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# Synthesis of nickel oxide/zirconia powders via a modified Pechini method

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## Abstract

NiO/YSZ powders as precursors for anode materials for solid oxide fuel cells were synthesized by a modified Pechini method. The effect of different chelating agents, e.g., ascorbic and citric acid, on the thermal decomposition of gels and on the morphology of final products, was studied. Thermal decompositions of the obtained gels were completed at around 700 °C. The grain size of the prepared materials was in the nanometre range but they grouped into larger agglomerates with sizes in the range from 14.9 to 8.6 μm. After ball milling in ethanol, the size of these agglomerates was reduced by around 60%. Sintering temperature as low as 1300 °C could be attained. A correlation between the metal ion concentration and the temperature of maximum shrinkage rate was established. The results show that the powders prepared with ascorbic acid could be used for preparation of SOFC anodes.

*Keywords:* Sol–gel processes; Ascorbic acid; NiO–YSZ powders; Fuel cells

## 1. Introduction

High temperature solid oxide fuel cells (SOFCs) are very efficient devices for the electrochemical conversion of chemical energy of fuels into electricity. The most widely studied and used SOFC system consists of an yttria-stabilized zirconia (YSZ) layer as an electrolyte, a nickel and YSZ (Ni–YSZ) cermet as an anode, an electrically conducting oxide based on lanthanum manganites $La_{1-x}M_xMnO_3$ (M = Sr, Ca) as a cathode, and lanthanum chromites doped with Sr, Ca or Mg as an interconnect material.[1] The anode composite materials are usually manufactured by a solid state method, where separately prepared nickel oxide and YSZ powders are subsequently subjected to homogenization, sintering and reduction to form a Ni–YSZ cermet. Many authors have recently focused toward alternative preparation techniques such as spray pyrolysis,[2] chemical vapour deposition,[3] combustion synthesis[4] and sol–gel synthesis.[5] One of the methods in which sol transforms into gel, is also the so-called Pechini process which is a low cost, high simplicity, low-temperature synthesis.

The Pechini-type methods exploit the preparation of homogeneous precursors on a molecular level and enable the preparation of multicomponent metal oxides with very good homogeneity.[6–8] The method is based on the formation of metal-citric acid complexes. The subsequent polymerization of free CA and coordinated CA with ethylene glycol results in formation of a polymeric resin. The homogenous polymeric precursor contains exactly the same metal stoichiometry as the desired product. This is because the metal-CA complexes are thermally stable at medium temperatures (∼130°C) and could be "frozen" in a polymer network while preserving the initial stoichiometric ratios of metal ions in the starting solution. The immobilization of metal cations in such a highly branched polymer can prevent, or at least reduce, the cation mobility during heat treatment which preserves a good dispersion of cations in the product.[7]

The final processing step in the preparation of SOFC anode involves sintering which hardens the product and provides the necessary continuity of different phases in the composite material.[12] The parameters of sintered material such as sintering temperature and density depend mainly on the characteristics of starting powder. The use of different synthesis methods and preparation conditions, i.e., reaction temperature, pH and the concentration of the reactants, result in variations of the product properties.

In the present study, a modified Pechini-type process is used for preparation of NiO–YSZ powders. The modification con-

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sists of introducing a complexing agent, e.g., ascorbic acid, to the starting solution. For comparison, gels with citric acid were prepared by the same procedure. The samples were synthesized by setting the initial concentration of metal ions in the solution at 0.1, 0.05 and 0.01 mol $L^{-1}$. Additionally, samples without metal ions were also prepared. The influence of the metal ions concentrations and the effect of complexation agents on the properties of final powders were studied. Thermal decomposition of the prepared gels was investigated by TG/DTA analysis. The calcination and crystallization behaviour was studied by X-ray diffraction (XRD). The calcination temperature was 900 °C. The products were characterized by specific surface area (BET) and particle size (laser diffraction granulometry) measurements. The sintering behaviour of the powders was studied using a heating microscope. The grain sizes were estimated by scanning electron microscopy (SEM).

## 2. Experimental procedures

Nickel oxide/yttria-stabilized zirconia powders were prepared via a modified Pechini method. The procedure is illustrated in Fig. 1. The starting precursors of $NiCl_2 \cdot 6H_2O$, $ZrCl_4$, $Y_2O_3$ (all analytical grade) were added to 50 mL of distilled water and heated to around 40 °C. After the dissolution of $Y_2O_3$ in a strongly acidic solution of Ni, Zr salts, the rest of the distilled water was added. Ascorbic (AA) or citric (CA) acid and ethylene glycol (EG) were added into this solution as complexation/polymerization agents. The amount of yttrium in the starting reaction mixture was selected so that the final molar ratio of $Y_2O_3$ to $ZrO_2$ was 10: 90 (10 mol% YSZ). The molar ratios of carboxylic acid:EG:metal ions in the solution were 2:1:1. The pH of the prepared solution was adjusted to 8 by adding gaseous ammonia. After that the solution was heated up to around 90 °C.

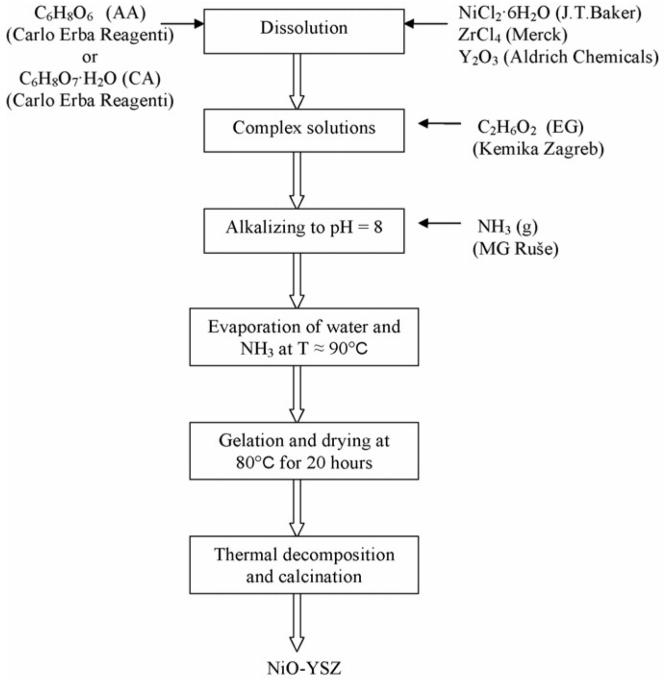

Fig. 1. A flow chart illustrating the preparation of samples.

Table 1
Composition of polymeric precursor

| Sample | $C_M$ (mol $L^{-1}$)[a] | $C_{EG}$ (mol $L^{-1}$) | $C_A$ (mol $L^{-1}$) | $C_C$ (mol $L^{-1}$) |
|---|---|---|---|---|
| A1 | 0.1 | 0.1 | 0.2 | |
| A2 | 0.05 | 0.05 | 0.1 | |
| A3 | 0.01 | 0.01 | 0.02 | |
| C1 | 0.1 | 0.1 | | 0.2 |
| C2 | 0.05 | 0.05 | | 0.1 |
| C3 | 0.01 | 0.01 | | 0.02 |

[a] $C_{(Ni^{2+})} = C_{(Zr^{4+}+Y^{3+})}$.

Within 4 h, its pH was lowered to a value around 5—due to evaporation of ammonia and water. The obtained solution was placed into a drying oven where it was maintained at 80 °C for about 20 h to promote polyesterification reactions. During drying, a substantial amount of water was removed from the samples. The obtained polymeric gel was calcined for 1 h in air at different temperatures to burn and remove all the remaining organic materials. The sintering behaviour of as-prepared powders was studied on samples calcined at 900 °C for 1 h. The powders were subsequently milled in ethanol for three hours in a planetary ball mill (Pulverisette 5, Fritsch), dried and compacted by uniaxial pressing (60 MPa) into cylindrical pellets of a 6 mm diameter. The green densities of the prepared pellets were in the range from 35 to 43% of the theoretical value of 6.2525 g $cm^{-3}$. The shrinkage of the samples during sintering was measured using a Leitz–Wetzlar heating microscope by heating them to 1550 °C at a constant heating rate of 10 °C $min^{-1}$. The densities before and after sintering were estimated by measuring the mass and the geometric dimensions of the pellets. The theoretical density was calculated from lattice parameters.

The designation of samples and their polymeric precursor composition is listed in Table 1, where A and C denote ascorbic and citric acid, respectively; $C_M$, $C_{EG}$, $C_A$, $C_C$, are the concentrations of metal ions, ethylene glycol, ascorbic acid and citric acid, respectively.

Thermal analysis (TG/DTA) of the dried gels was performed on a Netzsch STA 409 thermoanalyzer in air at a heating rate of 10 °C $min^{-1}$, using $\alpha$-$Al_2O_3$ as a reference. The crystal structures were identified by a powder X-ray diffractometer (XRD, Brukers D4 Endeavor) employing Cu K$\alpha$ radiation ($\lambda$ = 1.5406 Å). Powder crystallite size was determined with an X-PAS software using the Scherrer equation[9] and X-ray diffraction line broadening of (1 1 1) peak for YSZ and (0 1 2) peak for NiO. A Micrometrics Gemini 2370 instrument was used to determine the specific surface area of samples. After being dispersed in ethanol, the particle size distribution of samples was determined by laser beam diffraction (Microtrac FRA9200). The morphology of synthesized powders was determined using a scanning electron microscope (Jeol T300).

## 3. Results and discussion

### 3.1. Thermal analysis

Thermal behaviour of the samples listed in Table 1 and their decomposition was studied by thermal analysis. For comparison,

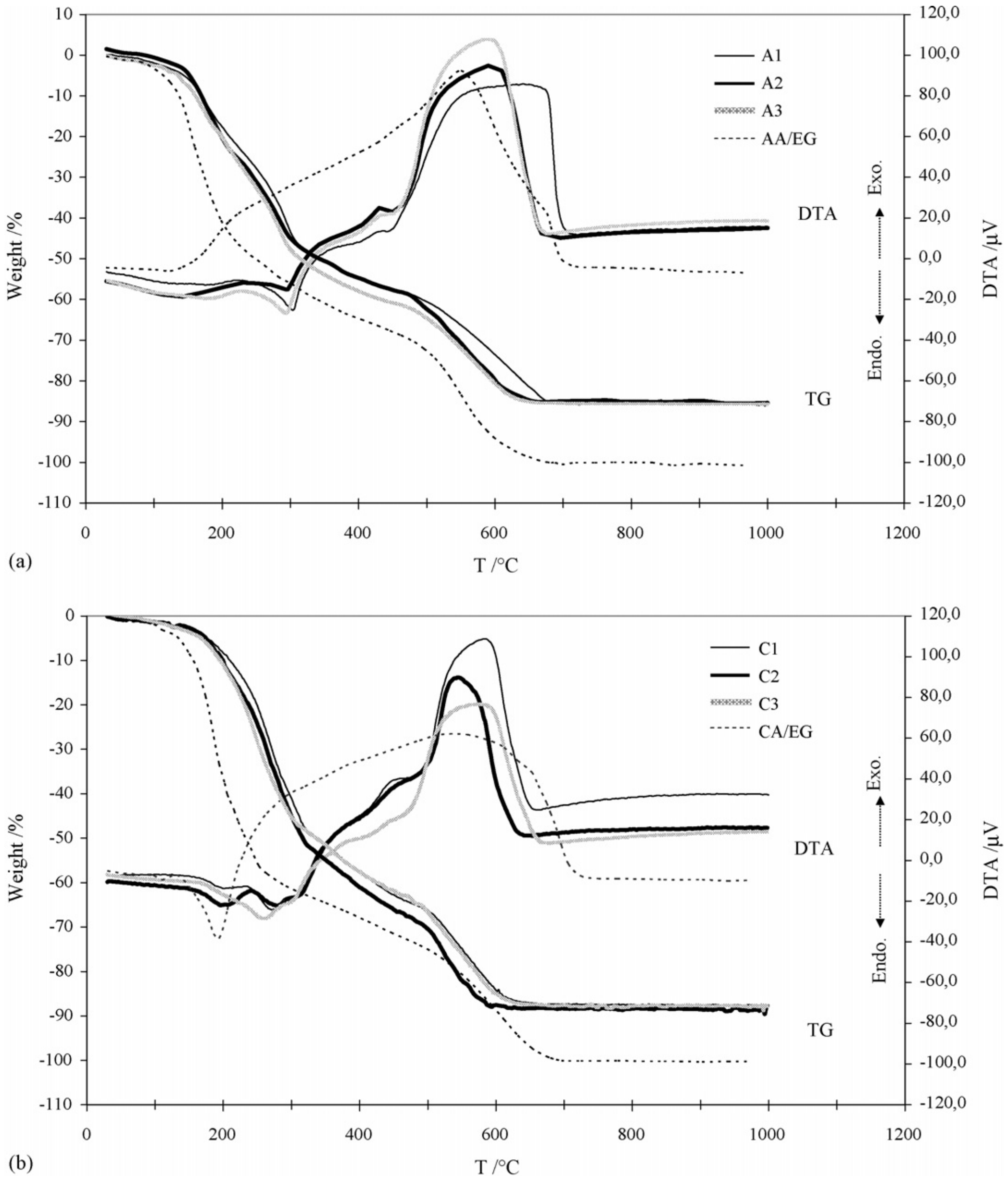

Fig. 2. Combined TG–DTA curves for samples prepared with (a) ascorbic and (b) citric acid.

reference gels without metal ions (AA/EG and CA/EG) were prepared. Representative TG and DTA curves of the samples are shown in Fig. 2.

Samples AA/EG and CA/EG decompose in three steps in the temperature range from 80 to 700 °C. An endothermic peak for the sample CA/EG is observed at 200 °C which, according to the literature,[10] corresponds to a superposition of two different reactions: dehydration of gel and evaporation of excessive ethylene glycol from the dried gels. In AA/EG gels this peak is less pronounced. In the temperature range from 200 to 700 °C both samples decompose exothermally. According to the literature[10], this section corresponds to the combustion of polymeric gel.

The TG/DTA curves show that all samples prepared with the addition of metal ions decompose in a similar way. The decomposition takes place in several steps with weight losses of around 86%. The first endothermic part of the process is followed by a strong exothermic region in the temperature interval from 80 to 700 °C. The exothermic effect in the temperature range from 150 to 500 °C is much smaller if compared with the samples without metal ions, taking into account also the difference in the initial sample weight. This suggests that the presence of metal-carboxylic acid complexes in samples has a reducing effect on the pyrolysis of organics. In the temperature interval from 500 to 700 °C the course of DTA curves (Fig. 2) is affected by the composition of the samples, e.g., by the initial metal ion concentrations.

### 3.2. Calcination of samples

XRD patterns of the powders synthesized with different carboxylic acids are shown in Fig. 3. The samples were calcined for 1 h at 900 °C. The XRD patterns for samples C1 and A1 prepared

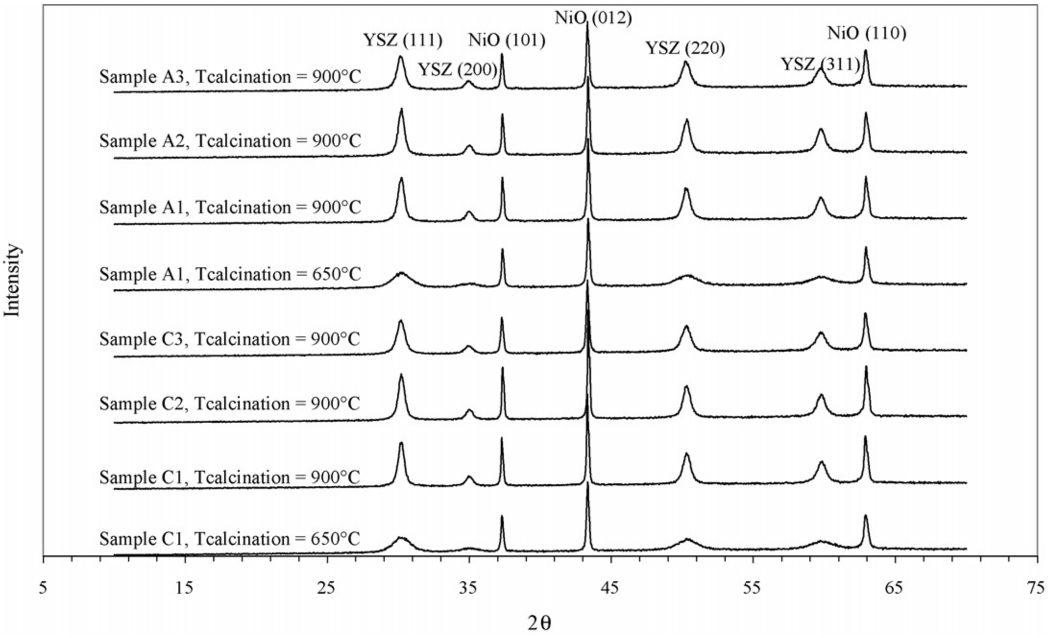

Fig. 3. X-ray diffraction patterns of NiO–YSZ powders calcined at 650 °C (samples C1 and A1) and at 900 °C for 1 h.

at 650 °C are added to illustrate the crystallization behaviour at lower temperatures. In all cases, two main phases corresponding to YSZ and NiO can be found. The higher background and the broader peaks obtained in samples calcined at 650 °C indicate a poorly crystallized powder mixture. For the samples heated up to 900 °C the background diminishes and the peaks become sharper and more intense.

From X-ray broadening of the peaks, the average crystallite size was calculated using the Scherrer equation. The values obtained for samples calcined for 1 h in air at different temperatures are presented in Table 2. With increasing temperature of calcination, the mean crystallite size of YSZ (plane (1 1 1)) increases from 6 to 16 nm and for NiO (plane (0 1 2)) from 42 to 48 nm. The results indicate that calcination at higher temperatures enables Y-doped zirconia to acquire larger crystallite sizes and higher crystallinity. The calcination temperature of 900 °C was selected for further investigation of the particle properties.

The effect of the complexation agents and metal ion concentration in the precursors on the crystallization behaviour of NiO–YSZ powders was also studied. A comparison of crystallite sizes obtained from X-ray diffraction patterns (Table 2) shows that the use of different carboxylic acids has a very small effect on the average crystallite size of the products. On the other hand, the lowest metal concentration (samples A3 and C3) produced somewhat smaller average crystallites of NiO and YSZ phases than if higher metal concentrations were used.

### 3.3. Specific surface area and particle size

The results of BET analysis of NiO–YSZ powders calcined at 900 °C are given in Table 2. The specific surface areas for powders prepared with ascorbic acid were in the range from 18.4 to 20.5 $m^2 g^{-1}$ while those with citric acid were in the range from 12.0 to 19.6 $m^2 g^{-1}$. Thus, the samples prepared with ascorbic acid exhibited somewhat higher specific surface area. However, it was observed that in both cases the lowering of the metal ions concentration in the precursor solution led to an increase in the specific surface area of the final products.

Table 2
Crystallite size ($D_{YSZ}$, $D_{NiO}$) calculated from XRD patterns, specific surface area ($S_{BET}$), average grain size ($d$) estimated from SEM micrographs and median particle size ($d_{50}$) measured with laser diffraction granulometer for samples calcined at 900 °C for 1 h

| Samples | $T_c$ (°C) | $D_{YSZ}$ (nm) | $D_{NiO}$ (nm) | $S_{BET}$ ($m^2 g^{-1}$) | $d$ (nm) | $d_{50}$ (μm)[a] | $d_{50}$ (μm)[b] |
|---|---|---|---|---|---|---|---|
| A1 | 650 | 5.5 | 41.9 | | | | |
| A1 | 900 | 15.7 | 47.7 | 18.4 | 570–860 | 12.1 | 5.1 |
| A2 | 900 | 16.8 | 46.3 | 19 | 450–1150 | 11.4 | 4.8 |
| A3 | 900 | 13.6 | 44.8 | 20.5 | 280–470 | 14.9 | 5.7 |
| C1 | 650 | 5.9 | 42.9 | | | | |
| C1 | 900 | 16.3 | 47.9 | 12.0 | 370–940 | 14.6 | 6.0 |
| C2 | 900 | 16 | 50.4 | 14.2 | 470–1100 | 10 | 3.8 |
| C3 | 900 | 12.3 | 42.6 | 19.6 | 200–400 | 8.6 | 3.3 |

$T_c$, calcination temperature.
[a] Median particle size for samples before milling in ethanol for 3 h.
[b] Median particle size for samples after milling in ethanol for 3 h.

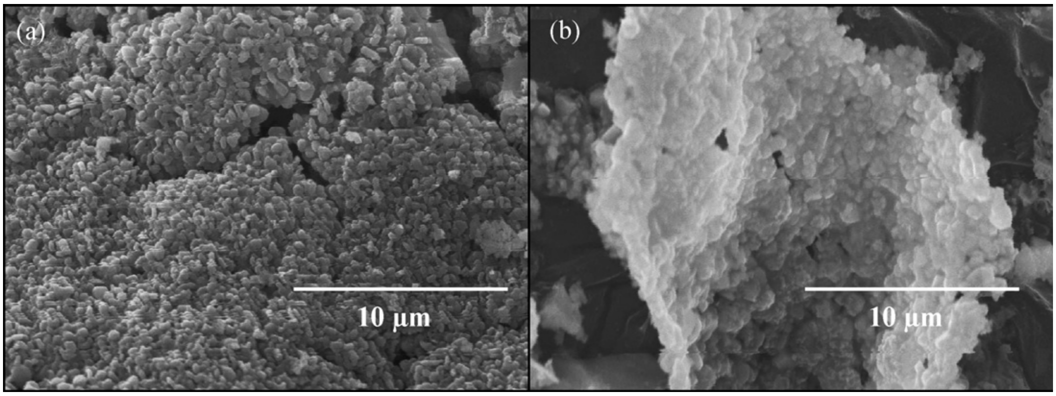

Fig. 4. Representative SEM micrographs of NiO–YSZ powders prepared from (a) ascorbic and (b) citric acid. Samples were calcined for 1 h at 900 °C.

Typical SEM photomicrographs of powders are shown in Fig. 4. The agglomerates of NiO–YSZ samples are similar in all powders prepared from the same precursors. The agglomerates prepared with citric acid were denser, as can be seen from Fig. 4(b). All agglomerates were composed of smaller particles, i.e., grains. Their average sizes (*d*), which were estimated from SEM micrographs, are displayed in Table 2. The use of the total metal concentration of 0.05 mol $L^{-1}$ (samples A2 and C2) gave the largest grains while the concentration of 0.01 mol $L^{-1}$ (samples A3 and C3) gave the smallest grains.

The median particle size of the calcined and subsequently ball milled samples was determined by laser granulometry. The size interval of powders calcined for 1 h at 900 °C was in the range from 0.4 to 70 μm. The median particle sizes ($d_{50}$) obtained from the cumulative curves ranged from 8.7 to 14.9 μm, as seen from Table 2. For samples prepared with citric acid the median particle size decreased with lowering of the initial metal concentration. This effect is not so evident in the samples prepared with ascorbic acid.

The particle size of the samples determined by laser granulometry was higher than the grain size found in SEM micrographs. The frequency particle size distribution confirmed that grains created during calcination formed larger agglomerates of various median sizes (Table 2).

### 3.4. Sintering behaviour

The sintering behaviour of NiO–YSZ composites was studied by a heating microscope. Both the calcined and compacted powders (a representative curve of sample A1 is shown in Fig. 5(a)) exhibited the presence of two different shrinkage rates. This effect confirms the presence of different agglomerates in samples. Therefore, the products were subsequently ball milled in ethanol for 3 h. The median particle size was reduced (Table 2) for around 60%. The dried samples were compacted with uniaxial pressing using a pressure of 60 MPa. The densification rates vs. temperature for pellets are shown in Fig. 5(b). Samples A1 and C1 prepared with the highest concentration of metal ions in the precursors showed higher relative green densities (38.8 and 42.5% of the theoretical density) then samples A2, A3, C2 and C3 (37.3, 35.3, 39.9, and 35.5% of the theoretical density). The sintering curves for all six samples have the onset of shrinkage at a similar temperature (around 900 °C). Based on the course of the sintering curves, they can be divided into three groups con-

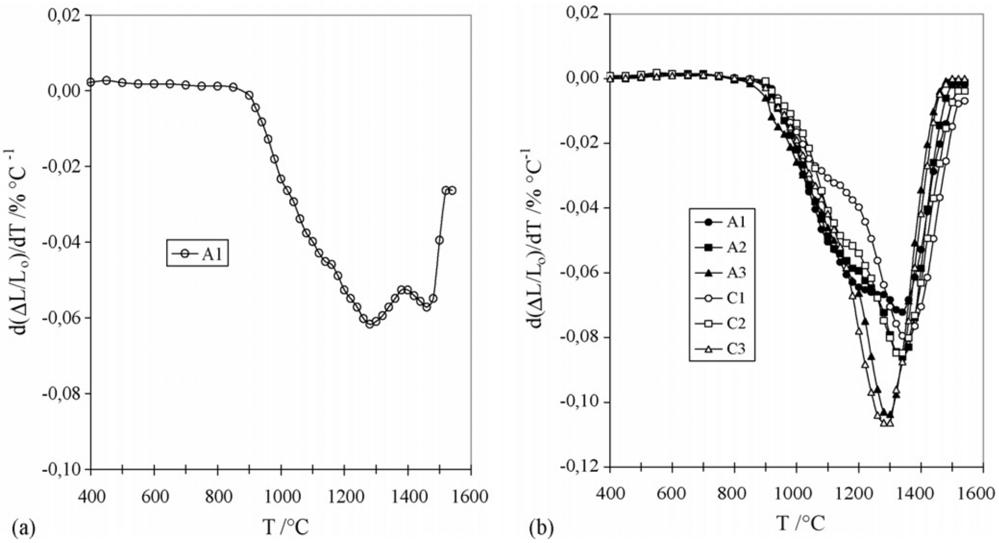

Fig. 5. Linear shrinkage rate as a function of temperature for calcined (a) and ball milled powders (b).

sisting of the following samples: (a) C1 and C2, (b) A1 and A2, and (c) A3 and C3. The curves exhibit only one distinct peak, reflecting the presence of a single heating rate. The maximum densification rates for samples A1, A2, A3, C1, C2 and C3 were achieved at 1360, 1340, 1300, 1380, 1340 and 1300 °C, respectively. Relative densities of the sintered samples varied from 98.1 to 98.9% of the theoretical value (98.8, 98.9 and 98.8% for samples A1, A2 and A3; 98.2, 98.1 and 98.1% for samples C1, C2 and C3). Thus the decrease in the starting concentration of metal ions gave products which exhibited the decrease in the temperature of maximum shrinkage rate.

As shown before, the decrease of the concentration of metal ions increases the specific surface area and decreases the average grain and crystallite size. In powders with smaller particles the mass transport during the densification is faster. This effect leads to a decrease in the temperature of maximum shrinkage rate.[11]

## 4. Conclusions

NiO–YSZ powders with particle sizes ranging from hundreds of nanometers to several micrometers have been prepared by a modified Pechini-type sol–gel method. According to this method, a homogeneous polymer precursor is formed from metal chlorides, ethylene glycol and ascorbic (or citric) acid. The precursor is subsequently calcined. NiO–YSZ powders prepared by the use of different complexing agents exhibited good crystallization at 900 °C. The relative sintered densities of around 98% of the theoretical value were achieved with average particle sizes around 5 μm. The powders prepared with ascorbic acid had a higher specific surface area than those obtained with citric acid. The thermal behaviour of samples was influenced by the initial metal ion concentration. It was found that the grain size and the crystallite size in the products were most reduced when the lowest metal concentration ($C_M = 0.01\ \mathrm{mol\,L^{-1}}$) was used for the preparation of samples. In that case powders with grain sizes in the range from 200 to 470 nm and a specific surface area of ca. $20\ \mathrm{m^2\,g^{-1}}$ were obtained. These samples had the lowest sintering temperature, i.e., about 1300 °C. From the results it can be concluded that the Pechini gel route modified by the use of ascorbic acid as a complexation agent could be employed for preparation of pure NiO–YSZ powders.

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