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High-Performance Solid-Oxide Fuel Cell Cathodes Based on Cobaltite Nanotubes

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Fuel cells are one of the most promising devices for environmentally clean power generation by converting chemical energy directly into electrical energy.[1] Among them, solid-oxide fuel cells (SOFCs) have the advantage of allowing the use of different fuels such as hydrogen or hydrocarbons. Significant effort has been devoted to lower the operation temperature of these devices giving rise to the intermediate temperature SOFCs (IT-SOFCs) which operate at 500−700 °C, avoiding degradation problems due to thermal cycling or diffusion at interfaces and reducing the cost of the interconnection materials.[1,2]

Nanostructured materials have recently attracted great interest due to their novel properties.[3−5] They have already been used in power generation and storage devices, such as lithium-ion batteries, low-temperature fuel cells, etc.[5] These materials are not employed in conventional SOFCs since grain growth is expected to occur at the typical operation temperatures of these devices. However, their use in IT-SOFCs deserves to be evaluated since grain growth can be minimized at this operation temperature range. In this work, we present a new type of highly porous nanostructured cathodes which exhibit very low polarization resistance, prepared from $La_{0.6}Sr_{0.4}CoO_3$ nanotubes following a very simple procedure.

Tubular structures formed by assembled manganite nanoparticles have been successfully synthesized by Levy et al.[6] and Leyva et al.[7] These structures are likely to have a very high specific area and have recently been suggested as cathodes for SOFCs.[8] However, manganites are not good candidates for IT-SOFC because they are poor ionic conductors in this temperature range.[9−11] In this sense, it is better to choose cobaltites for this type of SOFCs. We have chosen the $La_{0.6}Sr_{0.4}CoO_3$ compound since it is nowadays one of the most used cathodes in IT-SOFCs due to its significant mixed ionic-electronic conductivity in this temperature range.[9]

We synthesized $La_{0.6}Sr_{0.4}CoO_3$ (LSCO) nanotubes by using the pore wetting technique to obtain tubular structures. Commercial polycarbonate membranes with pore size of 800 nm were used as template and filled with a nitrate precursor solution. The membranes were further treated under microwave radiation for a few minutes and then calcined at 750−900 °C for 10 min, obtaining the perovskite desired structure, as confirmed by X-ray diffraction. Nanotubes calcined at 800 °C exhibited a crystallite size of about 20 nm and BET specific surface area of 43 m^2/g, showing that nanotubes are formed by disagglomerated crystallites. This high specific surface area is expected to be very useful to prepare a high-performance cathode. A detailed study on the synthesis process is currently in progress. Preliminary results showed that the perovskite structure can be obtained at temperatures as low as 750 °C, but the resulting tubes have comparatively worse mechanical properties. These properties can be enhanced by increasing the calcination temperature, but it is limited to around 900 °C in order to retain the nanotube structure.

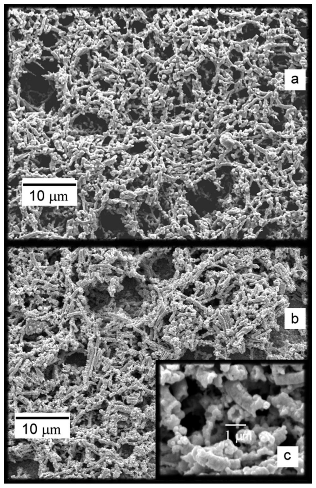

Figure 1. SEM micrographs of LSCO cathodes painted with a LSCO/IV mass ratio of 1:2 and treated for 3 min at 1200 °C (FF1200) (a) and for 1 min at 1100 °C (FF1100) (b and c). In panel c, it can be observed that the hollow structure is retained in the case of the FF1100 treatment.

We painted CeO_2-10 mol% of Sm_2O_3 (SDC) electrolytes with an ink made with LSCO nanotubes calcined at 800 °C and a commercial ink vehicle (IV). Typical processes to attach the electrodes to the electrolyte involve temperatures around or higher than 1000 °C and times of about 1 or 2 h, with slow heating and cooling rates. In our case, this option is not adequate for the preparation of a nanostructured cathode. Then, we developed an original method to attach the cathodes by heating the sample at 1000−1200 °C with fast heating and cooling rates (around 200 °C/min) and dwell times of 1−10 min. In addition, this method allowed us to obtain a cathode in a time of several minutes. This process derives from a nonconventional method for ceramic sintering known as “fast-firing”.[12,13]

Figure 1 displays SEM micrographs of LSCO cathodes painted with a LSCO/IV mass ratio of 1:2 and treated for 3 min at 1200 °C (FF1200) (a) and for 1 min at 1100 °C (FF1100) (b). It can be noted that both cathodes are highly porous at the meso- and nanoscales, the former being due to the ink vehicle and the latter undoubtedly a result of the original nanostructured tubular shape. In Figure 1c, it can be observed that the hollow structure was retained in the cathode treated at 1100 °C. After the thermal treatment, the grain size of the nanotubes increased to 150−200 nm. The typical thickness of the films was about 10 μm.

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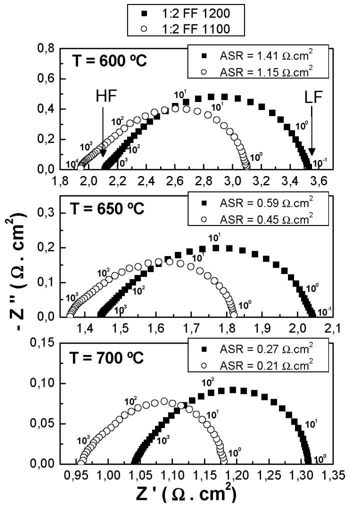

Figure 2. Nyquist plots, measured on symmetrical LSCO/SDC/LSCO cells, of cathodes painted with a LSCO/IV mass ratio of 1:2 and treated for 3 min at 1200 °C (1:2 FF1200) (■) and 1 min at 1100 °C (1:2 FF1100) (○).

Impedance spectroscopy measurements were performed on symmetrical LSCO/SDC/LSCO cells for 600, 650, and 700 °C in air atmosphere. Figure 2 shows the evolution of the Nyquist plots with temperature for the cathodes previously shown in Figure 1. The high-frequency intercept of the electrode impedance on the real axis is the total resistance of the electrolyte. The impedance arcs observed in Figure 2 are the sum of the charge-transfer impedances plus a chemical impedance associated with non-charge-transfer processes.[10] The difference between the low-frequency (LF) and the high-frequency (HF) intercepts on the real axis is the area-specific resistance (ASR).

The lower ASR of the 1:2 FF1100 sample compared to the 1:2 FF1200 one is mainly due to a reduction of the low-frequency arc, which is associated with non-charge-transfer processes, such as oxygen surface exchange, solid-state diffusion, and gas-phase diffusion.[10] The high specific surface area and porosity at the meso- and nanoscales of the LSCO nanotube cathode promotes these processes since this architecture facilitates gas distribution in the electrode and increases the number of reaction points. This is probably the main reason for their high performance. The values of ASR found in this work are substantially lower than those reported in the literature for many cobaltite-based cathodes,[9,10,14−18] reaching 0.21 Ω•cm² at 700 °C for the 1:2 FF1100 sample.

We also evaluated cathodes treated for 10 min at 1000 °C. They exhibited a high porosity, but larger values of ASR were found (0.33 Ω•cm² at 700 °C). This may be due to a poor contact between the nanotubes. A significant improvement in the contact could be obtained by mixing the nanotubes with a LSCO nanopowder or by preparing LSCO nanotube/SDC nanopowder composite cathodes.

The influence of the LSCO/IV ratio was also examined. The optimum LSCO/IV ratio was 1:2 (Figure 2), while cathodes prepared with lower or higher concentrations of LSCO nanotubes showed lower performance. For example, the ASR at 700 °C was 0.31 and 0.57 Ω•cm² for 1:1.5 FF1100 and 1:3 FF1200 samples, respectively. It is worthy to note that substantially good electrical properties were obtained even for cathodes prepared with a low concentration of LSCO nanotubes in the precursor ink.

The long-term stability of the hollow nanostructure requires further study since a short fast-firing treatment was used to attach the cathode to the electrolyte. However, a good behavior is to be expected since the typical operation temperatures of these cathodes are much lower than the dwell temperature of the fast-firing treatment. In this work, the stability of these materials was proved only during a few hours. Long-term tests will be conducted to address this matter, taking into account its great importance in technological applications.

We also tested LSCO nanotube/Ag composite cathodes, which have the advantage of lowering the temperature required to attach the cathode to the electrolyte. Preliminary results showed that a very good performance can be obtained, exhibiting at 700 °C a similar ASR than the 1:3 FF1200 sample (0.57 Ω•cm²), but larger for lower temperatures, indicating a higher activation energy. Further study of this type of cathodes is needed in order to optimize their performance.

In summary, we have synthesized cobaltite nanotubes and used them to build a new architecture for IT-SOFCs cathodes with very low polarization resistance. We have developed a very fast and simple method to attach them to the electrolyte which allows the retention of its original nanostructure. The ASR of these novel cathodes is much lower than that reported in the literature for materials exhibiting conventional microstructures, reaching satisfactory values for technological applications. However, further investigation is required in order to evaluate their long-term stability. The present work opens a path for a new generation of nanostructured electrodes. Nanotubes of other mixing conducting materials with better intrinsic properties, such as the recently discovered $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$,[19] may exhibit an additional improvement of the cathode performance. Finally, it is worth mentioning that this new architecture, which increases the number of reaction sites, deserves to be investigated for anode materials since a similar enhanced performance could be obtained.

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Supporting Information Available: Experimental procedure and more details on material characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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