

Synthesis and characterization of NiO-8YSZ powders by coprecipitation route

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Abstract. Nickel oxide – 8 mol% yttria stabilized zirconia (NiO-8YSZ) powders containing 25 to 75 wt% of NiO were prepared by coprecipitation. The entire process includes the reaction of metals aqueous chloride solutions (heated at 95 °C) with ammonium hydroxide, washing steps of the resulting gel, butanol azeotropic distillation treatment to prevent the formation of hard agglomerates, drying, calcination and ball milling. The yield of precipitation of metals was determined by inductively coupled plasma atomic emission spectroscopy analysis (ICP-AES). Powders were characterized by X-ray and laser diffraction, infrared analysis, gas adsorption (BET) and scanning electron microscopy. It was observed that zirconium and yttrium hydroxides are easily precipitated in alkaline medium, while nickel precipitation yield is in the range of 80 to 95% due to the formation of soluble complexes. NiO appears as a second phase in synthesized powders and contributes to decreasing of specific surface area and agglomerate mean size.

Introduction

The incorporation of metallic nickel or nickel oxide particles in yttria stabilized zirconia (YSZ) ceramics has made possible the development of mixed ionic-electronic composites applied in solid state ionic devices such as solid oxide fuel cell electrodes and flow sensors [1-5]. Ni-YSZ can also be used as thermal barrier coating (TBC) to reduce the mismatch strains between the coatings and the metallic substrate [6]. The advantages in choosing NiO/Ni, as a second phase, include its low cost, the stability over a wide range of temperatures, the limited solubility in solid solution (< 2mol% at 1600 °C) and the absence of reaction products or intermediates phases [1-7].

In recent years, increasing efforts directed towards the development of NiO-YSZ synthesis and ceramic processing is due to the great interest in fuel cell technology for high efficiency, environmental friendly power generation. State-of-the-art anode for Solid Oxide Fuel Cells (SOFC) is a nickel-8 mol% yttria stabilized zirconia (Ni-8YSZ) composite, obtained by reduction in situ of NiO-8YSZ cermet. The nickel particles, forming a percolative network, have a high catalytic activity for hydrogen oxidation and are responsible for transporting electrons from the electrode reaction site to the external circuit. YSZ matrix supports nickel particles, inhibits coarsening by sintering during SOFC operation and gives a thermal expansion coefficient close to the other cell components [2-4].

Mechanical mixing of powders is the technique usually employed for the manufacture of NiO-YSZ anode [4]. However, a uniform distribution of nickel particles in the ceramic matrix is difficult to be assured as a consequence of differences in powder densities and size distributions. For a better control of anode microstructure, several techniques such as mechanical alloying [8], coprecipitation [9-11], polymeric precursors [12] and combustion [13, 14] have been proposed for synthesis of NiO-YSZ powders.

In the case of YSZ powders, coprecipitation of zirconium and yttrium hydroxides is the most important synthesis method for industrial scale, due to its simplicity, low cost and high efficiency

[15]. For this reason, the main purpose of this work is to establish a coprecipitation route to obtain high sinter-reactive NiO-YSZ powders with controlled chemical composition. Washing steps with organic liquids, azeotropic distillation technique and wet milling were also employed to reduce the state of agglomeration of calcined powders.

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) were the precursors used in this investigation. Nickel cation concentration was fixed at 0.1 molar and appropriate amounts of yttrium and zirconium solutions were mixed to produce a final composition corresponding to 8 mol% yttria stabilized zirconia containing 25 – 75 wt% NiO. Pure YSZ and NiO powders were also prepared for comparison purposes.

The coprecipitation reactions were carried out by spraying the mixed metal chlorides (heated at 95°C, excepted for YSZ sample) into vigorously stirred 7.5 molar ammonium hydroxide solution. After the precursor addition water was added twofold the final volume of mother liquor and the pH readjusted at 9.5. In order to enhance nickel precipitation, the resulting suspensions were reheated at 95°C with continuous stirring, cooled to room temperature and aged for 24 hours. The precipitates were filtered in vacuum and washed with distilled water to remove Cl^- ions. To avoid the formation of hard agglomerates the precipitates were washed with ethanol and submitted to a butanol azeotropic distillation treatment. The resulting powders were oven-dried at 80°C for 24 hours, calcined at 800°C for 1 hour and submitted to ball milling in ethanol for 15 hours using zirconia balls.

The chemical composition of coprecipitated products (dissolved in hydrochloric acid) was determined by inductively coupled plasma atomic emission spectroscopy analysis (Spectro Flame M 120E - Spectro Analytical). Nickel hydroxide crystal structure was analyzed by infrared spectroscopy (670 FT – IR, Nexus) and X-ray diffraction (D8 Advance, Bruker-AXS). Calcined and milled powders were characterized by X-ray diffraction for phase identification, scanning electron microscopy (XL30, Phillips) for observation of particle and agglomerate morphology, laser diffraction (granulometer 1064, Cilas) for determination of agglomerate size distribution, gas adsorption (Nova 1200, Quantachrome) for BET surface area measurements and helium pycnometry (Micromeritics, AccuPyc 1330) for density measurements.

Results and Discussion

Table 1 shows the yield of precipitation of metal cations and the sample chemical compositions. As expected, the experimental conditions allowed almost a total recovery of Zr^{4+} and Y^{3+} ions in the precipitates. This behavior is a consequence of selecting a higher pH (9.5) for the precipitation reactions. In hydrochloric medium, the formation of zirconium and yttrium hydroxides occurs at a pH range of 1.9 - 4.2 and at pH 6.78, respectively [16, 17]. Nickel hydroxide precipitates as a light green gel, with a yield between 78 – 95%. In this case, the ammonia excess, used to assure the coprecipitation of zirconium and yttrium hydroxides, contributes to lower the nickel hydroxide precipitation, due to the formation of a soluble nickel amino-complex ($[Ni(NH_3)_n]^{2+}$) that gives a blue color to the mother liquor [18].

Table 1: Yield of precipitation of zirconium, yttrium and nickel ions in mixed hydroxides and sample chemical compositions.

Sample code	Nominal composition	Yield of precipitation (%)			Real composition
		Zr ⁴⁺	Y ³⁺	Ni ²⁺	
YSZ	8YSZ	100	100	-	8YSZ
25NZY	25 wt% NiO : 8YSZ	99	100	87	22 wt% NiO : 8YSZ
50 NZY	50 wt% NiO : 8YSZ	97	100	78	39 wt% NiO : 8YSZ
75NZY	75 wt% NiO : 8YSZ	99	100	90	68 wt% NiO : 8YSZ
NiO	NiO	—	—	95	NiO

As-dried zirconium and yttrium coprecipitated gel is amorphous. Nevertheless, nickel hydroxide can exist in two polymorphic forms, α - and β -Ni(OH)₂, which transform to γ - and β -NiOOH by oxidation, respectively. These structures differ from each other in terms of their crystal structure, short-range structure and degree of hydration [19].

According to infrared spectra showed in Fig. 1a, after precipitation and drying, nickel hydroxide sample is obtained as β -Ni(OH)₂ [20]. Free hydroxyl bands are observed at 3640 and 520 cm⁻¹ while Ni-O lattice vibration appears at 460 cm⁻¹. Characteristic bands due to the presence of free hydration water and several adsorbed ions appear at 1640 cm⁻¹ and 1400 – 1500 cm⁻¹, respectively.

X-ray diffraction pattern (Fig. 1b) confirms the formation of β -Ni(OH)₂ due to the absence of (001) diffraction peak at $2\theta = 11^\circ$. As α -Ni(OH)₂, β polymorphic form crystallizes in hexagonal system with the brucite type structure. The main difference between these phases is related to the stacking of layers along the c-axis. For β -Ni(OH)₂, layers are perfectly stacked along the c-axis with an interlamellar distance of 4.6 Å; while for the α -Ni(OH)₂ layers are completely misoriented with the presence of water molecules and anionic species within the Van der Waals gap, resulting in a c-spacing of 7.5 Å. This feature explain the poor stability of α -Ni(OH)₂ in alkaline medium [21, 22].

X-ray diffraction patterns of the calcined and milled powders (Fig. 2) show the formation of a mixture of rhombohedral nickel oxide and tetragonal and /or cubic yttria stabilized zirconia for samples 25 – 75NZY. The relative intensity of each phase increases with the weight percentage.

Fig. 3 and Table 2 show that agglomerate mean size and specific surface area of oxide powders decrease with increasing NiO content, in the range of 0,80 - 0,15 μm and 60 – 20 m².g⁻¹, respectively. As can be observed by scanning electron microscopy (Fig. 4), the high specific surface area of YSZ sample is a consequence of reduced size of particles that constitute the agglomerates. NiO and NiO-YSZ powders are formed by sub-micrometric particles with a minor tendency to agglomeration. Powder densities increase with NiO addition.

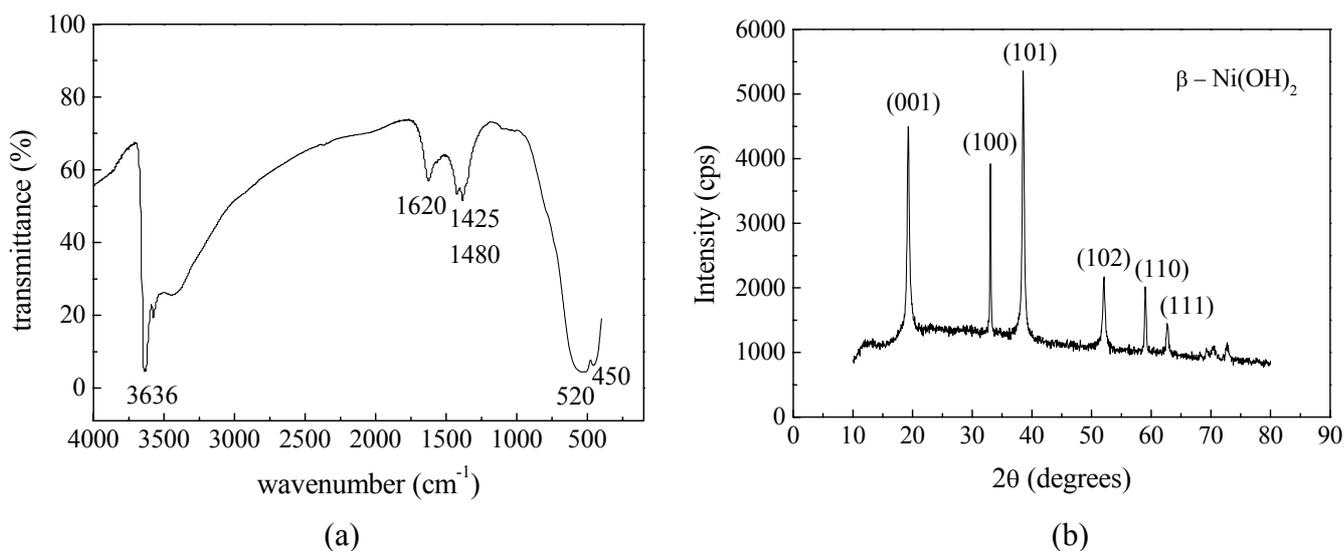


Fig. 1: Infrared spectra (a) and X-ray diffraction pattern (b) of as-dried nickel hydroxide sample.

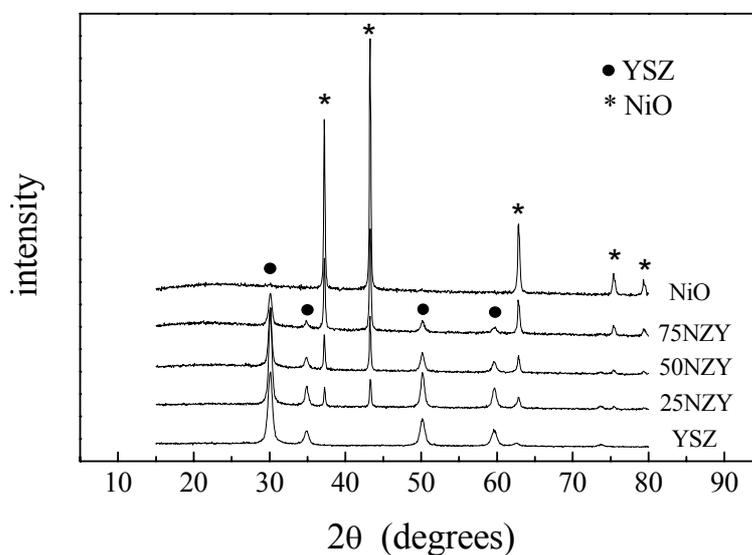


Fig. 2: X-ray diffraction pattern of calcined and milled YSZ, NiO and NiO-YSZ powders.

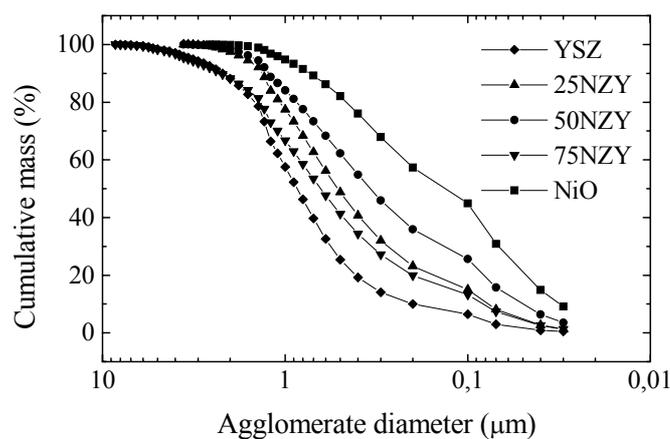
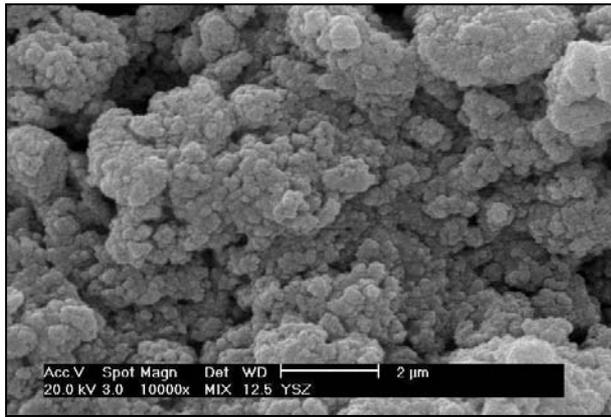


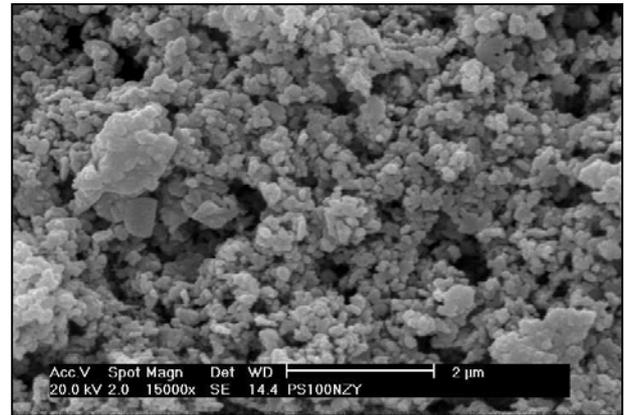
Fig. 3: Cumulative size distributions of calcined and milled YSZ, NiO and NiO-YSZ powders.

Table 2: Agglomerate mean size, specific surface area and density of calcined and milled YSZ, NiO and NiO-YSZ powders.

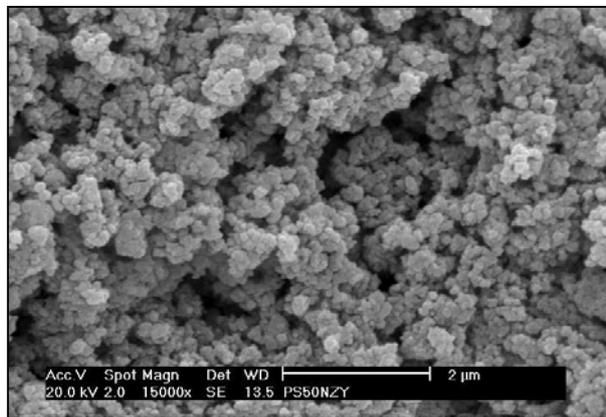
Sample	Agglomerate mean size (μm)	Specific surface area ($\text{m}^2 \cdot \text{g}^{-1}$)	Density ($\text{g} \cdot \text{cm}^{-3}$)
YSZ	0.80	60.2	5.34
25NZY	0.50	28.9	5.82
50 NZY	0.30	23.2	6.00
75NZY	0.60	16.0	6.40
NiO	0.15	20.1	6.52



(a)



(b)



(c)

Fig.4: SEM micrographs of YSZ (a), NiO (b) and 50 wt%NiO-YSZ (c) powders.

Conclusions

Coprecipitation has demonstrated to be a promising technique for synthesis of NiO-8YSZ powders. To overcome the difficulties related to the formation of nickel soluble complexes, the concentration of metals (zirconium, yttrium and nickel) in the starting precursors mixture has to take into account

the precipitation yield such chemical species. After washing steps, butanol azeotropic distillation treatment, calcination at 800 °C and ball milling, a submicron nickel oxide dispersed throughout a YSZ ceramic powder was produced.

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