



Short communication

# Low-temperature preparation by polymeric complex solution synthesis of Cu–Gd-doped ceria cermet for solid oxide fuel cells anodes: Sinterability, microstructures and electrical properties

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## ABSTRACT

A homogeneous dispersion of fine CuO in a gadolinia-doped ceria (CGO) ceramic matrix by the polymeric organic complex solution method has been achieved. Highly sinterable powders were prepared by this method after calcining the precursor at 600 °C and attrition milled. The powders consist of individual particles of few tens of nanometer in size with a low agglomeration state. The isopressed compacts were sintered in air at 1000 °C and reducing in N<sub>2</sub> 90%–H<sub>2</sub> 10% atmosphere to form Cu–CGO cermets. The microstructures showed a uniform distribution of porous metallic Cu particles surrounded by microporous spaces. The influence of Cu content in Cu–CGO cermets on the electrode performance has been investigated in order to create the most suitable microstructure. The electrical properties of Cu–CGO cermets have been also studied using impedance spectroscopy, in the temperature range from 150 to about 700 °C in argon atmosphere. These measurements determined a high value of electrical conductivity at 700 °C, similar to that corresponded to pure metallic copper.

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## 1. Introduction

The development of economically competitive solid oxide fuel cells (SOFCs) required lowering the operation temperature and the utilization of novel anode materials and microstructures capable of efficiently utilizing hydrocarbon fuels [1]. Ni-cermet have been commonly used as anode material for SOFCs due to its high catalytic activity for the dehydrogenation of hydrocarbons as well as a high electronic conductivity. However, Ni forms carbon fibers above 700 °C, a serious problem since these fibers can completely fill the anode compartment [2,3]. Cu is found to be one possible anode material used for direct utilization of hydrocarbon fuels in SOFCs, because it is relatively inert to hydrocarbon reactions, particularly coking, compared to Ni, and also Cu exhibit a high electronic conductivity and relatively low cost [4–6]. It is essential to develop compatible electrodes with the electrolyte and with high performance [7]. Given that CeO<sub>2</sub>-based materials, i.e., those doped with Gd<sub>2</sub>O<sub>3</sub> (CGO) are an upcoming alternative solid electrolyte to yttria stabilized zirconia (YSZ) in IT-SOFC applications [8], then, Cu–ceria cermets would be a much recommended electrode in order to realize a practical solid oxide fuel cell which operates at low temperatures and with the possibility of utilizing hydrocarbon fuels.

The important functions of the ceria particles in the Cu-doped ceria cermet would be to (a) supply oxide ions to the TPB, (b) suppress the sintering of Cu, and (c) match the thermal expansion coefficients between the cermet and the doped ceria electrolyte.

The main problem is that Cu has a low melting point that makes it difficult to apply conventional ceramic processing methods to fabricate cermets containing Cu. With Ni–CGO, the usual method for producing the cermet involves calcining mixed powders of NiO and CGO and then, after forming, the sintering process. Given that a good densification of CGO is necessary to ensure the stability of the composite during the reduction process, then heating to at least 1500 °C is required and, because Cu<sub>2</sub>O melts at 1235 °C, it is not possible to prepare a Cu–CGO cermet using this approach. Therefore, a good powder preparation method, in order to achieve much more reactive and sinterable powders, becomes necessary. Gorte et al. [4] have successfully prepared Cu-cermet anodes by adding Cu after preparing a porous layer of YSZ on a dense YSZ electrolyte layer. Cu is added by aqueous impregnation with a concentrated solution of Cu(NO<sub>3</sub>)<sub>2</sub>, followed by calcination to decompose the nitrate and form the oxide. As an alternative, Sin et al. [9] propose an anodic cermet of Ni/Cu alloy and gadolinia-doped ceria with advantages respect to typical Ni–YSZ anode for the direct electrochemical oxidation of hydrocarbons.

Therefore, the development of a process as simple as possible leading to produce CuO–CGO at very low temperature is an objective intensively investigated. The preparation of complex metal

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oxides by the combustion synthesis has become an important area of research because of promising results of this technique compared to the conventional method [10]. Currently, powders with good sinterability have been obtained using mixtures with carboxylate, urea and/or glycine [11] with the additional advantage of obtaining the complex oxide powders directly from the precursor solution. Therefore, the combustion synthesis could be, in principle, a good method leading to prepare the composite powder of Cu–CGO. However, this uncontrolled synthesis temperature may be the cause for obtaining relatively poor sinterable powders [12]. As a low cost and simple alternative, with excellent results, is that based on the chelation of complex cations leading to the formation of an intermediate resin, which, on charring and calcining, leads to a sinterable powder [13]. This method generates less carbon residues than other similar techniques of synthesis [14].

In this work, metal–ceramic composite (Cu–Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub>) mixed conductor prepared by the polymeric organic complex solution method has been studied. The influence of Cu content in Cu–CGO cermet on the electrode performance has been investigated in order to create the most suitable microstructure. Electrical properties of Cu–CGO cermets have been also determined.

## 2. Experimental procedure

CuO–Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>1.95</sub> powders (CuO–CGO) with two different proportions (40/60 and 50/50 wt%) were prepared by the polymeric organic complex solution method. Aqueous solutions of corresponding nitrates were mixed by stirring with nitric acid (65%) (10 ml) and ethylene glycol (80 ml) to make a gel. The as-obtained solutions were treated thermally in three steps, 80 °C for 2 h, 120 °C for 3 h to obtain a syrup-like gel, and finally 150 °C to obtain a black resin which is heated around 230 °C and up to a vigorous exothermic reaction occurred which converted the resin into an expanded porous solid. After combustion the material had a black colour which remained throughout all the powder processing. After milling in an agate mortar, the as-obtained powder (around 20 g) was calcined at 600 °C for 5 h and then attrition milled for 2 h in ethanol with zirconia ball media. The powders were characterized by differential thermal (DTA) and thermogravimetric (TG) analysis (Perkin-Elmer 7), X-ray diffraction (Siemens D5000 with Cu K $\alpha$ ), and Field Emission Microscopy FE-SEM (Hitachi S-4700). The complex polymeric gel, resin and derived powders were also analysed by Fourier transform infrared (FTIR) spectroscopy (model Perkin-Elmer 1760X) and SEM in a Zeiss Microscope (model DSM 950, Oberkochem, Germany). For sintering, the powder was isopressed in pellets at 200 MPa. Pore-size distributions of compacts were obtained by nitrogen adsorption measurements at 77 K (Accusorb 2100, Micromeritics). Shrinkage during sintering, at a heating rate of 10 °C min<sup>-1</sup> without holding, was followed in a dilatometer (Netzsch 402E of Geratebau, Bayern, Germany). Density of sintered bodies was measured by the Archimedes method with distilled water. After sintering pellets in air at 1000 °C for 1 h, the samples were reduced using a N<sub>2</sub>/H<sub>2</sub> (90/10%) atmosphere at 700 °C for 4 h. After polishing and thermal etching, the microstructures of the sintered samples (non-reduced and reduced) were examined by scanning electron microscopy. Impedance was measured from 150 up to 700 °C in argon using a LF Impedance analyser (model HP-4294A, Hewlett-Packard).

## 3. Results and discussion

### 3.1. Powder characterization

The simultaneous TG/DTA curves for the 50/50 wt% CuO–CGO polymeric gel heated at 150 °C is shown in Fig. 1. From 200 up to about 400 °C a strong and wide exothermic effect is present in

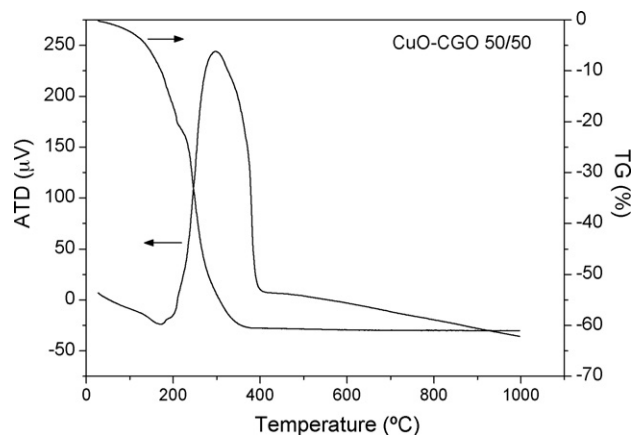


Fig. 1. TG and DTA curve corresponding to the gel precursor of the CuO–CGO (50/50 wt%) composition.

the DTA curve. Such an exothermic effect is associated with the decomposition–oxidation of the metal–chelates and the evolved gases. The TG curve shows a total weight loss of about 60% up to 1000 °C, due to evolution of carbon compounds (CO or CO<sub>2</sub>) and elimination of nitrates (N<sub>2</sub>, NO and NO<sub>2</sub>). Fig. 2 shows XRD patterns of 50/50 CuO–CGO resin, after combustion and that calcined at 600 °C. After the probable formation of an EG–metal polymerized complex is produced, the auto-combustion leads to the crystallization of CuO and CGO powders. In fact this X-ray diffraction pattern is very similar to that corresponded to the same powder calcined at 600 °C.

Fig. 3(a)–(d) shows representative SEM photographs of the 50/50 polymeric gel calcined at different temperatures. The syrup-like gels obtained after heating the solutions at 120 °C showed a black resin at 150 °C formed by large agglomerates which embedding all the cations. Heating the resin up to combustion, it is converted into an expanded porous solid. In a general sense, these powders showed the morphology of agglomerates containing pores and voids caused by the escaping gases during the violent combustion process. The powders calcined at 600 °C for 5 h and attrition milled for 2 h, show the microstructure of the spherical agglomerates surfaces, in which the primary particle can be observed. The individual particles were a few tens of nanometer in size with a low agglomeration state and consequently highly sinterable.

Fig. 4 shows the FTIR spectra of the as prepared EG–metal nitrate–water–nitric acid solution (50/50) and of its decomposition products at selected temperatures. The IR spectrum of the

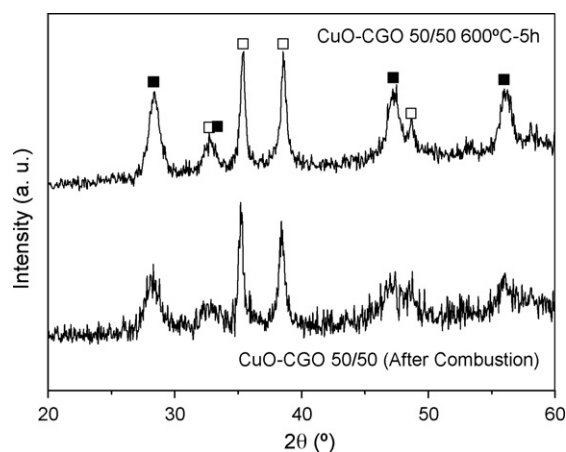


Fig. 2. XRD patterns of 50/50 wt% CuO–CGO resin after combustion and calcined at 600 °C for 5 h. (■) CGO; (□) CuO.

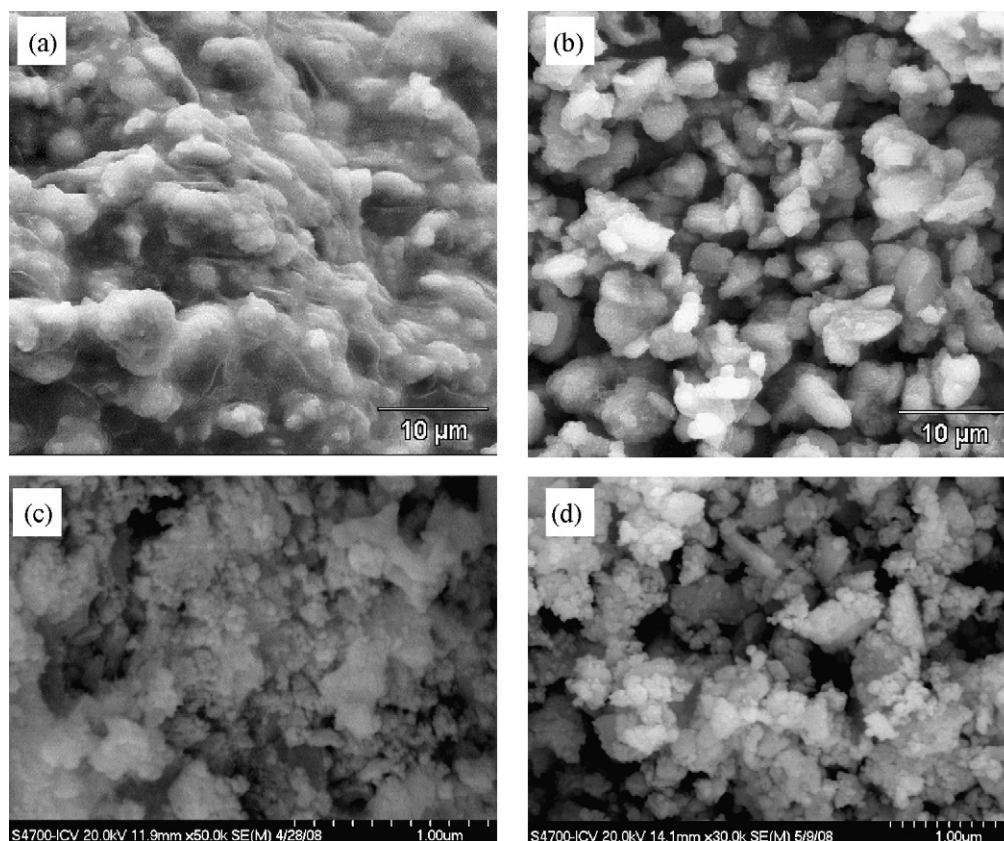


Fig. 3. SEM micrographs of the 50/50 wt% polymeric gel precursors heated at 120 °C (a), 150 °C (b), up to combustion (c) and that calcined at 600 °C (d).

solution heated at 80 and 120 °C was quite complex but a broad absorption band at about  $3400\text{ cm}^{-1}$  attributable to the stretching vibration of the hydrogen-bonded OH groups, was present. The absorption band at  $2950\text{--}2875\text{ cm}^{-1}$  is attributed to the stretching vibrate ion mode of the  $\text{CH}_2$  group of which low intensity can be attributed to a probable partial oxidation of ethylene glycol. The

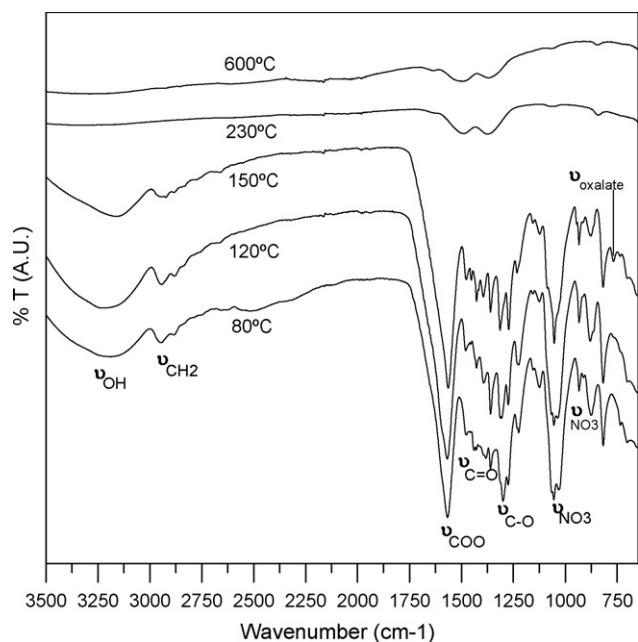
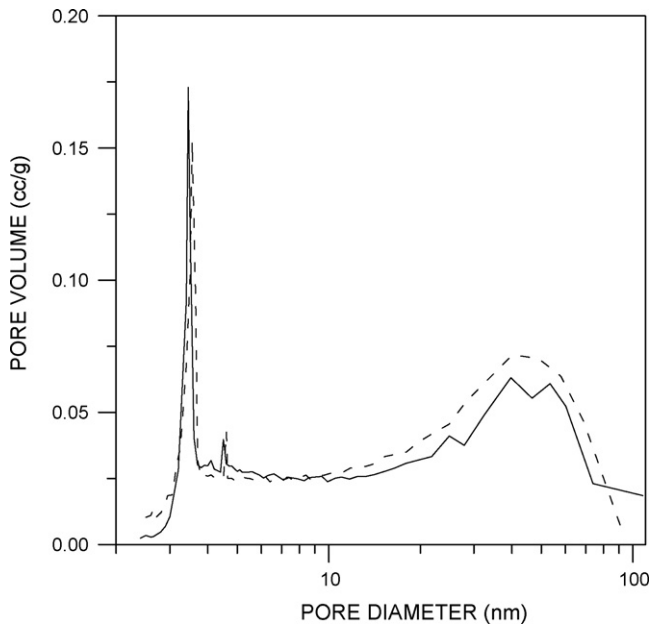


Fig. 4. FTIR transmission spectra of the 50/50 wt% CuO–CGO polymeric gel heated at the indicated temperatures.

carboxylate anion ( $\text{COO}^-$ ) stretching and the  $\text{C=O}$  groups, are also shown by the appearance of a strong absorption band at  $1570\text{ cm}^{-1}$  and around  $1380\text{ cm}^{-1}$ . The bands located at  $1300\text{ cm}^{-1}$  are associated to the stretching vibration of the  $\text{C-O}$  bonds. Those bands detected at  $1440$ ,  $1060\text{--}1030$  and  $880\text{ cm}^{-1}$  indicate the presence of nitrate ions in the polymeric gel. In this process, firstly proposed by Anderson et al. [15] it is believed that during the preparation of the polymeric gel at 80 °C and further drying at 130 °C, the ethylene glycol is, at least, partially oxidized by the nitrate ions leading to the formation of carboxylic acid groups ( $\text{HCOO}^-$ ) and/or ( $-\text{COO}-\text{COO}-$ ) which can then act as the chelating end groups. The polymeric gel heated at 150 °C showed, in addition, the presence of an absorption band at  $770\text{ cm}^{-1}$  attributable to the existence of some formate and/or oxalate ions. Chen et al. [16] and Wang et al. [17,18] reported that the heat treatment of the polymeric gel at 80 and 130 °C show the presence of crystalline peaks corresponding to the formation of formate or oxalate salts. For determining more precisely its composition it was analysed by XRD confirming the existence of oxalate salt. Finally, the absorption band at about  $660\text{ cm}^{-1}$  can be attributed to the presence of metal–oxygen bonds in the complex gel structure. Heating up to  $\approx 230\text{ °C}$  and promoting the combustion, all the previously mentioned absorption bands have practically disappeared in similar way to that corresponded to the powder heated at 600 °C. It seems to be that an auto-combustion process accompanied by a strong exothermic reaction in a very narrow temperature range, takes place during the decomposition of the partially oxidized ethylene glycol–metal dried polymeric gel. It is also assumed that such auto-combustion was catalysed by the nitrate ions, and took place as consequence of the reaction between the metal nitrate and the formed carboxyl groups through an oxidation–reduction process. Considering these first showed results it can be assumed that the method here used constitute a simple and low cost preparation process, comparatively with other

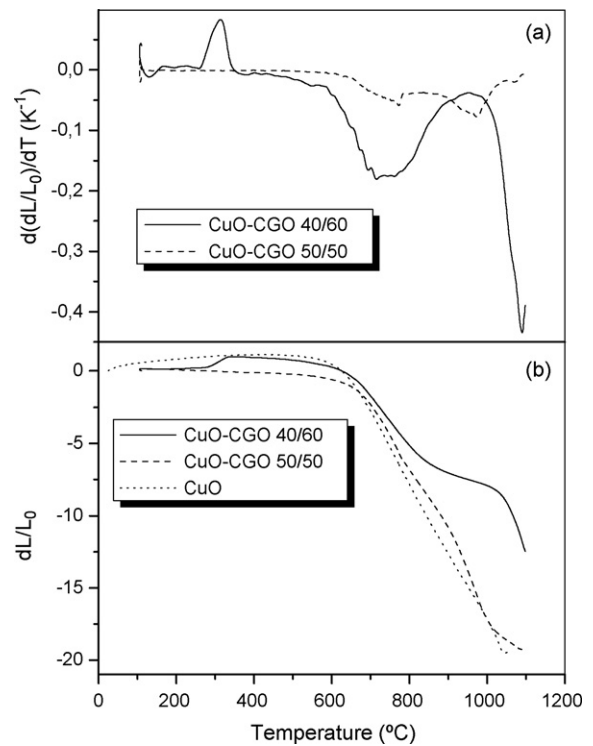


**Fig. 5.** Pore-size distributions of 50/50 wt% (---) and 40/60 wt% (—) CuO-CGO green compacts prepared from powder calcined at 600 °C for 5 h.

chemical preparation methods, leading to the low-temperature formation of a composite CuO-CGO by using cheap organic and inorganic reagents as metal nitrates, nitric acid, and ethylene glycol.

### 3.2. Sintering behaviour and microstructure developing

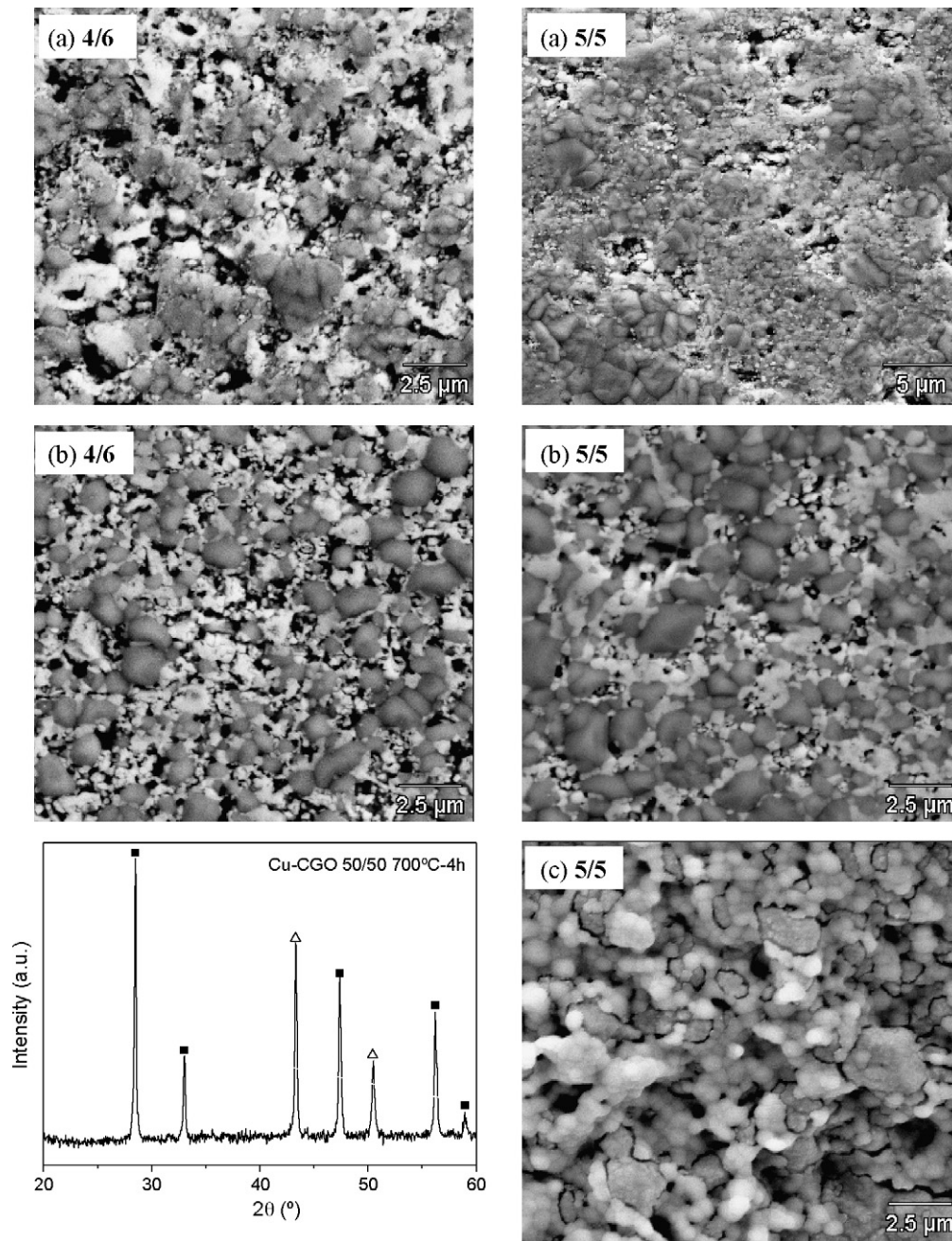
In spite of the different composition of the CuO-CGO powders, the green compacts pore-size distribution, Fig. 5, was very similar. We can divide the pore-size distribution in two well-defined regions: (1) pores with size smaller than the particle-size; (2) pores with size between 40 and 100 nm. The first ones can be considered thermodynamically unstable, and those larger than the particle-size are thermodynamically stable. At the early stages of sintering the smaller pores will be rapidly eliminated due larger driving force and the shorter diffusion distances and that occurs at very low temperature. Pore-size higher than the particle-size will needs higher temperatures to eliminate the pores. These results clearly affect the sintering process as it can be observed in Fig. 6. The shrinkage rate curves of CuO-CGO composites, 50/50 and 40/60, indicate that the sintering process takes place with the appearance of two maximum shrinkage peaks: a small one at about 750 °C, consequence of the very small pores detected in the porosimetry, and a higher one at 1000 °C for the composition containing 50% of CuO and around 1100 °C for the composite with lower CuO content. The second peak of the shrinkage rate shifted to lower temperatures when the CuO content increases up to 50 wt%, could be explained in base to the CuO content. In the same way, while the shrinkage curve, Fig. 6b corresponding to the CuO-CGO 50/50 remain almost constant at temperatures higher than 1050 °C, indicating an almost fully densification at this temperature; this curve continues dropping even at temperatures higher than 1100 °C for the composite with lower CuO content. The difference in the shrinkage behaviour between them can be due to the higher sintering characteristics of the CuO powder, i.e., CuO particles have a higher contraction and this phenomenon allow a normal sintering process of the CGO ceramic phase with trapped CuO particles into. In fact, the curve corresponding to the sample with higher CuO content is quite similar to that corresponding with the pure CuO, also shown in this figure. Ran et al. [19] explain that the addition of CuO enhance the sintering activity of 3Y-TZP, resulting in an extremely fast densi-



**Fig. 6.** (a) Shrinkage rate spectra and (b) linear shrinkage behaviour of CuO-CGO composites vs. sintering temperature.

fication between 750 and 900 °C. A similar effect could be applied for CGO ceramics.

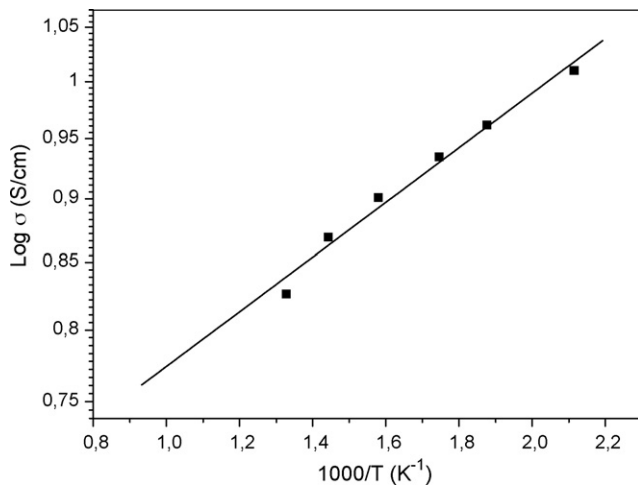
Fig. 7 shows the microstructure after sintering in air at temperatures between 950 and 1000 °C for 1 h. Although the contrast between CuO and CGO is low because of the small difference in average atomic weight, it was possible to distinguish with relative clarity between two kinds of grains, by using back-scattered electrons, darkish and brighter. EDX analysis revealed that the darkness grains were CuO, and brighter-looking grains were CGO. Although the densification process is initiated a very low temperature ( $\approx 700$  °C), samples sintered at 950 °C, Fig. 7a for both compositions showed microstructures with low densification. The sintering necks between the ceramic particles were not well formed and that could affect negatively the consistence of the ceramic. Also, it must be mentioned the different particle-size of the CuO and CGO particles. CuO exhibited a particulate size from 1 to 4  $\mu\text{m}$  and the CGO phase remains almost in a nanometric range. The poor structural stability of the samples heated at 950 °C caused the rupture of the sample during the reduction process inciting an increase of the sintering temperature up to 1000 °C, always below the melting temperature of CuO. As it can be observed in Fig. 7b, at 1000 °C samples containing 50 wt% of CuO exhibited better microstructures than samples with the lower CuO content, that is, a homogeneous distribution of CuO phase and higher density ( $\approx 94.5\%$ ). The grain size of CGO does not depend on sintering temperature (CGO grain size increased only up to about 0.3  $\mu\text{m}$  at 1000 °C for 1 h), these results indicate that the presence of CuO grains intergranularly located retard the grain growth of CGO grains, it is the phenomenon namely known as pinning effect. Clearly the CuO phase showed a better sintering behaviour at low temperatures in compare with the CGO phase. CuO sinters quite early, thus the sintering behaviour of the mixture moves closer to that of pure CuO and that agree the results observed from the dilatometric analysis in which only the curve corresponding to the sample with higher CuO content is quite similar to that corresponding with the pure CuO.



**Fig. 7.** SEM micrographs of composite 50/50 CuO–CGO (5/5) and 40/60 (4/6) sintered in air at 950 °C for 1 h (a), 1000 °C for 1 h (b) and (5/5) sintered at 1000 °C for 1 h and then reduced (c), XRD is included. (■) CGO; (△) Cu.

For all of that, the microstructure corresponding to composites with 50/50 content seems to be adequate for preparing Cu–CGO cermets by an appropriate reduction process (700 °C for 4 h using a  $N_2/H_2$  (90–10%) atmosphere), see Fig. 7c. The micrograph showed Cu–CGO cermets, as proved by the XRD analysis, with a uniform distribution of porous/spherical Cu particles surrounded by CGO particles. The Cu particles present a similar average grain size as before reduction, which indicate that a grain growth process does not take place during reduction process. The observed microstructures could enhance significantly the performance characteristics of Cu–CGO anode cermets, because, as it is known, that depends strongly of the Cu particles distribution in the ceramic matrix, increasing the number of active sites at the boundary between Cu (electronic conductor), CGO (ionic conductor) and fuel.

From the above results it seems clear the success of preparing cermets Cu–CGO having appropriate microstructures for using as anodes for SOFC. In this work, in which the requirements for sintering are very hard, considering the low sintering temperature needed to avoid the melting of CuO phase, it is crucial the development of a method, which permitting the preparation of low-agglomerated and highly homogeneous CuO–CGO oxide nano-sized powders, lead to the achievement of defect-free compacted green bodies with a very narrow pore-size distribution. This allows a strong densification process at temperatures much lower than usual. The ratio pore-size to particle-size is an important parameter in determining whether the pores can be completely removed after sintering, leaving a full-dense ceramic body. The smaller the ratio, the easier the pore can be eliminated. Less agglomeration in the starting powder and associated with a smaller pore-size/particle-



**Fig. 8.** Arrhenius plot for the total electrical conductivity of the 50/50 wt% Cu-CGO cermets.

size ratio after consolidation ensure a better sinterability of the ceramic. In this way, it must be noted that the proposed synthetic route based on the preparation of polymerized complex solutions has result to be an excellent non-expensive method for preparing nanosized powders exhibiting clear advantages in compare, i.e. with the conventional ones, or even wet chemical processes as coprecipitation, in which the strong forces due to dissolution–reprecipitation during synthesis form necks and/or subsequent solid necking due to sintering resulting in hard agglomerates or even aggregates. The powders as-obtained constitute by softer and looser agglomerates are crucial for succeed of the ulterior compacting and sintering process as mentioned.

### 3.3. Electrical characterization

The function of metallic phase in the composite material is to serve as an electrocatalyst for hydrogen oxidation and to provide the anode with high electrical conductivity. To satisfy these conditions, the metallic phase must become continuous. Kawada et al. [20] have demonstrated that the preparation process is of importance in controlling the electrode stability and performance and it has been shown that optimization of the anode microstructure by decreasing the particle-size of the Ni phase would increase the length of Ni–CGO triple phase boundaries, and thus improve the anodic performance. Studies [21,22] on Ni/rare-earth-doped ceria cermets preparation are focused towards achievement of a uniform distribution of fine Ni particles in the ceramic matrix using different preparation techniques. In our case copper grains can act as a continuous metallic medium allowing the electrons to migrate throughout the material. The easiest way to verify the continuity of the copper phase is to measure the electrical conductivity of the cermets. According to the impedance measurements, samples with 50 wt% of CuO are electronically conducting. The relatively high value of electrical conductivity at 700 °C which is close to the conductivity of pure metallic copper ( $70 \text{ S m}^{-1}$  at 700 °C) proves that the copper phase is continuous. From the Arrhenius plot (Fig. 8), it can be seen that the equation fits the data over the temperature range studied and that the electrical conductivity decrease with

increasing temperature, which is characteristic from a pure metallic electronic conductor. This behaviour verifies again the continuity of the copper phase, with predominant Cu–Cu contacts, demonstrating that there is not sintering of Cu particles.

### 4. Conclusions

Nanomeric powders of  $\text{CuO-Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  with highly sinterizable characteristics were prepared by the polymeric organic complex solution method. The sintering temperatures of compacts are significantly reduced (1000 °C), specially considering that normal sintering of CGO ceramic powders require temperatures even higher than 1500 °C. Besides, that sintering temperature is well below the melting point of CuO and sufficiently low for controlling the strong grain growth of the CuO particles in the ceramic matrix. Cermets Cu–CGO obtained by reduction of the sintered composites with 50 wt% of CuO presented a uniform distribution of Cu particles surrounded by a pore space and by the CGO particles. These cermets have metallic-type electronic conductivity that confirms a good percolation. Finally, this method constitutes an excellent non-expensive alternative to conventional ceramics methods for producing anodes for IT-SOFCs, and the intention is that all the components were built up one by one, and then, the temperature of sintering for each successive component must be lower than that of the preceding component. Electrodes will be applied on the sintered electrolyte and then sintered.

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