

## Physical and Microstructural Characterization of Cathode, Composite Cathode and Electrolyte Ceramics to ITSOFC

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**Abstract.** The  $(\text{La}_{0.60}\text{Sr}_{0.40})(\text{Co}_{0.20}\text{Fe}_{0.80})\text{O}_{3-\delta}$  - LSCF,  $(\text{Ce}_{0.90}\text{Gd}_{0.10})\text{O}_{1.95}$  - CGO composites and LSCF were deposited by wet powder spraying deposition method for the purpose of investigating their potential use in Intermediate Temperature Solid Oxide Fuel Cells. The interlayers are necessary between CGO electrolytes and LSCF cathodes in order to improve the performance of these materials. LSCF powders synthesized by citrate technique were calcined at 900 °C for 4 h and, their LSCFCGO composites and LSCF suspensions deposited on CGO substrate and, sintered in 1100 °C for 1 h, were formed pseudo-perovskite. The ceramics materials were analyzed by X-ray diffraction (XRD) and chemical composition of different half-cells layers by scanning electron microscope with energy dispersive (SEM-EDS). The results are in agreement with the literature and indicate that route studied is adequate for crystal structures formation compatible with films the 35  $\mu\text{m}$  thick total for study of conductivity between the cathode and the electrolyte.

### Introduction

Recently, there are significant efforts for the development of Intermediate Temperatures Solid Oxide Fuel Cells - ITSOFC. When these devices are operated at temperatures considered intermediate (between 500 and 700°C), reduces the degradation of constituent components and extends the system life, beyond increase the amount of materials which may be used (1, 2).

For this fuel cell type, can be used inexpensive materials such as stainless steel. However, the decrease operating temperature reduces the ionic conductivity in electrolyte and gases kinetics transport electrons to electrodes, influencing the device final performance. To reduce the electrolyte resistance, a common practice is to decrease thickness (2) or introducing a source high ionic conduction, such as gadolinium-doped cerium oxide  $(\text{Ce}_{0.90}\text{Gd}_{0.10})\text{O}_{1.95}$  - GDC or samarium-doped cerium oxide  $(\text{Ce}_{0.90}\text{Sm}_{0.10})\text{O}_{1.95}$  - SDC (3, 4). Moreover, to develop an ITSOFC device with high electrochemical performance, it is desirable to reduce polarization resistors (2, 3).

The ITSOFC is an electrochemical device of electric power generation alternative, which by chemical energy from the hydrogen and oxygen reaction, produces electricity, heat and water vapor (1).

The unit cell this device consists of three ceramic materials: cathode (positive pole), electrolyte and anode (negative pole). The material typically used as cathode is the mixed oxide cathode  $(\text{La}_{0.60}\text{Sr}_{0.40})(\text{Co}_{0.20}\text{Fe}_{0.80})\text{O}_{3-\delta}$  - LSCF, which has the function of oxygen reducing and generate electrons to the external circuit. The electrolyte used is GDC with the function of transporting oxygen ions to the anode. Finally, the anode used is a GDC composite with the function of hydrogen oxidizing, generating electric current, thermal energy and water vapor (2, 3). The LSCF has been used as cathode due to high mixed conductivity (electronic and ionic) and adequate catalytic activity for oxygen reduction reaction (ORR) (3-6).

For best ITSOFC performance are studies needed with unit cells, consisting mainly part cathode and electrolyte, due mainly contact region between the electrolyte, cathode and oxygen (triple phase boundary - TPB), responsible for ORR. To increase the ionic and electronic conductivity, and improve the catalytic activity in the O, a functional layer composed of mix LSCF with CGO (LSCFCGO) is formed between electrolyte material and cathode (3-5).

The LSCFCGO aids in adhesion between cathode and electrolyte and improves the LSCF cathode performance as main (5-8). The LSCF has characteristics such as porosity for the gases transport, electronic and ionic conductivity, oxidizing atmospheres stability and electrolyte compatibility. The CGO must be dense enough, possess high ionic conductivity and oxidizing atmospheres stability (1, 5).

In this work, LSCF particulates were prepared by citrate technique and LSCFCGO by mechanical mixing, using the LSCF synthesized with CGO commercial. The ceramic composed of cathode layers, cathode composite and electrolyte was characterized by X-ray diffraction (XRD), density by Archimedes principle and scanning electron microscopy (SEM) using energy dispersive (EDS).

## Materials and Methods

The CGO commercial substrates (electrolyte) were shaped in cylindrical pellets form of 15 mm diameter and 0.50 mm thickness, with uniaxial and isostatic hydraulic press. The pellets were sintered at 1500°C for 1 h.

The starting materials used in LSCF synthesis were the following reagents:  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  e  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , with purities 99.99% (Aldrich), citric acid and ethylene glycol, PA (Merck). The LSCF particulate were synthesized with x equal to 40 mol% strontium by citrate technique, which originally consisted in mixing nitrates of each element in required proportions with distilled water. The citric acid and ethylene glycol in ratio 60:40 by weight were mixed under stirring and heating to 60°C. Individual solutions of each precursor were added to the citric acid solution and ethylene glycol under stirring and heating to 80°C. At this stage, the water was evaporated to obtain a viscous liquid. The nitrate in the form of NOX was evaporated, the process polyesterification occurring, fixing and distribution of long chain cations and organic, yielding a resin. The next step involved the evaporation of residual nitrate and conversion of resin during particulate calcination at 900°C for 4 h.

The LSCFCGO composites were prepared by mechanic mixture involving the LSCF and CGO particulates. The mixture was held in atritor mill for 4 h and calcined at a rate of 5°C/min to 500°C for 2 h, and following to 900°C for 10 h. Were made three different proportions (weight %): 75% LSCF with 25% CGO (LSCFCGO31), 50% each (LSCFCGO11) and 25% LSCF with 75% CGO (LSCFCGO13). For composite depositions was used in formation gradient starting with CGO electrolyte, LSCFCGO13, LSCFCGO11, LSCFCGO31 and ending with film composed only LSCF.

The cathode and composite cathode films were prepared by wet powder spraying on substrate electrolyte. The suspensions were prepared in ethanol with organic binder and dispersant for stabilization LSCF or LSCFCGO particulate. Were then used 69% (by weight) of LSCF or LSCFCGO in ethanol, 4% (by weight) of polyethylene mine (PEI) as dispersant and 27% (by weight) of ethyl cellulose as binder. The cathode and cathode composite were applied in electrolyte surface using an airbrush with a nozzle diameter of 2 mm and distance to substrate of 200 mm.

## Results and Discussion

The sintered ceramics were characterized by bulk density (Archimedes principle) and XRD. The CGO sintered substrate in addition the films LSCFCGO and LSCF micrometric films obtained by wet powder spraying, making the half-cell cathode/electrolyte were characterized by SEM and EDS.

From the values apparent densities (Table 1) for LSCF, LSCFCGO composite and CGO samples were calculated porosities (in %) corresponding to each material at different sintering temperatures.

According Tab. 1, it was found that the porosities values are in agreement with literature (5-8). The LSCF ceramic samples require porosity between 35 and 40% for efficiently performance as ITSOFC cathode. According to the results, it is possible obtain a porosity of 39% at a sintering at 1050°C for 1 h and nearly 33% at a sintering of 1100°C also for 1 h.

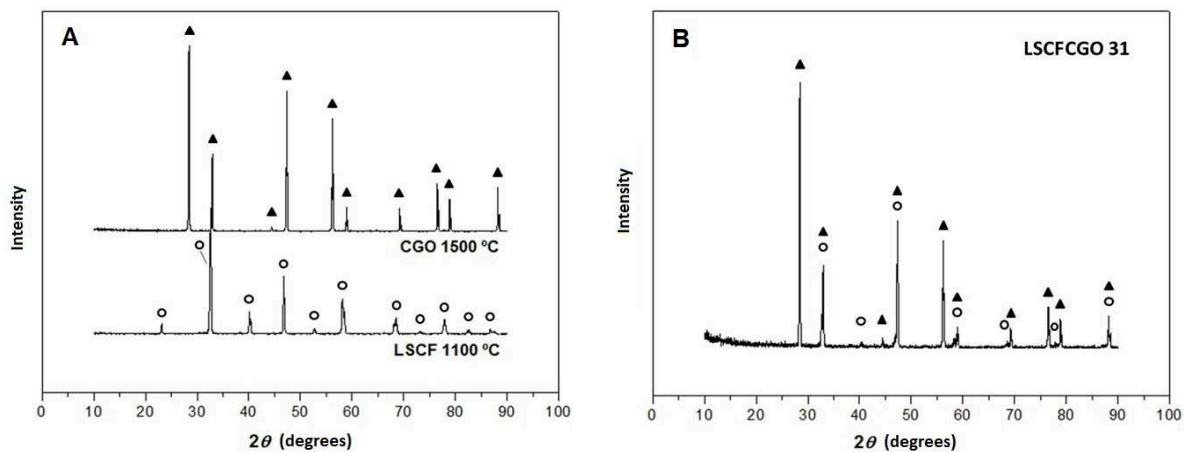
Table 1. Ceramics porosity (%) sintered at different temperatures.

Temperature [°C]	LSCF	LSCFCGO	LSCFCGO	LSCGCGO	CGO
1000	43.09	-	-	-	-
1050	39.43	-	-	-	-
1100	32.94	31.49	28.07	14.95	30.47
1200	19.47	-	-	-	19.67
1300	-	-	-	-	13.30
1400	-	-	-	-	9.83
1500	-	-	-	-	5.26

The composites samples were presented lower porosity as increasing the amount of CGO on its composition. The CGO sample may be sintered between 1400 and 1500°C to have a porosity below 10% and perform electrolyte function<sup>(3,4)</sup>.

The Fig. 1 shows the X-ray diffractograms of LSCF and CGO ceramic films (A) and LSCFCGO films (B, C and D). The presence of LSCF and CGO phases were confirmed by the XRD patterns in Fig.1 (A). In Fig. 1 (B, C and D), confirmed the LSCF presence with intense CGO peaks. The crystal structure is orthorhombic type for LSCF and cubic for CGO, according with database JCPDS No. 89-1268 and 75-16, respectively. The XRD patterns confirm the relationship of each constituent phase in the different compositions of LSCFCGO.

Based on these results, there is a gradual increase in intensities peaks corresponding to CGO when compared to LSCF.



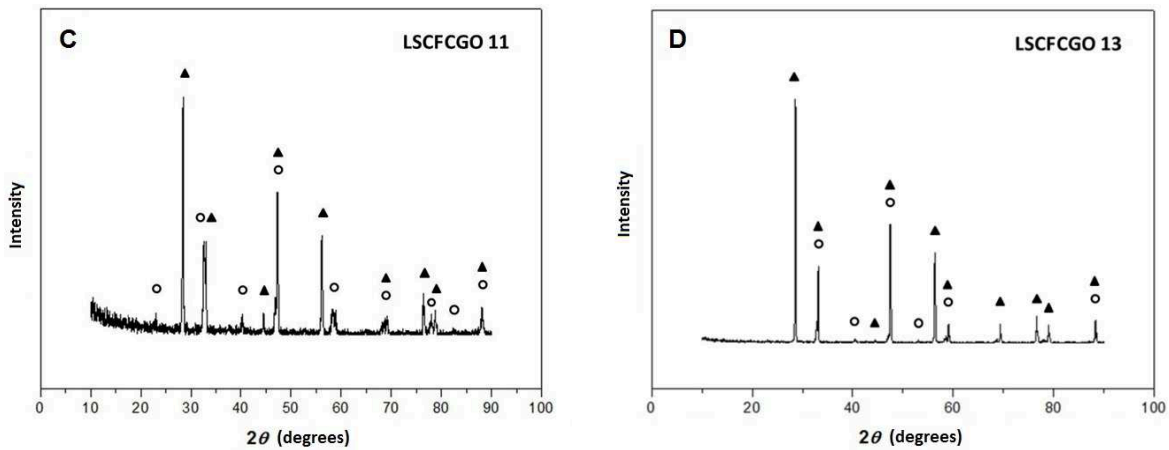


Fig. 1. XRD patterns of CGO and LSCF ceramic films (A), LSCFCGO31 (B), LSCFCGO11 (C) and LSCFCGO13 (D).

The micrographs obtained by SEM-EDS (Fig. 2 and 3) show the cross sections of LSCF / LSCFCGO (in gradient) / CGO sintered with their respective peaks of chemical elements forming each film and substrate.

A qualitative analysis shows that the CGO substrate is dense enough to be used as a solid electrolyte, and the LSCF and LSCFCGO films have adequate porosity and good adhesion with the electrolyte. The films morphologies formed from LSCF and LSCFCGO are similar to morphology observed by Leng *et al.*<sup>(1)</sup>, where the films were fabricated by screen printing.

The characteristic peaks of LSCF films; LSCFCGO films or CGO substrate, obtained by EDS confirms the presence of chemical elements constituting the films with total thickness of 5  $\mu\text{m}$  for LSCFCGO film (Fig 2.) consisting of three materials composites and 35  $\mu\text{m}$  LSCF and LSCFCGO films (Fig. 3).

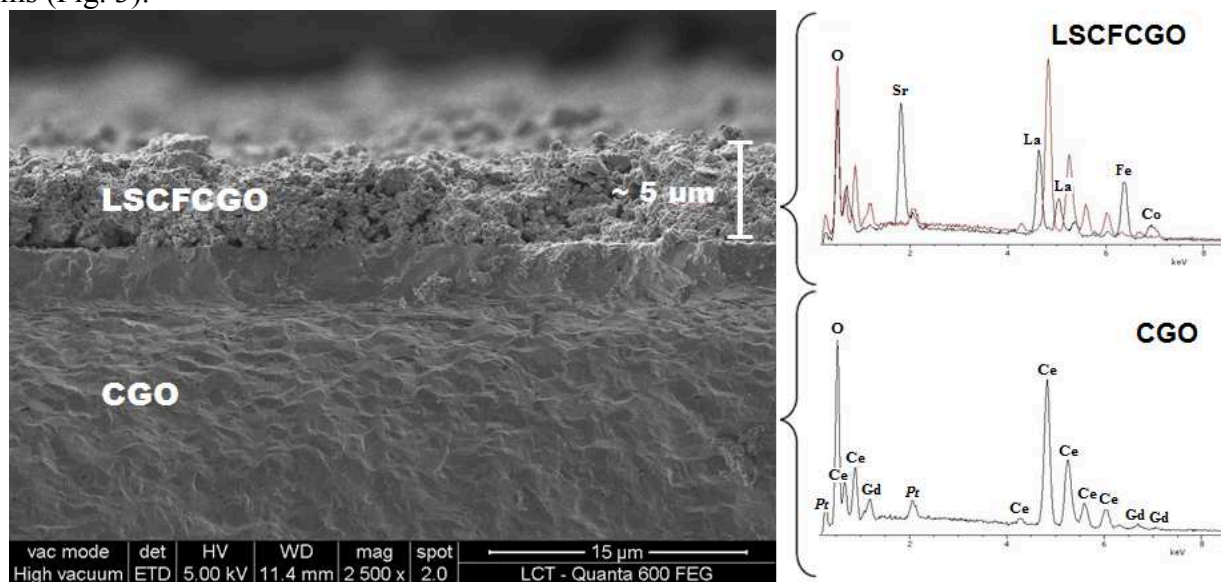


Fig. 2. Micrograph of LSCFCGO film cross section on the CGO substrate, obtained by SEM-EDS.

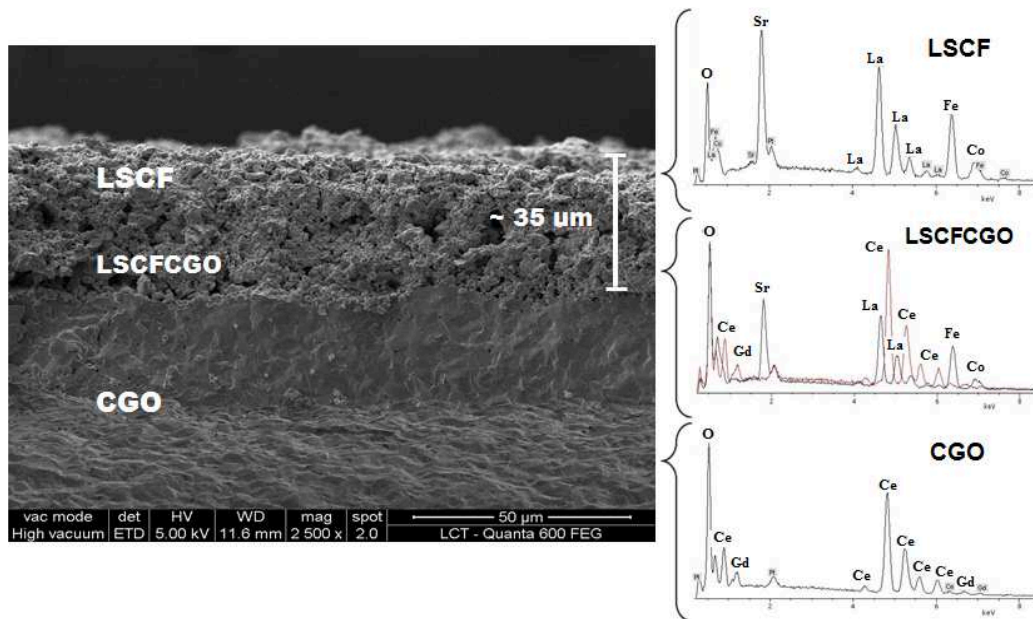


Fig. 3. Micrograph of LSCF and LSCFCGO film cross section on the CGO substrate, obtained by SEM-EDS.

For LSCFCGO film was deposited three layers for each composite, while for LSCF film was deposited a total of 12 layers. Each layer was fabricated with deposition steps and drying periods in air, to obtain the required thickness as a cathode for assembling the ITSOFC unit cell.

## Conclusions

The XRD patterns of LSCF and CGO films micrometric and LSCFCGO substrate confirmed the formation of orthorhombic perovskite-type crystal structure distorted (for LSCF) and cube (for CGO).

The micrograph confirmed the films to both the porous microstructures LSCF film (> 30%) and LSCFCGO and dense enough (<10%) to the substrate CGO. The presences of chemical elements were confirmed by EDS and the films had thicknesses of 35 μm (LSCF) and 5 μm (LSCFCGO).

The technique known as wet powder spraying deposition is adequate for the micrometric film formation and adherent to the electrolyte, spraying particulates dispersed on the surface clean of electrolyte and suitable for unit cells assembly consisting of cathode/electrolyte/anode.

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