Journal of Power Sources 196 (2011) 9276–9283

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

# Electrochemical performance of nanostructured $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ and $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ cathodes for IT-SOFCs

L.M. Acuña [a], J. Peña-Martínez [b], D. Marrero-López [b], R.O. Fuentes [a], P. Nuñez [b], D.G. Lamas [a,c,*]

[a] CINSO (Centro de Investigaciones en Sólidos), CITEFA-CONICET, J.B. de La Salle 4397, (1603) Villa Martelli, Pcia. de Buenos Aires, Argentina
[b] Departamento de Química Inorgánica, Universidad de La Laguna, (E-38200) La Laguna, Tenerife, Spain
[c] Laboratorio de Caracterización de Materiales, Facultad de Ingeniería, Universidad Nacional del Comahue, Buenos Aires 1400, (8300) Neuquén, Pcia. de Neuquén, Argentina

ARTICLE INFO

*Article history:*
Received 20 June 2011
Received in revised form 19 July 2011
Accepted 20 July 2011
Available online 27 July 2011

*Keywords:*
Nanocrystalline materials
Intermediate-temperature solid-oxide fuel cells
Cathode
Mixed ionic-electronic conductor
Cobaltite

ABSTRACT

The electrochemical performance of nanostructured cathodes for IT-SOFCs based on perovskite-type mixed ionic/electronic conductors (MIECs) is investigated. Different compounds ($La_{0.6}Sr_{0.4}CoO_{3-\delta}$ and $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$) and synthesis methods (freeze-drying and citrate complexation) were evaluated. These materials exhibited excellent performance (area-specific resistance values in the range of 0.05–0.20 $\Omega\,cm^2$ for an operating temperature of 700 °C), which improved with decreasing grain size. This performance can be attributed to the high specific surface area of these nanostructured cathodes, thus dramatically increasing the number of active sites for the oxygen reduction reaction. Under these conditions, the electrochemical properties are mainly controlled by oxide ion diffusion through the MIEC cathode, which becomes faster with decreasing grain size.



## 1. Introduction

Nanostructured materials attract great interest due to their novel properties. They have already been used in power generation and storage devices, such as lithium-ion batteries, low-temperature fuel cells, among others [1]. These materials have limited applications in Solid-Oxide Fuel Cells (SOFCs) because grain growth is expected to occur at the typical operation temperatures of these devices. Nevertheless, their use in intermediate-temperature SOFCs (IT-SOFCs) is currently under investigation because grain growth is reduced by operating in this temperature range. Cathodes based on nanostructured mixed ionic/electronic conductors (MIECs) are particularly interesting because the number of active sites for the oxygen reduction reaction (ORR) is expected to increase dramatically due to the increase in the specific surface area [2–6].

Recent works showed that nanostructured cathodes prepared from $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ nanotubes exhibit low polarization resistances at intermediate temperatures [2,6]. Initially, their enhanced performance was mainly attributed to their high surface-to-volume ratio, increasing the number of reaction sites with the surrounding gas, when compared to an ordinary microstructured cathode [2]. However, a subsequent study showed that oxide ion diffusion enhances with decreasing particle size [6]. This result is similar to the improvement of ionic transport previously reported in nanostructured $CeO_2$-based electrolytes [7]. Therefore, further investigation is essential to elucidate the electrochemical processes behind the enhanced electrochemical performance of nanostructured MIEC cathodes. In this sense, the study of other compositions and/or nanostructures could be very important. The $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ perovskite deserves particular attention because it is considered as a serious candidate for IT-SOFC cathode due to its high performance for the ORR [8–11].

In this work, we evaluated nanostructured $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) and $Sm_{0.5}Sr_{0.5}CoO_{3-\delta}$ (SSC) cathodes prepared from nanopowders synthesized by two different wet-chemical methods: freeze-drying and citrate complexation. They were used to prepare pastes with an organic vehicle and deposited on $Gd_2O_3$-doped $CeO_2$ (GDC) electrolytes. To retain the original nanostructures in the final cathodes, we use a conventional sintering process at moderate temperatures. The area-specific resistance (ASR) was evaluated using electrochemical impedance spectroscopy (EIS) on symmetrical [cathode/electrolyte/cathode] cells, measured in air. These nanostructured cathodes exhibit very high performance, which is enhanced significantly with decreasing grain size, as in the case of the above-mentioned studies on cathodes based on LSC nanotubes. Their electrocatalytic properties for the ORR are discussed in detail.

* Corresponding author at: Laboratorio de Caracterización de Materiales, Facultad de Ingeniería, Universidad Nacional del Comahue, Buenos Aires 1400, (8300) Neuquén, Pcia. de Neuquén, Argentina. Tel.: +54 299 4490350; fax: +54 299 4490329.
*E-mail address:* diego.lamas@fain.uncoma.edu.ar (D.G. Lamas).

0378-7753/$ – see front matter © 2011 Published by Elsevier B.V.
doi:10.1016/j.jpowsour.2011.07.067

**Table 1**
Phase (space group) and morphological data of LSC and SSC powders synthesized by citrate and freeze-drying (FD) methods and calcined at different temperatures. *d*: average crystallite size determined by Scherrer's equation. $D_{SEM}$: average grain size determined from SEM observations. $S_{BET}$: BET specific surface area. $D_{BET}$: average particle size determined from BET specific surface area (see text).

| Powder | Synthesis method/calcination temp. | Space group | *d* (nm) | $D_{SEM}$ (μm) | $S_{BET}$ ($m^2\ g^{-1}$) | $D_{BET}$ (μm) |
|---|---|---|---|---|---|---|
| LSC | Citrate/1100 °C | $R\bar{3}c$ | >200 | ≈1 | 2.1 | 0.44 |
| | FD/1100 °C | $R\bar{3}c$ | >200 | ≈0.5 | 2.1 | 0.44 |
| | FD/900 °C | $Pm\bar{3}m$ | 30 | ≈0.25 | 6.1 | 0.16 |
| SSC | Citrate/1100 °C | $I4/mmm$ | >200 | ≈2 | 0.62 | 1.4 |
| | FD/1100 °C | | 150 | ≈1 | 1.5 | 0.61 |
| | FD/900 °C | | 25 | ≈0.25 | 4.0 | 0.22 |

## 2. Experimental procedure

### 2.1. Synthesis and characterization of LSC and SSC nanopowders

LSC and SSC nanopowders were prepared by freeze-drying and citrate complexation methods, starting from $Sr(NO_3)_2$ (Aldrich, 99%), $La(NO_3)_3{\cdot}6H_2O$ (Aldrich, 99.999%), $Co(NO_3)_2{\cdot}6H_2O$ (Aldrich, 98%) and $Sm(NO_3)_3{\cdot}6H_2O$ (Aldrich, 99.9%). These nitrates were first assessed by thermogravimetric analysis to assure the correct cation composition.

The citrate complexation route was carried out using citric acid (Aldrich, 99%) as the complexing agent [12,13]. Each nitrate compound was dissolved in distilled water separately and then mixed to obtain a nitrate solution with the appropriate stoichiometry. A citric acid solution was added at a ligand/metal ratio ($L\,M^{-1}$) of 2 and left under continuous stirring for 24 h. Afterwards, evaporation at 200 °C yielded a homogeneous gel, which was calcined at 1100 °C for 1 h to eliminate the organic material and to obtain the perovskite phase. Samples obtained using this method will be referred hereafter as LSC-citrate and SSC-citrate.

Using the freeze-drying method [14], a stoichiometric solution was prepared from metal nitrates in distilled water, and an ammonium-EDTA solution was added at a molar ratio $L\,M^{-1} = 0.5$ as a complexing agent. The pH was adjusted to 7 by adding nitric acid. The solutions were flash frozen in liquid nitrogen and then dehydrated in a Heto Lyolab 3000 freeze-dryer. The resulting precursors were treated at 300 °C for 1 h, grounded and finally calcined at 900 °C for 5 h. These materials will be referred hereafter as LSC-FD and SSC-FD.

For structural characterization, X-ray power diffraction (XPD) patterns were collected with a PANalytical X'Pert PRO diffractometer equipped with a primary monochromator (Cu $K\alpha_1$ radiation) and an X'Celerator detector. Scans were recorded in the range of $2\theta = 20–80°$, with steps of 0.03° for 2 h. The average crystallite size (*d*) was calculated using Scherrer's equation [15].

BET-specific surface areas ($S_{BET}$) were determined using a surface area analyzer (Gemini™ 2365, Micromeritics Instrument) with nitrogen as the adsorptive. Prior to the analysis, all samples were degassed at 250 °C under vacuum for several hours. The average grain size was estimated from these results using the equation $D_{BET} = 6/(S_{BET}\,\rho)$, where $\rho$ is the theoretical (crystallographic) density.

The powder morphology and electrolyte/electrode interfaces were analyzed with scanning electron microscopy (SEM) with a JEOL JSM-6300 microscope.

### 2.2. Preparation and characterization of LSC and SSC cathodes

The electrocatalytic properties of the LSC and SSC cathodes for the ORR were studied with electrochemical impedance spectroscopy (EIS) using symmetric [cathode/electrolyte/cathode] cells.

Dense GDC pellets of about 1.0 mm thickness and 10 mm diameter, prepared from commercial powders ($Ce_{0.8}Gd_{0.2}O_{1.9}$, Nextech Materials) and sintered at 1400 °C for 5 h, were used as electrolytes. A slurry of the different powders mixed with Decoflux™ as the binder was deposited on each side of the GDC electrolyte, and then sintered at different temperatures in the range of 850–950 °C to determine an optimum sintering temperature that yields both an appropriate electrolyte–electrode adherence and the lowest ASR values. Platinum paste (Metalor™) fired at 800–850 °C for 30 min was used as the current collector.

The impedance spectra of these symmetric cells were measured in static air in the temperature range of 400–700 °C using a frequency response analyzer (Solartron 1260) in the frequency range from 0.02 Hz to 1 MHz with an excitation voltage of 50 mV.

## 3. Results and discussion

### 3.1. Crystal structure and morphology of LSC and SSC powders

Table 1 summarizes the space group (phase), the average crystallite size and the results of the morphological analysis for all the as-synthesized LSC and SSC nanopowders.

Single-phase perovskite-type powders were obtained after calcination of LSC-FD and SSC-FD at 900 °C for 5 h and LSC-citrate and SSC-citrate at 1100 °C for 1 h. Figs. 1 and 2 show XPD patterns of LSC and SSC powders, respectively. These figures compare the two synthesis methods studied in this work, i.e., citrate complexation and freeze-drying.

In the case of LSC-citrate powders calcined at 1100 °C, the reflections in Fig. 1 exhibit the typical splitting of a rhombohe-

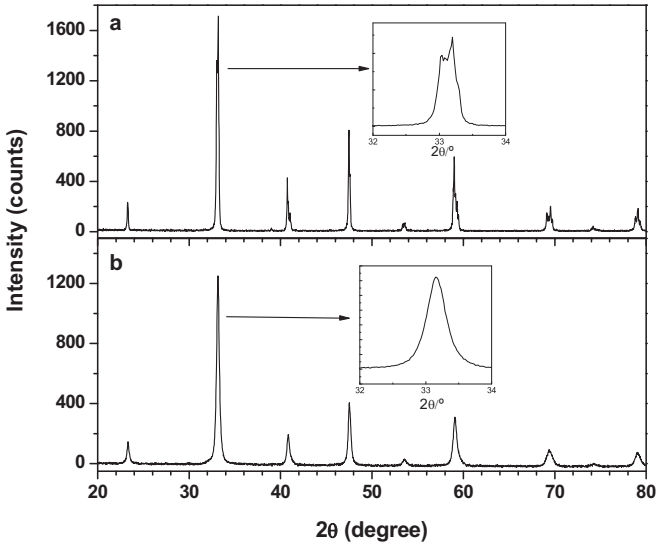


**Fig. 1.** XPD patterns of LSC powders: (a) synthesized by the citrate complexation method and calcined at 1100 °C and (b) synthesized by the freeze-drying method and calcined at 900 °C. In the former case, all reflections correspond to the rhombohedral phase, while in the latter, they are ascribed to the cubic phase.