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Present several items on ceria-based ceramic electrolytes: synthesis, additive effects, reactivity and electrochemical behaviour

J. R. JURADO
Instituto de Cerámica y Vidrio, ICV-CSIC. Antigua Ctra. Valencia Km. 24,300.
Arganda del Rey 28500, Madrid. Spain
E-mail: jrjurado@icv.csic.es

Ceria-doped electrolytes have been extensively studied, because they are promising candidates for intermediate temperature solid oxide fuel cells (ITSOFC). In this work, several relevant aspects, such as powder synthesis, small additive effects, reactivity of electrode/electrolyte and interface microstructure were described. The combustion synthesis is a really suitable synthesis route to achieve, at low temperatures, finely, homogeneous and reactive powders for ceria based electrolytes. The presence of small amounts of titania is beneficial, since it produces a significant reduction of the grain boundary resistance. On the other hand, the reactivity of the ceria electrolyte against lanthanum-NiO perovskites at high temperatures (1475 °C), enhances both the $LaNiO_{3-\delta}$ decomposition and the diffusion of Ni and La ions as is noted in the reactivity analysis.

1. Introduction

Most of the effort in SOFC development is nowadays focussed on intermediate temperature solid oxide fuel cells (IT-SOFCs). For this purpose, relatively high ionic conductivity for suitable solid electrolytes is required at intermediate temperatures, and ceria-based materials could have sufficient high ionic conductivity at temperatures so low as 600 °C, which is appropriate for electrolyte candidates in such devices. Actually, doped-ceria based materials are considered the most promising conducting solid electrolyte for ITSOFC applications. In a recent review, Steele [1] reported the current state of the art Ceria-doped ceramics. In that appraisal the following key aspects were pointed out:

1) The original ceria-doped gadolinia (CGO) composition is still the best choice for ITSOFC applications, eventually at 500°C, and it is not clear that ceria-doped samarium would be a better candidate [2].
2) Pure ceria-powder is a key factor in reducing the grain boundary electrical resistance.
3) It is not clear that the addition of minor co-dopants such as Pr_6O_{11} [3] has any beneficial effect (increasing ionic domain), for clean CGO ceramics.

In any case, after the evaluation of ceria electrolytes in an electric generator ITSOFC by Milliken *et al.* [4], one has been persuaded that these types of ceramics provide sufficient electrical efficiency to consider that ceria-doped mixed conductors are suitable for application in SOFC electric generators.

Minor interest has been found in the literature about three important aspects of using ceria-doped ceramics for ITSOFC applications: 1) New routes of synthesis, such as, hydrothermal synthesis [2], oxalates coprecipitation [5, 6] etc. 2) Search of minor co-dopants to decrease the grain boundary resistance by reaction with silica [7]. 3) Finally, the reactivity between the electrodes and the electrolyte in order to build a suitable interface.

Wet-chemical synthesis methods produce ceramics single or multioxide powders with high sinterability, high surface area, well-defined chemical compositions and homogeneous distribution of the elements. In spite of the quality of the powders produced and although powder synthesis can be achieved at low temperature, many solution processes are complicated and lengthy procedures which limit their applicability.

In the past few years, combustion synthesis of multicomponent ceramic oxides has been gaining reputation as a straightforward preparation process to produce homogeneous, very fine, crystalline and unagglomerated powders, without the intermediate decomposition and or calcining step [8–10]. The basis of the Combustion Synthesis Technique comes from the thermochemical concepts used in the field of propellants and explosives [11]. Briefly, to produce a mixed oxide by combustion, a saturated aqueous solution containing the desired metal ions and a suitable organic fuel is brought to a boil, until the mixture ignites and a self-sustaining and rather fast combustion reaction takes off, resulting in a dry oxide powder. Redox reactions such as this are exothermic in nature and ignite at temperatures much lower than the oxide phase formation temperature. The heat released by the reaction causes the temperature to rise very fast and sustains it, even in the absence of an external heat source, at the high level ($>1000\,^\circ$C) necessary for the synthesis to occur. The large amounts of evolved gases result in the formation of a foam whose structure is transmitted to the oxide produced. The method consists of establishing a simple valency balance, irrespective of whether the elements are present in the oxidiser or the fuel components of the mixture, to obtain the stoichiometric composition of the redox mixture which corresponds to the release of the maximum energy for reaction. Given that the metal cations are mixed in a liquid phase, the boiling liquid sustains the homogeneity of the mixture and the reaction is very fast, the resulting powder is also homogeneous, the oxide particles are very fine and the high temperature reached is usually enough to promote their crystallisation.

One of the aims of this research is to prepare fine powders (combustion synthesis) capable of leading to dense materials with high electrical and mechanical performance. Another objective is try to reduce the effect of silica content on grain boundary resistance, which produces the ohmic losses in the interfaces, by using small amounts of alumina and titania in order to clean (scavenger effect) the grain boundaries and take away the silica to the triple points [5, 7, 12].

Finally, in this work the reactivity between ceria doped ceramics and a perovskite oxide such as $LaNiO_{3-\delta}$ is considered. Furthermore the interface between the components will be studied and considered as a candidate for the cathode in ITSOFCs.

2. Experimental

2.1. Preparation and EIS characterisation of several ceria-based materials by combustion synthesis

The ceria based ceramics were synthesised by combustion reactions employing Aldrich hydrate nitrate salts, $Ce(NO_3)_3.6H_2O$, $Ca(NO_3)_2.6H_2O$, $Gd(NO_3)_3.6H_2O$ and $Y(NO_3)_3.6H_2O$ as cation precursors. Aldrich urea, $CO(NH_2)_2$, was used as fuel. Batches were calculated on a basis of 5 g of cerium nitrate, with those reactants in a molar proportion. The reactants were first melted in a wide-mouth vitreous silica basin (300 cm^3) by heating up to 300 °C on a hot-plate inside a fume cupboard, under ventilation at this temperature the ignition took place and the reaction was rapid (5 minutes) and produced a dry, mostly white and very fragile foam, that readily crumbled into powders accompanied by a great volume increase, when compared to the original volume of liquid. Further details on the combustion reaction can be found elsewhere for other systems [9, 11]. The as-prepared powders were characterised by XRD using a SIEMENS D-5000 diffractometer, also HTEM Hitachi H-9000 and SEM-EDX Zeiss DSM 950. After sintering at 1450 °C for 4 hours, axial pressed disk pellets of 1 cm in diameter and 2 mm thickness were electroded onto both faces with platinum paste, and then calcined at 800 °C for 30 minutes. The impedance spectroscopy spectra (EIS) were obtained in a hot sample holder in the temperature range of 150 to 800 °C, by using an impedance analyser HP 4192 in the frequency range of 10 to 10^7 Hz.

2.2. The effect of additives (alumina and titania) on boundaries. Cathodic polarisation curve

Samples of $(CeO_2)_{0.92}(Gd_2O_3)_{0.08}$ (CGO) with 1 mol% TiO_2 and 1 mol% Al_2O_3 as additives were prepared by solid state reaction. The raw materials were attrition milled for 2 hours in iso-propanol, and calcined at 1100 °C for 4 hours and then attrition milled again for 2 hours and sieved to 65 μm. Disk pellets were isopressed at 200 MPa and sintered at 1500 °C for 4 hours. Archimedes density measurements, SEM, XRD, EIS and conductivity as a function of oxygen partial pressure methods were also used. A three electrode configuration, using silver paste as the working electrode and platinum paste as reference and counter electrodes, was performed. A polarisation curve was obtained using the AUTOLAB (Electrochimie) Impedance Interface Electrochemical Equipment.

2.3. Reactivity and interface between Ceria doped ceramics and a perovskite oxide such as $LaNiO_{3-\delta}$

$LaNiO_{3-\delta}$ was produced by the combustion technique [10]. The hydrated nitrate salts $Ni(NO_3)_2.6H_2O$, and $La(NO_3)_3.6H_2O$ were used as cation precursors with a stoichiometric amount of urea as the fuel. The obtained powders were calcined at 800 °C and then characterised by XRD, SEM, TEM and BET. BET specific surface area was determined by a Quantachzome Quantasort apparatus. Disk samples prepared using a mixture of $LaNiO_{3-\delta}$ and CeO_2 with a molar ratio of 1 : 1 were fired at 1475 °C for 4 hours and those of 3 : 7 were calcined at 1050 °C for 2, 4, and 8 hours of soaking times. A layer of $(CeO_2)_{0.92}(Y_2O_3)_{0.04}(CaO)_{0.04}$(CYCa) powder was deposited by uniaxial pressing onto a thicker green layer of $LaNiO_{3-\delta}$, and then co-firing at 1400 °C for 4 hours. XRD and SEM-EDAX were employed for microstructural characterisation. Preliminary electrical conductivity measurements by EIS were also conducted to evaluate the phase transformation.

3. Results and discussion

3.1. Preparation and electrical characterisation of several ceria-based materials by combustion synthesis

The combustion reaction of urea is extremely exothermic and should provide the heat needed for the synthesis reactions of the precursor nitrates. The amount of urea satisfies the enthalpy requirements for complete decomposition at 25 °C and release of all the corresponding gases. In this case the temperature is high enough to promote the synthesis of the ceria fluorite structure and the single oxides no longer are reaction products, as seen in Fig. 1. The XRD pattern of the as-prepared powders showed finely and nano crystalline powders with $(CeO_2)_{0.92}(Y_2O_3)_{0.04}(CaO)_{0.04}$ fluorite single phase structure. There are no second phases of any

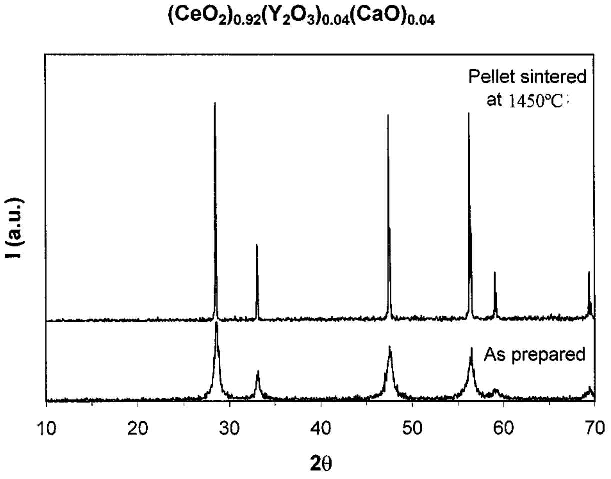


Figure 1 XRD pattern of the as-prepared powders and pellet sintered at 1450 °C of CeO_2-Y_2O_3-CaO.

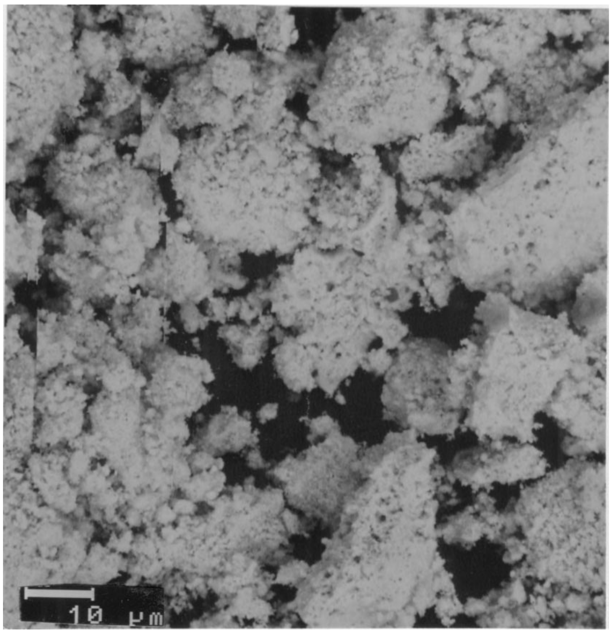


Figure 2 SEM micrograph of the as-prepared powder of $(CeO_2)_{0.92}(Y_2O_3)_{0.04}(CaO)_{0.04}$.

significant reaction products present, such as carbonates and nitrates, which normally appear in the synthesis of other materials [10]. When the as-prepared powders were observed by SEM-EDX (see Fig. 2), a very fine homogeneous material with sponge features is noted, and the particle size is extremely small (~15 nm), with a mono-modal grain size distribution. By EDX no silica peak was observed which is an indication that for this method we can obtain clean powders. However, we need to get more accurate information about the final silica content by Inductively Coupled Plasma Chemical (ICP) Analysis. By TEM, individual crystals could be clearly perceived by alternating bright/dark fields. Typically, quite spherical agglomerates of 50 nm size, of very fine crystals (ca.15 nm) could be seen, Fig. 3, for the powder $(CeO_2)_{0.92}(Gd_2O_3)_{0.08}$. The narrow particle size distribution of the calcined stoichiometric powder, practically monosized, suggests that it might display low packing density although its high specific surface area should ensure good sinterability.

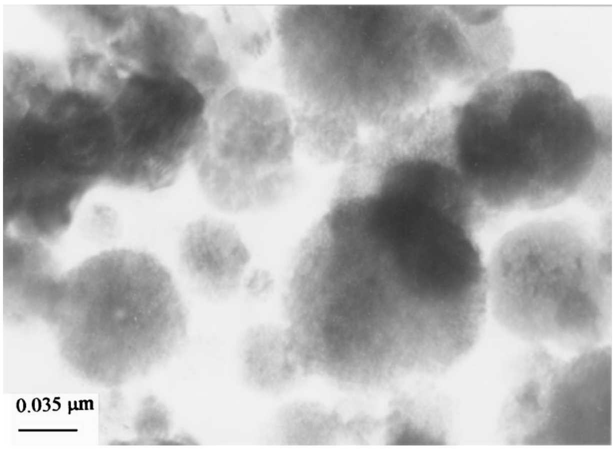


Figure 3 TEM micrograph of the $(CeO_2)_{0.92}(Gd_2O_3)_{0.08}$ as-prepared powder.

In this work, after uniaxially pressing (MPa) into pellets, a relative density of 95% was obtained in all samples investigated. The submicron features of the as-prepared powders promote densification but associated with unsuitable powder morphology and lower powder packing might cause abnormal grain growth and hinder densification, but the density achieved is sufficient to make preliminary EIS studies in air. The EI spectra of Ceria doped gadolinia (CGO) and ceria-doped yttria plus calcia CYCa, (Figs 4 and 5), shows high electrical conductivity of the grain interior and the size of the grain boundary arcs are small. That fact could be due to the synthesis method, the powders were achieved in only two simple steps. This indicates that the samples come from clean powders. Although, one cannot say that any silica is in the grain boundary, but the grain boundary arc might be considered as an intrinsic grain boundary contribution rather than a silica effect [1]. The activation energies for CGO is 0.73 eV, and 0.82 eV for the CYCa pellet, which were expected. Conclusively, the valency based molar proportions of reactants proposed by propellant chemistry can be conveniently used to successfully produce suitable ceria-doped electrolyte precursors. The powders will have a high compositional control and homogeneity, which 'really transform', at very low temperature (300 °C in 5 minutes), in a simple vitreous silica basin, on a simple hot plate, to a fluorite ceria single phase, without any second phases, impurities, reaction products, etc. The key factors of this method are: 1) Liquid solution mixture of precursors and fuel and 2) Ignition at 300 °C. Further, it is worth mentioning that the synthesis of ceria for any wet-chemical methods and/or solid state routes require exposure to temperatures in the range of 800–1100 °C for some hours and repeated intermediate drying, grinding and sieving steps. Again, the combustion synthesis technique could be a much simpler and more reliable route to synthesise these compounds.

3.2. The effect of additives (alumina and titania) on boundaries and electrochemical analysis

In this part it is demonstrated that undoped ceria-gadolinia samples with an amount of silica of 0.05% wt.

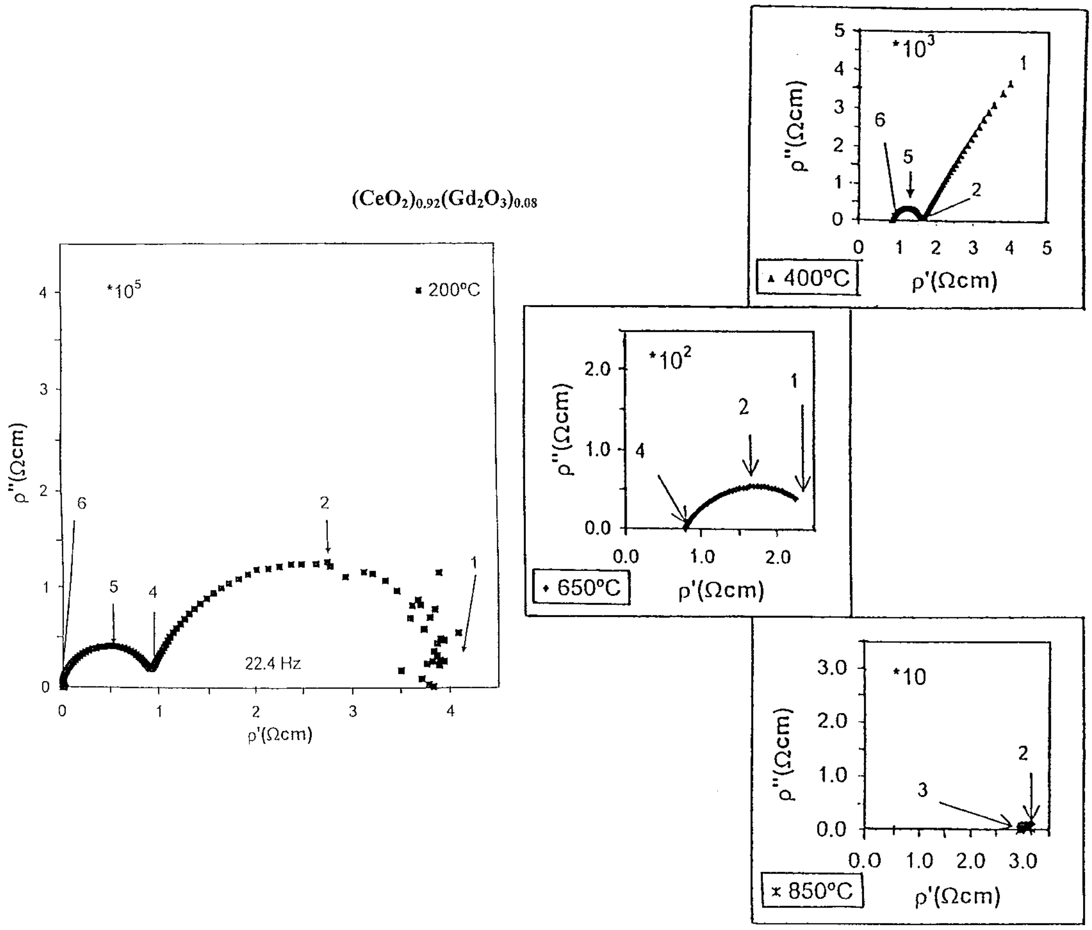


Figure 4 Impedance spectra in air of the $(CeO_2)_{0.92}(Gd_2O_3)_{0.08}$ sintered pellet.

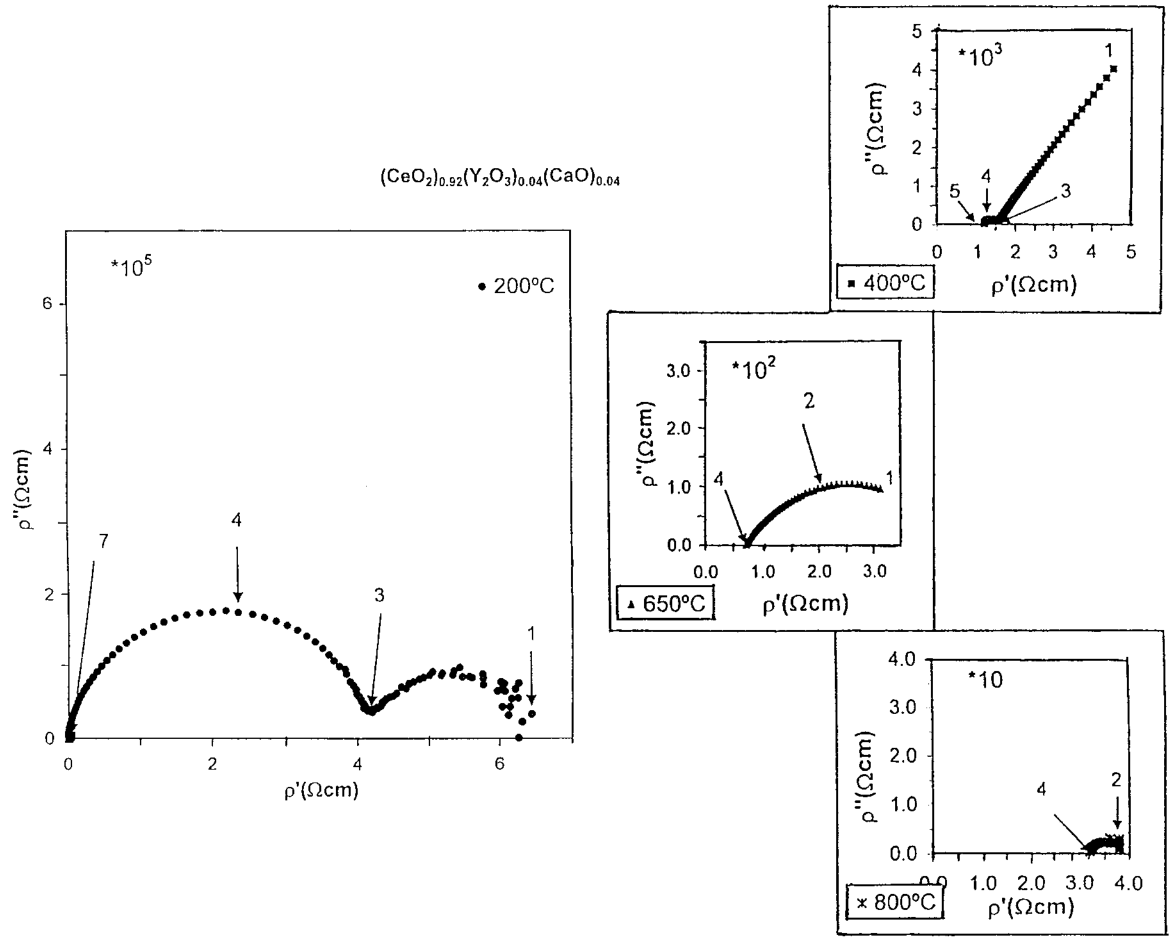


Figure 5 Impedance spectra in air of the $(CeO_2)_{0.92}(Y_2O_3)_{0.04}(CaO)_{0.04}$ sintered pellet.

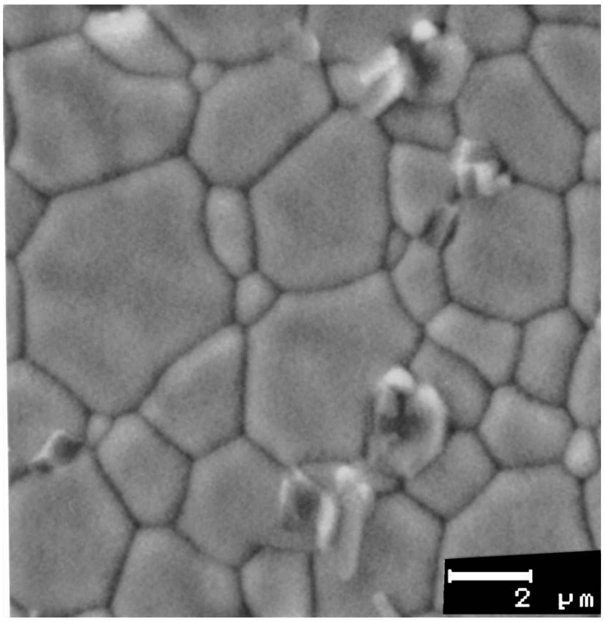


Figure 6 Microstructure of $(CeO_2)_{0.92}(Gd_2O_3)_{0.08}(TiO_2)_{0.01}$ sintered body.

can have the grain boundary electrical resistance behaviour modified by using a small amount, up to 1 mol%, of TiO_2 and Al_2O_3. Fig. 6 shows the microstructure of the minor titania co-doped materials. A non-exaggerated grain growth is noted. The relative density of compact ceramic bodies is superior to 98% (sintering temperatures of 1450 °C/4 h). The residual porosity is located at the grain boundaries. All of these features are related to a compact and well-developed microstructure. The fresh fracture of these samples is transgranular and can be associated to improvement toughness value, which is around 3 MPa. A second phase located at the grain boundaries, identified by a small XRD peak as $Gd_2Ti_2O_7$ with a pyrochlore structure was also found. The grain boundary electrical resistance of the undoped sample with the amount of silica mentioned above is two times superior to that minor titanium co-doped sample, and also a slight increase in the bulk conductivity was also detected. On the contrary, when alumina is added, the grain boundary resistance increases one and a half orders of magnitude. In one way, a beneficial effect of titania addition is noted in the grain boundary conductivity contribution, which could be attributed to the presence of a conducting second phase at the boundaries and silica is partially removed towards the triple points.

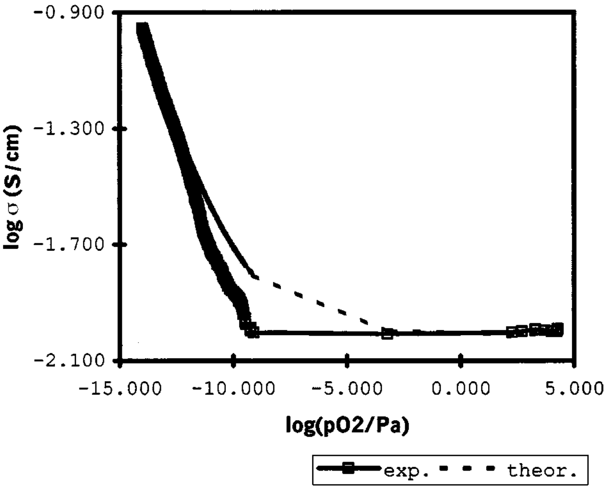


Figure 7 Log of conductivity of $(CeO_2)_{0.92}(Gd_2O_3)_{0.08}(TiO_2)_{0.01}$ as a function of pO_2 (750 °C).

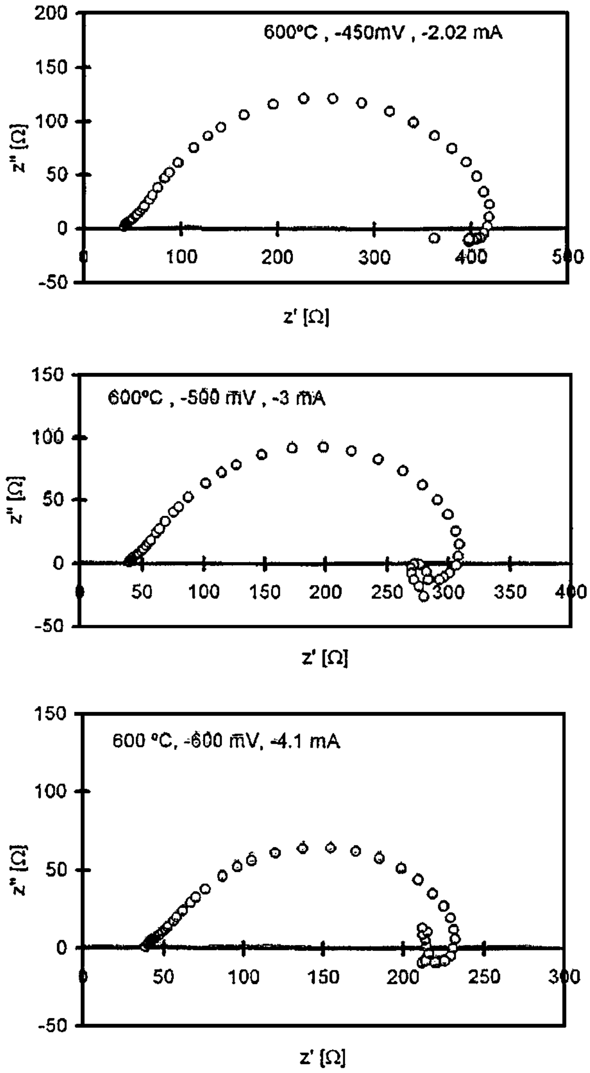


Figure 8 Impedance spectra in air obtained during cathodic polarisation measurement at different temperatures.

For the next electrochemical studies, the CGO composition with titania was selected. In Fig. 7, the log of conductivity as a function of oxygen partial pressure at 750 °C was plotted. An electrolyte domain from 5 to 10^{-12} Pa (pO_2) with a conductivity value of 0.035 S/cm is achieved. The n-type conductivity region curve is fitted to a -1/4 slope, which corresponds to the chemical defect diagram expected in this mixed conductor. The impedance spectrum obtained during the cathodic polarisation is shown in Fig. 8, a cathodic voltage of -450 mV vs. air was applied with a current density of -20 mA/cm^2 at a temperature of 600 °C. By fitting the EIS spectra using a non-linear least squares method, three contributions to the total impedance were identified and an equivalent circuit fit to the data was found [12]. A pure resistance, which can be ascribed to the electrolyte contribution, is associated in series with a parallel combination of a resistance with a single Warburg line in the frequency range of 10^4 to 10^{-2} Hz. This parallel combination can be ascribed to a partial

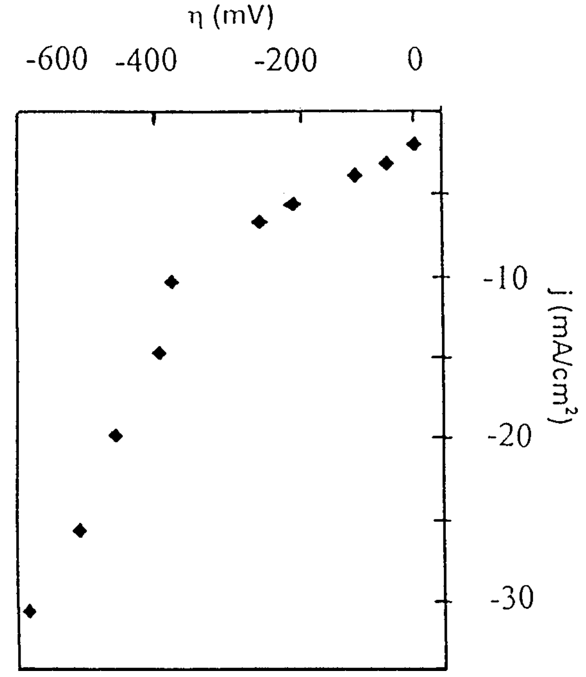


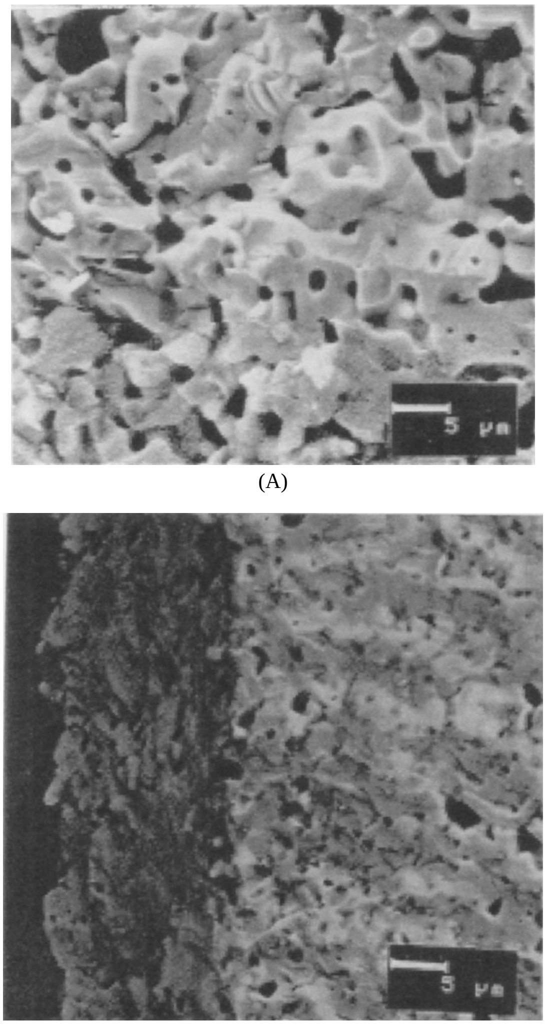
Figure 9 Cathodic polarisation curve in air at 600 °C.

rate-determining step identified as uniform diffusion of atomic oxygen through the silver electrode. That subcircuit is associated in series with a parallel combination of a resistance and a constant phase element (CPE). That result is different from that reported by Van Herle and McEvoy [13], who observed a non-uniform oxygen diffusion through a silver cathode in an O_2, Ag/YSZ cell.

The cathodic polarisation curve obtained is shown in Fig. 9, where the current density vs. overpotential is plotted. The overpotential departs from Butler-Volmer theory. The overpotential curve reaches a plateau in that plot, where an increase in overpotential occurs without a significant increase in current. It seems to reach a limiting value and after reaching that limiting value, if the overpotential is increased, the current density increases significantly indicating a decrease in the polarisation cell resistance, according to Wang and Nowick [14], using platinum as a working electrode. This unusual fact could be due to a reduction effect of the electrolyte in those ranges of overpotential and current density. Further work is now in progress in order to replace silver by a LSFC (Lanthanum, Strontium, Iron, Cobalt) perovskite as a working electrode.

3.3. Reactivity and interfaces between Ceria doped ceramics and a perovskite oxide such as $LaNiO_{3-\delta}$

The reactivity of $CeO_2/LaNiO_{3-\delta}$ mixtures [15] was studied. Above 900 °C, $LaNiO_{3-\delta}$ decomposes to several La-Ni-O oxides and ceria seems not to modify the $LaNiO_{3-\delta}$ decomposition. However, La ions enter into ceria lattice, as identified by XRD studies. According to the EIS spectra in the $(CeO_2)_{0.92}(Y_2O_3)_{0.04}(CaO)_{0.04}$/La-Ni oxide 1 : 1 mixture, the La_2O_3 incorporation inside the CeO_2 electrolyte lattice determines an increment in the grain interior conductivity on the original-base electrolyte $(CeO_2)_{0.92}(Y_2O_3)_{0.04}(CaO)_{0.04}$. Moreover, the presence of NiO as a secondary phase and the La_2O_3 diffusion breakdown influence both the grain boundary and the electrolyte microstructure (see Fig. 10 A). Consequently, the contribution of grain boundary to the total resistance of the sample increases. The SEM-EDX analysis of the $(CeO_2)_{0.92}(Y_2O_3)_{0.04}(CaO)_{0.04}$/La-Ni Oxide interface formed at 1400 °C is shown in Fig. 10B. A good adherence and match between both phases are shown. The high reaction temperature could enhance both phenomena, the $LaNiO_{3-\delta}$ decomposition and the diffusion, as is noted in the reactivity analysis [15]. However, the NiO dominated self-diffusion towards the interface builds a barrier, which retains La_2O_3 diffusion since, La might be captured in the La-Ni-O oxide structures. Because of the negligible NiO diffusion into the CeO_2 electrolyte and the La ions retention in the above mentioned structures the CeO_2 electrolyte does not suffer any significant modification. The absence of traverse cracks and the excellent adherence between both phases, indicate acceptable thermomechanical behaviour.



(A)

(B)

Figure 10 SEM micrograph of the (A) microstructure of the CeO_2-Y_2O_3-CaO/La-Ni-O oxide 3:7 mixture and (B) The microstructure of the interface of CeO_2-Y_2O_3-CaO/La-Ni-O oxide.

4. Conclusions

1. Combustion synthesis is a reliable and suitable synthesis route to achieve, at low temperatures, finely,

homogeneous, and reactive powders for ceria based electrolytes.

2. The presence of small amounts of titania in CGO is beneficial, since it produces a significant reduction of the grain boundary resistance.

3. The reactivity of the ceria electrolyte CYCa against lanthanum-NiO perovskites at high temperatures (1475 °C), enhances both the $LaNiO_{3-\delta}$ decomposition and the diffusion of Ni and La ions, as is noted in the above reactivity analysis. A good adherence and match between both phases was shown. The absence of traverse cracks and the excellent adherence between both phases indicate an acceptable thermomechanical behaviour.

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