

## Deposition of strontium-doped lanthanum manganite suspensions by wet powder spraying

Rubens Chiba<sup>1,a</sup>, Reinaldo Azevedo Vargas<sup>1,b</sup>, Marco Andreoli<sup>1,c</sup>,  
Emília Satoshi Miyamaru Seo<sup>1,d</sup>

<sup>1</sup>Nuclear and Energy Research Institute - *IPEN/CNEN - SP*  
Materials Technology and Science Center - *CCTM*  
Components and Raw Materials SOFC Laboratory  
Av. Prof. Lineu Prestes, 2242 - Cidade Universitária (USP)  
CEP 05508-000 - São Paulo - Brazil  
<sup>a</sup>rchiba@ipen.br, <sup>b</sup>ravargas@ipen.br, <sup>c</sup>mandreol@ipen.br, <sup>d</sup>esmiyseo@ipen.br

**Keywords:** solid oxide fuel cell, strontium-doped lanthanum manganite, cathode, thin films, wet powder spraying.

**Abstract.** The compound strontium-doped manganite lanthanum ( $\text{La}_{0,85}\text{Sr}_{0,15}\text{MnO}_3$  - LSM), deposited in the form of thin films in yttria-stabilized zirconia substrate ( $\text{Y}_2\text{O}_3/\text{ZrO}_2$  - YSZ), is of basic importance as cathodic material of the solid oxide fuel cells (SOFC). In this work, the LSM was synthesized by the citrate technique and characterized by X-ray fluorescence spectroscopy (XRF), phase analysis light scattering granulometry (PALS), X-ray diffractometry (XRD) and scanning electron microscopy (SEM). In the wet powder spraying, was used an airbrush and the LSM sample deposited to the YSZ substrate was sintered and characterized by SEM. The conclusions had allowed to establish preliminary conditions for preparation of LSM suspensions by wet powder spraying.

### Introduction

The high-temperature solid oxide fuel cells (SOFC) represent the basic building block for power generation in a variety of applications energy systems for residences, industrial cogeneration systems, and utility central station power production. These devices offer a clean, pollution-free technology to electrochemically convert gaseous fuels such as hydrogen, natural gas or gasified coal into electricity at high efficiencies. These fuel cells provide many advantages such as high efficiency, reliability, modularity, fuel adaptability, and low levels of  $\text{NO}_x$  and  $\text{SO}_x$  emissions [1-5]. An others advantages include less noise of the solid oxide fuel cells and because of their high temperature of operation (900 - 1000 °C), natural gas fuel can be reformed within the cell stack eliminating the need for an expensive, external reformer system [3].

The operating of the SOFC and reactions principals (equations 1 and 2) involved inside are presented in Figure 1 [6]. When an external load is applied to the cell, oxygen from the air is reduced at specific reaction sites in the porous air electrode to produce oxygen ions. At 1000 °C, these ions migrate through the solid electrolyte from the cathode to the anode where the fuel is oxidized to release electrons to an external load.

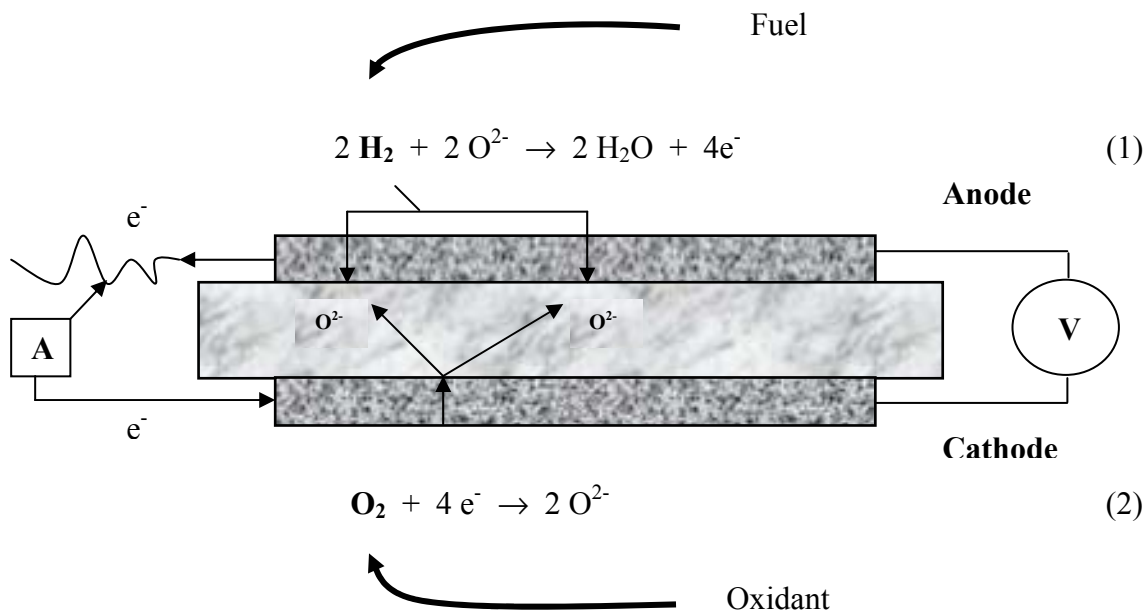


Figure 1 - Schematic diagram of the SOFC, indicating how oxidation of the fuel generates electric current to the external load.

Among the various designs, the planar type is claimed to have the advantages of high power density per unit volume and low production costs [7,8]. In this design, the lanthanum strontium manganite (LSM) and lanthanum strontium cobalt ferrite (LSCF) are two of the most common materials used as porous air electrode for reduction reactions in SOFC [1,9]. In particular, the  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ , a complex oxide with a perovskite structure, shows desirable properties such as good electronic conductivity, chemical compatibility with electrolyte, thermal expansion coefficient similar to that of the electrolyte, and adheres to the electrolyte during thermal cycling [1,3,9].

Various methods have been reported for synthesis of LSM powders, such as sol-gel, coprecipitation, amorphous citrate, and combustion [10-14], and there have been several successful methods reported to fabricate thin LSM, but for porous structures, the wet powder spraying (WPS) and screen-printing processes are well established methods because are low cost routes, being easy to use and suitable for mass production [15, 16].

Wet powder spraying requires the formulation of a well dispersed slurry of powder, binder, etc. Conditions for formation of defect free flat films by controlled binder burnout and sintering may be obtained from a detailed characterization of the microstructure and density of sintered bodies [15].

In this paper,  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  powder was prepared by the citrate technique (Pechini method modified) for x value equal 0.15 and further processed by wet powder spraying, using an airbrush [17]. According to Schuller and Stover [15], wet powder spraying is in use for the cathode layer deposition with layer thicknesses of more than 50  $\mu\text{m}$ .

## Materials and Methods

**Preparation of YSZ electrolyte substrates.** The YSZ electrolyte substrates were prepared by conventional ceramic process. The commercial Tosoh YSZ powder (TZ-8Y, Tosoh Corporation, Tokyo, Japan) were pressed into pellets of 15 mm in diameter and 0,5 mm in

thickness, using presses hydraulic uniaxial and isostatic. The green pellets were sintered at 1500 °C for about 1 h to strengthen their mechanical property.

**Starting LSM powder preparation.** The departure materials used in the synthesis of the LSM had been the following reagents: hexahydrated lanthanum nitrate, with 99,99 % purity; strontium nitrate, with 99,93 % purity; tetrahydrated manganese nitrate, with 99,99 % purity (Aldrich); acid citric e ethylene glycol, P.A. (Merck).

The powders of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  had been synthesized for x equal 15 mol % of strontium ( $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$  - LSM), gotten by the citrate technique, that consisted initially in the mixture of nitrates of strontium, manganese and lanthanum, in the required ratios with distilled water. Acid citric and ethylene glycol in ratio 60:40 in weight is mixed in becker and kept under agitation and the heating at 60 °C. The individual solutions of each precursor are added to the citric acid solution of more ethylene glycol under agitation and heating to the temperature between 80 and 110 °C. In this stage, the water is evaporated until the attainment of a viscous liquid. The nitrate in the  $\text{NO}_2$  form initially is evaporated, occurring polyesterification, fixing and distributing cations to long of organic chain and, getting itself a resin. The following stage consists of the evaporation of residual nitrate and of transformation of the resin in dust of LSM, calcination of the resinous material to air the 1100 °C for 12 hours for a complete synthesis of the reaction and elimination of residual carbon.

#### **Preparation of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ composition cathode films by wet powder spraying.**

Suspensions of a carrier liquid ethanol, an organic binder, an organic dispersant and the LSM ceramic powder are used. The ingredients for preparation of suspension were 68.29 wt% of LSM powder in ethanol with 4.26 wt% of oil fish as dispersant, and 27.44 wt% of ethylcellulose as binder. The cathode layer was applied onto the sintered YSZ electrolyte substrate by using an airbrush with nozzle size (diameter) about 2 mm and distance to substrate around 100 mm.

### **Results and Discussion**

From the results of the analysis of X-ray fluorescence spectrometry (XRF - *SHIMADZU, EDX900HS*), were calculated the molar values of the constituent elements of LSM powder. The concentrations values of the constituent elements of the initial composition ( $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ ), are next with the values of the synthesized composition obtained in this synthesis ( $\text{La}_{0.81}\text{Sr}_{0.19}\text{MnO}_3$ ).

In the phase analysis light scattering (PALS - *Brookhaven ZetaPlus*) were obtained the particle average sizes of LSM powders with value of 0.70  $\mu\text{m}$ .

In the analysis by scanning electron microscopy (SEM) is observed the particles morphology of LSM powders (Figure 2) in the form of agglomerates with the particle sizes are inferior 1  $\mu\text{m}$  and are homogeneous particles have been are presented.

The Figure 3 show the diffractogram obtained by X-ray diffractometry (XRD - *Rigaku Multiflex*) of LSM powders, had presented hexagonal crystalline structure, and the calculated lattice parameters of the crystalline structure were  $a = b = 5.5096 \pm 0.0021 \text{ \AA}$  and  $c = 13.3218 \pm 0.0002 \text{ \AA}$ .

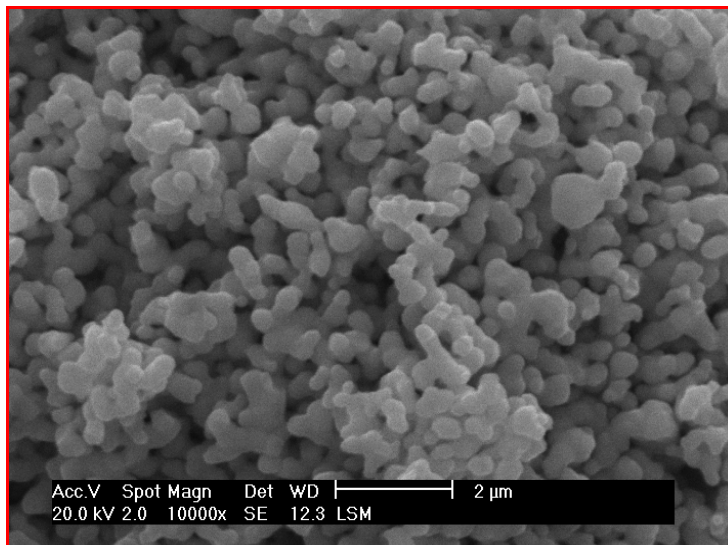


Figure 2 - Micrograph obtained by SEM of LSM powders.

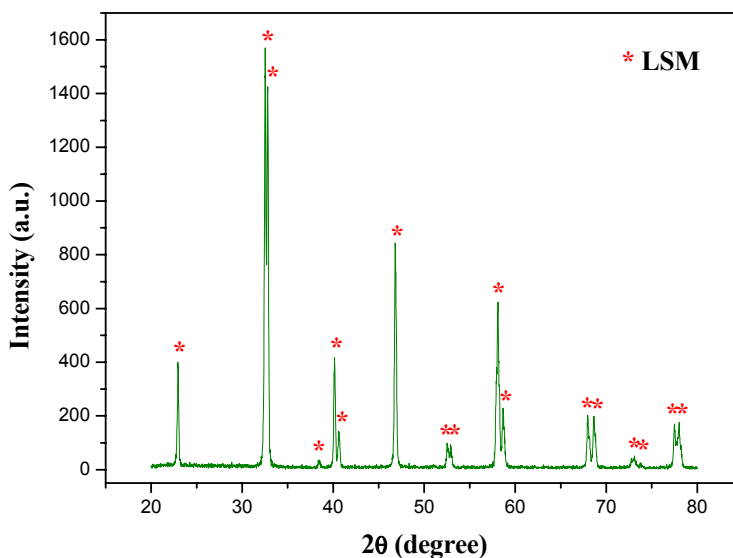


Figure 3 - Diffractogram obtained by XRD of LSM powders.

Microstructural investigation was carried out to observe the overall quality of the LSM films which include surface uniformity, shape of the pores and their distribution, and thickness of LSM film. A scanning electron microscope (*PHILIPS - XL30*) was used for this study. The film thickness over the entire surface was found to be fairly uniform with variation of  $\pm 10 \mu\text{m}$  and a homogeneous pores distribution (Figure 4). A SEM photograph (Figure 5) of the film surface shows the required porous structure of the fabricated LSM films.

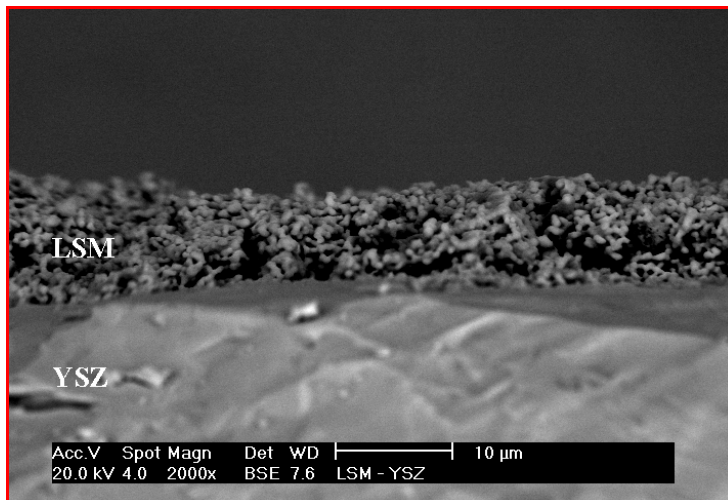


Figure 4 - Cross section of LSM films on YSZ substrate.

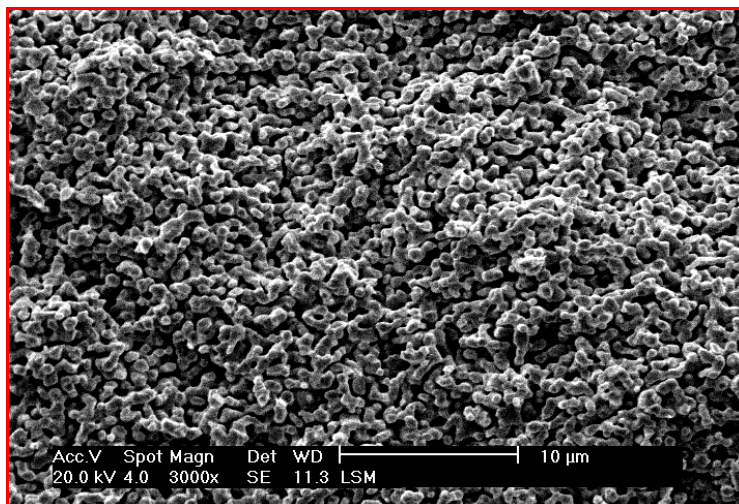


Figure 5 - Typical pore morphology of LSM films.

## Conclusion

The synthesis by the citrate technique of strontium-doped lanthanum manganite powders is possible. The analyses by XRF, had shown that the synthesis was efficient in the attainment of composition LSM, with values around calculated stoichiometric

The micrograph obtained by SEM, had shown that the particle sizes are in the form of agglomerates and are inferior at 1 μm. The results obtained by PALS are with particle average sizes of 0.70 μm that prove the same results of micrograph.

The LSM powders were observed by XRD, presenting the formation of a main phase LSM with identification of hexagonal crystalline structure.

In the sintered sample of LSM films on YSZ substrate, were observed by SEM, film uniform with thickness variation of  $\pm 10 \mu\text{m}$  and a homogeneous pores distribution.

The LSM powders with the particle average sizes of 0.70 μm are homogeneous particles that can be conveniently used by wet powder spraying on YSZ substrate. Multiple coatings

are necessary to increase the film thickness until 40-50  $\mu\text{m}$  that is thickness adequate as cathode (air electrode) of SOFC.

The deposition of LSM suspensions by wet powder spraying are contributions for the study of LSM/YSZ (cathode/electrolyte) interface in the SOFC.

### Acknowledgements

The authors thanks to the *CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico)* for the financial support, as well as the friends and colleagues of the CCTM-IPEN (Celso V. de Morais, Chieko Yamagata, Glauson A. F. Machado, Nelson B. de Lima, Nildemar A. M. Ferreira, Rene R. Oliveira, Walter Kenji Yoshito) and CQMA-IPEN (Vera L. R. Salvador) for the analysis and contribution contained in this work.

### References

- [1] N.Q. Minh, T. Takahashi. *Sci. and Tech. of Ceram. Fuel Cells*. Amsterdam: Elsevier, 1995.
- [2] T. F. Fuller. *The Electrochem. Soc. Interface*. (1997), p. 26-32.
- [3] S.C. Singhal. *Solid State Ionics*, 135 (2000), p. 305-313.
- [4] S.P.S. Badwal, K. Foger. *Materials Forum*, 21 (1997), p. 187-224.
- [5] V. Karakoussis, M. Leach, R. van der Vorst, D. Hart, J. Lane, P. Pearson, J. Kilner, Report: EST F/01/00164, Crown Copyright, 2000.
- [6] W. Feduska, A.O. Isenberg. *J. of Power Sources*, 10 (1983), p. 89-102.
- [7] M. Mori and Y. Hiei. *J. Am. Ceram. Soc.*, 84 (2001), p. 2573-2578.
- [8] M. B. Kakade, S. Ramanathan, P.K. De. *British Ceramic Transactions*, 102 (2003), p. 211-215
- [9] S.P. Jiang. *Solid State Ionics*, 146 (2002), p.1-22.
- [10] S. Bilger, E. Syskakis, A. Naumidis, H. Nickel. *J. Am. Ceram. Soc.*, 1992, 75, p. 964-970.
- [11] S.T. Aruna, M. Muthuraman, P.C. Kashinath. *J. of Mater. Chemistry*, 7 (1997), p. 2499-2503.
- [12] T. Ioroi, T. Hara, Y. Uchimoto, Z. Ogumi, Z. Takehara. *J. of the Electrochem. Soc.*, 145 (1998), p. 1999-2004.
- [13] S. Tanasescu, N.D. Totir, D.I. Marchidan, A. Turcanu. *Mater. Res. Bull.*, 32 (1997), p. 915-923.
- [14] Q. Zhang, T. Nakagawa, F. Saito. *J. of Alloys and Compounds*, 308 (2000), p. 121-125.
- [15] E. Schuler, R. Vaben, D. Stover. *Advanced Engineering Materials*, 4 (2002), p. 659-662.
- [16] X. Ge, X. Huang, Y. Zhang, Z. Lu, J. Xu, K. Chen, D. Dong, Z. Liu, J. Miao, W. Su. *J. Of Power Sources*, 159 (2006), p. 1048-1050.
- [17] N. Oishi, Y. Yoo, I. Davidson. *J. Am. Ceram. Soc.*, 90 (2007), p. 1365-1369.