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NiO/YSZ nanoparticles obtained by new sol–gel route

C. Suciu[a,*], A.C. Hoffmann[a], E. Dorolti[b], R. Tetean[b]

[a] *Department of Physics and Technology, University of Bergen, Allegaten 55, 5007 Bergen, Norway*
[b] *Faculty of Physics, Babes-Bolyai University, 400084 Cluj–Napoca, Romania*

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Abstract

This paper discusses the production in one single synthesis step of a binary mixture of YSZ particles and NiO particles as precursor powder for the manufacture of SOFC anodes. Three parameters were varied, each over two levels: (i) the temperature of the calcination step involved in the production process, (ii) the proportions of the two organic precursors: sucrose and pectin and (iii) the proportions of YSZ and NiO. The particles, and the calcination process involved in their production, are analyzed by TGA, TEM, SEM, XRD and BET adsorption. It is shown that the relative particle sizes are near-optimal for the production of SOFC anodes and that the particles consist either of pure cubic YSZ or pure cubic NiO. The particle sizes indicated by the various analysis methods are consistent. The particle size and the degree of crystallinity of the particles increase with increasing calcination temperature, while it appears that the process is rather forgiving for changes in the sucrose:pectin ratio. SEM studies show that the powder produced already has good connectivity between the YSZ and the NiO particles, respectively, which is good for the functionality of the resulting anode.

Keywords: Ni/YSZ; Nanoparticles; Solid oxide fuel cells; Sol–gel processing; Calcination temperature; Organic precursors

1. Introduction

The conversion of chemical energy directly to electrical energy in fuel cells, rather than having to take the detour around thermal and mechanical energy involved in conventional power generation process, is a fundamentally different principle for electrical power generation making much higher efficiencies possible. It is, therefore, in spite of some technical and economic obstacles, likely to become a cornerstone in the future electrical power generation industry, particularly as we move from coal- and oil-based fuels toward natural gas, and, eventually as these resources deplete, to hydrogen as an energy carrier.

Several types of fuel cell exist, each with their advantages and disadvantages [1]. This paper concentrates on solid oxide fuel cells (SOFC), which have the distinction of being the type of fuel cell operating at the highest temperature (approximate range 700–1000 °C at present). Advantages of SOFCs include high cell efficiencies, cost-effective catalysts and fuel flexibility. SOFCs are able to process natural gas directly without the need for external prereforming to produce hydrogen. Among their disadvantages are the long start-up and shut-down times dictated by the high operating temperature, making them less suitable for some applications, such as primary power units for transportation.

Some urgent research priorities for SOFCs are

1. Decreasing the cell internal resistance (or “polarization losses”) to enable higher current densities through the cells, decreasing the volume/weight of an SOFC installation for a given throughput.
2. Increasing the robustness toward disturbances either in the temperature or the chemical environment.
3. Reducing manufacturing costs.

In this paper we are concerned with the cost-effective production of precursor powders for the production of high-efficiency SOFC anodes, thus addressing research priorities 1 and 3.

Traditionally anode materials are binary mixtures of particles consisting of nickel (Ni) and particles consisting of yttria-doped zirconia (YSZ). Other materials are being developed, see the recent review by Fergus [2]), but Ni/YSZ is still the preferred material.

The performance of the anode, in terms of minimal electrode polarization loss and minimal degradation during operation,

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[*] Corresponding author.
E-mail address: crina.suciu@ift.uib.no (C. Suciu).

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depends strongly on its microstructure, and therefore on the precursor powders [3,4]. It is important that both an ionically conducting network is formed by the YSZ particles and an electronically conducting one is formed by the Ni particles, and that the contact line between the two networks and the gas-phase, which is the “triple-phase-boundary” where the electrochemical reaction can take place, is large. Furthermore, the relative size of the particles is important, the YSZ particles need to be much smaller than the Ni particles to minimize degradation due to Ni-particle sintering and coarsening during operation [3]. Wilkenhoener et al. [5] discuss the beneficial effects of adding YSZ nanoparticles to the precursor powder mixture to avoid such degradation and coarsening.

The standard way of producing the anode precursor powder mixture is to produce the two types of powders separately and mix them in a mill. However, it would be advantageous to produce the powder mixture in one processing step. A number of methods for doing this have been published, they are reviewed by Jiang and Chan [3]. Most relevant to the study in this present paper is the work of Razpotnik and Macek [6] where a modified Pechini-type sol–gel method was used to produce Ni/YSZ powders for the production of SOFC anodes. They mixed solutions of chlorides of the metal constituents with either ethylene glycol, ascorbic acid or citric acid to form a polymeric precursor, and subsequently calcined this reaction mixture to produce nanoparticles. These particles were strongly agglomerated. The agglomerate size was in the micron-range, while the primary particle size was 200–470 nm. Using ascorbic acid to form the polymeric precursor resulted in powders with a higher specific surface area – up to 20 $m^2\,g^{-1}$ – than when using citric acid.

Some of the present authors (CS and ACH) have recently presented a new sol–gel route for the production of zirconium nanoparticles, using the ubiquitous, environmentally friendly and cost-effective organic precursors sucrose and pectin [7]. Sucrose and pectin have been proven to be better organic precursors than the traditional ones, e.g. ethylene glycol, citric acid and glycerol. The importance of pectin as a gelling agent in the food industry is well known, and obtaining a gel with a high level of homogeneity is also important in the sol–gel method to produce very small particles. In a subsequent article they showed that this same method is suitable for producing YSZ nanoparticles even with a very low temperature in the calcination step [8,9]. Different sucrose pectin ratios were investigated and the ones found to be optimal have been chosen for the present study. This present work investigates whether this method is suitable for producing a binary Ni/YSZ powder mixture for SOFC anodes directly in one single step.

2. Objectives

The objectives of this work is thus to devise a new, environmentally friendly and cost-effective, one-stage process for the production of a complete, nano-sized Ni/YSZ powder mixture suitable for SOFC anodes, based on the new sol–gel process where sucrose and pectin are used as organic precursors.

Table 1
Composition of the samples (wt%)

Ni:YSZ	Sucrose:pectin	Water (ml)	Sample designation
50:50	100:1	300	A1
	100:4	300	A4
60:40	100:1	300	B1
	100:4	300	B4

3. Experimental procedure

3.1. Synthesis

Zirconium tetrachloride ($ZrCl_4$, Sigma–Aldrich, technical purity), yttrium nitrate hexahydrate ($Y(NO_3)_3{\cdot}6H_2O$, Sigma–Aldrich, 99.9% purity) and nickel nitrate hexahydrate $Ni(NO_3)_2{\cdot}6H_2O$ (Merck KGaA, 99% purity) were used as raw salts. The appropriate quantities for a final composition of 8 mol% $Y_2O_3$to ZrO_2 were calculated and used. Two final Ni/YSZ mass ratios were used: 50:50 and 60:40. In order to obtain the optimal particle morphology and at the same time a narrow particle size distribution, a range of compositions of the precursors were tried out. These are given in Table 1.

The procedure is illustrated in the form of a flow chart in Fig. 1. The starting raw salts are dissolved in about 300 ml distilled water at a temperature of about 90° C on a warming plate under continuous stirring forming a clear solution. The sucrose:pectin mixture is added to the solution to act as complexation/polymerization agents. The final solution, having the pH of 0.5–1, is maintained on the warming plate at a temperature lower than 110° C for about 3 h.

During these 3 h the gel is formed from the clear solution, the solution starts to evaporate slowly and in the end a xerogel is obtained. The xerogel is then calcined to obtain NiO/YSZ powder. Two maximum calcination temperatures were used: 800 and 1000 °C. The heating/cooling rate during the calcination was 100 ° C per hour, and the temperature was kept constant at two plateaus at 500 ° C for 1 h and at the maximum calcination temperature for 1 h.

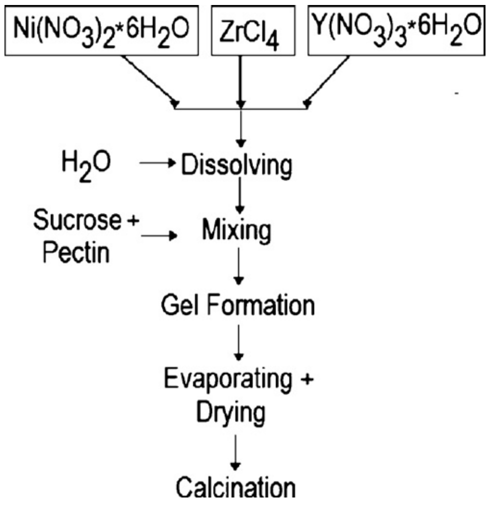

Fig. 1. A flow chart illustrating the preparation of samples.

Addition of sucrose and pectin to the solution of the metal cations forms a polymer matrix in which the Ni^{2+}, $Zr^{4+}$and Y^{3+} cations are distributed through the polymeric network structure. Sucrose, which is always in excess, acts as a strong chelating agent and as a pattern material. The chelated complex mass is obtained by polymerization via gel formation. In the case of sucrose solution (aqueous solution), NO_3^- ions helps to hydrolyze the sucrose molecule into glucose and fructose which are afterwards oxidized to gluconic acid or polyhydroxyl acid. Gluconic acid contains both carboxylic acid group and hydroxyl groups which can participate in the complexation of metal ions and may form branched polymer with pectin. Pectin chains form very large, long layers and sucrose molecules may bind between this layers. In the present process, metallic ions (e.g. Zr^{4+}, Ni^{2+}) are bound by the sucrose molecule and the resulting complex molecule is trapped between pectin layers. During calcination this polymeric metal ion complex is decomposed into CO_2 and H_2O and a large amount of heat is generated. The products from this process are gaseous, and their escape from the reaction mixture prevents agglomeration by ensuring that the mixture remains porous. Thus fine particles, which are only moderately agglomerated, are formed as the final powder. This mechanism, and the role played by sucrose and pectin in the formation of YSZ powders, is discussed in more detail in Ref. [8].

3.2. Results and discussion

Thermal analyses were performed on dried gel using a Derivatograph Q 1500 (MOM Hungary). An example of the diagrams obtained is shown in Fig. 2. During the experiments, the sucrose quantity is always in excess so the TG/DTA curves show that all samples prepared decompose in a similar way. An endothermic effect (marked 1 in the figure) starts at 100 ° C and continues until 200 °C. This effect is associated with a mass loss of 12%, and can be due to water loss. From 200 ° C until 400 ° C an exothermic process (2) takes place, probably due to decomposition of the organic components. Starting at 400 ° C two other exothermic effects can be distinguished: the first one between 400 and 475 ° C (3) and the second one between 475 and 800 ° C (4). These effects can be due to the formation of the $ZrO_2$and NiO structures and the formation of the solid solution between $Y_2O_3$and ZrO_2, which results in a cubic crystal structure. The mass loss during these exothermic effects is 52%, giving a total mass loss of 64%.

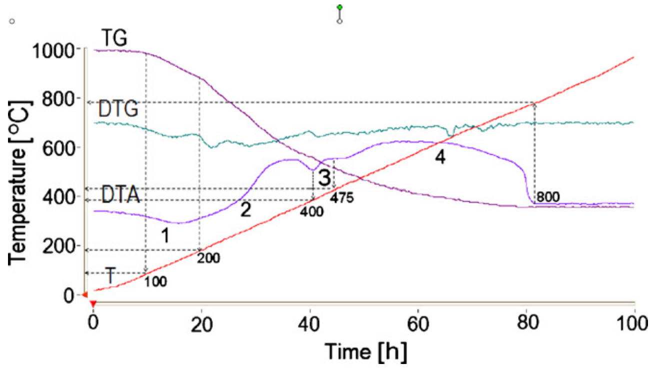

Fig. 2. The thermal analysis of the Ni/YSZ gel sample. The mass axis is not indicated in the figure, but runs from 100% at the top of the *y*-axis to 0% at the origin, such that the mass% loss can be read directly off the plot.

The specific surface area of the samples was determined using a Gemini 2380 surface area analyzer from Micromeritics. The results of BET analyses of the NiO/YSZ powders are given in Table 2.

Assuming the particles to be round and using a density of 6285 kg/m^{3}for the A samples and 6362 kg/m^3 for the B samples, the Sauter mean diameter of the particles can be estimated from the specific surface area (see Table 2). The specific surface decreases – and the particle size increases – with increasing calcination temperature.

X-ray diffraction, XRD, was carried out with Cu K α radiation on a Bruker diffractometer. The intensities were measured from 20 ° to 100 ° with a step size of 0.02 ° and a counting rate of 3 s per scanning step. Structure refinement was performed according to the Rietveld technique, supported by the FULLPROF computer code [10,11] under the assumption of Thompson–Cox–Hastings line profile. XRD patterns of the powders synthesized with different sucrose:pectin ratios are shown in Figs. 3 and 4. The obtained patterns show the presence of two main phases, NiO and ZrO_2, with a cubic *Fm* −3 *m* type structure. The presence of other phases such as an amorphous one, single Y_2O_3, ZrO_2 tetragonal or monoclinic, single Ni or $Ni(OH)_2$ was not observed. A well-crystallized powder mixture is indicated even for the four samples calcined at 800 °C. The larger peak width in these four patterns compared to the four

Table 2
Specific surface area of the samples

Sample	Calcination temperature (°C)	Specific surface area		Particle size (nm)
		BET singlepoint (m^2/g)	BET multipoint (m^2/g)	
A1	800	148.54	144.02	6.63
A1	1000	54.81	53.11	18.0
A4	800	15.75	15.27	62.5
A4	1000	5.70	5.56	172
B1	800	168.21	161.27	5.85
B1	1000	62.03	60.09	15.7
B4	800	13.87	13.43	70.2
B4	1000	5.48	5.26	179

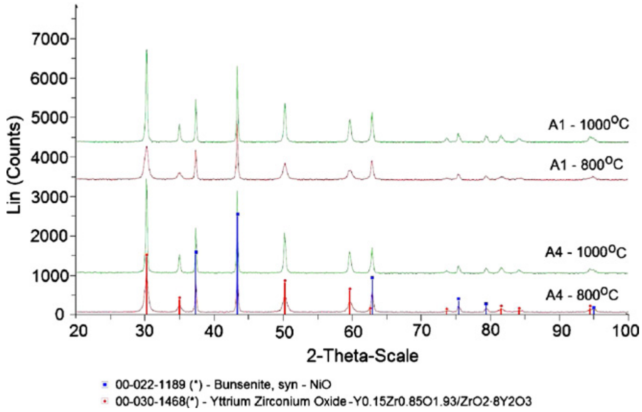

Fig. 3. The XRD spectra of the A samples calcined at 800 and 1000 °C.

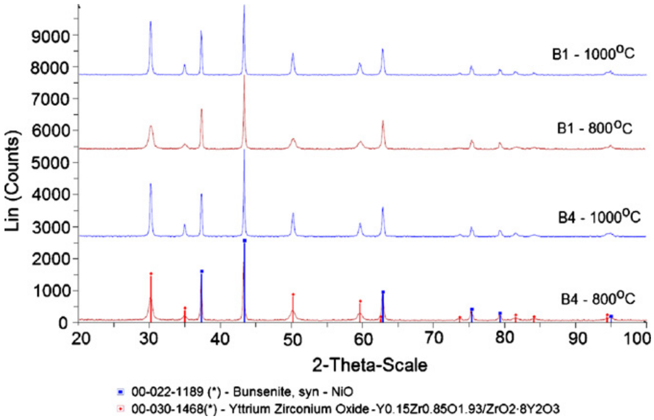

Fig. 4. The XRD spectra of the B samples calcined at 800 and 1000 °C.

Table 3
Atomic distances for NiO and ZrO_2 structures

Structure	Site	Distances (Å)	Number of near neighbours	Notation
NiO	4a	2.09	2	4b
		–	–	4a
	4b	–	–	4b
		2.09	2	4a
ZrO_2	4a	5.14	6	4a
		2.23	8	8c
	8c	2.23	4	4a
		2.57	6	8c

calcined at 1000 ° C indicates a smaller crystallite size for the lower calcination temperature.

The detailed structure was investigated using the CARINE program to obtain the interatomic distances and to show the reliability of the new method. The interatomic distances are very similar between the samples, and thus only the structures of NiO and ZrO_2 in sample A4 calcined at 1000 ° C are presented in Table 3. Due to the fact that the interatomic distances are exactly the same, i.e. that the structural parameters have no major differences, the obtained compounds can be said to be crystalographically analogous. Based on the obtained interatomic distances the NiO and ZrO_2spatial structures are presented in Figs. 5 and 6 confirming the crystal configurations characteristic of NiO and ZrO_2 and the reliability of the new method.

The mean crystallite size was calculated from full width at half maximum (FWHM) of the diffraction peaks according to Scherrer's formula (as quoted in [12]). For the A samples, calcined at 800 °C, the mean crystallite sizes of the NiO and YSZ phases are about 37 and 11 nm, respectively. When increasing the calcination temperature to 1000 ° C these values increased to 53 and 31 nm, respectively. All the values are given in Table 4. The XRD data are in good agreement with the TEM studies reported below. The results indicate that calcination at higher temperatures enables Y-doped zirconia to acquire larger crystallite sizes and a higher degree of crystallinity. A study of the table reveals that the use of different sucrose:pectin ratios has only little effect on the average crystallite size of the final products. We note that the BET and TEM results indicate a somewhat more significant effect of the sucrose:pectin ratios on the particle size. We have to leave this issue somewhat in the open at this stage, however, since there are uncertainties associated with all three methods, due, for example, to the formation of solid necks between the particles, and non-sphericity of the particles.

Typical *transmission electron microscopy* (TEM) pictures, obtained by a JEOL-JEM-1011 transmission microscope, of all the investigated powders are shown in Figs. 7 and 8.

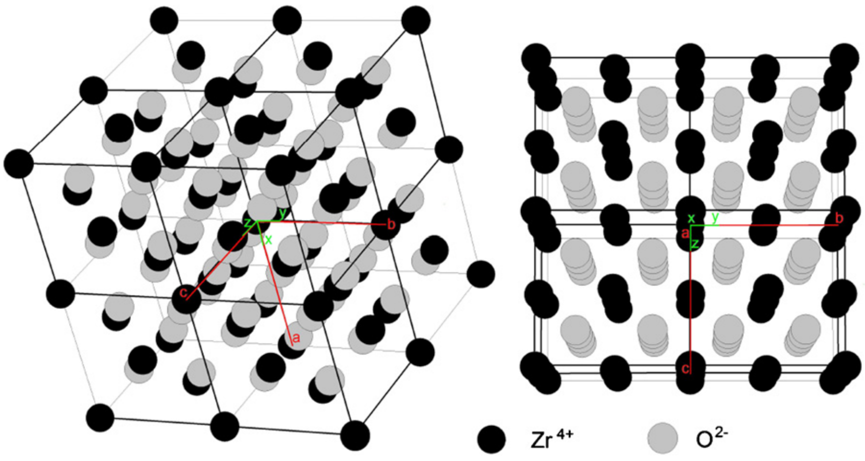

Fig. 5. ZrO_2 spatial configuration.

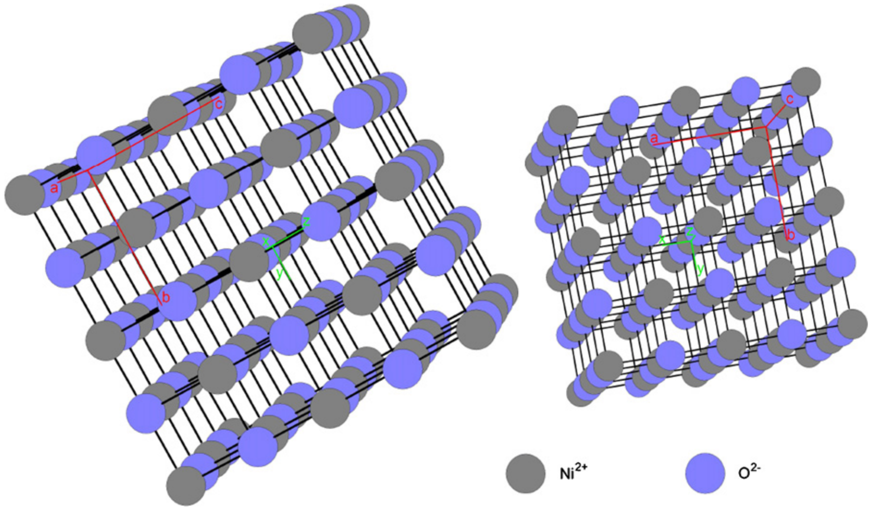

Fig. 6. NiO spatial configuration.

The samples were dispersed in water under stirring and one drop taken from the solution was deposited on a copper grid, which previously had undergone a carbon deposition process under vacuum followed by a glow discharge. The agglomerates of NiO/YSZ samples are quite similar in all final powders. The mean particle size estimated from the pictures are shown in Table 4. The A samples have the largest range of particle sizes from 28 to 71 nm, the smallest sizes at a calcination temperature of 800 °C. The mean particle sizes of the B samples appear to be much more uniform between samples and between the calci-

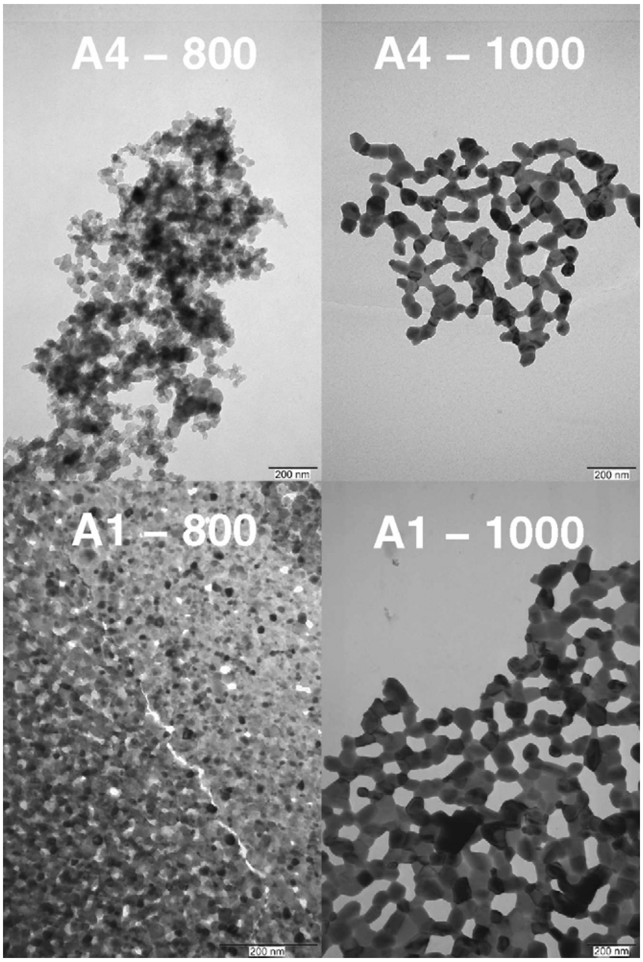

Fig. 7. TEM images of the A samples calcined at 800 and 1000 °C.

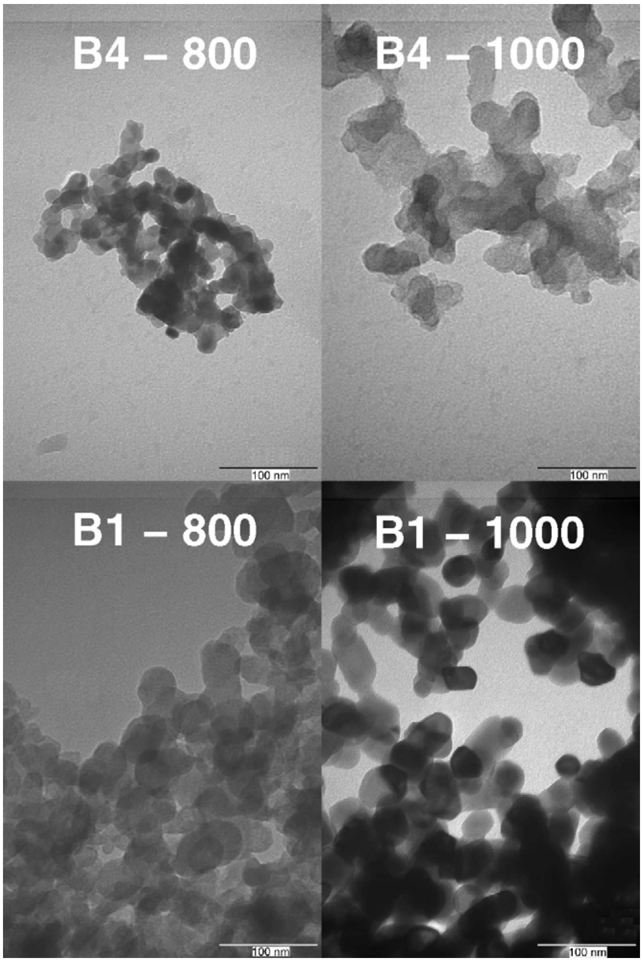

Fig. 8. TEM images of the B samples calcined at 800 and 1000 °C.

Table 4
Crystallite size (NiO, YSZ) calculated from XRD patterns and mean particle size estimated from TEM pictures

Sample	Temperature (°C)	NiO crystallite size (XRD) (nm)	ZrO_2crystallite size (XRD) (nm)	Mean particle size (TEM) (nm)
A1	800	37	11	28
A1	1000	53	31	71
A4	800	39	11	35
A4	1000	58	32	64
B1	800	44	11	30
B1	1000	53	28	31
B4	800	40	11	28
B4	1000	60	28	30

nation temperatures, ranging from 28 to 31 nm, again the lower size found at a calcination temperature of 800 °C. The TEM investigations are in general in good agreement with the XRD data. Unfortunately, the two types of particles (NiO and ZrO_2) cannot be distinguished visibly. It was, however, possible to use the analytical capabilities of the SEM microscope to determine the elements present in small regions of the obtained powders as described below.

The *scanning electron microscopy* (SEM), a Zeiss, SUPRA 55VP microscope was used for further analysis of the samples. Aluminium stubs covered with carbon tape were used to enter the samples into the microscope. Fig. 9 presents the results of the sample A4 calcined at 800 ° C using a magnification of 116,878 times and the accelerating voltage of 10.0 kV. The sample was investigated at three different points and the presence of Ni, Zr and O elements was recorded. The weight ratios of each element for all three analyzed points have been determined from the EDAX spectra and are presented in Table 5. The detection of Al and C is due to the presence of the supporting stubs. Based on the XRD spectra, which have shown the presence of only NiO and ZrO_2phases, it can be assumed that other forms of Ni or Zr are not present in the final powders.

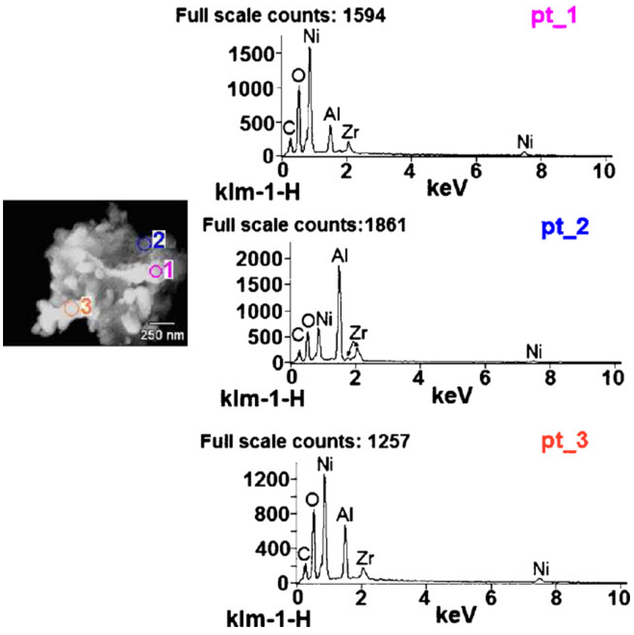

Fig. 9. SEM image of the A4 samples calcined at 800 °C.

Table 5
The weight ratios of individual elements of the A4 sample calcined at 800 °C

Point	Ni (wt%)	Zr (wt%)	O (wt%)	Al (wt%)	C (wt%)
pt_1	52.32	4.68	28.68	4.70	9.62
pt_2	25.62	10.62	24.17	25.90	13.69
pt_3	47.84	5.40	27.56	8.58	10.63

4. Conclusions

Binary mixtures of NiO and YSZ particles in two different compositions were synthesized by a new sol–gel method using sucrose and pectin as organic precursors. The method allowed the preparation of binary mixtures of pure particles in one step at relatively low cost and at a reduced calcination temperature compared to conventional methods. Moreover, the product particles had quite uniform particle sizes within each type. The YSZ particles were smaller than the NiO particles, which, as mentioned in the introduction, is optimal for SOFC anode performance.

This process is simple and cost-effective and reasonably easy to transfer to an industrial scale.

Thermal analysis studies indicate the NiO and YSZ phases are completely formed at 800 °C. The XRD patterns show the presence of NiO and YSZ in cubic forms in all the samples, and indicate no other phases.

TEM, SEM and XRD analyses agreed in showing that the particle size increases with increasing calcination temperature, and all the analysis techniques agreed reasonably well in terms of the particle and crystallite sizes.

The obtained particle mixtures can be used to fabricate cermet anodes. During calcination, the metal ion complex is decomposed and large amount of gases and heat are generated. The degree of porosity of the gel is a direct consequence of the amount of gases that escape during calcination treatments. The resultant composite powders provided good connections of YSZ grains and NiO grains without a milling process, and this may result in a relatively low polarization loss in an anode produced directly from the composite powder as produced.

The obtained particles are all smaller than 135 nm and a comparison between the estimates for the crystallite size and the particle size indicates that the particle consist of one to two crystallites in the case of YSZ particles and several crystallites in the case of NiO particles. The electrical properties of the obtained materials and their sintering properties will be reported in the near future.

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