Synthesis and characterization of cobaltite nanotubes for solid-oxide fuel cell cathodes

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Abstract. La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-\delta}$ oxides are good candidates for solid oxide fuel cell (SOFC) cathodes because these materials present high ionic and electronic conductivity, and compatibility with Cerium Gadolinium Oxide (CGO) electrolytes allowing a lower operation temperature. In this work, we report the synthesis of La$_{0.4}$Sr$_{0.6}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (LSCF) nanotubes prepared by a porous polycarbonate membrane approach, obtaining different microstructures depending on sintering conditions. The structure and morphology of the nanotubes and deposited films were characterized by X-ray diffraction, transmission and scanning microscopy. Finally, we obtained nanostructured films of vertically aligned LSCF tubes deposited over the whole surface of CGO pellets with diameter up to 2.5cm in a direct and single step process.

1. Introduction
Solid oxide fuel cells (SOFC) are electrochemical devices whose efficiency is theoretically very high for power generation, and have become a great candidate for future energy generation due to its possible fuel flexibility [1]. Their main disadvantage is the high work temperature (800-1000°C), which brings new challenges and difficulties with materials and structure stabilities. Therefore a high effort is currently made to lower the work temperature without loosing the SOFC benefits in the so called intermediate temperature SOFC (IT-SOFC) [1, 2]. For that purpose a lot of research is made to find new materials or to improve the performance of the different cell components: cathode, anode, electrolyte and interconnection materials. In the cathode case, it is necessary to know which of the oxygen reduction steps is the rate determining step that may be present due to major losses coming from lowering work temperature [3].

On one hand, the use of mixed ionic and electronics conductors like La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-\delta}$ (LSCF) as cathode material, to replace the simple electronics conductors, allows that the oxygen reduction reaction may take place over all cathode surface and not be limited to triple phase boundary region [4]. On the other hand, the microstructure also has a strong influence in cathode performance, which may be substantially improved using nanostructures [5, 6]. It is interesting to identify the rate determining step by modelling the electrochemical response of cathodes with different micro or nanostructures. The system complexity involves several associated parameters such as porosity, grain size, thickness, tortuosity, etc.

Hollow and solid cylindrical nanometric structures of mixed valent manganese oxide-based compounds have been obtained by Leyva et al by wetting sacrificial porous substrates [7][8]. Sacanel et al synthesized LSC and LSCF nanotubes by denitration process [9], Bellino et al
painted electrolyte surfaces with an ink made with LSC nanotubes (previously obtained by pore wetting technique) and attached them with a high temperature thermal treatment [6].

In this work, the synthesis and characterization of vertically aligned tubular nanostructures of LSCF (from now on nanotubes) were deposited on cerium gadollinium oxide pellets. The synthesis was made through an acetate approach and polymeric porous membrane acting as mould. Then, a nanostructured electrode of simple and well defined geometry could be obtained which may allow a system analysis by simple models.

2. Experimental

La_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O_{3−δ} tube structures were prepared by the acetate route [10] and porous polycarbonate membrane (characteristic pore diameters of 200, 400 and 800nm) acting as a mould or template [8]. Stoichiometric amount of SrCO_{3}, Co(CH_{3}COO)_{2}.4H_{2}O, Fe(CH_{3}COO)_{2} and La_{2}O_{3} were mixed in acetic acid solvent (0.1M) under reflux and magnetic stirring. The polycarbonate membrane pores were filled with the acetate solution by two different methods: capillarity and vacuum. In the first one the membrane was submerged in the solution and left in ultrasound for 5 minutes to help filling the pores by capillarity effect. In the later one, the membrane was placed over a silicate filter and the solution was forced to pass through the membrane making vacuum at the other side of the filter.

Each membrane, with its pores filled with the acetate solution, was pretreated in a microwave oven with exposure times ranging from 30 to 300 seconds. Then it was positioned over a Ce_{0.9}Gd_{0.1}O_{2−δ} (CGO) pellet (up to 2.5 cm of diameter) acting as substrate and fired at 400°C for 2 hours and then to 800°C for 6 hours to complete the synthesis of the perovskite phase.

The obtained tube structures were characterized by X-ray diffraction (XRD) with a Philips PW 1730/10 diffractometer with Cu Kα radiation using a low background Si monocrystal substrate. The morphology was characterized by scanning (SEM) and transmission (TEM) electron microscope (Philips 515 and Philips CM-200UT, respectively). Dark field, bright field and high resolution images acquired with TEM were used to determine grain size distributions and interplanar distances.

3. Results and Discussion

Figure 1 shows SEM images corresponding to samples made with (a) ultrasound and (b and c) vacuum with different pore filling methods. Nanotubes made with the vacuum method have thicker walls, better defined surface and endings than those prepared with ultrasound method. The ultra-thin wall tubes prepared with ultrasound-capillarity method can be noted by the transparency of some tubes at Fig. 1(a). The complete filling of the membrane pores is not

Figure 1. SEM images of nanostructures formed with a) capillarity filling method, b) vacuum method with home-made equipment and c) vacuum method with commercial filtering system adapted to the used membranes.
Table 1. Crystallite size and residual structural tension calculated from XRD.

| Sample       | Crystallite Size (nm) | Residual strain (%) |
|--------------|-----------------------|---------------------|
| bulk         | 30 ± 1                | 0.38 ± 0.02         |
| 400nm-60s    | 19 ± 1                | 0.54 ± 0.02         |
| 400nm-120s   | 21 ± 1                | 0.49 ± 0.02         |
| 800nm-30s    | 22 ± 1                | 0.47 ± 0.02         |
| 800nm-60s    | 21 ± 1                | 0.50 ± 0.02         |

assured using this method, while the vacuum system forces the solution to pass through the pores. It can also been observed that commercial vacuum system allows to obtain more homogeneous walls thickness with less external roughness than home-made equipment.

SEM images were used to characterize the morphology and the presence of hollow nanostructures for all characteristic pore size used. The microwave exposure time influence is shown in Fig. 2(a) for samples made with the commercial vacuum filling method. Measurements showed a decrease of tube diameters with higher exposure time but these results may be hindered by the measurement dispersion. The shrinkage rate (deduced from the final diameters as a function of the initial pore size in Fig. 2(b)) was higher for bigger pore membrane size due to more available space for diameter reduction in larger pores. The wall thickness was not significantly changed by microwave exposure times while it is reduced when using smaller pore diameters (e.g. walls thickness measured from SEM images were ∼100nm for 800nm samples and ∼60nm for 400nm samples).

A comparison of XRD analysis corresponding to a nanotubes sample and to a bulk sample (prepared as a pressed pellet of solution crystallized powder), with the same final thermal treatment, is displayed in Figure 3. Additional reflections, corresponding to precursors oxides, were observed only in the powder sample diffractogram meaning that the used temperature was not enough for complete LSCF phase formation. On the contrary, the microwave pretreatment

![Figure 2](image1.png)

**Figure 2.** a) Final tube diameters for several synthesis conditions (■ 800nm, ▲ 400nm, ▼ 200nm) and b) structure shrinkage for different characteristic diameters of template.

![Figure 3](image2.png)

**Figure 3.** Bulk sample and nanostructured film X-ray diffractograms with the same final thermal treatment. Perovskite phase reflections are indicated with vertical lines.
helps to reduce the synthesis temperature of the perovskite phase in the nanostructured film where only LSCF peaks were observed.

Crystallite sizes and residual structural tensions were calculated for nanotubes made with all pore sizes and also for the bulk sample using the 47.3° reflection of the x-ray diffractogram (see Table 1). All the nanostructured samples showed similar results but their residual strain were significantly higher than one corresponding to the bulk sample and the crystallite size were lower which may be explained by the confinement produced by tube walls. TEM images were acquired from colloidal suspension of 200 and 800nm pore diameter samples. From Figure 4 it can be seen that tube walls are more irregular than observed at SEM images (difference due the better resolution of TEM), diameter and wall thickness have been measured for single tubes obtaining: (550±30)nm and (58±7)nm, respectively for 800nm diameter template, (145±10)nm and (41±7)nm for 200nm diameter template. Diameters showed similar values in comparison with SEM images measurements. TEM diameter values measured along the axis direction on individual tube had a 5% dispersion. Wall thickness measurements from TEM images resulted on smaller values than those obtained from SEM images due to better resolution, and similar values were found between 200 and 800nm samples.

Grain size distribution has been obtained from dark field TEM images of both samples, resulting a mean value of 30nm (ranging from 12 to 85nm) for 800nm sample and 14nm (from 4

Figure 4. a) 800nm sample TEM bright field image used for individual structure characterization, b) dark field image of same sample used for measurement of crystalline single domain and c) 200nm sample bright field TEM image.

Figure 5. a) Final sample of nanotube monolayer full covering a 2.5cm diameter CGO pellet. b) SEM image of long range distribution of nanotubes deposited over the CGO pellet. c) detail of layer surface showing the alignment between nanotubes.
to 70nm) for 200nm sample, these values are similar to those found for crystallite size at XRD for 800 and 200nm template samples. Planar length of (2.74 ± 0.01)Å and (3.78 ± 0.06)Å were obtained from HRTEM images which can be identified with 110 and 012 planes of LSCF phase rhombohedral structure [11].

Once the synthesis process was optimized, vertically aligned nanotubes monolayer films were obtained, full covering CGO pellets of diameters up to 2.5cm (Figure 5). This optimization for LSCF tubes deposition film requires the use of commercial vacuum method for pore mould filling, drying the membrane surface before the thermal pre-treatment (microwave exposure time of 60 second), and final synthesis onto CGO pellet at 800°C.

4. Conclusions
Hollow tubular structures were synthesized through an acetate solution approach and polycarbonate porous mould technique for several nominal pore diameters (200, 400 and 800nm). Morphological characterization of these structures was made through images acquired by SEM and TEM. We observed that the best tubular structure formations were reached with commercial vacuum filling method and the measurements of final tube diameters result on decreasing values with higher microwave exposure times. These values were lower than characteristic mould pore size and the rate of shrinkage was higher for bigger pores. Diameter dispersion along tubes axis was between 6 and 9% and similar wall thickness were measured for samples made by different mould sizes.

X-ray diffractograms showed perovskite phase formation at 800°C (final thermal treatment temperature) which is lower than the temperature necessary for bulk samples. Lower crystallite size and higher tension were calculated from x-ray diffractograms for nanotubes than those for a bulk sample due to tube walls confinement. Distribution mean values of grain sizes obtained at dark field TEM images are comparable with XRD average crystallite size.

Nanostructured films of vertically aligned LSCF tubes were deposited over the whole surface of CGO pellets with diameter up to 2.5cm at the same time of final thermal treatment in a direct and single step process. LSCF films deposited over the two sides of CGO pellets, forming symmetrical cells, will allow to carry out the study of electrode reaction through the electrochemical impedance spectroscopy technique.

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