

Characterisation of Y-PSZ and PR-doped Y-PSZ obtained by unconventional methods for sofc applications

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The effect of method of preparation, including the traditional ceramic method and several sol-gel methods have been studied on the molar composition $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.04}$ and $(\text{ZrO}_2)_{0.82}(\text{Y}_2\text{O}_3)_{0.04}(\text{Pr}_2\text{O}_3)_{0.05}$ praseodymium doped samples. Powder fired at 500°C was sieved at 60 μm , uniaxially pressed and fired at 1.600°C for 2h. The resulting compacts were characterised by XRD, SEM-EDX, density measurements, toughness strength and Vickers microhardness. The results indicate that colloidal samples stabilises tetragonal zirconia polymorph showing the best densification and electrical conductivity behaviour, praseodymium addition stabilises cubic zirconia improving the microhardness and densification of the material.

Keywords: YSZ, Unconventional methods, praseodymium.

Caracterización de y-psz e y-psz dopada con pr obtenida mediante métodos no convencionales para aplicaciones en sofc

Se ha estudiado el efecto del método de preparación, incluyendo el método cerámico tradicional y varios métodos sol-gel, sobre las composiciones $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.04}$ y $(\text{ZrO}_2)_{0.82}(\text{Y}_2\text{O}_3)_{0.04}(\text{Pr}_2\text{O}_3)_{0.05}$. Los polvos calcinados a 500°C se tamizaron a 60 μm , se prensaron uniaxialmente y se sinterizaron a 1600°C durante 2h. Los compactos resultantes se caracterizaron mediante XRD, SEM-EDX, medidas de densidad, tenacidad y microdureza Vickers. Los resultados indican que en las muestras coloidales se estabiliza el polimorfo tetragonal de la circonia mostrando la mejor densificación y el mejor comportamiento en conductividad eléctrica. Las adiciones de praseodimio estabilizan la circonia cúbica mejorando la microdureza y densificación del material.

Palabras clave: YSZ, Métodos no convencionales, praseodimio.

1. INTRODUCTION

Pure zirconia, ZrO_2 , is monoclinic at room temperature, tetragonal between 1170 and 2370°C, and cubic up to the melting point at 2680°C. The stabilisation of tetragonal zirconia polymorph at room temperature by addition of yttria, magnesia, ceria or calcia allows to be obtained ceramics tougher due to the martensitic tetragonal \rightarrow monoclinic zirconia phase transformation (1). The mechanical properties of tetragonal zirconia depend on several parameters such as doping concentration, zirconia particle size and microstructural characteristics such as shape, grain size or densification (2). Zirconia solid electrolyte materials, however, are usually based on the cubic zirconia lattice which avoids structural problems related to the martensitic transformation. This polymorph is also stabilized by the addition of magnesia, ceria, calcia or yttria. At fuel cell operating temperature, the maximum ionic conductivity is observed in the yttria-zirconia system at the yttria content of 8 mol% (3), but the low mechanical properties of cubic zirconia make its application difficult. One possible approach to improving the properties is to precipitate tetragonal zirconia on the surface by substituting Y_2O_3 by CaO or MgO (4), which is why these ternary systems are currently studied. Other ternary systems using CeO_2 and TiO_2 (5-6), or transition metals (Fe, Mn and Cr) (7) as dopants have also been investigated recently in order to find out the effects of small additions of dopant on the structure and conductivity of YSZ (yttria stabilized zirconia).

Cubic zirconia has an adequate ionic conductivity at the required operating temperature. However, temperature by solid state reaction yields high porosity material, the conductivity of which quickly reduces when the operating temperature falls. Non-conventional

synthesis methods, such as sol.gel (8), and adequate doping have been studied in order to avoid the poor densification of the material (9-10).

The aim of the present paper was, therefore, to study the influence of both, the synthesis method and the praseodymium addition on the sinterability of powders, as well as their effect on stability and their mechanical properties in Y-PSZ (yttria partially stabilized zirconia).

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of powders

Samples with a molar composition $(\text{ZrO}_2)_{0.82}(\text{Y}_2\text{O}_3)_{0.04}(\text{Pr}_2\text{O}_3)_{0.05}$ (CEPr, doped with Pr) prepared by the ceramic method and several unconventional methods were studied and compared with a molar composition $(\text{ZrO}_2)_{0.92}(\text{Y}_2\text{O}_3)_{0.04}$ (CE undoped). According to the ZrO_2 - Y_2O_3 phase diagram (11), the composition of undoped samples appears in the two-phase (cubic and tetragonal zirconia) region.

For synthesis, the ceramic method, a colloidal route, citrate polymerisation, and polymeric gels obtained by hydrolysis-condensation of alkoxides, were used and compared for both compositions. ZrO_2 (baddeleyite) of a commercial technical grade supplied by SEPR, Y_2O_3 (Aldrich) and Pr_6O_{11} (Rhône Poulenc) were used as the Zr, Y and Pr precursors for the ceramic method. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Merk), $\text{Y}(\text{CH}_3\text{CHOO})_3 \cdot \text{H}_2\text{O}$ (Aldrich) and $\text{Pr}(\text{CH}_3\text{CHOO})_3 \cdot 3\text{H}_2\text{O}$ (Johnson Matthey) were employed instead of commercial technical grades in the unconventional processes. Zirconium (IV) n-propoxide (Flucka) was used as the Zr precursor in the case of polymeric gels.

2.1.1. CERAMIC METHOD (CE AND CEPR)

To prepare the compositions, the appropriate amounts of commercial oxides, used as precursors, were mixed and ball-milled in acetone for 20 minutes. Residual acetone was then removed by evaporation, and the resulting dried powder was finally homogenized in an agate mortar.

2.1.2. COLLOIDAL METHOD (CG AND CGPR)

In this method, a solution was obtained by dissolving $ZrOCl_2 \cdot 8H_2O$ in water (0.8 M) at 70°C with continuous stirring followed by the addition of $Y(CH_3CHOO)_3 \cdot H_2O$ (0.07 M) thirty minutes later. The resulting mixture was left for 1h under the same stirring and heating conditions to provide the basic CG solution. The CGPr solution was prepared by the appropriate addition of $Pr(CH_3CHOO)_3 \cdot 3H_2O$ (0.12 M). With both solutions, when a homogeneous dispersion was reached, a concentrated ammonia solution was added drop wise until gelation occurred at pH= 5-6. The resulting light yellow and homogenous gel was aged and dried at room temperature in the open air and then crushed and ground in an agate mortar.

2.1.3. CITRATE PROCESS (CI AND CIPR)

In order to use the citrate process $ZrOCl_2 \cdot 8H_2O$, $Y(CH_3CHOO)_3 \cdot H_2O$ (CI sample), and $Pr(CH_3CHOO)_3 \cdot 3H_2O$ (CIPr sample) precursors were dissolved under the same conditions as above for the colloidal method. Then, a solution prepared at 70°C with anhydrous citric acid and ethylene glycol (both from Panreac) in a molar ratio 1:1 was added to form a homogenous dispersion of the precursors. Immediately afterwards, concentrated ammonia solution was added drop wise until pH= 5 to avoid the coprecipitation of the Zr, Y and Pr precursors. The resulting solution was heated, with stirring up, to 70°C for 3h in order to promote the polyesterification. The polyester was dried at 90°C and submitted to a "charring" treatment at 250°C to eliminate organics.

2.1.4. POLYMERIC METHOD (PG AND PGPR)

To prepare the PGPr sample, praseodymium(III) acetate, acid catalyst (3 M HNO_3), acetylacetone and water were added and refluxed at 70°C in the ethanol media with continuous stirring. Two hours later, zirconium (IV) n-propoxide was added to the solution and hydrolysed at 70°C for 6h with continuously stirring. After this time, yttrium acetate was added maintaining the same refluxed conditions for 4 days.

Firstly, in sample without praseodymium (PG sample), the Zr precursor was added together with acid catalyst, acetylacetone and water in ethanol and hydrolysed in the same conditions above mentioned (70°C/6h). Finally, yttrium acetate was added maintaining refluxed condition for 4 days. Gelation, five days after reflux has finished, and drying were performed at room temperature in the open air. The dried gels obtained were yellow coloured.

The molar ratio conditions in samples prepared by polymeric method were: acid: zirconium(IV) n-propoxide=1:0.18, acetylacetone: zirconium(IV) n-propoxide= 1:1, water: zirconium(IV) n-propoxide= 4:1, and ethanol: zirconium(IV) n-propoxide=1:26 molar ratio.

To compare directly the behaviour of the prepared powders no washing and deagglomeration was carry out in any of the method.

2.2. Firing and characterisation of samples

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were carried out in air on raw powders contained in a Pt crucible with a Perkin-Elmer instrument (DTA 1700, TGA7). The heating rate was 10°Cmin⁻¹ to 25°C from 1100°C. Powdered alumina was used as the reference substance.

The raw powders were fired in air at 500°C for 12h to eliminate organic compounds and then were sieved to 60 µm, uniaxially pressed (20 MPa) and fired at 1.600°C for 2h. This treatment caused zirconia stabilization and sintering simultaneously. The sintered compacts were characterised by XRD (X-ray diffraction), to determinate the cell parameters, SEM-EDX (scanning electron microscopy-energy dispersion X-ray) and density measurements. Vickers microhardness and K_{IC} measurements were also carried out polished samples embedded in an epoxy matrix.

XRD powder diffractograms were obtained using a Philips X-ray diffractometer using CuK_{α} radiation. Microstructural analysis by SEM-EDX were carried out using a LEICA LEO440I equipped with an Oxford LYNK EDX system. Density measurements were determined by the Archimedes method in water. Microhardness values were measured from indentations of a Vickers diamond pyramid in a Matsuzawa indenter. The load on the sample was 200 g with 25 seconds loading time.

Electrical behaviour of sintered materials has been studied by complex impedance spectroscopy in an LF Impedance Analyzer 4192A supplied by Hewlett-Packard.

3. RESULTS AND DISCUSSION

DTA and TG curves of representative raw gel samples are shown in Fig. 1 and XRD of the DTA residues are also presented in Table I.

TABLE I. XRD RESULTS AND COLOUR OF SAMPLES.

SAMPLE	Raw	DTA-TG*	500°C/12h	1.600°C/2h
CE	M(vs)Y(vw) white	M(vs)Y(w) white	M(s)Y(vw) white	C(vs)M(m) white
CG	N(s) white	T(s) white	T(w) white	T(vs) white
CI	N(s) white	T(s)M(w) white	T(w) white	T(vs)M(s) white
PG	A white	T(vs) white	T(w) gray	T(vs) white
CEPr	M(vs)Y(vw) Pr(vw) gray	M(vs)Y(m) Pr(m) gray	M(vs)Y(vw) Pr(vw) gray	C(vs) yellow
CGPr	N(s) green	C(m) yellow	C(vw) yellow	C(vs) yellow
CIPr	N(s) green	C(m) yellow	C(vw) yellow	C(vs) yellow
PGPr	A green	C(m) yellow	C(vw) gray	C(vs) yellow

*DTA-TG treatment resulting powder. Crystalline Phases: N (NH_4Cl), A (Amorphous), T (tetragonal zirconia), M(monoclinic zirconia), C (cubic zirconia), Pr (Pr_2O_3), Y (Y_2O_3). Peak intensity: vs(very strong), s(strong), m(medium), w(weak), vw(very weak).

In colloidal samples (Fig 1a) the DTA curves show two endothermic peaks at 140-300°C related to a weight loss detected in the TG curves in the same temperature range, which could be ascribed to the evaporation of residual water and chloride entrapped in the gel (9). From 350 to 420°C an exothermic peak may be seen associated

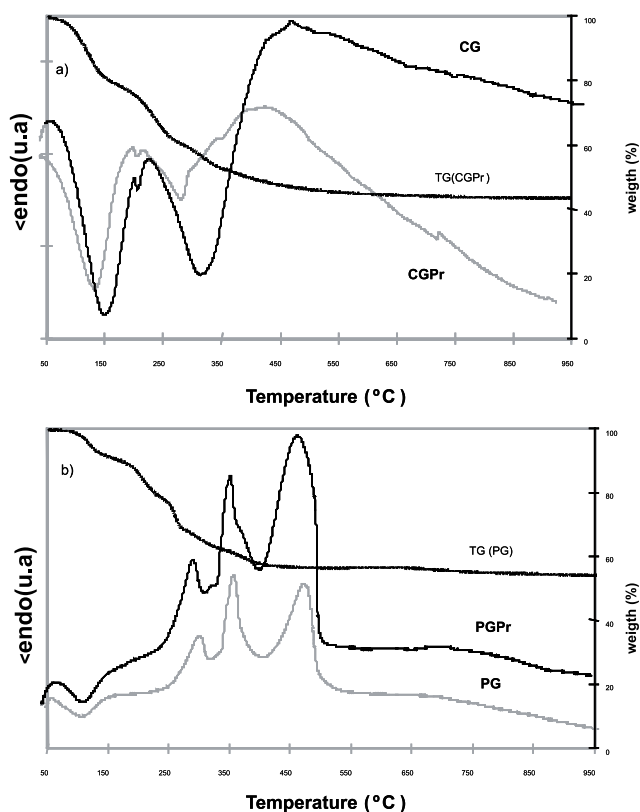


Fig. 1. a) DTA curves of colloidal samples: CG (undoped), CGPr (doped), and TG curve of doped colloidal sample (CGPr); b) DTA curves of polymeric samples: PG (undoped), PGPr (doped), and TG curve of undoped polymeric (PG).

with a weight loss of 8% due to decomposition of acetate groups. The weak exothermic peak around 450°C in CGPr and at 470°C in CG is ascribed to zirconia crystallization detected by XRD of residues (see Table I).

DTA-TG curves of polymeric samples (Fig. 1b) show the endothermic peaks associated with the evaporation of solvent (120-250°C) and three exothermic peaks at 300, 350 and around 450°C. The peaks at 300 and 350°C are associated with a weight loss as shown in the TG curve, indicating that they can be ascribed to the oxidation of organics and to the decomposition of acetate groups respectively. The last strong exothermic peak around 450°C in PGPr and at higher temperature (470°C) in PG can be ascribed to a pyrolysis process of organometallic intermediate compounds (12). The zirconia crystallization, detected by XRD of the residue (see Table I), would not be observed in these curves due to strong exothermic peak above mentioned.

According to the ATD-TG results for all the gel samples, the temperature associated with zirconia crystallization is around 470°C in undoped samples and 450°C in doped samples. Praseodymium not only decreases the crystallisation temperature but also stabilises the cubic zirconia polymorph as opposed to tetragonal zirconia stabilization. Cubic or tetragonal zirconia are detected as the single phase in all gel samples by XRD of the residue except in the CI sample in which monoclinic zirconia is also detected (Table I).

However, DTA and TG curves of a doped ceramic sample (not shown) showed only a weak endothermic peak at 270°C, related to a weight loss of ~1% due to Pr₆O₁₁ decomposition.

The XRD results (Table I) show that the raw powders were amorphous in the polymeric samples. Colloidal and citrate samples

show the presence of present ammonium chloride crystallised from the ammonia addition, and the ceramic samples show peaks associated with oxide precursors. Powders calcined at 500°C for 12h had wide peaks of medium intensity associated with the tetragonal zirconia as identified by Garvie (13) except in the case of the ceramic samples which remain unreacted. XRD results in sintered samples at 1600°C for 2h indicate that undoped samples had a different behaviour: ceramic and citrate undoped samples (CE and CI) show a mixture of monoclinic and tetragonal zirconia phases. Colloidal (CG) and polymeric samples (PG) show only the tetragonal polymorph as the stable phase (characterised doublet tetragonal peaks (002)_v, (200)_v, (202)_v, (220)_i and (113)_v, (311)_i were detected by DRX). However, doped samples show the cubic phase as stable for all the methods and had a yellow colour. These results are in accordance with the DTA-TG analysis discussed above.

Lattice parameters measurements by POWCAL and LSQC calculation programmes (14) for the cubic and tetragonal crystalline phases are given in Table II. The measurements indicate, in agreement with literature data (15), a decrease in the tetragonal cell volume from the ASTM value in the undoped samples: the a and b crystalline parameters are similar to the ASTM values and the c parameter decreases significantly. However, the cubic yttria-stabilized zirconia cell parameters are between 5.10-5.12 Å (15). The doped samples with Pr show an increase for these crystallographic parameters indicating the introduction of the doping cation into the cubic structure; because the effective Zr⁴⁺ ionic radius (0.84 Å) for 8-fold coordination proposed by Shannon (16) is lower than Pr ionic radius (Pr³⁺ = 1.14 Å or Pr⁴⁺ = 0.99 Å).

TABLE II. CELL PARAMETERS, THEORETICAL DENSITIES AND MECHANICAL MEASUREMENTS.

SAMPLE	Cell	Parameters	ρ(%)	Hv (GPa)	K _{IC} (MPa·m ^{1/2})
	a=b(Å) JCPD 5.12 Å t-ZrO ₂	c(Å) JCPD 5.25 Å t-ZrO ₂			
CE	5.122(4)	5.155(4)	80	1.3(6)	-
CG	5.106(1)	5.164(1)	92	9.3(2)	4.8(2)
CI	5.118(6)	5.163(9)	87	6.7(1)	4.7(1)
PG	5.110(3)	5.152(4)	82	5.3(3)	-
	a=b(Å) JCPD 5.09 Å c-ZrO ₂	c(Å) JCPD 5.09 Å c-ZrO ₂			
CEPr	5.163(1)	5.163(1)	81	4.6(3)	-
CGPr	5.167(1)	5.167(1)	90	10.8(2)	2.4(2)
CIPr	5.168(1)	5.168(1)	91	7.4(2)	1.8(2)
PGPr	5.169(1)	5.169(1)	88	6.0(1)	-

Table II also shows the sintering and microhardness data for the samples. The density values were calculated by the additive method, considering both Pr³⁺ and Y³⁺ ions as in solid solution in the cubic zirconia lattice, whose cell volume is calculated from the lattice parameters measurements.

Sintered compacts densified relatively poorly (80 and 92% theoretical) indicating that the samples had not reached the final step of densification. The method of synthesis has a great influence on densification. Gel samples densified better than ceramic samples, and the polymeric method was the poorest for densification of the gel techniques for both doped and undoped samples. Only colloidal (CG) and citrate (CIPr) samples reached the intermediate step of densification. The characteristics of the agglomerates in the presintered powders (powders fired at 500°C) explain these results: the agglomerates in the ceramic samples were more chemically heterogeneous, non-uniform in size and higher size than agglomerates in samples prepared by

unconventional methods. These last samples were characterised by good chemical homogeneity, more homogenous size distribution and with monolithic aspect, especially colloidal samples. These results indicate that, in the thermal treatment where zirconia stabilization and sintering are simultaneous, samples prepared by the ceramic method, whose precursors have larger particle and crystallite sizes, and samples prepared by the polymeric method with a homogenous crystallisation mechanism, have the worst densification characteristics. However, methods with a heterogeneous crystallisation mechanism, such as citrate or colloidal, gave the best results. Pr doping improves densification except in colloidal samples where it was reduced by the Pr addition.

SEM micrographs of representative samples are shown in Fig. 2. CE sample shows a grained microstructure with extensive grain boundaries and large degree of open porosity (Fig. 2a), the grain size being $\sim 3\text{-}6\ \mu\text{m}$. Polymeric samples (Fig. 2b) show a porosity intermediate between that for ceramic and the other gel samples. Colloidal (Fig. 2c) and citrate (Fig. 2d) microstructures show a relatively low closed porosity. In polymeric and citrate samples, it was difficult to determine grain size. In contrast, the colloidal samples show a clear grain boundary with grain size of $6\text{-}12\ \mu\text{m}$. These results are in agreement with the densification obtained. No sample shows closed porosity typical of final step of densification. Colloidal and citrate samples with lower porosity have the highest density and the ceramic sample with a high level of open porosity has the lowest.

EDX analysis (not shown) indicated a homogeneous dispersion of both Y and Pr. The homogeneous distribution of praseodymium is consistent with substitutional solid solution of the Pr in the zirconia lattice.

From the Vickers microhardness results in Table II the following may be highlighted: i) gels samples have greater microhardness than ceramic samples; colloidal samples stand out with 9.3 (CG) and 10.8 GPa (CGPr), ii) Pr doping substantially improves the microhardness of all samples. However, the crystallization of cubic zirconia in colloidal or citrates samples doped with praseodymium diminishes the toughness strength from 4.8 and 4.7 $\text{MPa}\cdot\text{m}^{1/2}$ to only 2.4 and 1.8 $\text{MPa}\cdot\text{m}^{1/2}$.

These results agree with the densification obtained and the microstructures observed. Colloidal samples have low porosity, large size grain and consequently a greater microhardness. The low microhardness in ceramic samples is explained by the open porosity and the monoclinic zirconia detected by XRD in undoped sample (CE) (Table I).

The colloidal and citrate samples were characterized by complex impedance spectroscopy. The impedance spectra evolution with temperature of CG and CIPr samples are shown in Figure 3 and the Arrhenius plot of bulk contribution of samples is presented in Figure 4.

From Figure 4 the energy of activation is 1.03 eV for CG and 1.14 eV for CGPr, citrates present higher values 1.18 and 1.33 eV. At 1000°C CG shows $0.025\ \text{S}/\text{cm}$ of measured conductivity and doped samples two degrees of magnitude lower, but CI sample lowers three degrees.

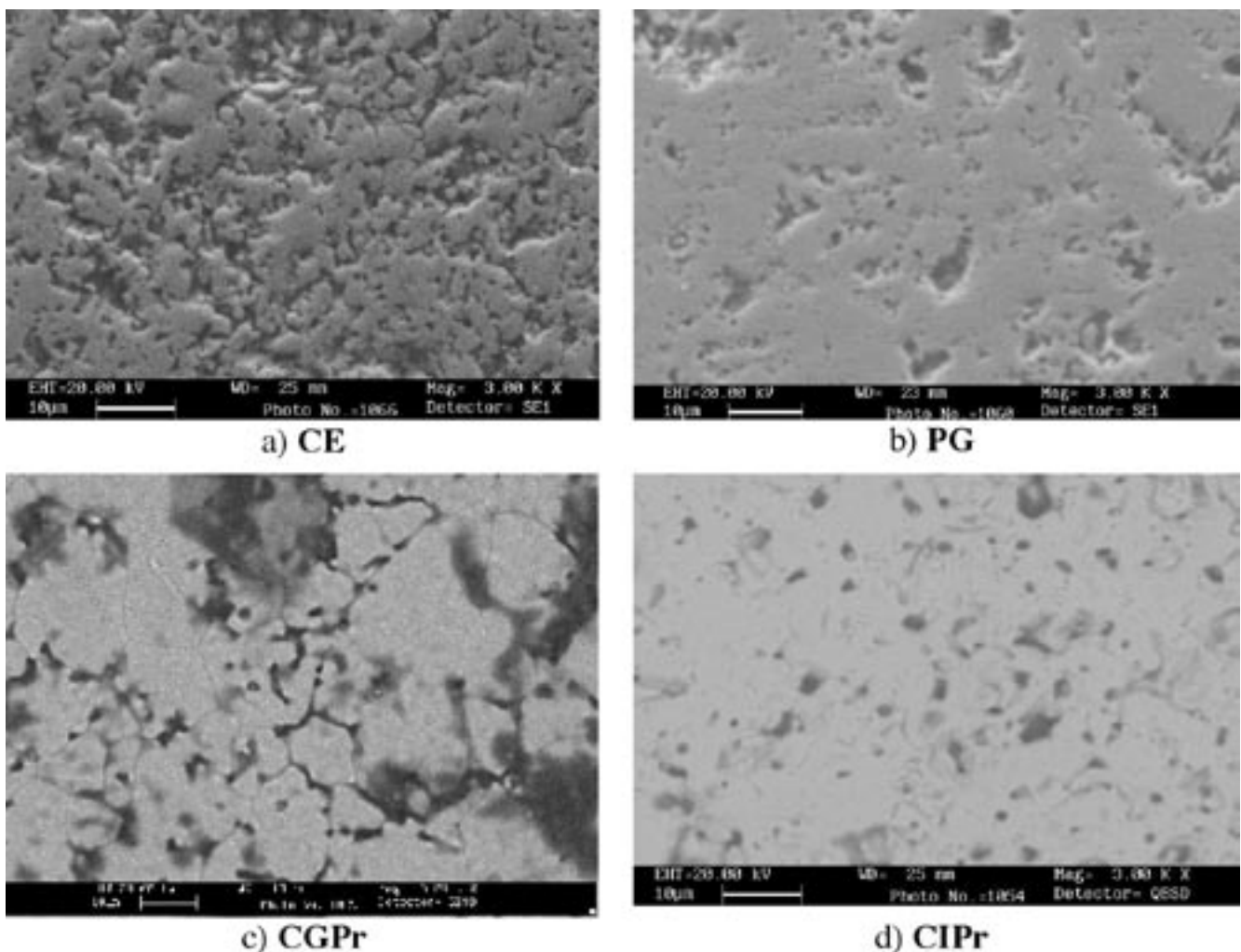


Fig. 2. SEM micrographs of representative samples sintered at 1600°C for 2h: a) CE (undoped ceramic), b) PG (undoped polymeric gel), c) CGPr (doped colloidal gel), d) CIPr (doped citrate).

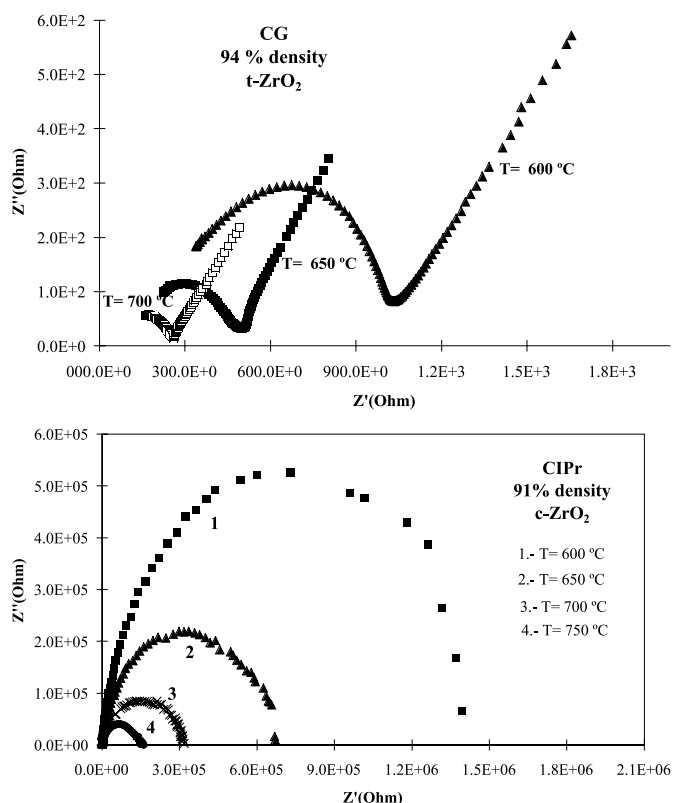


Fig. 3. Impedance spectra evolution with temperature of CG and CIPr

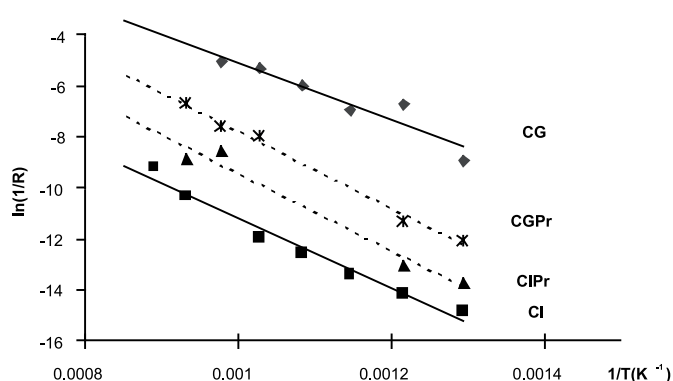


Fig. 4. Arrhenius plot of bulk contribution of samples colloidal and citrates samples. R= resistance (Ω), T= Temperature (K)

4. CONCLUSIONS

- i) The influence of the method of synthesis on the reactivity is more relevant in undoped than in doped samples. Colloidal and polymeric gels allow complete stabilisation of the tetragonal zirconia structure; monoclinic zirconia is also detected in citrate and ceramic samples.
- ii) The synthesis method generates important differences in microstructure: very high grains and a high degree of open porosity in ceramic samples, and lower closed porosity with a bigger grain size in gels. Specimens prepared by polymeric route have a level of porosity intermediate between that for ceramic and the other gel samples.
- iii) Powders of intermediate reactivity (citrate and colloidal gel) show the best sintering (low level of closed porosity) and the highest microhardness. Colloidal gel samples showed non-porous microstructure and high Vickers microhardness. In contrast, those routes whose reaction rate depends to a large

degree on the particle size of the precursors, such as ceramic or routes with a tendency to form amorphous material such as polymeric, showed the lowest densification and the lowest microhardness.

- iv) Praseodymium addition stabilised cubic zirconia rather than the tetragonal form by the formation of a substitutional solid solution.
- v) Praseodymium addition improved Vickers microhardness properties in all samples prepared by all the routes but the toughness strength was reduced to 50% due to crystallization of cubic zirconia.
- vi) Undoped colloidal sample showed the best conductivity measurements (0.025 S/cm at 1000°C) and the lowest energy of activation. CG presents good expectations and with a better processing it would be possible to improve the densification which is necessary in an electrolyte to avoid the combustible and oxidant gases mixed. In these conditions, CG can become an interesting solid electrolyte for SOFC applications.

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