

## Characterization of LSCF-based composite and LSCF as cathodes for intermediate temperature SOFCs

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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 particles synthesized by citrate technique were calcined at 900 °C for 4 h and, their LSCF-CGO 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, significant effort has devoted to the development of Intermediate Temperature Solid Oxide Fuel Cells (ITSOFCs). Operating in intermediate temperature (500-700 °C) not only reduces the degradation of fuel cell stack components and prolongs the lifetime of fuel cell systems, it also widens materials selection. In addition, cheap stainless steel materials can be used as interconnect at intermediate or low temperatures. However, decreasing the operating temperature reduces both electrolyte conductivity and electrode kinetics; hence the cell performance is hindered in these temperatures. To reduce the increase in electrolyte resistance due to decreasing operating temperature, it is a common practice to decrease the thickness of yttria-stabilized zirconia (YSZ) electrolyte [1-5] and/or to source for high ionic conducting electrolyte materials such as doped lanthanum gallate [2-7] or doped ceria [6,7,8]. Besides, to develop high performance ITSOFCs, it is desirable to design with low polarization resistance operating in these temperatures [5-7].

Due to its high electronic and ionic conductivities as well as high catalytic activities for oxygen reduction [3-6], mixed ionic-electronic conductor  $(\text{La}_{1-x}\text{Sr}_x)(\text{Co}_y\text{Fe}_{1-y})\text{O}_{3-\delta}$  - LSCF has been considered to be one of most promising cathode materials for intermediate or low temperature SOFCs, especially with ceria based electrolyte. One of the commonly used methods to improve cathode performance is to add an ionic ally conducting second phase, such as YSZ [1,4] or ceria based electrolyte [1,3,6,7] into the electronically conducting electrode material, typically LSCF.

The ITSOFC is an electrochemical device of alternative energy generation, that by means of the chemical reactions energy of the hydrogen and oxygen gases is converted into water and electric and thermal energies [1].

The unity cell is composed for three ceramic materials nominated of cathode, electrolyte and anode. The used material as cathode is the LSCF, that it has the function to reduce the oxygen gases together with electrons of the external circuit. The used electrolyte is the  $(\text{Ce}_{0.90}\text{Gd}_{0.10})\text{O}_{1.95}$  -CGO,

with the function of migrate the oxygen ions from cathode to anode and, the used anode is the Ag-CGO, with the function to oxidant oxygen ions with the hydrogen gases fed, generating electricity and water [2,3].

For optimum performance of the ITSOFC in generally, it is necessary to study the half-cells consisting of cathode and electrolyte, because the region of contact between cathode, electrolyte and oxygen gas, responsible for the oxygen reduction reaction, called Triple Phase Boundary (TPB). For an increase of the ionic and electronic conductivities, and the catalytic activity of the reduction reaction of the oxygen gas, a functional layer of composite cathode of LSCF and CGO is conformed between the cathode and the electrolyte [5-8]. The mixing to form the LSCF-CGO composite has been shown to increase the adhesion of the cathode materials to the CGO electrolyte [1,8].

The LSCF-CGO composite can perform better than pure LSCF as the cathode [1,8]. On the other hand has also been used as anode materials for the direct oxidation of methane in intermediate temperature and shown to have no formation of carbon deposits [1]. The characteristics such as enough porosity for the gases transport, raised electronic and ionic conductivities, stability in oxidant atmospheres, compatibility with the electrolyte and raised catalytic activity for oxygen reduction for LSCF cathode and LSCF-CGO composite cathode are necessary and, the CGO electrolyte, in turn, must be dense, solid, present high ionic conductivity and excellent stability in oxidant and reducing environments [1,9,10].

In this work,  $(\text{La}_{0.60}\text{Sr}_{0.40})(\text{Co}_{0.20}\text{Fe}_{0.80})\text{O}_{3-\delta}$  - LSCF particles was prepared by citrate technique. LSCF-based composite cathodes were prepared from the mixture between LSCF particles and commercial  $(\text{Ce}_{0.90}\text{Gd}_{0.10})\text{O}_{1.95}$  particles, emphasizes the ceramics characterized by X-ray diffractometry (XRD) and cathode/electrolyte solid oxide half-cells, characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) techniques.

## Materials and Methods

**Preparation of CGO electrolyte substrates:** The CGO electrolyte substrates were prepared by conventional ceramic method. The commercial Tosoh YSZ powder (*TZ-8Y, Tosoh Corporation, Tokyo, Japan*) were pressed into pellets of 15 mm in diameter and 0.50 mm in thickness, using presses hydraulic uniaxial and isostatic. The green pellets were sintered at 1500 °C for about 1 h to strengthen their mechanical property.

**LSCF and LSCF-CGO particulates preparation:** The departure materials used in the synthesis of the LSCF had been the following reagents:  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , with 99.99 % purity (Aldrich); acid citric and ethylene glycol, P.A. (Merck). The powders of LSCF had been synthesized for x equal 40 mol % of strontium, gotten by the citrate technique, that consisted initially in the mixture of nitrates in the required ratios with distilled water. Acid citric and ethylene glycol in ratio 60:40 in weights is mixed in Becker and kept under agitation and the heating at 60 °C. The individual solutions of each precursor are added to the citric acid solution of more ethylene glycol under agitation and heating to the temperature between 80 °C. In this stage, the water is evaporated until the attainment of a viscous liquid. The nitrate in the  $\text{NO}_2$  form initially is evaporated, occurring polyesterification process, fixing and distributing cations to long of organic chain and, getting itself a resin. The following stage consists of the evaporation of residual nitrate and transformation of the resin, calcination of the resinous material to air the 900 °C for 4 hours for a formation of LSCF particulates. The LSCF-GDC composites were prepared by mixing between LSCF and GDC particulates. The mixture was ground for 24 h and then calcined by heating in air at a rate of 5 °C  $\text{min}^{-1}$  to 500 °C and held for 2 h, and then to 900 °C and held for 10 h before drying.

**Preparation of cathode films by wet powder spraying:** Suspensions of a carrier liquid ethanol, an organic binder, an organic dispersant and the LSCF or LSCF-CGO particulates are used. The ingredients were 69 wt% of LSCF or LSCF-CGO in ethanol with 4 wt% of PEI as dispersant, and

27 wt% of ethyl cellulose as binder. The cathode and cathode composite layers were applied onto the sintered CGO electrolyte substrate by using an airbrush with nozzle size (diameter) about 2 mm and distance to substrate the 100 mm.

## Results and Discussion

The ceramics formed by uniaxial pressing were characterized by XRD. The CGO substrate formed by uniaxial pressing and the LSCF-CGO and LSCF thin films by wet powder spraying forming the cathode/electrolyte solid oxide half-cells were characterized by SEM and EDS. The Fig. 1 shows the X-ray diffractograms of LSCF and CGO ceramics (A) and LSCF-CGO composites (B, C e D).

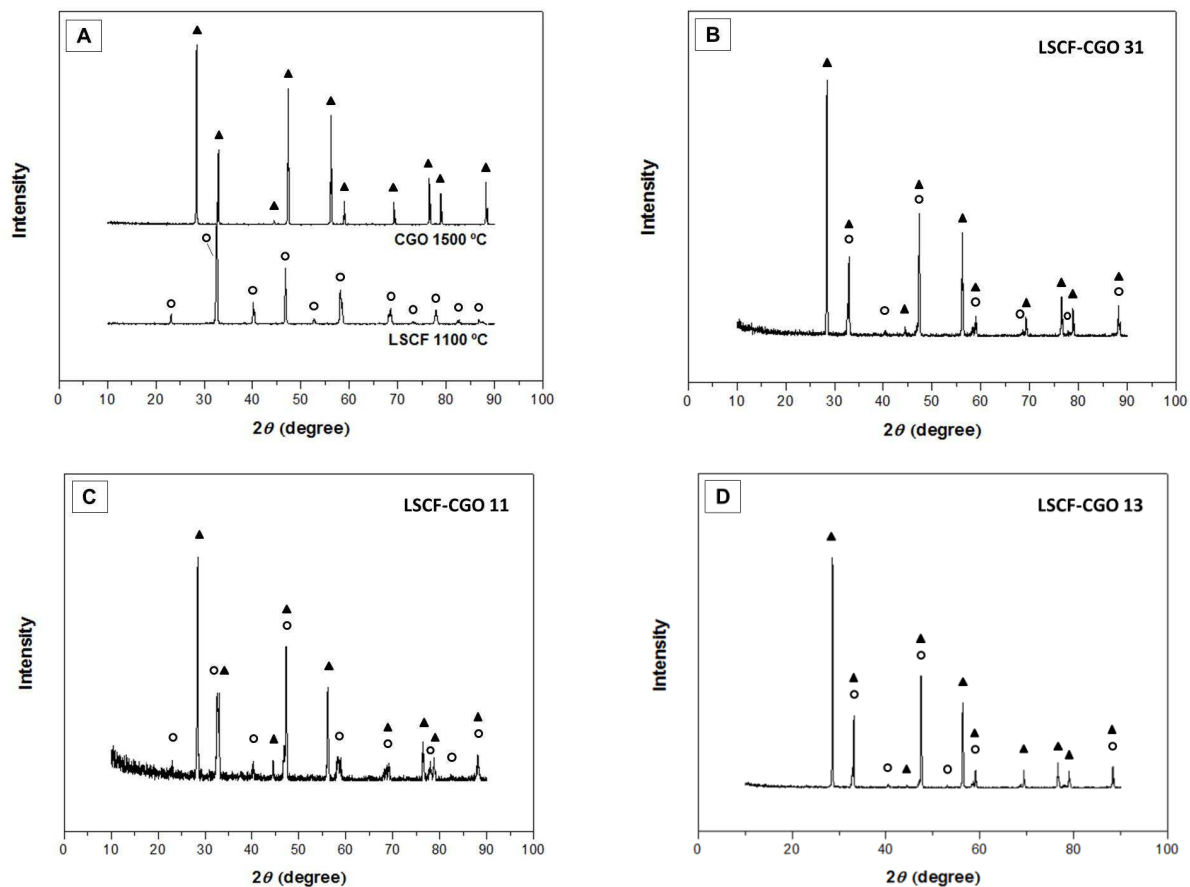


Fig. 1 - Diffractograms of LSCF and CGO ceramics (A), LSCF-CGO 13 ceramic (B), LSCF-CGO 11 ceramic (C) and LSCF-CGO 31 ceramic (D) obtained by XRD.

The particles of LSCF-CGO composites were fabricated in proportion (wt %) with 75 % LSCF to 25 % and called LSCF-CGO 31. We produced two more mass variations of these materials: 25 % LSCF to 75% CGO (LSCF-CGO 13) and 50 % to each one (LSCF-CGO 11). In step LSCF-CGO composites depositions were carried out in the form of gradient starting with the composite electrolyte which has the largest CGO concentration and arriving at the cathode and which has the largest LSCF concentration.

The presence of LSCF or CGO single phases was confirmed in the ceramic, as observed in Fig. 1(A). In Fig. 1(B, C and D) confirm the presence of the LSCF phase [11] with peaks of intensity of CGO phase, which the analysis realized for all cathode composites. The crystalline structure of phase LSCF is orthorhombic and CGO phase is cubic, in according to data base JCPDS N°89-1268 and JCPDS N°75-161, respectively.

The XRD patterns confirm the matching of each composite constituent phases, respectively. Based on these results, as it increases the amount CGO in the composite increases the intensity of peaks corresponding to this oxide up  $2\theta$  approximately 60 degrees, thereby decreasing the intensity of LSCF peaks.

The micrographs observed by SEM, shows the cross sections of the sintered and fractured half-cells of the thin films of LSCF and LSCF-CGO plus LSCF on CGO substrates, with its respective characteristic peaks of the chemical elements of each film and substrate obtained by EDS, as presented in Fig. 2 and Fig. 3.

A qualitative analysis of the half-cells allows verify that CGO substrate observed by SEM is dense, enough to be used as solid electrolyte, and the LSCF and LSCF-CGO thin films present porous with good adherence between the cathode and electrolyte. The morphology of the LSCF and LSCF-CGO ceramic films is similar that one observed for Leng *et al* [1], whose films were formed by the screen printing technique.

The characteristic peaks of LSCF and LSCF-CGO films and CGO substrate, obtained by EDS, confirm the presence of the chemical elements and had presented thickness of approximately 30  $\mu\text{m}$  (Fig. 3) and 5  $\mu\text{m}$  (Fig. 2), respectively. For the LSCF-CGO film, 3 layers were deposited for formation of the thin film, whereas for LSCF film, 12 layers were deposited. Each layer was formed realizing the deposition with intermediate stages of drying in air for the attainment of the desired thickness.

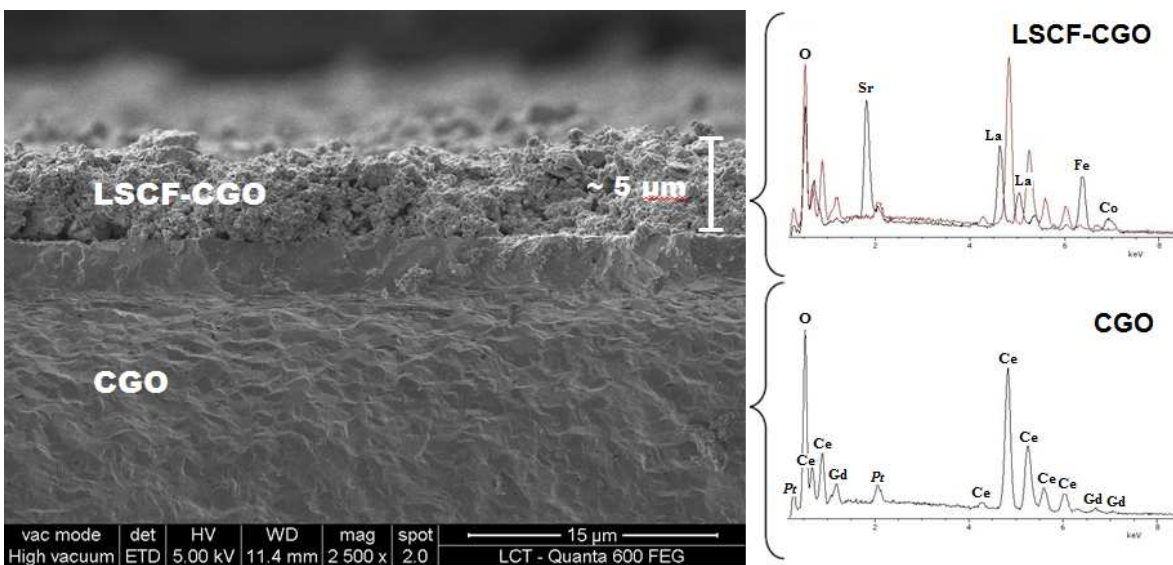


Fig. 2 - Micrograph of the cross sections LSCF-CGO thin films on CGO substrate obtained by SEM-EDS.

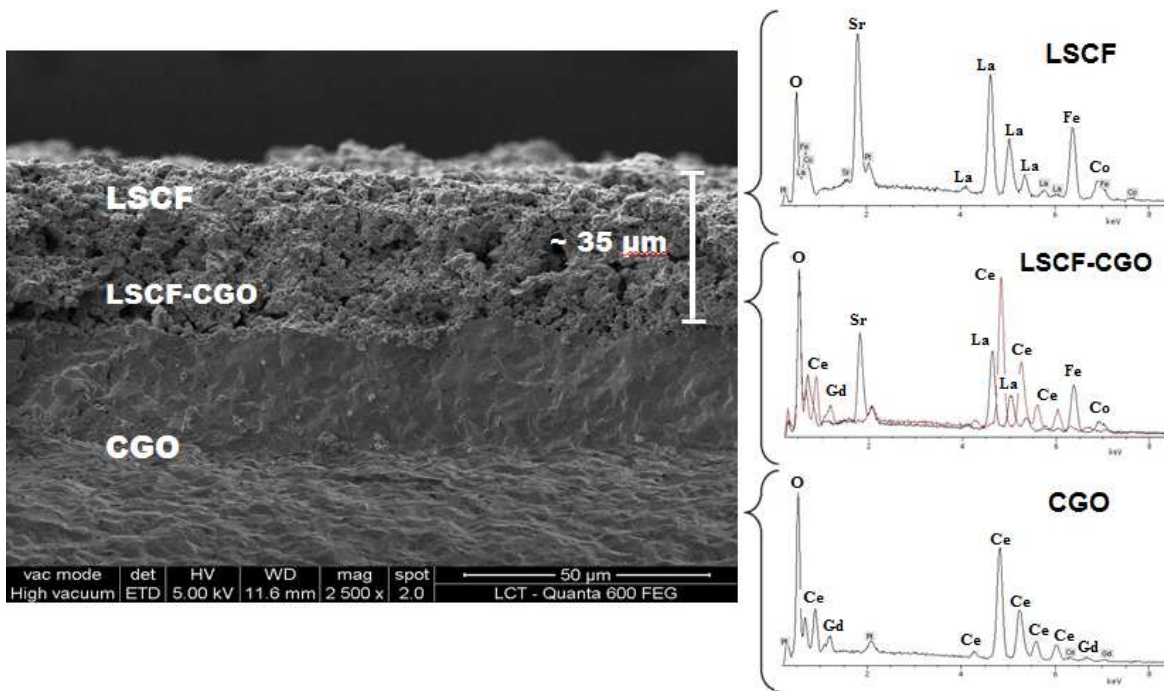


Fig. 3 - Micrograph of the cross sections LSCF and LSCF-CGO thin films on CGO substrate obtained by SEM-EDS.

## Conclusions

The diffractograms of the LSCF and LSCF-CGO thin films and of the CGO substrates confirm the presence of the formed phases of orthorhombic perovskite (LSCF) and cubic perovskite (CGO) crystalline structures.

The micrographs of LSCF and LSCF-CGO films, confirm porous microstructures and for CGO substrates, dense microstructures were observed. The presences of the chemical elements in the half-cells were confirmed by EDS.

The uniaxial pressing and wet powder spraying forming techniques had shown to be possible the manufacture of LSCF porous thin films adherent on CGO dense substrates, as well as adequate for the study of the cathode/electrolyte solid oxide half-cells.

The characteristic peaks of LSCF and LSCF-CGO films and CGO substrate, obtained by EDS, confirm the presence of the chemical elements and had presented thickness of approximately 30 μm and 5 μm, respectively.

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