

## Effect of Cobalt-Doped Electrolyte on the Electrochemical Performance of LSCFO/CGO Interfaces

L. Baqué<sup>a</sup>, K. P. Padmasree<sup>b</sup>, M. A. Cenicerros Reyes<sup>c</sup>, H. Troiani<sup>a</sup>, M. D. Arce<sup>a</sup>, A. Serquis<sup>a</sup>, and A. Soldati<sup>a</sup>

<sup>a</sup> CONICET, CAB-CNEA, Av. Bustillo 9500, S. C. de Bariloche, R8402AGP, Argentina

<sup>b</sup> CINEVESTAV Unidad Saltillo, Apartado Postal 663, Saltillo, 25000, Mexico

<sup>c</sup> CIQA, Blvd. Enrique Reyna Herosillo 140, Saltillo, 25294, Mexico

In this work, we have studied  $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}/\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$  / $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  symmetrical cells containing  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$  electrolytes synthesized with and without the addition of cobalt as sintering aid. Electrochemical impedance spectroscopy results indicate that both electrolyte and cathode impedance response are affected by the addition of Co to the electrolyte, despite using cathodes with similar nano/microstructure according to scanning electron microscopy observations. Transmission electron microscopy characterization revealed the formation of columnar structures at the cathode/electrolyte interface of the cell with Co-doped electrolyte. These columnar structures would negatively affect the cell performance hindering the diffusion of oxide ions from the cathode to the electrolyte.

### Introduction

Solid oxide fuel cells (SOFCs) are efficient and environmental friendly devices which directly convert hydrogen and fossil fuels into electric energy. The operation temperature of these devices is mainly determined by the nature of its electrolyte. Conventional SOFCs are composed of yttria-based electrolytes requiring operation temperatures around 1000 °C, whereas ceria-based electrolytes have allowed reducing the temperature down to the 500-700 °C range (1). Nevertheless, these materials require sintering temperatures in the 1300-1600 °C range to achieve complete densification, which produces very large grain sizes and poor mechanical properties. In the last years, several research works have demonstrated that the addition of transition metals oxides is effective in improving the densification and thus, lowering the sintering temperatures of ceria-based electrolytes (2-4). Such research efforts generally focalize on how the addition of these sintering aids affects the properties (density, sintering temperature, conductivity) of the electrolyte. Nonetheless, it is well established that SOFC performance depends not only on the characteristics and performance of its individual components (i.e. cathode, electrolyte and anode) but also on their interfaces (5,6). Hence, a comprehensive study on how the addition of electrolyte sintering aids affects the cell performance is still missing.

In this work, the microstructural and electrochemical properties of  $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}/\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}/\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (LSCFO/CGO/LSCFO) symmetrical cells were studied. CGO electrolytes were synthesized with and without the addition of cobalt as sintering aid. LSCFO nanostructured cathodes with high

electrochemical performance were deposited by spin coating techniques on both sides of the electrolyte pellets. The assemblies were studied by Scanning Electron Microscopy (SEM), Electrochemical Impedance Spectroscopy (EIS), and Transmission Electron Microscopy (TEM).

## Experimental

The  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$  powders with and without the addition of 1at.% Co sintering aid were prepared by a molten-salt route described elsewhere (7,8). The starting materials used were high purity (Aldrich, >99+ %) analytical grade cerium nitrate, gadolinium nitrate, cobalt nitrate hexahydrate and sodium hydroxide. Doped ceria powders were uniaxially pressed to form pellets and then sintered at 1500°C for 6 h. The obtained substrates were ~ 1.3 mm thick. Independently,  $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  powders were prepared by an acetic acid-based method reported elsewhere (9). These powders were dispersed in an ink and deposited onto both sides of CGO substrates by the spin coating technique. Afterwards, these assemblies were heat treated at 900°C, resulting in a symmetrical cell configuration used for electrochemical measurements. Cathode covered the entire electrolyte surface reaching a geometric area ( $A$ ) of ~0.8 cm<sup>2</sup>.

Impedance measurements were performed in the 300-500°C temperature range under pure oxygen. Impedance spectra were recorded using a potentiostat/impedance analyzer Autolab (Eco Chemie BV) within the 10<sup>-3</sup>-10<sup>6</sup> Hz frequency range. Platinum grids, slightly pressed on electrodes, were used as current collectors. LSCFO/CGO/LSCFO cells were mechanically fractured and mounted in a SEM sample holder in order to observe its surface and cross-section by using a Philips 515 scanning electron microscope. TEM site-specific lamellae including the cathode/electrolyte interface were prepared by a Dual beam SEM/FIB (Focused Ion Beam) FEI Quanta 200 3D microscope. TEM images were obtained using a Philips CM 200 UT microscope. Point elemental analyses were done using an Energy Dispersed Spectroscopy (EDS) EDAX system coupled to the TEM.

## Results and discussion

### Scanning electron microscopy

Figures 1a and b show cross-section SEM images of LSCFO/CGO/LSCFO cells with and without the addition of Co as sintering aid. CGO electrolyte containing Co looks very dense while CGO substrate without Co presents considerable large pores. Images acquired with higher magnification (see Figure 1d) reveal that the CGO electrolyte without Co has elongated pores, although they do not penetrate the substrate from side to side. The presence of such pores on the electrolyte would compromise the gas impermeability (in the case thin electrolytes) as well as its mechanical properties. In fact, the LSCFO/CGO/LSCFO cell without Co was unintentionally broken during mounting for SEM analysis likely because of its higher brittleness.

The cathode microstructure is similar for both LSCFO/CGO/LSCFO cells (see Figures 1c and d) with a thickness of roughly 4-5 μm. In addition, the cathode/electrolyte interface shows good contact between them in both cells.

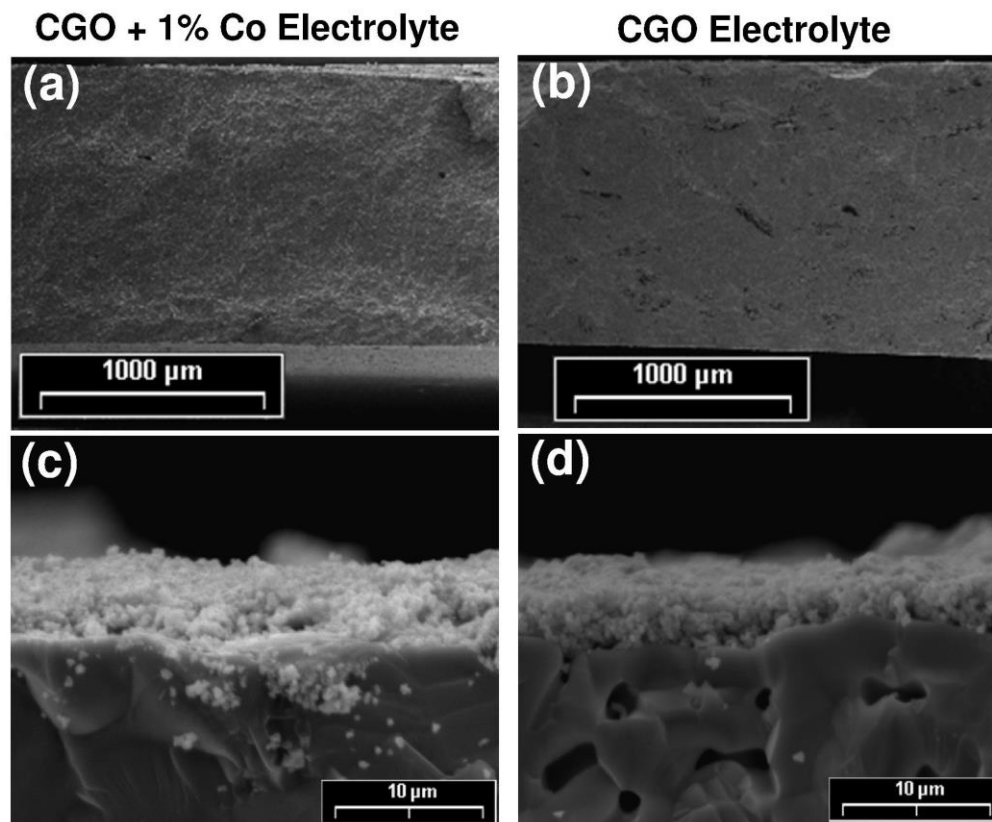


Figure 1. Cross-section SEM images of LSCFO/CGO/LSCFO cells (a,c) with and (b,c) without the addition of 1 at.% Co as sintering aid. The cathode is on top and the electrolyte is at the bottom in (c) and (d).

### Electrochemical impedance spectroscopy

The total electrical conductivity values of the electrolyte were estimated by using the expression  $\sigma = L/(R_{electrolyte} \cdot A)$  where  $\sigma$  is the conductivity,  $L$  is the electrolyte thickness,  $R_{electrolyte}$  is the electrolyte resistance (estimated as explained in (10)), and  $A$  is the cell area. The Arrhenius plot of the total electrical conductivity values for CGO electrolytes with and without the addition of Co is displayed in Figure 2(a). Electrolyte with Co doping has conductivity values up to two times higher than CGO electrolyte without sintering aid. This difference reduces to 1.2 times at higher temperatures because of the lower activation energy of the Co doped electrolyte (i.e.  $0.61 \pm 0.02$  eV vs  $0.72 \pm 0.03$  eV). The higher conductivity values of Co-doped electrolyte would be mainly caused by its higher density as observed by SEM.

Cathode area specific resistance ( $ASR_{cathode}$ ) values were evaluated by using the equation  $ASR_{cathode} = R_{cathode} \cdot A$  where  $R_{cathode}$  was estimated as detailed in (10) and  $A$  is geometric area of the cell. The corresponding Arrhenius plot can be seen in Figure 2b. The cell containing a CGO electrolyte with the addition of Co presents  $ASR_{cathode}$  values 2-4 times higher than those of the cell without sintering aid. Such differences are likely to be originated in the cathode/electrolyte interfaces since both cathodes have similar nano/microstructure as characterized by SEM.

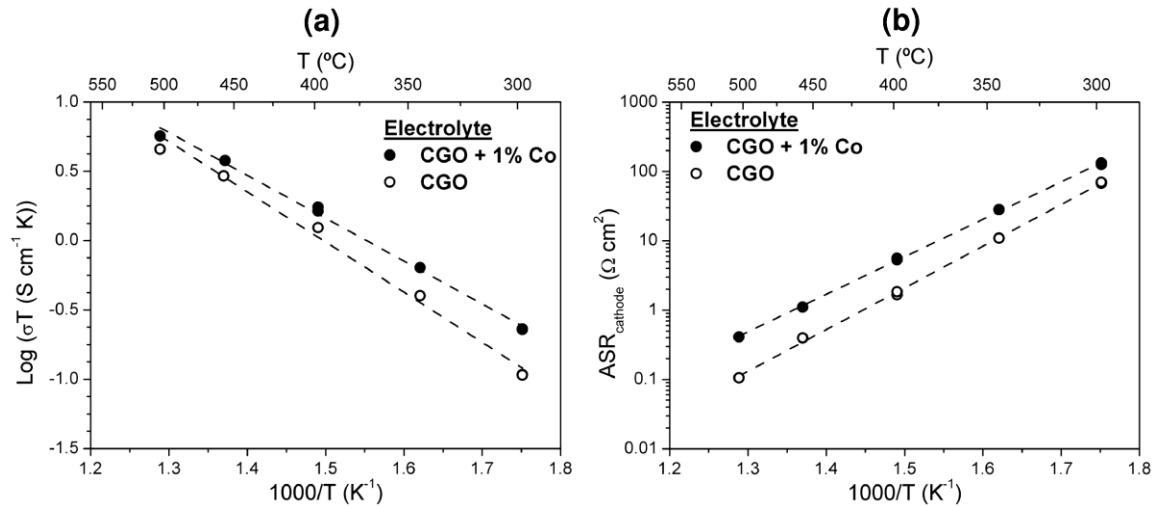


Figure 2. Arrhenius plots of (a) the total electrical conductivity values of the electrolyte and (b) the area specific resistance values of the cathode for LSCFO/CGO/LSCFO cells with and without the addition of 1 at.% Co as sintering aid. The dotted lines represent the linear fitting of values.

### Transmission electron microscopy

The cathode/electrolyte interface of the LSCFO/CGO/LSCFO with the addition of Co sintering aid was investigated by TEM. The formation of columnar grains attached to the electrolyte was observed along the cathode/electrolyte interface (see Figure 3(a)). Point EDS acquired at different spots surrounding the area reveals that these columnar grains are mainly composed of Co, Sr and Gd. In addition, these columnar grains seem to grow from a surface grain of the electrolyte rich in Gd. The formation of such phases at the cathode/electrolyte interface would hinder the oxygen ion transport to the electrolyte, hence increasing the  $\text{ASR}_{\text{Cathode}}$  values.

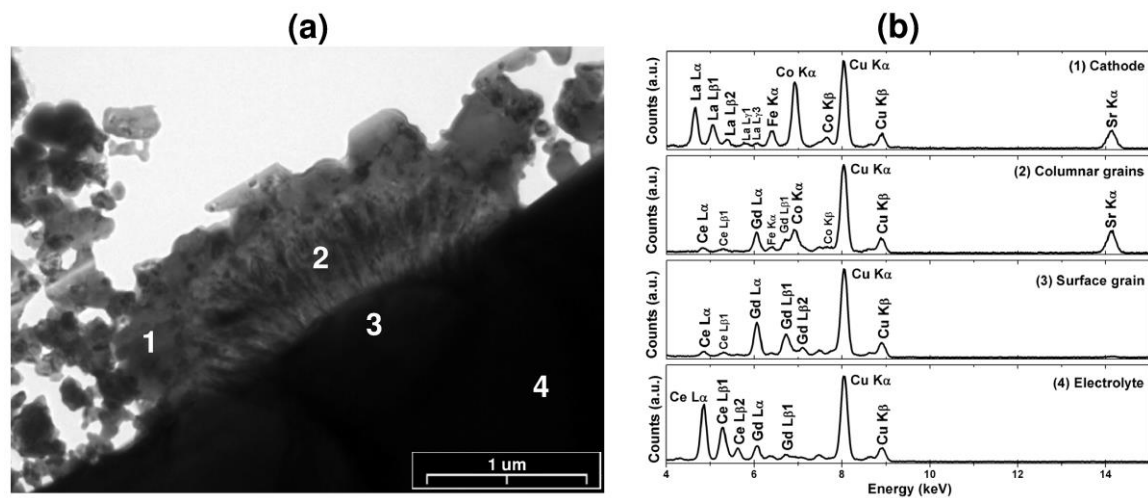


Figure 3. (a) Bright Field TEM image at the cathode/electrolyte interface of the LSCFO/CGO/LSCFO cell with Co doping. (b) Point EDS spectra acquired at the zones indicated in (a).

## Conclusions

The microstructure and the electrochemical performance of LSCFO/CGO/LSCFO cells containing electrolytes with and without the addition of 1at.% Co as sintering aid were studied. CGO electrolytes with Co doping are denser, have better mechanical properties, and present higher electrical conductivity. However, the LSCFO/CGO/LSCFO cells with the addition of Co have  $ASR_{cathode}$  values up to four times higher than those of the cell without sintering aid despite both cells have cathodes with similar nano/microstructure. These higher  $ASR_{cathode}$  values would be produced by the presence of columnar grains rich in Sr, Co and Gd at the cathode/electrolyte interface of the cell prepared with cobalt doping. Such columnar grains would hinder the oxygen ion transport from the cathode to the electrolyte. These results indicate that even though the use of sintering aids would improve the electrolyte properties, they could also negatively affect the cathode performance.

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