

## Properties of Sr-Doped Lanthanum Manganites for SOFC

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**Abstract:** The study of Sr-doped lanthanum manganites ( $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ) leads to solid oxide fuel cells (SOFC) cathodic material application. This material has been studied due to its excellent electrochemical, chemical and thermal stability performance, further electrolyte compatibility. This composition was prepared using traditional ceramic processing methods. The density about 93% of the theoretical was obtained for  $x = 0,5$ . The results obtained suggested that sintering temperature and type materials used for preparation powder of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  could influence the sintered density and porosity of the sintered samples. Vickers microhardness measurements showed similar behaviour for the samples prepared with different purity degrees of  $\text{La}_2\text{O}_3$ .

### Introduction

Solid oxide fuel cells, SOFCs, have attracted a great deal of interest in recent years as potential sources of electrical energy due to their high efficiency and low environmental hazard [1-3]. A fuel cell is a device that converts chemical energy to electricity and thermal energy. The main components of fuel cells are composed of cathode, anode, electrolyte, and interconnect. Fig. 1 shows a solid oxide fuel cell operating on fuel and air. In particular, the cathode must have a porous microstructure so that gaseous oxygen can diffuse through the cathode to the cathode/electrolyte interface [3]. Thus, the study of sintering behaviour of the cathode materials is composed a step important in the fabrication of SOFCs. In addition, the cathode with this porous microstructure must have mechanical properties for successful operation of a SOFC.

The perovskite-type strontium-doped lanthanum manganites have been studied as the most promising candidate material for the cathode of SOFCs [3-10]. With operating temperature up to 1000 °C in air or oxygen atmosphere, the cathode material has to meet the following requirements: high electron conductivity, thermal and chemical stability, compatibility with the solid electrolyte, sufficient porosity, and good adherence at the surface of the electrolyte [11]. Many surveys [10-16] have been published about synthesis processes of Sr-doped lanthanum manganites.

In the present work, were prepared  $\text{La}_{(1-x)}\text{Sr}_x\text{MnO}_3$  powder by high-temperature solid-state reaction of  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ , and  $\text{MnCO}_3$ . The purposes of the present study are to investigate the effects of powder agglomeration and sintering temperature on the sinterability of the obtained powder. The microstructure and Vickers microhardness of sintered samples are analyzed too.

It was evaluated the use of  $\text{La}_2\text{O}_3$  (lower purity), that was produced at IPEN, aiming the application of a raw material available in Brazil.

### Experimental

For experimental work  $\text{La}_2\text{O}_3$  (Aldrich, 99.999%; real density = 6.51 g/cm<sup>3</sup>; mean size diameter = 1.9 µm; surface area = 28.87 m<sup>2</sup>/g),  $\text{SrCO}_3$  (Aldrich, 99.995%; real density = 3.7

$\text{g/cm}^3$ ; mean size diameter = 2.2  $\mu\text{m}$ ; surface area = 30.48  $\text{m}^2/\text{g}$ ),  $\text{MnCO}_3$  (Aldrich, 99.9%; real density = 3.12  $\text{g/cm}^3$ ; mean size diameter = 0.5  $\mu\text{m}$ ; surface area = 5.18  $\text{m}^2/\text{g}$ ) and  $\text{La}_2\text{O}_3$  (obtained in IPEN, starting raw material Brazil, 71.80%; real density = 4.98  $\text{g/cm}^3$ ; mean size diameter = 1.2  $\mu\text{m}$ ; surface area = 24.82  $\text{m}^2/\text{g}$ ) were used for preparation  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  powder. The raw materials were mixed in isopropyl alcohol using attrition mill for 12 h. Powders different compositions in  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  were synthesized by high-temperature solid-state reaction of starting powders are given in reaction. 1.

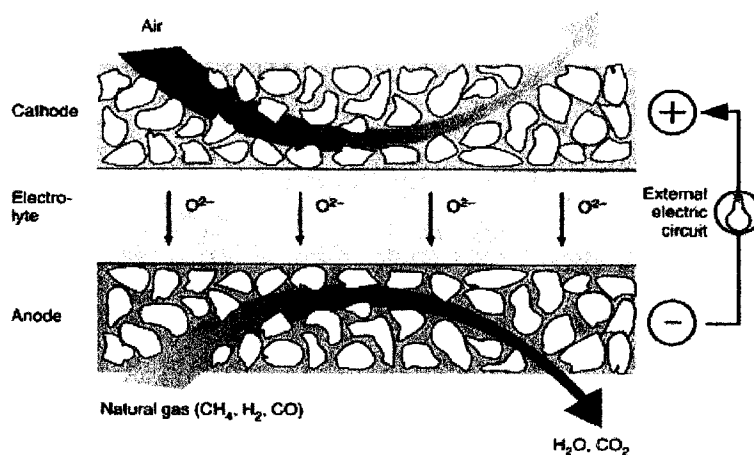
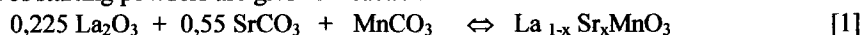


Fig. 1. Solid Oxide Fuel Cell

Two mixtures containing  $\text{La}_2\text{O}_3$  99.999%;  $\text{SrCO}_3$  99.995%; and  $\text{MnCO}_3$  99.9%; (MO2) and  $\text{La}_2\text{O}_3$  71.8%;  $\text{SrCO}_3$  99.995%; and  $\text{MnCO}_3$  99.9%; (MO3) were prepared.

The required amount of each raw material was dried at 80  $^{\circ}\text{C}$  for 24 h in kiln before of the mixing step. The resultant mixtures were calcined at 1200  $^{\circ}\text{C}$  for 12 h in argon atmosphere and pellets (10 $\phi$ x2.1 mm) were formed by dry-uniaxial pressing process up to 500 bars in steel dies and by a subsequent isostatic pressing under a pressure of 3000 bars. The green densities were calculated geometrically. Pellets were sintered at 1400  $^{\circ}\text{C}$  and 1500  $^{\circ}\text{C}$  for 4 h using a heating rate of 10  $^{\circ}\text{C}/\text{min}$  in air. After sintering, samples were characterized by X-ray diffraction (XRD), the microstructures were observed by scanning electron microscopy (SEM), the sintered densities were measured by the Archimedes method using ethanol, and Vickers microhardness measurements were obtained using load of 19.6 N.

## Results and discussion

The averaged green densities for MO2 and MO3 powders were 33 % and 36 % of theoretical density, respectively. The particle size distributions of both powders calcined at 1200  $^{\circ}\text{C}$  for 4 h and disintegrated in attrition mill presented relatively narrow size distribution (0.2 to 5  $\mu\text{m}$ ). The two powders showed the same agglomeration degree and particle size distribution [17].

X-ray diffraction spectra of sintered  $\text{La}_{(1-x)}\text{Sr}_x\text{MnO}_3$  at 1400  $^{\circ}\text{C}$  and 1500  $^{\circ}\text{C}$  for 4 h are shown in Fig. 2. The XRD patterns of the MO2 and MO3 sintered samples indicated the formation of a single-phase solid solution with perovskite-like structure, where the  $\text{Sr}^{2+}$  ions are expected to occupy  $\text{La}^{3+}$  sites. Based on the lattice parameters found by GHARBAGE et al.[18], a orthorhombic structure of  $\text{La}_{0.50}\text{Sr}_{0.50}\text{MnO}_3$  composition was determined for MO2 and MO3

sintered samples at 1400 °C. For sintered samples at 1500 °C, a slight modification to monoclinic structure of  $\text{La}_{0.60}\text{Sr}_{0.40}\text{MnO}_3$  composition was obtained. The monoclinic phase is established at higher temperatures (above 1500 °C).

For higher sintering temperatures, the sintered densities of the MO2 e MO3 samples are smaller, 91 % of theoretical density was achieved when the powder compact was sintered 1500 °C for 4h. On the other hand, the sintered density for both MO2 e MO3 samples approached 96% theoretical density at 1400 °C for 4h. Therefore, it might be suggested that the sintered densities for both samples can be controlled simply by sintering temperatures and low influence by agglomerated particles and green density of samples.

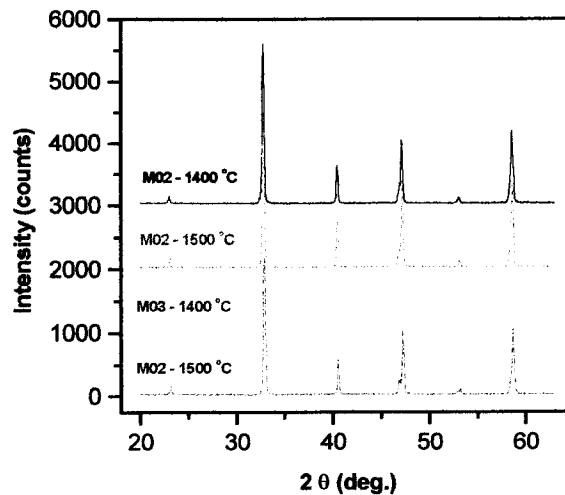


Fig. 2. XRD patterns of sintered  $\text{La}_{(1-x)}\text{Sr}_x\text{MnO}_3$  at 1400 °C and 1500 °C for 4 h.

The samples prepared with different purity of  $\text{La}_2\text{O}_3$  (71.80 % - MO3 or 99.999 % - MO2) showed the similar microstructures observed by SEM. Fig. 3 shows SEM micrographies of MO3 sintered samples at 1400 ( $\text{La}_{0.50}\text{Sr}_{0.50}\text{MnO}_3$ ) and 1500 °C ( $\text{La}_{0.60}\text{Sr}_{0.40}\text{MnO}_3$ ) for 4 h. The micrography (Fig. 3a) of sample sintered at 1400 °C shows small voids while the sample sintered at 1500 °C (Fig. 3b) large voids between aggregated lumps are observed. The sintered sample MO3 at 1400 °C shows that the lumps form small pores while for MO3 sintered at 1500 °C are observed large pores, indicating that the sintering is more completely achieved.

The results of microhardness are presented in Table 1. The microhardness obtained on the sintered samples at 1400 °C showed values slightly higher than on the sintered samples at 1500 °C. Basically, it was not observed any difference on microhardness values between the sintered samples with utilization of different concentrations of raw materials (MO3 - 71.80 %  $\text{La}_2\text{O}_3$  or - MO2 - 99.999 %  $\text{La}_2\text{O}_3$ ).

Table 1: Influence of purity of  $\text{La}_2\text{O}_3$  (71.80 % - MO3 or 99.999 % - MO2) and sintering temperature (1400 or 1500 °C) on microhardness Vickers

Material	$H_v$ [MPa] / 1400 °C	$H_v$ [MPa] / 1500 °C
MO2	7,58	4,79
MO3	8,74	4,82

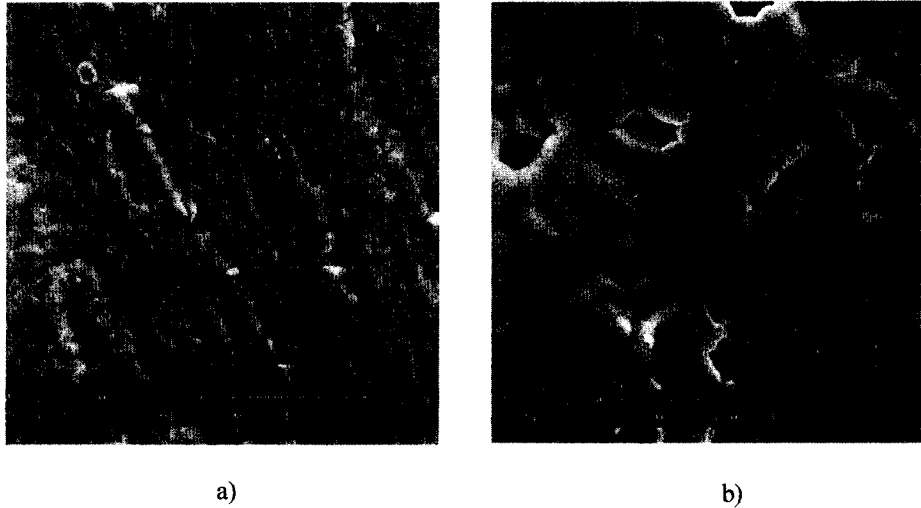


Fig. 3. SEM micrographs of samples obtained by sintering at a) 1400 °C / 4 h and b) 1500 °C / 4 h.

### Conclusion

The results obtained permitted the following conclusions to be established:

- The investigated compositions of the  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  sintered samples with  $x$  varying from 0 to 0,50 showed orthorhombic structure at 1400 °C and a slight modification to monoclinic structure at 1500 °C;
- It might be suggested that the sintered densities both samples can be controlled simply by sintering temperatures and low influence by agglomerated particles and green density of samples;
- The porosity of the sintered samples can be controlled by alteration of the sintering temperature;
- The microhardness showed values slight higher on the sintered samples at 1400 °C than at 1500 °C. However, any significant difference on microhardness was observed with utilization of different concentrations of raw materials.

### Acknowledgements

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