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Physico-chemical characterization of NiO/YSZ powders prepared by the citrate route

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NiO/YSZ powders prepared by the citrate route were characterized in order to check the effectiveness of this method for the preparation of materials suitable for solid oxide fuel cell application. Powders were obtained in the form of agglomerates of small YSZ and NiO particles (dimensions < 0.1 μm). Both stoichiometry of YSZ and NiO content derived by quantitative XRD analysis are consistent with the results of chemical analysis.

1. Introduction

The porous cermet Ni/YSZ is generally used as anode material in solid oxide fuel cells (SOFC). It displays better catalytic activity and has lower cost compared to other materials such as Ru/YSZ [1], CeO_2-based materials [2], transition metal oxide/YSZ solid solutions [3].

The electrochemical performance of the anode is generally improved by decreasing the YSZ particle size while the cell life is maximized by using a 50 wt% YSZ [4]. NiO particles must be uniformly distributed within the mixture in such a way that, after reduction, metallic nickel forms a fully connected net, ensuring maximum conductivity in the entire anode. Moreover, increasing the particle size of nickel results in decreasing the surface area of the metal and, consequently, the catalytic performance. Total reduction of NiO is prevented when large particles (diameter > 3 μm) are used [5]. To overcome these problems, various preparation methods have been proposed, including mechanical mixing of YSZ and NiO powders with the desired morphology, and chemical vapour deposition of nickel on YSZ, but no information is available on the characteristics of powders prepared by the so-called "wet chemical methods". This is quite surprising when considering the potentiality of these methods in preparing powders with high interdispersion of the two phases. It is the aim of this work to evaluate the possibility of producing NiO/YSZ powders suitable for application in SOFC technology by using wet chemical methods.

2. Experimental procedure

2.1. Powder preparation

NiO/YSZ powders were prepared according to a two-steps method recently developed in our laboratories [6]. The first step consists in the preparation of a mixture of metal citrates, from an aqueous solution containing $ZrO(NO_3)_2$, $Y(OOCCH_3)_3$ and $Ni(OOCCH_3)_2$ and citric acid, with 2.1 citric acid/metals molar ratio. Solid precursors were obtained using (a) a rotary evaporator at 333–353 K, under reduced pressure, or (b) a spray dryer (Lab Plant 03) with a flow of 150–200 ml h^{-1} of solution at 533–553 K.

In the second step, precursors were calcined in air at 1173 K for 8 h to give the final materials.

2.2. Characterization

Chemical analysis was performed by ICP-AES technique, using a Jobin Yvon 38 II Plus spectrophotometer.

The morphology of the powders was checked by scanning electron microscopy (SEM) with a Philips PSEM500 microscope. A standard gold-coating technique was used to prevent electrostatic charging.

Intimate particle morphology was determined by transmission electron microscopy (TEM, Philips 420T microscope), equipped with STEM facility.

X-ray powder diffraction patterns (XRD) were recorded on a computer-controlled Siemens D-500 diffractometer, operating in the θ/θ mode, equipped with a scintillation detector. Data were collected stepwise in the $20° \leqslant 2\theta \leqslant 140°$ angular region, with 0.03° 2θ step size and 3 s accumulation time. CuK_α radiation ($\lambda = 0.154\ 178$ nm) was used. The diffractometer was carefully calibrated using silicon (NBS 640) as the reference standard.

2.3. Quantitative phase analysis

Quantitative analysis was performed by full-profile fitting of the XRD pattern (Rietveld analysis), taking advantage of the equation recently proposed by Hill and Howard [7]

$$W_i = S_i M_i Z_i V_i / \Sigma_j S_j M_j Z_j V_j \qquad (1)$$

where W_i is the weight fraction, S_i the Rietveld scale factor, M_i the formula weight, Z_i the number of formula unit per unit cell and V_i the unit cell volume for the ith phase.

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Refinement was perfomed by using the software package WYRIET [8], A PC version of the DBW3.2S program [9]. The peak shape was described by the pseudo-Voigt function with refinable gaussian contribution, the angular dependence of the peak full-width at half-maximum (FWHM) by Caglioti *et al.*'s equation [10]. The calculated peak intensity was distributed over three FWHM on either side of the peak centre and the contribution of both $K_{\alpha 1}$ and $K_{\alpha 2}$ radiation (2:1 intensity ratio) to the reflection profile was considered. Background intensity was defined by a cubic polynomial with refinable coefficients. Starting values of unit cell parameters were determined by least-squares fit to the interplanar spacing of single strong reflections selected in the XRD pattern; the stoichiometry derived from chemical analysis was initially assumed for YSZ. Iteration was stopped as the shift/standard deviation ratio was less than 0.3 for all the parameters (normally after 15–20 iterations).

3. Results and discussion

3.1. Structural analysis

The powders obtained are made up of cubic YSZ and NiO. Because zirconia and NiO may react to give metastable solid solutions, which decompose over 1273 K [11], the stoichiometry of YSZ and phase abundance must be checked in relation to the overall chemical composition of the material. In fact, in the case of reaction, modification of electrical and mechanical properties of anode should be expected, owing to the decrease of nickel content and to the variation of thermal expansion coefficients.

Determination of YSZ stoichiometry may take advantage of the Vegard's type relationship between the unit-cell dimension of YSZ and yttria content. Owing to the significant discrepancies between the data reported in the literature [12, 13], the following equation was used, derived from data obtained on YSZ samples prepared in our laboratories [14]:

$$a = 0.000190[Y_2O_3] + 0.51225\,\text{nm} \qquad (2)$$

The effectiveness of the method was tested on samples prepared by mechanically mixing known amounts of YSZ (8 mol % Y_2O_3, from Nissan) and NiO (Carlo Erba). A very good fit of the XRD pattern was obtained (Fig. 1), with a resulting good agreement between the expected phase abundance and that determined by Equation 1 (Table I). Application of the

TABLE I Quantitative XRD results for standard NiO/YSZ mixtures

NiO (wt %)	YSZ (wt %)	S(NiO)[a] (× 10²)	S(YSZ)[a] (× 10²)	W(NiO) (wt %)	W(YSZ) (wt %)
25	75	0.644	0.625	25.4	74.6
		0.644	0.625	25.4	74.6
50	50	1.610	0.505	51.3	48.7
		1.610	0.507	51.2	48.8
75	25	2.830	0.303	75.5	24.5
		3.001	0.314	75.9	24.1

[a] $(MZV)_{NiO} = 21\,803$, $(MZV)_{YSZ} = 66\,047$ (see Equation 1).

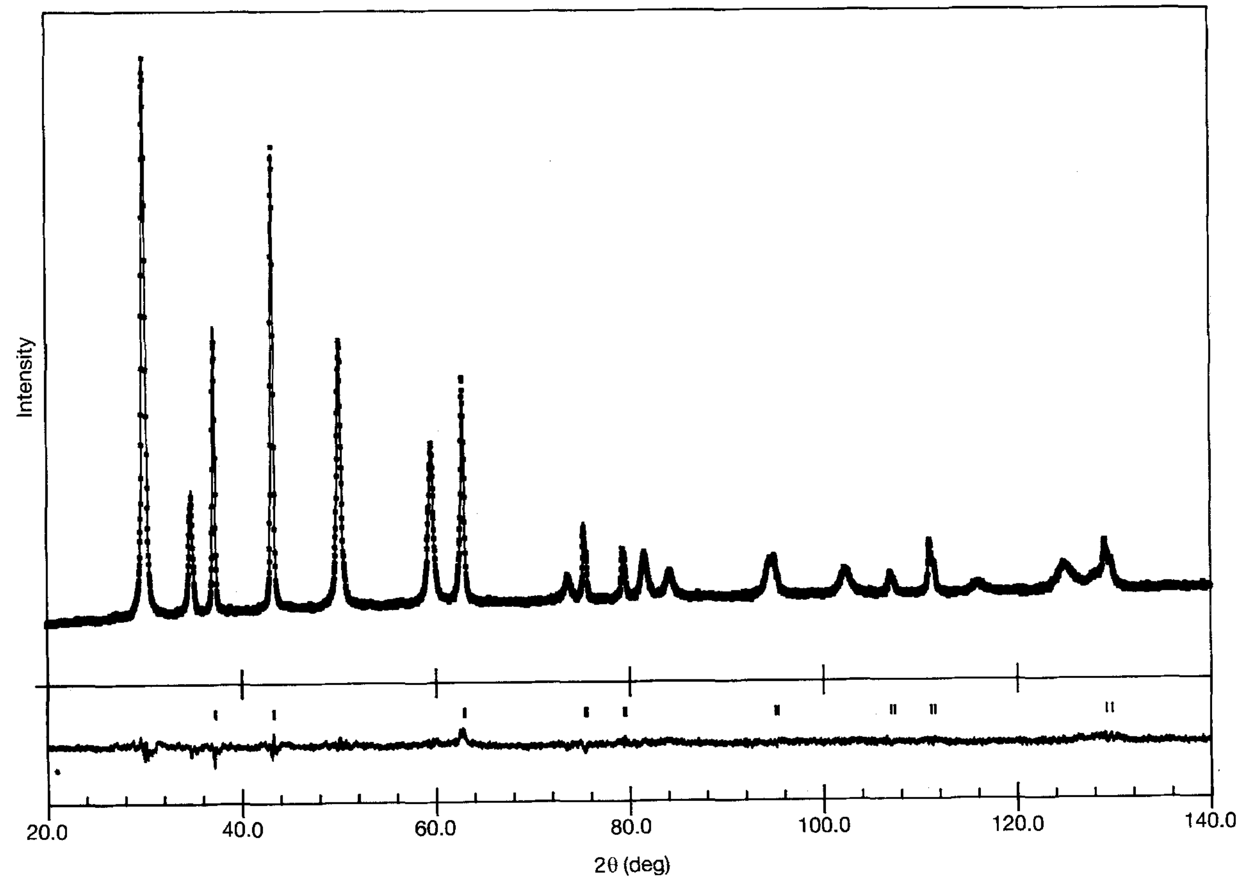

Figure 1 (■) Experimental, (——) calculated and (bottom) difference trace of X-ray diffraction pattern of an NiO/YSZ mixture (50/50 wt %). Vertical bars indicate the position of Bragg reflections of NiO.

TABLE II Analytical and crystallographical data for NiO/YSZ samples

Sample	Chemical analysis (wt %)			a_{YSZ} (nm)	Y_2O_3 (mol %)		NiO (wt %)	
	Ni	Zr	Y		Anal.[a]	XRD	Anal.[a]	XRD
1	55.7	17.5	4.07	0.514 35(6)	10.7	11.1	71.9	73.0
2	56.1	17.6	4.05	0.514 25(5)	10.5	10.6	71.4	70.8
3	30.3	36.5	8.95	0.514 47(6)	11.2	11.8	38.6	39.0
4	27.0	41.0	7.48	0.513 74(4)	8.6	7.9	34.4	35.2
5	34.6	34.8	8.32	0.514 3(1)	10.9	10.8	44.0	44.7
6	51.4	24.1	5.62	0.514 19(5)	10.6	10.2	62.2	63.0
7	56.1	17.6	4.05	0.514 1(1)	11.0	9.7	72.6	74.1
8	18.6	47.2	10.93	0.514 13(2)	10.6	9.9	23.4	23.3
9	35.0	34.4	7.99	0.514 2(1)	10.7	10.3	44.1	43.6
10	49.1	24.5	5.64	0.514 35(8)	10.7	11.1	62.1	61.3
11	47.0	24.1	5.62	0.514 38(9)	10.6	11.3	59.8	61.7
12	47.3	23.9	5.53	0.514 09(6)	10.6	9.7	60.2	61.9
13	47.8	24.4	5.76	0.514 14(3)	10.6	10.1	60.8	61.2
14	40.4	29.8	6.88	0.514 12(2)	10.5	9.7	51.4	50.7
15	37.6	32.4	7.36	0.514 18(3)	10.5	10.3	47.8	49.0
16	50.4	22.1	5.04	0.514 32(2)	10.5	11.0	64.1	64.3
17	55.9	18.1	4.24	0.514 27(2)	10.8	10.7	71.7	70.6
18	53.3	21.8	4.53	0.514 02(3)	9.7	9.3	67.8	68.0
19[b]	42.9	28.5	4.81	0.513 68(2)	8.0	7.6	55.0	56.5
20	44.2	28.5	5.15	0.513 77(3)	8.4	8.1	56.2	55.4

[a] Data reported are the average of three different evaluations; the deviation from the average values are: Ni < 0.3, Zr < 0.5, Y < 0.05 wt %.
[b] The sample contains 1.8 wt % monoclinic ZrO_2.

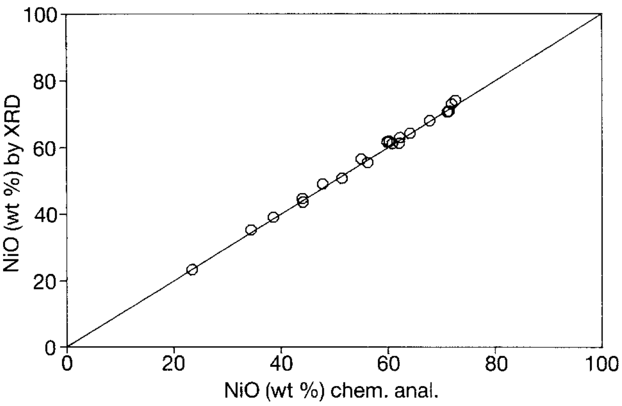

Figure 2 Comparison between NiO content determined by XRD and elemental analysis.

procedure to the analysis of samples produced by the citrate route gave YSZ stoichiometry and an NiO content in agreement with that expected on the basis of chemical analysis (Table II, Fig. 2).

3.2. Morphological analysis

Spherical agglomerates (1–10 μm in size) were observed in powders from precursors obtained from the spray-drier (Fig. 3a), irregular compact agglomerates (5–20 μm in size) in materials from the rotary evaporator (Fig. 3b). However, in both materials, X-ray maps (from STEM analysis) are indicative of very small (diameter < 0.1 μm) and very well interdispersed NiO and YSZ particles (Fig. 4a–c).

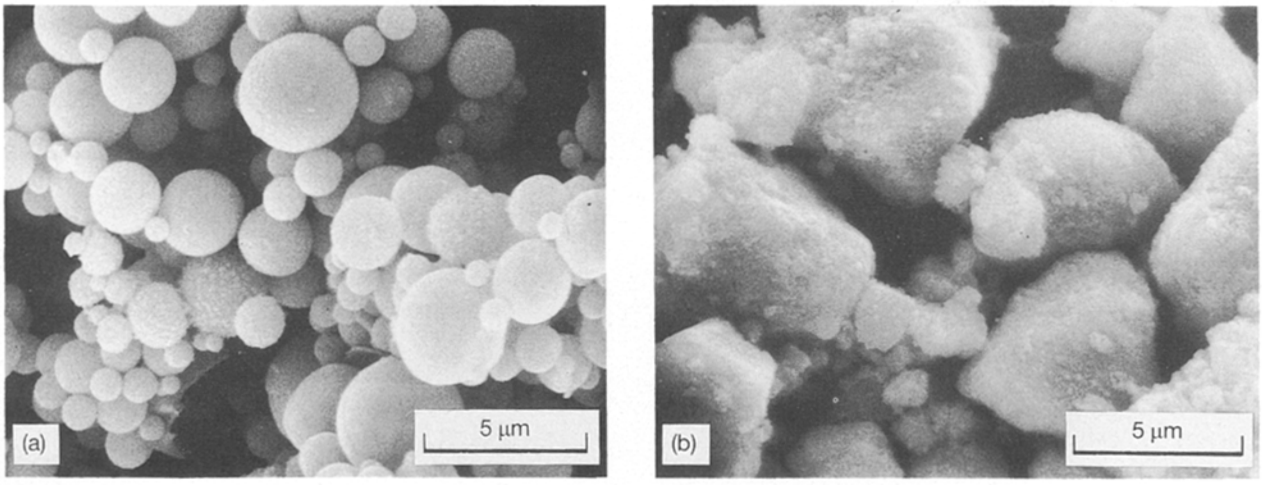

Figure 3 Typical morphology of NiO/YSZ powders obtained from (a) the spray drier and (b) rotary evaporation.

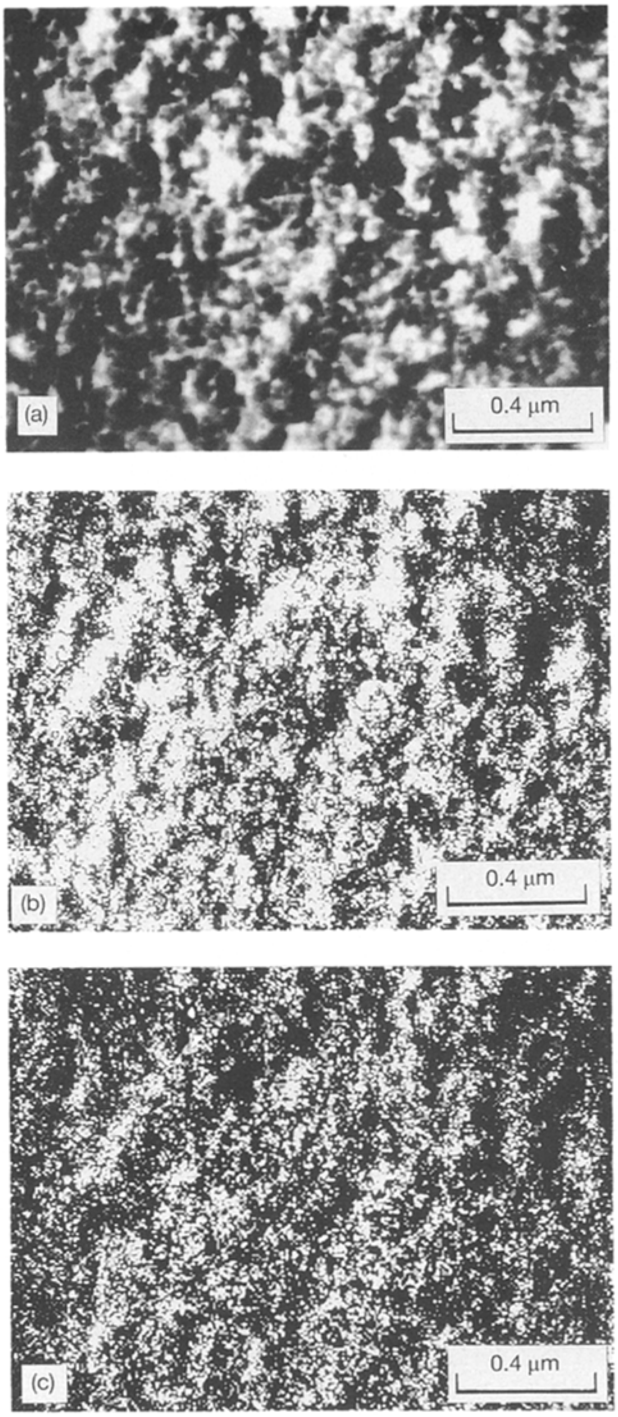

Figure 4 (a) Transmission electron micrograph, and X-ray maps showing the typical distribution of (b) nickel and (c) zirconium in NiO/YSZ samples.

The influence of particle morphology on the reduction behaviour of NiO, both as-synthesized and after sintering, was studied by temperature-programmed reduction (TPR); the results are published elsewhere [15].

4. Conclusion

NiO/YSZ cermet precursors were easily prepared by the citrate route. Powders in the form of spherical (from the spray-drier) or irregular aggregates (from the rotary evaporator) composed of small NiO and YSZ particles, were obtained. No macroscopic phase segregation was observed. Quantitative XRD analysis showed that both YSZ stoichiometry (i.e. Y_2O_3 content) and NiO content are very close to those expected on the basis of the composition of the starting solutions, which confirms that neither appreciable interaction between zirconia and NiO, nor segregation of secondary phases, occurs. Roentgenographic analysis may be fruitfully used for characterization of these materials, by replacing time-consuming chemical analysis.

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References

1. M. SUZUKI, H. SASAKI, S. OTOSHI and M. IPPOMATSU, in "Proceeding of the Second International Symposium on Solid Oxide Fuel Cells", Athens, July 1991, edited by F. Grosz, P. Zegers, S. C. Singhal and O. Yamamoto (Office for Official Publication of the European Communities, Luxembourg, 1991) p. 585.
2. M. MORGENSEN, *ibid.*, p. 577.
3. K. E. SWIDER and W. L. WORRELL, *ibid.*, p. 593
4. S. MURAKAMI, Y. AKIYAMA, N. ISHIDA, T. YASUO, T. SAITO and N. FURUKAWA, *ibid.*, p. 561
5. P.H. MIDDLETON, M. E. SEIERSTEN and B. C. H. STEELE, in "Proceedings of the First International Symposium on Solid Oxide Fuel cells", edited by S. C. Singhal (The Electrochemical Society, Pennington, NJ, 1989) p. 90.
6. T. P. LOCKHART, G. PIRO, M. F. GAGLIARDI and L. ZANIBELLI, EP 525 844 (03 Feb. 1993).
7. R. J. HILL and C. J. HOWARD, *J. Appl. Crystallogr.* **20** (1987) 467.
8. J. SCHNEIDER, in "Proceedings International Workshop on the Rietveld Method, Petten (NL), 1989", Abstract B17.
9. B. D. WILES and R. A. YOUNG, *J. Appl. Crystallogr.* **14** (1981) 149.
10. G. CAGLIOTI, A. PAOLETTI and F. P. RICCI, *Nucl. Instrum.* **3** (1958) 223.
11. T. H. ETSELL and S. N. FLENGAS, *Chem. Rev.* **70** (1970) 339.
12. K. HABERKO, *Ceram. Int.* **5** (1979) 1481.
13. S. P. TERBLANCHE, *J. Appl. Crystallogr.* **22** (1989) 283.
14. R. MILLINI, in "IEA SOFC Expert Meeting", Lausanne (CH), 5–6 November 1990.
15. C. PEREGO, L. ZANIBELLI, M. CATRULLO and G. PIRO, in " Proceedings of Third International Symposium on Solid Oxide Fuel Cells", Honolulu, 16–23 May 1993, edited by S. C. Singhal and H. Iwahara (The Electrochemical Society, Pennington NJ, 1993) p. 454.

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