

Densification Behaviour of Screen Printed Gadolinia-Doped Ceria Films: Effect of CuO

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Abstract

The effect of CuO on the densification of a Gadolinia doped Ceria ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$, GDC) deposited by screen printing on a GDC/NiO anode produced by tape casting was considered aiming to a complete co-firing of the anode-electrolyte half cell. A comparative study on a CuO-doped and undoped GDC revealed that the effect of CuO is strongly dependent on the thickness of the deposited layer and can lower of more than 100°C the temperature of co-firing of the anode-electrolyte half-cell. Chemical analysis did not reveal traces of CuO on the sintered GDC layer indicating that the oxide should evaporate from the electrolyte layer during sintering not affecting in this way its electrochemical properties.

Introduction

A critical point towards the commercialization of solid oxide fuel cells is decreasing the operating temperature while maintaining suitable electrochemical performances. Gadolinia doped Ceria ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$, GDC) is considered to be one of the most promising alternatives to yttria stabilized zirconia (YSZ) for application in solid oxide fuel cells operating at intermediate temperatures (IT-SOFC) [1]. In addition an important cost-reduction step comes from a simplified fabrication process. For this reasons, high performances anode-supported SOFC for low temperature operations are generally based on the co-firing of thin-film gadolinia doped ceria (GDC) deposited on a porous anode of GDC/NiO [2]. Screen printing offers several advantages over other techniques for the production of those films: thickness control, reproducibility, low cost and easy applicability to large scale production [3-4]. Unfortunately, open circuit voltage (V_{OC}) and power density values reported for screen printed electrolytes are often low as a consequence of cracks and/or porosity [5]. To limit these defects, the film is generally fired at temperatures higher than 1300°C causing the reduction of porosity in the anode and a detrimental effect on the ionic conductivity of GDC due to the reduction of Ce^{4+} to Ce^{3+} [1]. A lower sintering temperature for the electrolyte is therefore crucial to assure the production of an high performances cell reducing at the same time the chances of bending and different shrinkage of its components. Transition metal oxides (TMOs) are well-known for their ability to lower the sintering temperature of ceramics [6]. Whereas CuO is a commonly used sintering aid for GDC powders, there is no literature regarding its effect on the densification of layers deposited by screen printing. On the other hand several studies revealed the importance of the location and adding method of the dopant in order to maximize its efficiency [7]. Aim of this study was to evaluate the role played by CuO on the densification behaviour of GDC when the doped powder is used for a screen printing ink.

Experimental

Commercial NiO (JT Baker, USA, mean particle size of 1.0 μm and specific surface area (SSA) = 4.0 m^2/g) and gadolinia-doped ceria $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ powder (GDC, Fuel cell materials, USA, SSA = 9.16 m^2/g) were used as starting materials. The tape casting slurry was prepared by mixing the desired amounts of nickel oxide, GDC and pore former (Carbon black N99, Thermax, Italy) with the azeotropic mixture of methyl ethyl ketone (MEK, Sigma-Aldrich) and ethanol (EtOH, Sigma-Aldrich) as solvent and glycerine trioleate (GTO Fluka) as dispersant. The ratio of NiO/GDC was kept at 70/30 weight%. Poly-vinyl-butylal (PVB) (Butvar B98, Monsanto Co. St Louis, MO, USA) was selected as binder and polyethylene glycol (PEG-400, fluka) and benzyl butyl phthalate (BBP) (S160, Monsanto Co, St. Louis, MO, USA) were used as plasticizer in 1:1 weight ratio. GDC powders for electrolyte deposition were prepared by solid state reaction starting from stoichiometric amounts of high purity oxides (CeO_2 and Gd_2O_3 , both Aldrich 99.9%), which were treated at 1400°C for 6 h and ball milled by a planetary mill (Pulverisette 7, Fritsch) and afterwards doped with 3mol% CuO (Fluka, Germany) by ball-milling. The ink composition included other than the GDC powder, Butyl carbytol acetate (Fluka, Germany) as solvent, furoic acid (Fluka, Germany) as dispersant and ethyl cellulose as binder. Flow curves and thixotropical behaviour of the inks were obtained using a controlled-stress rotational rheometer (Bohlin C-VOR 120, Bohlin, Malvern, UK) equipped with serrated plates (diameter = 25 mm). The measurements were performed at 25°C setting the distance between the plates at 500 μm . Thermal analyses (STA 449 Netzsch Geraetebau GmbH, Selb, Germany) were performed to study the organic burn-out of the inks in air. The inks prepared were screen printed onto the NiO-GDC green tapes. (AUR'EL 900, AUR'EL Automation s.p.a., Italy). dried in air at room temperature and subsequently thermally treated in static air at 1400°C x 4 h. The microstructure of the sintered half-cells were analysed by scanning electron microscope (Stereoscan 360, Leica, Cambridge). Secondary Ion Mass Spectrometry (SIMS) analyses were done using a customized instrument where the monochromatic (6 keV) O^{2+} primary ion beam is generated in a mass-filtered duoplasmatron ion gun (DP50B, VG Fisons) whereas the ion detection is done by an EQS1000 (Hiden, UK) mass energy analyzer with high transmission 45° sector field electrostatic energy analyzer and a quadrupole mass filter. SIMS craters' depth were measured by a Tencor P-10 mechanical profiler (Tencor). Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analyses were performed on half-cells by a Thermo Elemental X7 ICP-MS (Thermo Scientific), coupled with a laser ablation system based on a Nd:YAG laser source (New Wave) working at 213 nm. Elemental concentrations were determined by scanning the electrolyte film surfaces by ablation lines (80 μm ablation spot size, 100 $\mu\text{m}/\text{sec}$ speed).

Results and Discussion

A key point for a successfully screen printing process is the quality of the ink [5]. Moreover, when the ink is used in a co-firing process, its composition must take in account the mutual interaction between its and the green tape organics. Terpeneol is one of the most common solvent for thick film screen printing inks for its low vapour pressure and rheological behaviour [8]. Unfortunately a first composition based on this solvent revealed its high compatibility with the binder used for the production of the GDC/NiO green tape. This affinity led to a partial swelling of the green anode just after deposition as can be clearly seen by the pictures presented in Fig. 1.



Figure 1. Photographs of the anode-electrolyte green bilayer taken five minutes after deposition. a) front, b) back.

Among the possible compound able to replace terpineol butyl carbitol acetate (BCA) is probably the most suitable one [8]. To test the compatibility between this solvent and the organics in the tape, rectangular pieces of the green anode (3 x 1.5 cm) were dipped in mixtures of 25, 50, 75 and 100 vol% of BCA in terpineol. All the tapes except the ones immersed in 100 vol% BCA presented strong effect of swelling just already 10 minutes after dipping (Fig. 2).

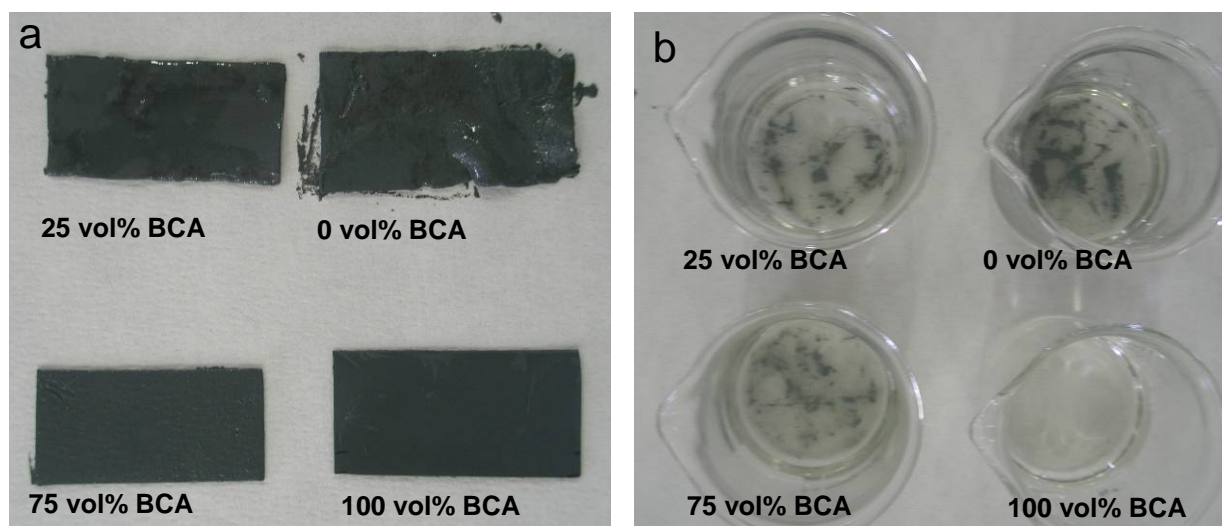


Figure 2. Swelling effect of terpineol on the GDC/NiO green tape. a) tapes after extraction from the solvent b) residuals of tapes left on the mixtures used for the dipping tests.

On the basis of these results the inks were formulated replacing terpineol with the more inert butyl carbitol acetate.

To identify the effect of the sintering aid on the film deposited, two inks, different only for the nature of the powder used, were prepared: one with pure GDC and the other with the same powder doped with CuO. The addition of the sintering aid did not change the rheological characteristics of the ink as shown by the flow and thixotropy curves presented in Fig. 3. As a consequence the two ink presented the same behaviour in printing.

Conversely, very different was the effect induced by CuO on the thermal decomposition of the ink. Fig 4 reports the TG/DTA analyses on the green anode tape and the two inks. The thermal processes of anode and electrolyte are important for effectively tailor the burn-out process. This is crucial step of the co-sintering process for the integrity of the final half-cell.

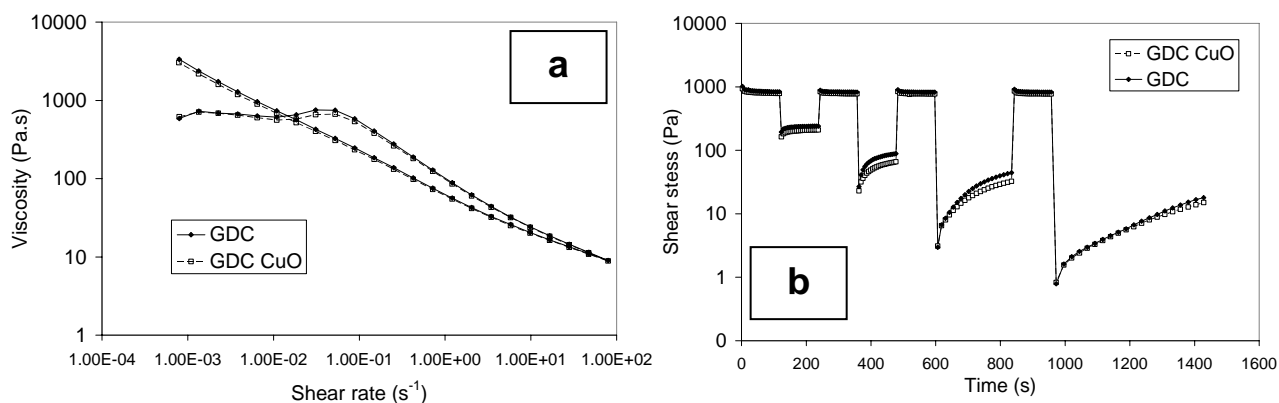


Figure 3. Rheological characteristics of the two inks made. a) flow curves; b) thixotropical behaviour.

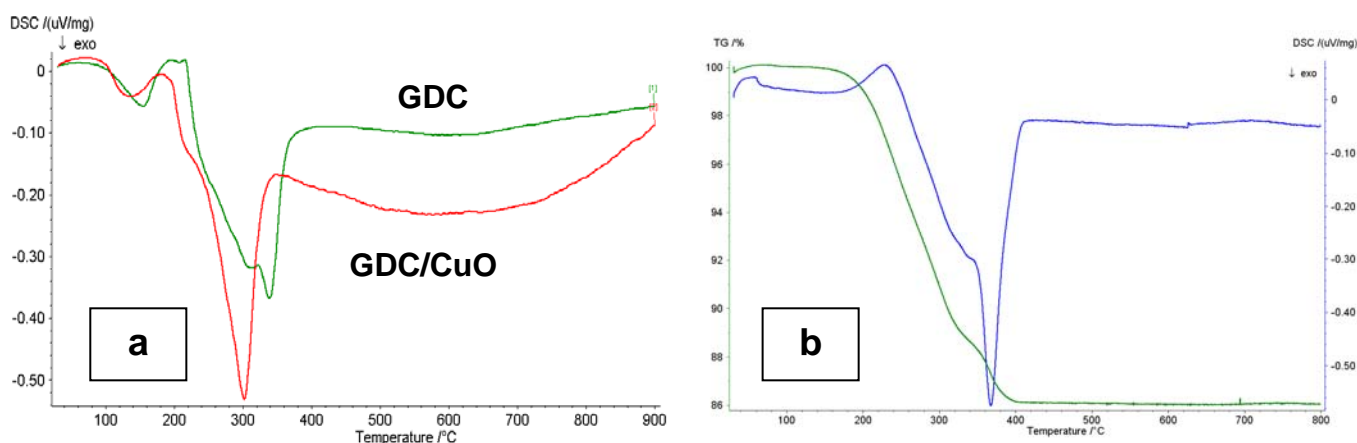


Figure 4. Thermal analyses on the two inks (a) and on the green tape (b).

The addition of CuO does not influence the solvent evaporation (160°C) but promotes the decomposition of the other organics in an single exothermic event at a temperature (300°C) well below the one of complete decomposition of the organics of the tape (Fig. 4b). This effect is probably linked to the amorphous film formed by CuO on the surface of GDC during heating that catalyze the oxidation of all the organics remained in a single step [9]. The shift plays an important role on the burn-out of the half cell. The debinding of the film in fact, must be lower than the one of the tape to leave a “free pass” to the organics coming out from it. Shifting the process to lower temperatures, the CuO lowers the chance to lead to cracks and defects. This effect can be clearly seen from the micrographs of Fig. 5 that show that the lower decomposition temperature leads, after burn-out and sintering, to an essentially crack-free surface of GDC/CuO compared to the one of GDC.

CuO has a strong influence also on the densification behaviour of GDC film. The micrographs presented in Fig. 6 show that the addition of 3mol% CuO leads to an almost full densification of the electrolytic layer

The main drawback connected to the use of CuO is its detrimental effect on the ionic conductivity of GDC. It has been reported that in bulk ceramic pellet densified with CuO, this oxide remains at the grain boundary of GDC affecting its conductivity [10]. For this reason SIMS and ICP-MS analyses were done on the sintered GDC/CuO half cell in order to evaluate the presence of copper oxide remained after the firing.

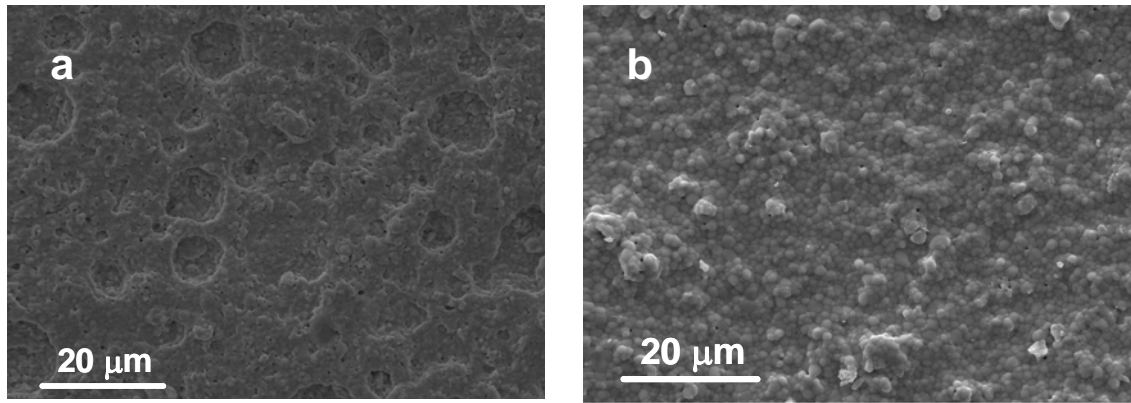


Figure 5. Effect of the burn-out cycle on the surfaces of GDC (a) and GDC/CuO (b) layers after sintering at 1400°C for 4h.

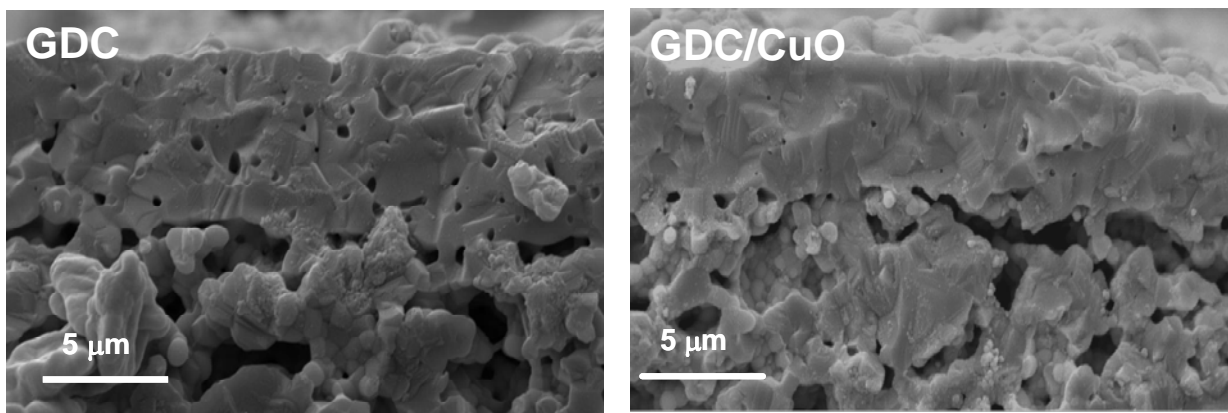


Figure 6. Micrographs of the sintered half cells.

The SIMS analyses did not show any presence of CuO (Fig. 7) while ICP, besides supporting the previous data, detected Sr (150 ppm) and La (10 ppm) present as impurities in the raw powders. This latter result confirm the CuO completely evaporates from the surface of the film during the co-firing process.

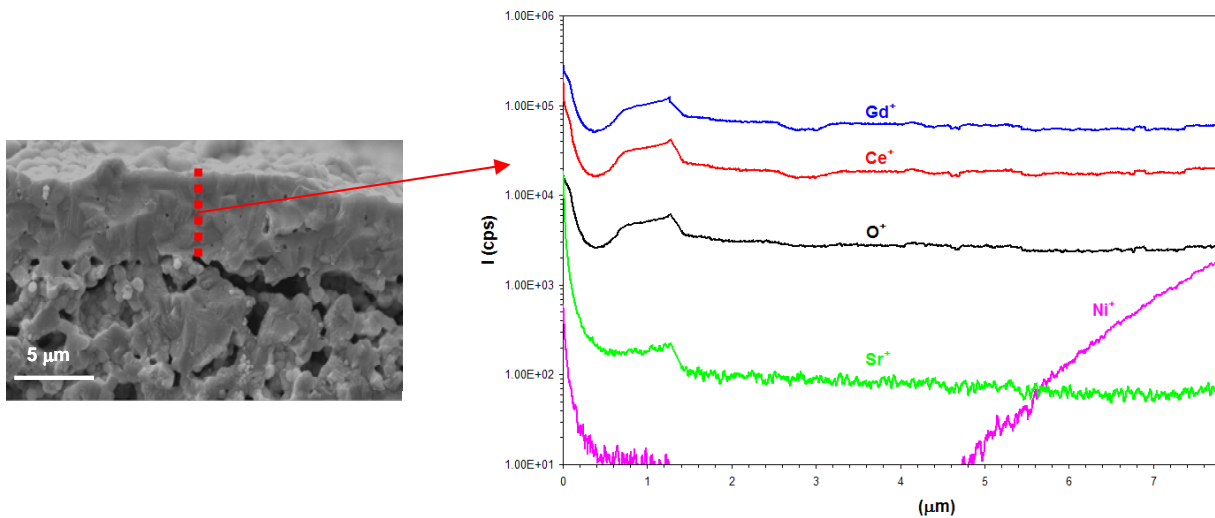


Figure 7. SIMS profile of the GDC/CuO half cell sintered at 1400°C for 4h

On the basis of these results, new tests were done sintering the half-green cell with GDC/CuO at 1300°C for 4h. The micrographs of the sintered bi-layer are presented in Fig. 8.

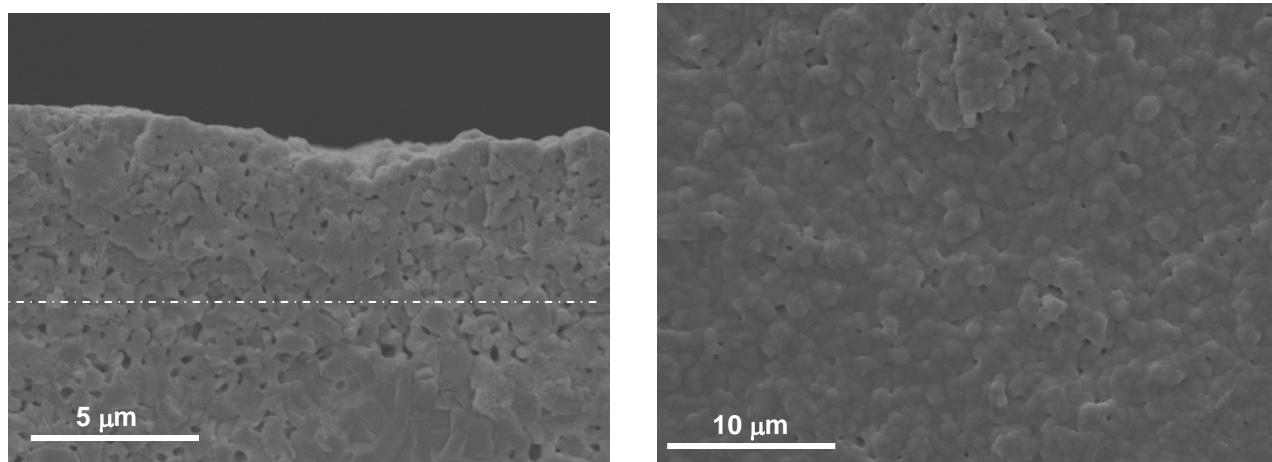


Figure 8. SEM micrographs of the GDC/CuO half cell sintered at 1300°C for 4h.

This sintering conditions are not strong enough to lead to a complete densification of the GDC film even with the use of the sintering aid. On the other hand, it has already been shown, that CuO allows the sintering of a GDC pellet at temperature as low as 900°C due to the formation of a liquid phase that improve the atom mobility [11]. The different behaviour observed can be related to the large diameter/thickness ratio of a film compared with the one of a bulk ceramic pellets. The liquid phase induced by CuO evaporates more rapidly from the surface of the GDC film than from the pellet. The high evaporation rate affects the sintering ability of the CuO in the film hindering its full densification. To check this assumption half cells with an higher electrolyte thickness were produced and treated at 1300°C x 4h. The micrographs reported in Fig. 9, show an improvement on the densification of the film and a well homogeneous surface.

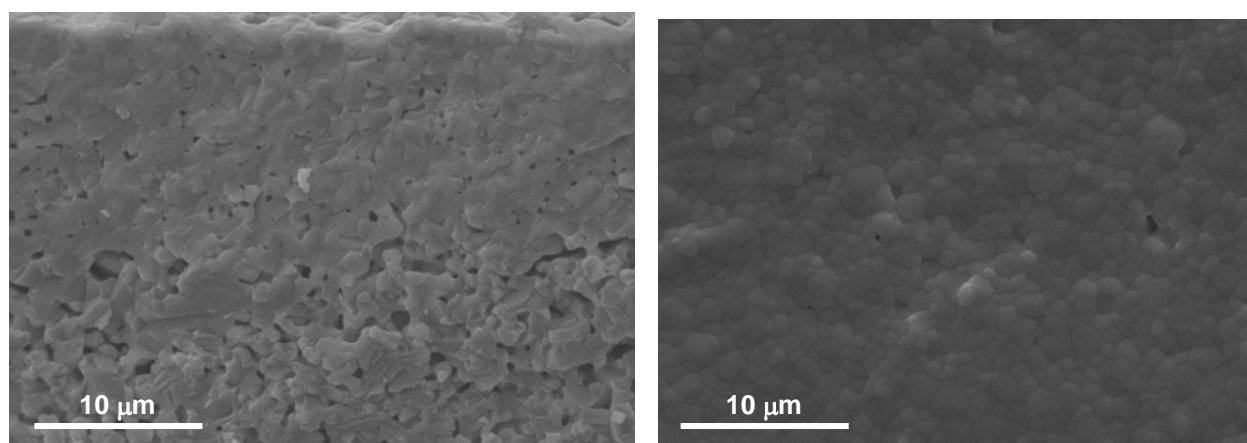


Figure 9. SEM micrographs of the half cell with a double thickness electrolyte treated at 1300°C for 4h.

The EDX and SIMS analyses on the bilayer showed that 1300°C x 4h are conditions strong enough to fully evaporate the copper oxide from the GDC matrix (Fig. 10).

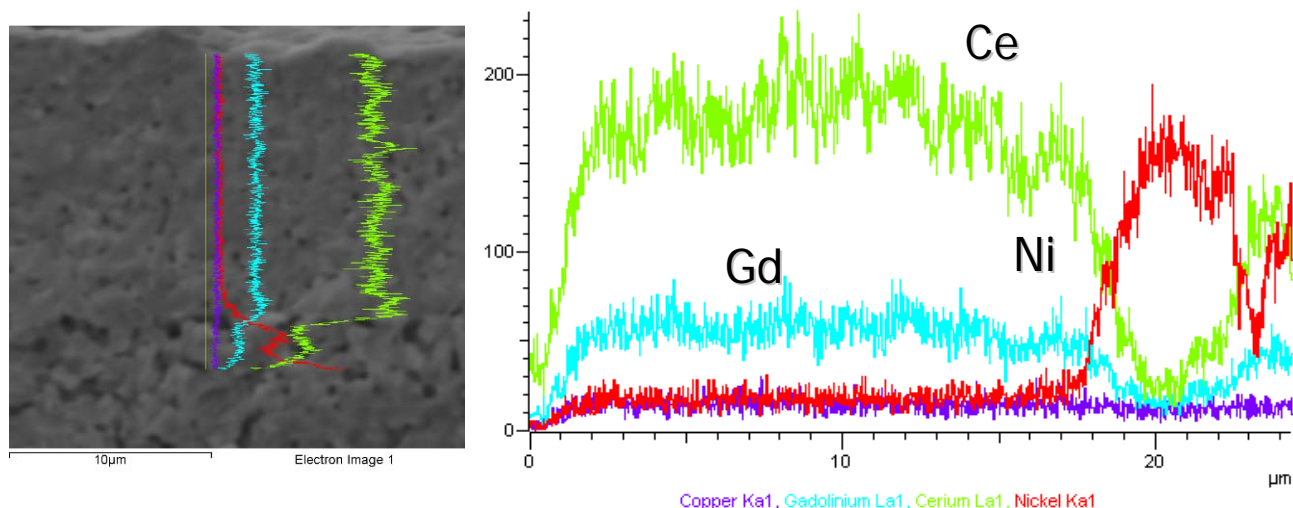


Figure 10. EDS analyses along the thickness of the GDC/CuO film treated at 1300°C for 4h.

On the contrary, CuO still remains in a pellet (diameter 20 mm, thickness 2mm) treated at the same temperature (Fig. 11) stressing the influence of the thickness of the layer on the diffusion path for the elimination of CuO.

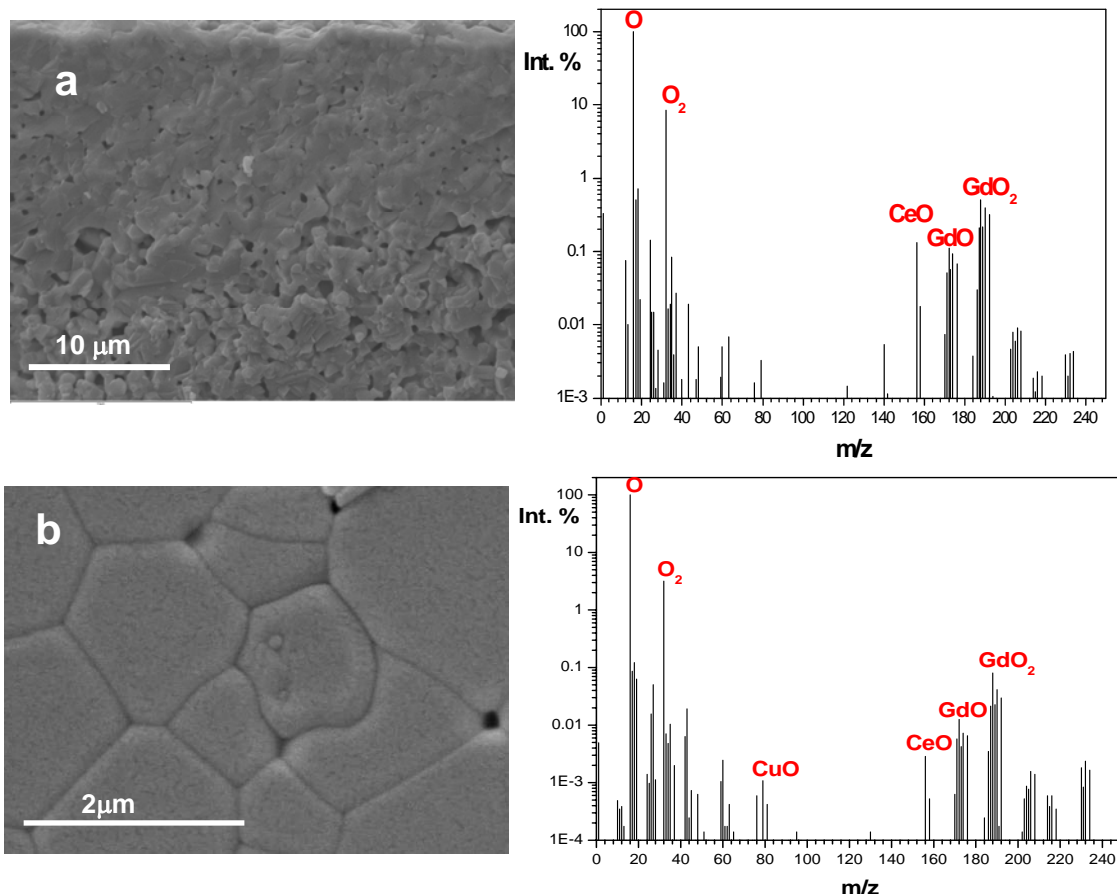


Figure 11. SIMS analyses of the half cell treated (a) and of a GDC pellet (diameter 20 mm, thickness 2mm) treated at 1300°C for 4h.

There is therefore a close relation between the CuO efficiency in densifying a screen printed GDC layer and the electrolyte thickness. The high surface area of the film

increases the rate of evaporation of the liquid phase induced by the CuO during sintering limiting its efficiency. On the other hand, this effect leads to a complete elimination of the sintering aid from the electrolyte layer not affecting in this way the ionic conduction of GDC.

Further studies are ongoing to evaluate the film thickness that can maximize the CuO densification efficiency assuring at the same time its complete elimination after firing.

Conclusions

The effect of CuO on the densification of a GDC layer deposited by screen printing on a GDC/Ni anode produced by tape casting was considered aiming to a complete co-firing of the anode-electrolyte half cell. A comparative study on a CuO-doped and undoped GDC revealed that the effect of CuO is strongly dependent on the thickness of the deposited layer and can lower of more than 100°C the temperature of co-firing of the anode-electrolyte half-cell. Chemical analysis did not reveal traces of CuO on the sintered GDC layer indicating that the oxide evaporates from the electrolyte layer during sintering not affecting in this way its electrochemical properties.

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