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Chemical and electrical properties of LSM cathodes prepared by mechanosynthesis

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HIGHLIGHTS

- We demonstrate scalability of mechanochemical method in order to obtain nanometric particle powder.
- Behaviour of obtained powder is superior to that of published reports and comparable to a commercial one.
- The proposed synthesis method is simple and implies less cost as it is at room temperature and atmosphere conditions.

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ABSTRACT

Mechanosynthesis of $La_{1-x}Sr_xMnO_3$ ($x = 0$, 0.25, 0.5, 0.75 and 1) was carried out at room temperature from stoichiometric mixtures of La_2O_3, Mn_2O_3 and SrO, obtaining monophasic powders with the perovskite structure. Physical properties of these materials and their chemical compatibility with the electrolyte yttria stabilized zirconia (YSZ), which depend strongly on the La/Sr ratio, were evaluated to corroborate availability to be implemented as cathode material in solid oxide fuel cells (SOFCs). Electrical conductivity values in air ranged between 100 and 400 S cm^{-1} in the temperature range of 25–850 °C. Samples presented low reactivity with YSZ in the working temperature range (600–1000 °C) maintaining the grain size small enough to preserve the catalytic activity for oxygen reduction.

1. Introduction

Solid Oxide Fuel Cells (SOFCs) have been widely studied in the last decade in order to reach a blue economy concept: "a zero emission world" [1]. SOFCs are specially interesting because of their advantages respect to the other types of fuel cells: theoretical efficiency of 80–90%, lower costs, fuel flexibility and better stability with time, although the operation temperature is still too high between 800 and 1000 °C for practical application [2,3].

Different mixed ionic-electronic conductors with perovskite structure have been proposed in the last few years as potential cathode materials for SOFC, such as cobaltites, ferrites, nickelates and double perovskites [3]; however, they usually exhibit chemical and thermal expansion incompatibilities with yttria stabilized zirconia (YSZ) electrolyte. Sr-doped lanthanum manganites, $La_{1-x}Sr_xMnO_3$ (LSM), are the most common cathode material used in SOFC systems due to their high stability under oxidant atmospheres and high temperatures compared to other alternative materials [4].

Synthesis of these materials has been extensively studied using different synthetic routes, but the mechanochemical method itself (not as activation) is not yet a common one [5]. Mechanochemistry is a relative simple process that uses high-energy ball mills and permits production among others of nanostructured mixed oxides [6]. The mechanical energy from impact and shear forces by application of a high frequency movement is transferred to the powder inducing solid state chemical reactions. One of the most important advantages of mechanochemistry is its capability to produce large material quantities at room temperature and in a very short time.

In the present work, a study of the chemical and physical properties of $La_{1-x}Sr_xMnO_3$ (LSM) system obtained by

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Table 1
Composition of the synthesized powder samples and milling time required to obtain 6 g of pure phases.

Phase	t (min)
P1 ($LaMnO_3$)	90
P2 ($La_{0.75}Sr_{0.25}MnO_3$)	90
P3 ($La_{0.5}Sr_{0.5}MnO_3$)	120
P4 ($La_{0.25}Sr_{0.75}MnO_3$)	120
P5 ($SrMnO_3$)	150

mechanosynthesis was carried out as small differences in the La/Sr ratio cause significant changes in the cathode performance. A structural study of this system, also prepared by mechanochemistry, was recently published by Sayagués et al. [7], although smaller amounts of samples were synthesized. A summary of the obtained structural results is presented here also to demonstrate the scalability of mechanochemistry. Chemical compatibility between cathode and electrolyte and electrical properties of the cathode were measured in a cell that was built using the synthesized LSM as cathode and YSZ as electrolyte.

2. Experimental

$La_{1-x}Sr_xMnO_3$ powder samples with different Sr content ($x = 0$, 0.25, 0.5, 0.75 and 1) were synthesized by a mechanochemical method using a planetary ball mill (model Micro-Mill Pulverisette 7, Fritsch) from stoichiometric mixtures of La_2O_3 (Aldrich 99.98%), Mn_2O_3 (Aldrich 99%) and SrO. The last one was obtained from calcination of $SrCO_3$ (Aldrich 98%) at 1200 °C for 12 h. This oxide mixture was placed into a hardened chromium steel jar along with 7 WC balls (26.4 g; Ø = 15 mm) and was milled at 600 rpm (disc and vial) in air to obtain 6 g of each sample. The different compositions and the required milling time to obtain single phase powders (**P** samples) are presented in Table 1. **P** samples were then uniaxially pressed into pellets of 12 × 5 mm (microstructural characterization) or 12 × 1 mm (total conductivity) and sintered in air at 1300 °C for 8 h with a heating rate of 10 °C min^{-1} and free cooling (**H** samples).

Structural characterization and phase identification were carried out by a PANalytical X'Pert Diffractometer. X-ray Diffraction (XRD) patterns were scanned between 10 and 80° in 2θ and step-scan mode, using a step of 0.05° and an acquisition time of 320 s. Peaks were indexed using X'Pert HighScore Plus and FullProff and WinPlot softwares [8,9] were used to do the fitting and calculate the cell parameters and the diffraction domain size (D). Scanning electron microscopy (SEM) images were obtained on Hitachi S5800 SEM-FEG (**H** samples) and Hitachi S-2400N (the electrode–electrolyte interface) microscopes. The compositional variation through the interface was analysed using Energy Dispersive X-ray Spectroscopy (EDX) in Hitachi S-2400N, which was equipped with a Bruker detector. Transmission Electron Microscopy (TEM and HRTEM) images and electron diffraction (ED) patterns were performed on a 200 kV Philips CM200 microscope equipped with a supertwin objective lens and a LaB_6 filament (point resolution = 0.25 nm) and a 300 kV TECNAI G2 F30 microscope with a field emission system (point resolution = 0.2 nm). The analysis of the HRTEM images was done with the Digital Micrograph software (Gatan Inc.). The samples were prepared by dispersion of the powder in acetone and droplets of the suspension were deposited onto a coated carbon copper grid.

The total conductivity of the pellets (**H** samples) was determined by the four-point Van der Pauw method between 100 and 900 °C during the cooling process [10]. The area-specific polarization resistance (ASR) values were obtained under symmetrical atmospheres in a two electrode configuration. Dense YSZ pellets (8% Y_2O_3 Tosoh), of 10 mm of diameter and 1 mm of thickness were obtained at 1400 °C for 5 h. The symmetrical cell of LSM cathode and YSZ electrolyte was prepared by screen printing using a slurry of 50 wt.% LSM (**P** samples) and 50 wt% Terpineol; and then sintered at 1100 °C for 1 h [10]. Impedance spectra of the cells was performed using a Solartron 1260 FRA, at open circuit voltage (OCV), in the 0.01–10^6 Hz frequency range with an *ac* signal amplitude of 50 mV. The spectra was analysed by using the ZView software [11].

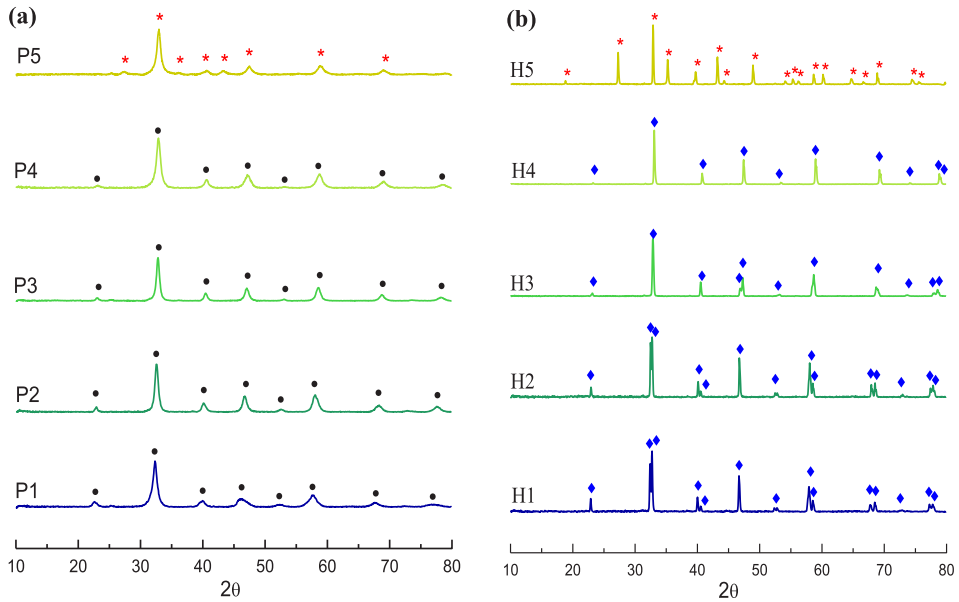

Fig. 1. XRD patterns for all synthesized samples: (a) **P1**–**P5** and (b) **H1**–**H5** (●*Pm-3m* cubic perovskite structure, ◆*R-3c* rhombohedral structure and ✻$P6_3/mmc$ hexagonal structure).