Synthesis and characterization of NiO-YSZ for SOFCs

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ABSTRACT

Nickel oxide and yttria-stabilized zirconia ceramic materials were prepared by three methods: physical mixture, a modified Pechini route, and impregnation with $Ni(NO_3)_2 \cdot 6H_2O$. Temperature-programmed reduction (TPR) analysis showed the presence of different reduction peaks for each sample and that the reduction temperature was influenced by the employed preparation procedure. Nickel oxide species are completely reduced at temperatures up to 1000 °C and their temperature-programmed reduction profiles indicated that a higher temperature reduction corresponds to a higher calcination temperature. Furthermore, the composites synthesized through impregnation presented nickel oxide species more easily reducible than those prepared by the two other methods. Scanning electron microscopy and X-ray photoelectron spectroscopy (XPS) evidenced a larger nickel oxide coating on yttria-stabilized zirconia for the composite synthesized through the impregnation method. The electrical conductivity of impregnation sample was 117 S cm^{-1} at 850 °C, a value three times higher than that of the physical mixture.

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1. Introduction

Solid oxide fuel cells (SOFCs) have presently become a promising system for generation of electric power due to their high conversion efficiency, the possibility of internal fuel reform, and their low pollutant emission. Most present SOFC developers use yttria-stabilized zirconia (YSZ) as electrolyte, strontium-doped lanthanum manganite (LSM) as cathode and Ni-YSZ ceramic-metallic composite (cermet) as supported anode materials.

Ni-YSZ cermet is an electronic conductive material formed during the SOFC stack operation by the reduction of NiO-YSZ used at the anode site during cell fabrication process. NiO-YSZ is an insulating material and its complete reduction to Ni-YSZ is necessary to assure good anodic performance. Ni-YSZ cermets have been used as SOFC anodes mainly due to their high electronic conduction, good electrochemical performance in the intermediate temperature range (750–850 °C) and high catalytic activity in reform reactions and the comparatively low cost of nickel [1]. The addition of YSZ, which acts as a metal particle support to the cermet initially investigated by Spacil [2], is a major improvement due to the largely increased contact zone between the electrolyte and the anode layer. The cermet allows oxygen ions (O^{2-}) to migrate from the electrolyte to the triple-phase boundary (TPB) in a more efficient way. It also assures a more uniform particle dispersion and prevents a probable Ni coalescence. In addition, the anode thermal expansion coefficient is compatible with that of the electrode [3,4] and thus prevents cracking and peeling off during cell manufacture and operation [5]. Previous studies demonstrate that the stability and electrical conductivity of Ni-YSZ anodes depend on the amount of nickel and the anode microstructure. The factors associated to anode microstructure include the reciprocal particle size of nickel and YSZ, the degree of agglomeration, and the nickel particle distribution in the YSZ matrix [5–11].

The physical mixture method is currently used to produce NiO-YSZ for SOFC anodes. Although this method is simple, it normally results in a material with larger particle size distribution due to a large difference in powder density that can induce the separation of the NiO and YSZ particles. On the other hand, the milling and grinding processes, normally used to prepare a mixture in a fine state of division, can introduce contaminants from the abrasive material. To obtain a complete solid-state reaction, the good proximity of reactants and the homogeneous distribution of each species were necessary due to the diffusion-controlled process. Therefore, several other synthesis methods have been investigated to produce NiO-YSZ powder having fine Ni particles uniformly distributed in the anode material with the objective to improve the SOFC anode operation stability and electrical properties [12–17]. Among these methods, the Pechini [14,16] and wet impregnation

[17–19] routes can be mentioned. The Pechini route uses the ability of weak polybasic acids, as citric acid, to form chelates with metallic ions, such as zirconium and nickel cations. The chelates can undergo polyesterification when heated with a polyhydroxyl alcohol and form a solid polymer resin in which the cations are uniformly dispersed. This process permits to get some chemically uniform materials without segregation. In the study of heterogeneous catalysts, the wet impregnation process is often used, and a recent a review of Jiang [18] focuses on the development and application of wet impregnation techniques for the fabrication of high performance and nano-structured SOFC electrodes. NiO-YSZ powder prepared from impregnation presents uniformly dispersed and nano-structured NiO that are physically adsorbed on YSZ [18].

In this work, NiO-YSZ ceramic powders with a typical composition of 50 wt.% NiO-YSZ were prepared by three methods: physical mixture, a modified Pechini route and impregnation. These ceramic materials were investigated by Electron Scanning Microscopy (SEM), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR) and Impedance Spectroscopy (IS). The purpose of this work is to get better understanding under the influence of three preparation methods on NiO-YSZ ratio on the ceramic surface, the morphology and the microstructure. The distribution of NiO on the surface of YSZ and the Ni-YSZ ratio on the composites were investigated by SEM and XPS. The NiO-YSZ support interaction and the reducibility of NiO-YSZ to Ni-YSZ were evaluated by TPR and the composite electrical properties were studied by IS.

2. Experimental procedures

2.1. Preparation of samples

NiO-YSZ ceramic powders with 50 wt.% NiO and 50 wt.% YSZ composition were prepared using three methods. The YSZ $[(Y_2O_3)_{0.08}(ZrO_2)_{0.92}]$ powder was prepared by aqueous ammonium coprecipitation [20], in which $ZrOCl_2 \cdot 6H_2O$ (Vetec) and Y_2O_3 (Aldrich) were used as precursors. The resulting suspension was filtered, washed with deionized water, and calcined at 1350 °C for 4 h. The obtained powder was denoted as YSZ and used in the three composite preparation routes.

2.1.1. Modified Pechini method

An aqueous solution of $NiCl_2 \cdot 6H_2O$ (30 wt.% Vetec) was added to a solution of citric acid (CA, Vetec) and water in appropriate amounts to solubilize the acid components. The resulting solution was stirred and heated at 60 °C for 2 h. Ethylene glycol (EG, Synth) was added to the solution in a molar ratio of CA/EG = 1/4, followed by stirring and heating at 90 °C for 5 h. The previously prepared YSZ was added to the solution, stirred and heated at 90 °C for 2 h. Heating the mixture at 180 °C for 40 min yielded a brown mixture, which was placed in an oven at 160 °C for 5 h. The glassy brown solid obtained was ground and the resin was calcined at 700 and 1200 °C for 3 h.

2.1.2. Impregnation method

YSZ was added to the $Ni(NO_3)_2 \cdot 6H_2O$ solution (30 wt.%) and the mixture was stirred and heated for 2.5 h until it reached 100 °C. The green paste formed was placed in an oven for 7 h. The powder formed was ground in an agate mortar and calcined at 700 and 1200 °C for 3 h.

2.1.3. Physical method

NiO was prepared under the same synthesis conditions used to prepare NiO-YSZ via Pechini route. YSZ was mixed with NiO in the presence of ethanol and the mixture was stirred for 21 h. The powder formed was ground in an agate mortar and calcined at 700 and 1200 °C for 3 h.

2.2. Sample characterization

Sample crystallographic characterization was performed by X-ray diffraction (XRD) in a Rigaku diffractometer (GeigerflexModel, semiautomatic) equipped with Cu Kα radiation. NiO crystallite size was determined by Scherrer equation [21].

Scanning electron microscopy (JEOL JSM 840A) was used to characterize the morphology and the microstructure of the composite powders and to evidence the presence of NiO on the YSZ surface. The composite Ni-Zr ratio was investigated by X-ray photoelectron spectroscopy in an ESCALAB-220ixL equipment from VG Scientific using Al Kα radiation (1486.6 eV) and an analyzer pass energy of 20 eV. The measured area of the samples was approximately 4 mm × 4 mm with the analyzer set to "large area mode". The probe depth is limited to about 2–3 nm, which is the mean inelastic scattering length for photoelectrons.

Temperature-programmed reduction analysis was carried out in a Quantachrome (ChemBET 3000Model) system. All the samples were pretreated in an inert atmosphere at 350 °C for 2 h prior to recording of the first TPR run. A soda-lime trap was connected in line so as to remove any moisture released during the TPR runs. The NiO-YSZ samples were reduced under 5% hydrogen and nitrogen gas flow of 20 cm³/min by heating from 100 to 900 °C at a constant rate of 10 °C/min.

For XPS and electrical characterizations, calcined composite powder pellets were uniaxially compacted (BOVENAU hydraulic press) at 200 MPa and sintered at 1350 °C for 4 h. The sintered pellets presented average diameter and thickness of 1.07 and 0.15 cm, respectively.

The impedance of the pellets was measured by two typical electrode methods at 25 °C under open circuit conditions using an Autolab PGSTAT302 potentiostat/galvanostat combined with a FRA2 impedance module and a computer. The electrical measurements were used to record the ohmic resistance. The impedance spectra in the frequency range from 1 MHz to 0.01 Hz were taken with signal amplitude of 5 mV. Before the electrical measurements, the pellet sides were coated with platinum and sandwiched between two platinum electrodes. During the experiments, highly pure nitrogen was flowed in the measurement apparatus.

3. Results and discussion

NiO-YSZ composites calcined at 700 and 1200 °C were characterized by XRD (Fig. 1). The diffractograms present peaks relative to the crystalline structures of NiO and YSZ (cubic structure), which evidences that the materials did not react at these temperatures. As can be noted, the peaks of the composites treated at 1200 °C are narrower, which indicates the larger crystallinity for the phases obtained. Table 1 presents the crystallite size of NiO from composites calcined at 700 and 1200 °C. Powders treated at 1200 °C presented a larger crystallite size due to particle coalescence effects.

The homogeneity of the NiO-YSZ composite is very important for the stability of the anodic material. Literature studies [14,22] report that the chemical synthesis methods result in materials more homogeneous than those obtained by physical mixture. Durán et al. [14] used the modified Pechini method and obtained more uniform NiO and YSZ particles in the preparation of NiO-YSZ composites when compared to those obtained by physical mixture and combustion methods [6,23,24]. Gong and co-workers [22] used the coprecipitation method and buffer solutions to produce NiO-YSZ composites. The materials obtained by this synthesis
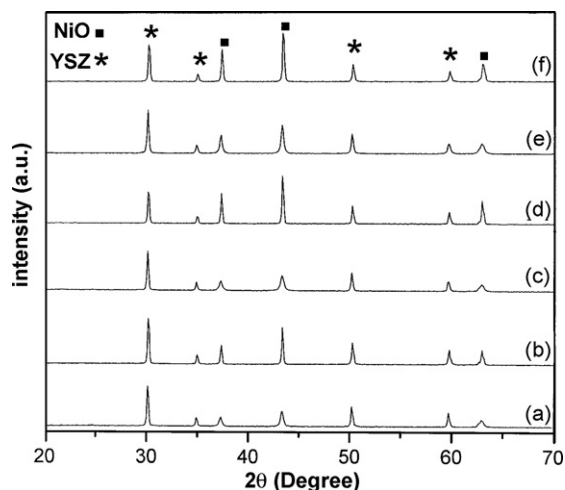
Fig. 1. XRD patterns of NiO-YSZ composite powders synthesized: by physical mixture and calcined at 700 °C (a) and at 1200 °C (b); by modified Pechini and calcined at 700 °C (c) and at 1200 °C (d); by impregnation and calcined at 700 °C (e) and at 1200 °C (f).

procedure present more uniform NiO distribution than the physical mixture methods, which influences the material conductivity. SEM micrographs of NiO-YSZ composites obtained for the three preparation methods are shown in Fig. 2. The images show the difference in the NiO particle magnitude and the formation of YSZ agglomerates with particles of the order of magnitude of 3.0 μm. The NiO particle size obtained by impregnation was of the order of magnitude of 0.8 μm, while the modified Pechini and physical mixture methods resulted in equal magnitudes of the order of 2.3 μm. Due to the large size of YSZ particles, very little surface area was available for NiO recovery and most NiO particles interacted with each other. The extension of YSZ surface coating by NiO could not be entirely clarified, but the impregnation synthesis method of NiO particles onto YSZ seems to lead to a larger coating than the physical mixture and modified Pechini methods, thus being the most efficient of the methods studied here. Jiang et al. [25] showed that the synthesis of Ni-YSZ cermet by impregnation inhibits grain growth of the Ni phase in the cermet and leads to Ni particles below ∼2 μm.

XPS has been extensively used to characterize nickel films deposited onto a variety of supports [26,27]. The interaction of nickel layers with ZrO_2 substrate [28] and the formation of NiO from exposure of the YSZ-supported nickel metal films to oxygen has been studied by this technique [29,30]. In the present work, XPS was used in order to calculate the Ni-Zr ratio on the surface of NiO-YSZ composites prepared by three different methods. Fig. 3 presents XPS spectra of Ni $2p_{3/2}$ with the respective satellites (sat) obtained for composites synthesized by physical mixture (Fig. 3a), modified Pechini (Fig. 3b), and impregnation (Fig. 3c) routes. The observed satellites are attributed to the electronic excitations from level 3d to 4s [31]. Fig. 4 presents XPS spectra of Zr $3p_{3/2}$ for the

Table 1
Size of NiO crystallites of composites synthesized by the three synthesis methods and calcined at different temperatures

Crystallite sizes (nm)					
Composite calcined at 700 °C			Composite calcined at 1200 °C		
Physical mixture	Pechini	Impregnation	Physical mixture	Pechini	Impregnation
47	30	10	(*)	(*)	58

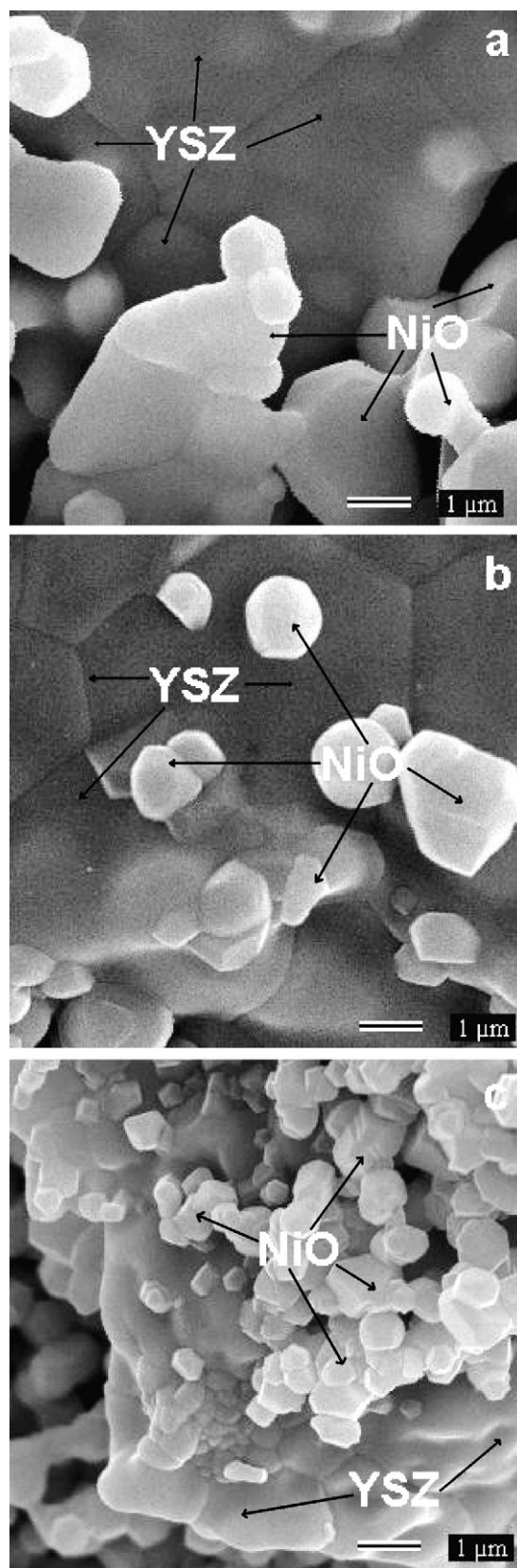Uncertainty: 10%. (*) For particle size over 0.2 μm, the method is not applicable.

Fig. 2. SEM micrographs of NiO-YSZ composites synthesized by physical mixture (a), modified Pechini (b), and impregnation (c) methods.
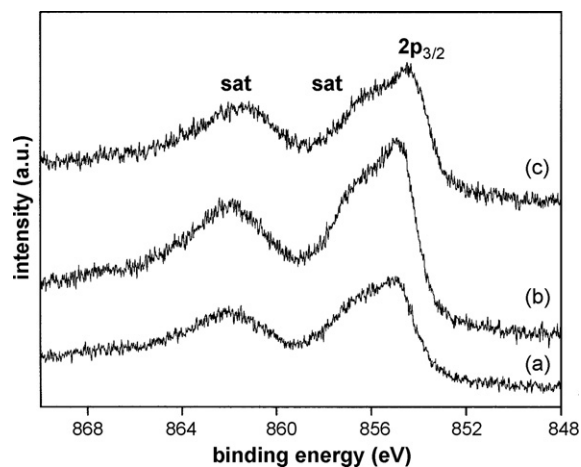
Fig. 3. XPS of Ni $2p_{3/2}$ of composites synthesized by physical mixture (a), modified Pechini (b), and impregnation (c) methods.

synthesized composites as prepared by the three methods. The peak areas of the Ni $2p_{3/2}$ line (and its satellites) and of the Zr $3p_{3/2}$ line were used to quantify the relative atomic concentrations of nickel and zirconium (C_{Ni}/C_{Zr}) according to the method described by Briggs and Seah [32] and with nickel and zirconium level sensitivity factors of 14.61 and 5.14 eV [33], respectively. Peak areas are presented in Table 2, as well as the C_{Ni}/C_{Zr} results.

Our results show that the physical mixture composite presented approximately the same amount of Ni and Zr on its surface (C_{Ni}/C_{Zr} = 1.4). The composites synthesized by modified Pechini and impregnation methods presented Ni-Zr ratios of 4 and 6, respectively. Therefore, the impregnation method yields more NiO on the YSZ surface, thus corroborating the SEM results.

Several TPR studies have been made to understand the interaction of different metal oxides with diverse supports [17,34–36], where the reduction temperatures are associated to the chemical interaction of the oxidized species with the corresponding support. At low temperatures, the most dispersed species having weak interaction surface are initially reduced while the species in closer interaction with the support are reduced at higher temperatures. In this work, the TPR technique was used to analyze the reduction temperature of NiO species and their interaction with the YSZ substrate. Mori et al. [17], studying the interaction between NiO and YSZ in the NiO-YSZ composite, found five peaks, four of them at temperatures lower than 900 °C, like in
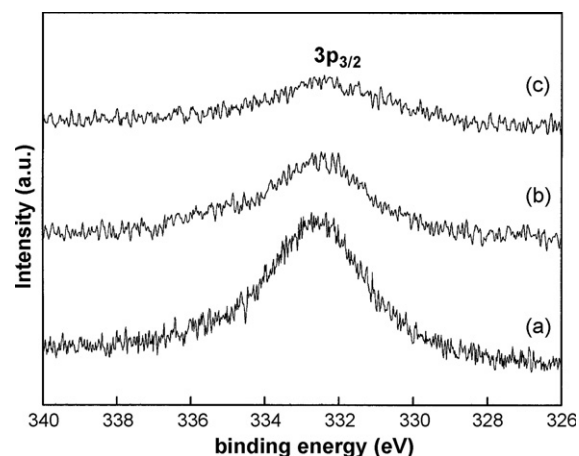

Fig. 4. XPS of Zr $3p_{3/2}$ of composites synthesized by physical mixture (a), modified Pechini (b), and impregnation (c) methods.

Table 2
Values of peak areas of Ni $2p_{3/2}$ and Zr $3p_{3/2}$ lines and values of atomic concentration ratios (C_{Ni}/C_{Zr}) of the NiO/YSZ composites prepared by the three synthesis methods

Preparation method	Peak areas (count. eV)		at. Concentration ratio
	Ni	Zr	C_{Ni}/C_{Zr}
Physical mixture	5252	1289	1.4
Pechini	9589	778	4.3
Impregnation	8369	472	6.2

our case. These peaks are associated with distinct NiO species at different levels of interaction with YSZ, when the percentage of NiO is about 5% in weight. Each of the four NiO species was assigned as follows: Peak I: NiO species with bulk-like property or weakly interacting with YSZ; Peaks II and III: these species are located on the surface of YSZ and interacted strongly with YSZ; Peak IV: NiO species incorporated in YSZ support. The reduction of this species is limited by the mass transfer rate in the solid. When the content of NiO was higher (61%), they obtained one broad peak, which involves the four previously described.

In Figs. 5 and 6 are presented the TPR profiles of the composites synthesized by the three routes and calcined at 700 and 1200 °C, respectively. As YSZ does not present any reduction peak at the analyzed temperature range, the TPR profile peaks are attributed to the reduction of different NiO species present in the composite. To evaluate the existence of the different NiO species, a Gaussian deconvolution analysis of the TPR profile was realized and the resulting reduction peaks were plotted (Figs. 5 and 6). For the three composites, four reduction peaks can be seen at different temperatures due to the presence of different oxide species. Table 3 shows the temperature obtained at the maximum of each reduction peak.
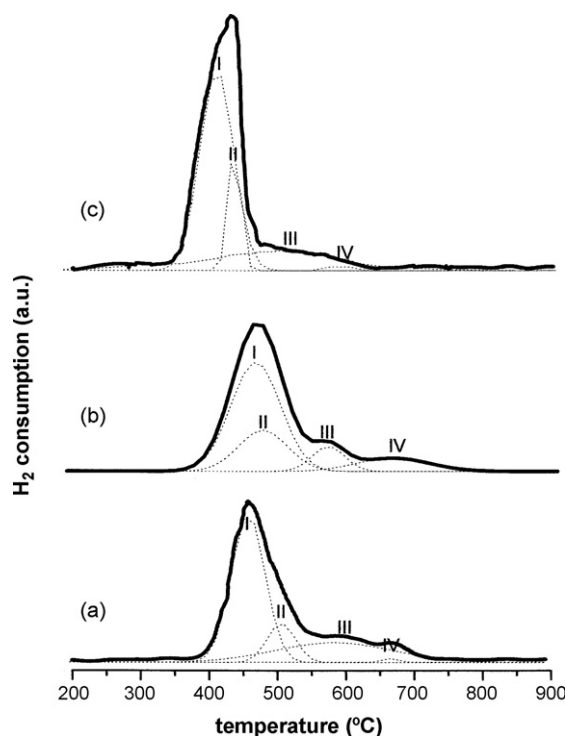

Fig. 5. (—) TPR profiles of NiO-YSZ synthesized by physical mixture (a), modified Pechini (b), and impregnation (c) methods and calcined at 700 °C. (- - -) Gaussian deconvolution of TPR profiles.
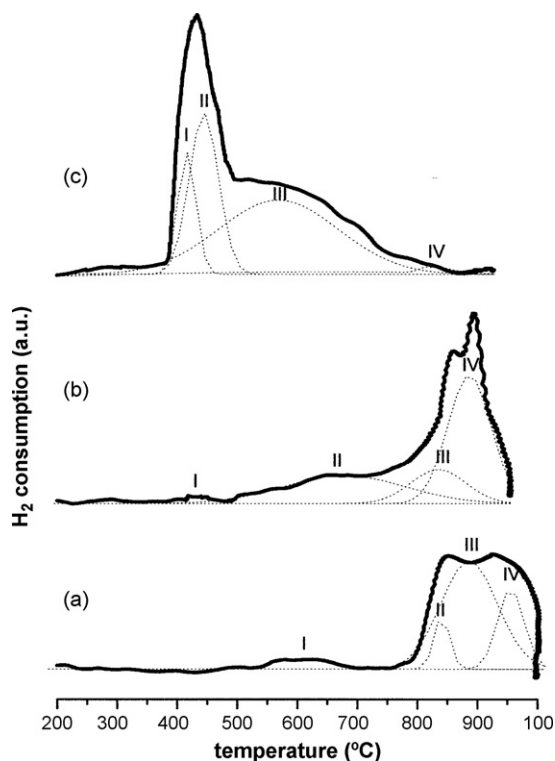
Fig. 6. (—) TPR profiles of NiO-YSZ synthesized by physical mixture (a), modified Pechini (b), and impregnation (c) methods and calcined at 1200 °C. (- - -) Gaussian deconvolution of TPR profiles.

The composites synthesized by impregnation and calcined at 700 and 1200 °C presented NiO species more easily reducible than those composites synthesized by physical mixture and modified Pechini methods. The reduction temperatures are also dependent on the calcination temperature. Ni composites calcined at 1200 °C present reduction temperatures higher than those treated at 700 °C due probably to a stronger interaction between NiO and YSZ. This behaviour has been described by other authors [14,17]. SEM shows rather similar images for the composites obtained by the modified Pechini method and the physical mixture methods (Fig. 2a and b). This explains the resemblance of the TPR profiles obtained. The modified Pechini method is a chemical synthesis route and a high interaction between NiO species and YSZ is expected.

Our SEM analysis revealed that the impregnation route resulted in YSZ species more extensively coated by NiO than those from the other synthesis methods, thus greatly favouring the interaction between NiO and the surface of YSZ. For the other samples, most of Ni oxides species seem to be inside YSZ, i.e. in the bulk of the composite, and consequently their reduction will be at higher temperatures. Furthermore, the particle size of Ni oxide species is smaller for the impregnated samples, also favouring their reduction. Thus, two factors are important to compare the reducing species types and the interaction of similar samples with a competition between them: (a) the quantity of this species on the surface and (b) the particle size. DRX, SEM and XPS analysis are in accordance with these results.

According to the impedance measurements, the electrical conductivity values of the pellets prepared from physical mixture, modified Pechini route, and impregnation powders were 40, 103 and 117 S cm^{-1}, respectively. These results show a high value of electrical conductivity for all samples [12]. The electrical conductivity of the pellets is due to the interconnecting network of Ni particles, which seems to be slightly better for the impregnation route.

4. Conclusions

The methods studied here for the synthesis of NiO-YSZ composites, physical mixture, modified Pechini, and impregnation were successfully used to produce powders with crystallographic, morphological and microscopy characteristics suitable for use in SOFC anodes.

Although the physical mixture and the modified Pechini routes promoted a stronger interaction between NiO and YSZ, the impregnation method led to a larger NiO coating on the YSZ surface and the NiO species obtained from this method are more easily reducible than from other, regardless of the calcination temperature used. This later factor can be considered as a great advantage once the reduction of NiO particles is made in situ in the beginning of cell operation and, in this case, the reduction process should be easier. It was verified that the NiO and YSZ particle sizes influence the composite reduction behavior more than the synthetic route. At 850 °C, the three studied samples present higher electrically conducting values as compared with those in the literature. Among the samples prepared here, those from impregnation route present values of about three times higher than the samples prepared by physical mixture.

References

[1] T. Setoguchi, K. Okamoto, K. Eguchi, J. Electrochem. Soc. 139 (1992) 2875.
[2] H.S. Spacil, Electrical device including nickel-containing stabilized zirconia electrode, US Patent 3 558 (1970) 360.
[3] J. Mizusaki, S. Tsuchiya, K. Waragai, H. Tagawa, A. Yoshihidi, Y. Kuwayama, J. Am. Ceram. Soc. 79 (1996) 109.
[4] G.E. Pike, C.H. Seager, J. Appl. Phys. 48 (1997) 5152.
[5] C.H. Lee, H.Y. Lee, S.M. Oh, Solid State Ion 98 (1997) 39.
[6] N.Q. Minh, J. Am. Ceram. Soc. 76 (1993) 563.
[7] Y.M. Park, G.M. Choi, Solid State Ion. 120 (1999) 265.
[8] D.W. Dees, T.D. Clark, T.E. Easler, D.C. Fee, F.C. Mrazek, J. Electrochem. Soc. 134 (1978) 2141.
[9] S. Primdahl, M. Mogensen, J. Electrochem. Soc. 144 (1997) 3409.
[10] J. Abel, A.A. Kornyshev, W. Lehnert, J. Electrochem. Soc. 144 (1997) 4253.
[11] T. Kawada, N. Sakai, H. Yokokawa, M. Dokiya, M. Mori, T. Iwata, J. Electrochem. Soc. 137 (1990) 3042.
[12] M. Marinsek, K. Zupan, J. Maeek, J. Power Source 106 (2002) 178.
[13] A. Li, R. Guo, J. Li, Y. Chen, W. Liu, Ceram. Int. 29 (2003) 883.
[14] P. Durán, J. Tartaj, F. Capel, C. Moure, J. Eur. Ceram. Soc. 23 (2003) 2125.
[15] T. Fukui, S. Ohara, M. Naito, K. Nogi, Power Tech. 132 (2003) 52.
[16] M.P. Pechini, Method of preparing lead and alkaline earth titanates and niobates and casting methods using the same to form a capacitor, US Patent 3 330 (1967) 697.
[17] H. Mori, C. Wen, J. Otomo, K. Eguchi, H. Takahashi, Appl. Catal. A 245 (2003) 79.
[18] S.P. Jiang, Mater. Sci. Eng. A 418 (2005) 199.
[19] K.R. Han, Y. Jeong, H. Lee, C.-S. Kim, Mater. Lett. 61 (2007) 1242.

Table 3
Reduction temperature obtained from the maxima of the deconvolution curves (Figs. 5 and 6) of NiO present in the composites calcined at 700 and 1200 °C

Preparation method	Reduction peaks (°C) of NiO-YSZ calcined at 700 °C				Reduction peaks (°C) of NiO-YSZ calcined at 1200 °C			
	I	II	III	IV	I	II	III	IV
Impregnation	410	437	480	580	415	450	565	830
Pechini	465	478	580	670	430	680	830	890
Physical mixture	460	500	580	680	620	830	900	950

[20] A.P. Santos, Síntese e caracterização de zircônias estabilizadas com uma mistura de terras-raras de origem brasileira, Federal University of Minas Gerais, Brazil, Master, 1993.
[21] A.K. Cheethan, P. Day, Oxford Sci. Pub. Oxford (1957) 80.
[22] Y. Li, Y. Xie, J. Gong, Y. Chen, Z. Zhang, Mater. Sci. Eng. B86 (2001) 119.
[23] S.J. Kim, W. Lee, W.J. Lee, S.D. Park, J.S. Song, E.G. Lee, J. Mater. Res. 16 (2001) 3621.
[24] S.T. Aruna, M. Muthuraman, K.C. Patil, Solid State Ion 111 (1998) 45.
[25] S.P. Jiang, Y.Y. Duan, J.G. Love, J. Electrochem. Soc. 149 (2002) 1175.
[26] M.C. Wu, P.J. Moller, Surf. Sci. 279 (1992) 23.
[27] B. Ealet, E. Gillet, V. Nehasil, P.J. Moller, Surf. Sci. 318 (1994) 151.

[28] D. Sotiroposlou, S. Ladas, Surf. Sci. 408 (1998) 182.
[29] S. Zafeiratos, S. Kennou, Surf. Sci. 482 (2001) 266.
[30] S. Zafeiratos, S. Kennou, Surf. Sci. 532 (2003) 402.
[31] G.K. Wertheim, S. Hüfner, Phys. Rev. Lett. 28 (1972) 1028.
[32] D. Briggs, M.P. Seah, In: J. Wiley (Ed.), Practical Surface Analysis—Auger and X-Ray Photoelectron Spectroscopy, vol. 1, 1996.
[33] Handbook XPS and AUGER, Surface Science, FISONS Instruments, 1991.
[34] W.S. Dong, H.S. Roh, K.W. Jun, S.E. Park, Y.S. Oh, Appl. Catal. A 226 (2002) 63.
[35] W.P. Dow, Y.P. Wang, T.J. Huang, J. Catal. 160 (1996) 155.
[36] Y. Zhang, B. Liu, B. Tu, Y. Dong, M. Cheng, Solid State Ion 176 (2005) 2193.