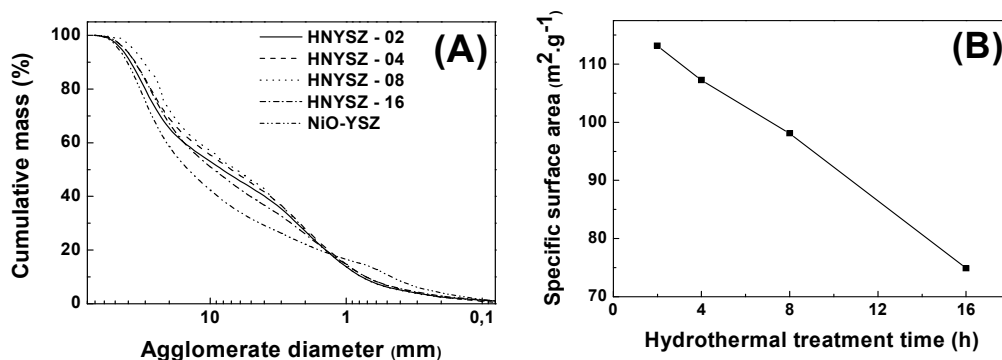


Fig. 2 – (A) Cumulative size distributions of NiO-YSZ powders obtained after calcination and milling and of  $\beta$ -Ni(OH)<sub>2</sub>-YSZ hydrothermally aged powders (HNYSZ samples), (B) Specific surface area of hydrothermally aged powders.

Fig. 3.A shows TG-DTA curves of  $\beta$ -Ni(OH)<sub>2</sub>-YSZ powder submitted hydrothermal treatment at 200°C for 16 h. The composite started to decompose at about 280°C. The major weight loss happened rapidly between 297 and 341 °C. The initial weight loss of about 5% represented the removal of the physically adsorbed water molecules. The followed weight loss of about 13% is caused by the decomposition of Ni(OH)<sub>2</sub> to NiO. The DTA curve shows an endothermic peak at 100°C due to evolution of absorbed water and a sharp endothermic peak at 336°C related to the decomposition of Ni(OH)<sub>2</sub> [ 15, 16].

The curve of the thermal decomposition of powders synthesized by coprecipitation (Fig. 3.B) shows two different stages: dehydration and further decomposition to NiO-YSZ. The first event of weight loss, corresponding to the removal of free water molecules and organic solvents, occurs slowly and gradually between 25 and 280°C. The second event that occurs in the range between 280°C and 380°C is associated to the removal of hydroxyl group linked to cations.

SEM and TEM micrographs of synthesized powders (Fig.4) show that samples of the two series are agglomerated with differences in particle size distributions. Those prepared by hydrothermal treatment have heterogeneous particle size distribution. Probably, larger particles size correspond to nickel

hydroxide and the smaller ones to YSZ. The homogeneous size distribution and spherical morphology of NiO-YSZ powders obtained in calcined serie may be a consequence of milling step.

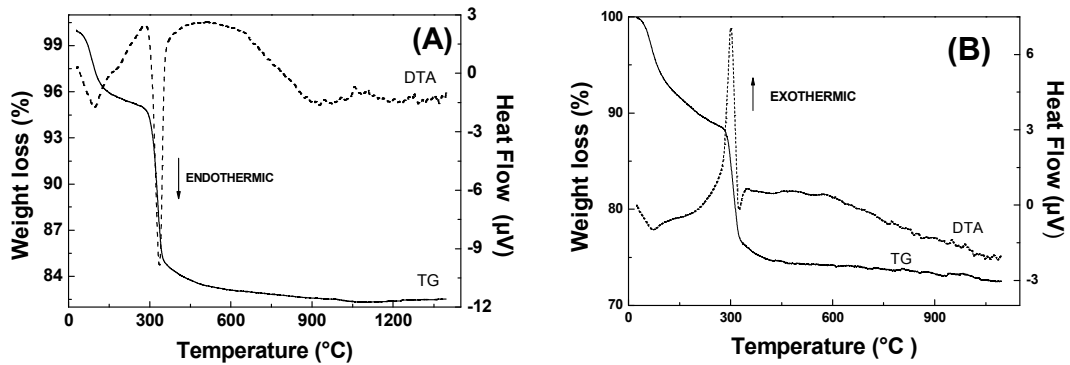


Fig. 3 – (A) TG/DTA curves of NiO-YSZ precursor powder: (A) submitted hydrothermal treatment at 200°C for 16 hours and (B) obtained after coprecipitation synthesis

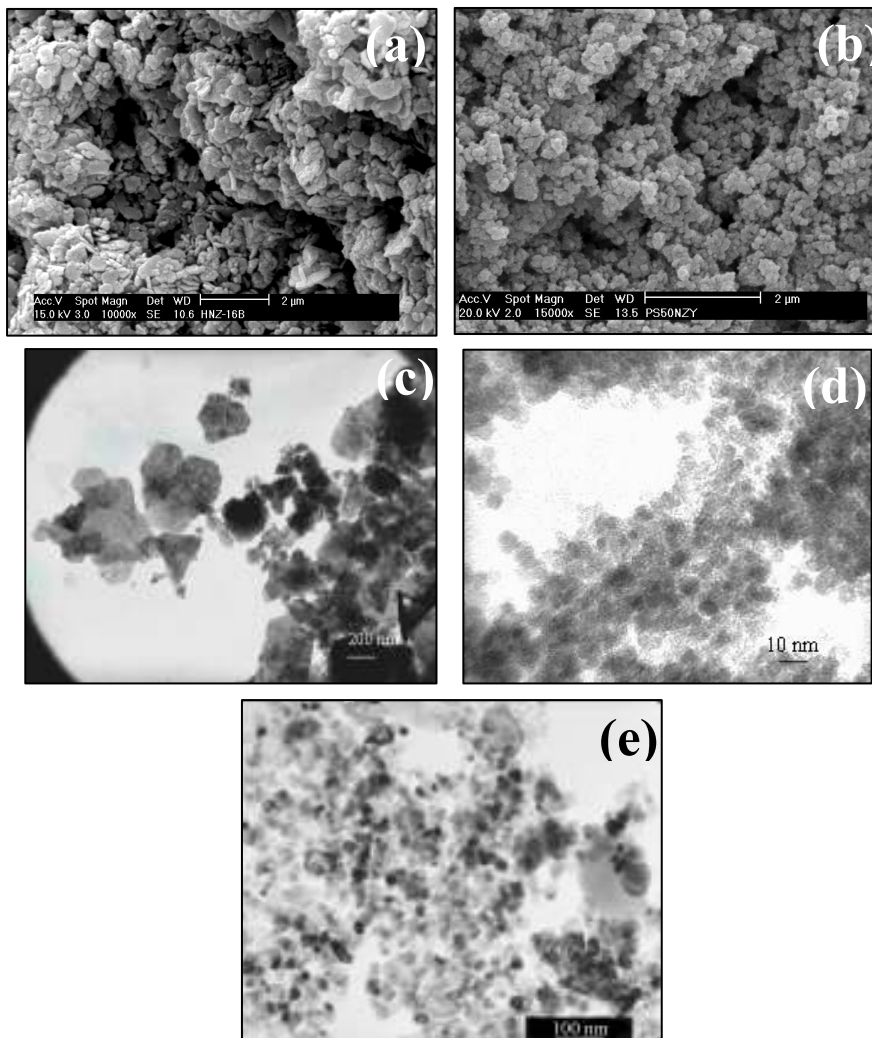


Fig.4 – SEM and TEM micrographs of synthesized powders :  $\beta$ -Ni(OH)<sub>2</sub>-YSZ hydrothermally aged powders (a, c and d) and NiO-YSZ obtained after calcination and milling (b and e).

Linear shrinkages and linear shrinkage rates of NiO-YSZ based ceramics, as a function of sintering temperature, are illustrated in Figs. 5 (A) and 5 (B). Samples prepared by hydrothermal ageing (H) shows a clear reduction of dimension between 300 and 400 °C due to transformation of Ni(OH)<sub>2</sub> to NiO. This behaviour was not observed for calcined powders (CP), which no shrinkage was detected until 1050°C. Maximum densification rates were observed at 1300°C for calcined powders and 1350°C for hydrothermal powders treated for 2 hours at 200°C. For others samples maximum densification rates occur above 1350°C and cannot be observed due to equipment limitations.

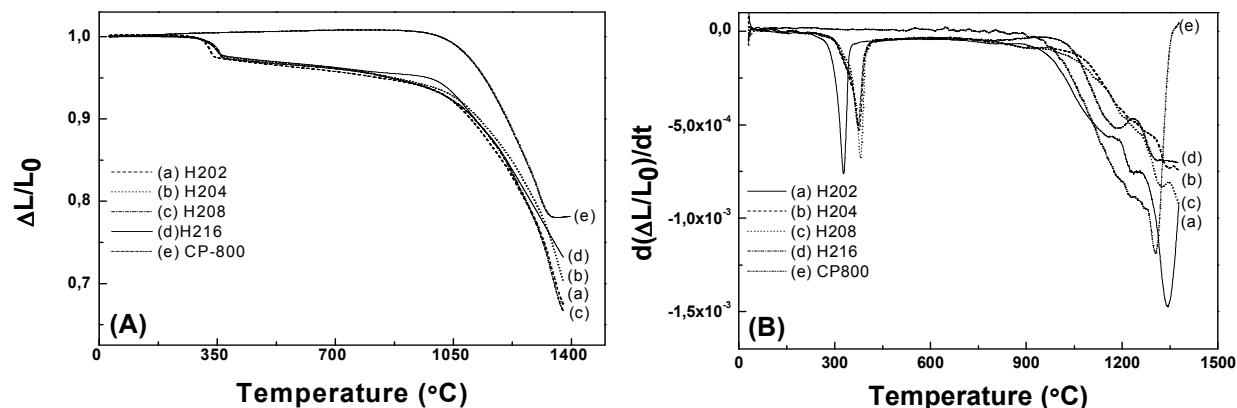


Fig. 5 – (A) Linear shrinkages of NiO-YSZ based ceramics as a function of sintering temperature and (B) Linear shrinkage rates of NiO-YSZ based ceramics as a function of sintering temperature.

The density evolution of NiO-YSZ ceramic samples sintered in air at 1350°C for 1 hour, as a function of hydrothermal treatment time, is shown in Fig. 7. Table 1 indicates that employing 16 hours of hydrothermal treatment at 200°C, density value is comparable to that obtained without hydrothermal treatment and calcining and milling (98%DT).

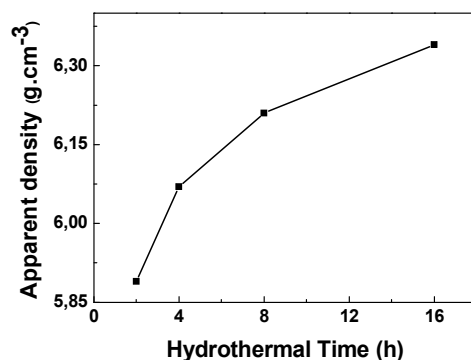


Fig. 7 - Apparent density of NiO-YSZ ceramic samples sintered in air at 1350°C for 1 hour, as a function of hydrothermal time.

Table 1 – Apparent and relative density of NiO-YSZ ceramics

Sample Code	Apparent density (g/cm <sup>3</sup> )	Relative density (%TD)
NiO-YSZ (calcining/milling)	6.35	98.4
HNYSZ-16 (hydrothermal treatment)	6.34	98.3

## Conclusions

The association of hydrothermal treatment to coprecipitation route allows the production of zirconia–nickel hydroxide nanometric powders crystallized at low temperatures (200°C). Transformation of nickel hydroxide to oxide may occur during sintering without deleterious effect to ceramics. The major advantage of this procedure is the elimination of calcining and milling from coprecipitation synthesis process, which requires the employment of high temperatures and greater electric power consumption. Density as high as 98% DT may be obtained for NiO-YSZ ceramics sintered at 1350°C. For SOFC application a lower sintering temperature can be employed considering that 40% of open porosity is needed to form a percolative network for hydrogen oxidation.

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## References

- [1] R.J. Gorte, J.M.Vohs: *Current Opinion in Colloid & Interface Science*, 14, (2009), p. 236
- [2] Bangwu Liu, Yue Zhang: *Journal of University of Science and Technology Beijing* Volume 15, Number 1, (2008), p. 84
- [3] A. Atkinson, S. Barnett, R.J. Gorte, J.T.S.Irvine, A.J. McEvoy, M. Mogensen, S.C. Singhal, J. Vohs: *Nat. Mater.* 3 (2004), p. 17
- [4] W.Z. Zhu, S.C. Deevi: *Mater. Sci. Eng. A*, 362 (2003), p.228
- [5] T. Setoguchi, K. Okamoto, K. Eguchi: *J. Electrochem. Soc.* 139 (1992), p. 2875
- [6] S.P. Jiang, S.H. Chan: *J. Mater. Sci.*, 39, (2004), p. 4405
- [7] F.Tietz, F. J. Dias, D. Simwonis, D. Stover, *J. Eur. Ceram. Soc.*, 20 (2000), p.1023
- [8] C.M. Grgicak, R.G. Green, W.F. Du, J.B. Giorgi, *J. Am. Ceram. Soc.*, 88 [11], (2005) 3081
- [9] W. K. Yoshito, M. A. Scapin, V. Ussui, D. R. R. Lazar, J.O.A. Paschoal: *Materials Science Forum* Vols. 591-593 (2008), p. 777
- [10] S. L. R. Guo, J.Li, Y. Chen, W. Liu: *Ceram. Int.* 29 (2003), p. 883
- [11] W. K. Yoshito, V. Ussui, D. R. R. Lazar, J. O. A. Paschoal: *Mater. Sci. Forum* 498-499 (2005), p. 612
- [12] E. P. Stambaugh: *Materials & Design*, Vol. 10, N° 4, (1989), p. 175
- [13] X. Wang, H. Luo, P. V. Parkhutik, A. – C. Millan, E. Matveeva: *J. Power Sources* 115 (2003), p.153
- [14] C.C. Yang: *Inter J. Hydrogen Energy* 27 (2002) p. 1071
- [15] E. Zhang, Y. Tang, Y. Zhang, C. Guo, L. Yang: *Materials Research Bulletin* 44 (2009), p. 1765
- [16] Zhen-Hua Liang, Ying-Jie Zhu, and Xian-Luo Hu: *J. Phys. Chem. B* 108, (2004), p. 3488