Materials Science Forum Vols. 660-661 (2010) pp 746-751
Online available since 2010/Oct/25 at www.scientific.net

doi:10.4028/www.scientific.net/MSF.660-661.746

CRYSTALLINE STRUCTURE AND MICROSTRUCTURAL CHARACTERISTICS OF THE CATHODE/ELECTROLYTE SOLID OXIDE HALF-CELLS

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Keywords: solid oxide half-cells, cathode, electrolyte, strontium-doped lanthanum manganite, yttria-stabilized zirconia.

Abstract. The solid oxide fuel cell (SOFC) is an electrochemical device generating of electric energy, constituted of cathode, electrolyte and anode; that together they form a unity cell. The study of the solid oxide half-cells consisting of cathode and electrolyte it is very important, in way that is the responsible interface for the reduction reaction of the oxygen. These half-cells are ceramic materials constituted of strontium-doped lanthanum manganite (LSM) for the cathode and yttria-stabilized zirconia (YSZ) for the electrolyte. In this work, two solid oxide half-cells have been manufactured, one constituted of LSM cathode thin film on YSZ electrolyte substrate (LSM - YSZ half-cell), and another constituted of LSM cathode and LSM/YSZ composite cathode thin films on YSZ electrolyte substrate (LSM - LSM/YSZ - YSZ half cell). The cathode/electrolyte solid oxide half-cells were characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The results have been presented with good adherence between cathode and electrolyte and, LSM and YSZ phases were identified.

Introduction

The solid oxide fuel cell (SOFC) is an electrochemical device of alternative energy generation, that by means of the chemical reactions energy of the hydrogen and oxygen gases is converted into water and electric and thermal energies [1].

The unity cell of the SOFC is composed for three ceramic materials nominated of cathode, electrolyte and anode. The used material as cathode is the strontium-doped lanthanum manganite ($La_{0.75}Sr_{0.15}MnO_3$ - LSM), that it has the function to reduce the oxygen gases together with electrons of the external circuit. The used electrolyte is the yttria-stabilized zirconia (ZrO_2/Y_2O_3 - YSZ), with the function of migrate the oxygen ions from cathode to anode. And, the used anode is the cermet yttria-stabilized zirconia - nickel ($ZrO_2/Y_2O_3/Ni$ - YSZ/Ni), with the function to oxidate oxygen ions with the hydrogen gases fed, generating mainly electricity and water [2,3].

For optimum performance of the SOFC, it is necessary to study the half-cells consisting of cathode and electrolyte, because the region of contact between cathode, electrolyte and oxygen gas, responsible for the oxygen reduction reaction, called Triple Phase Boundary (TPB).

For an increase of the ionic and electronic conductivities, and the catalytic activity of the reduction reaction of the oxygen gas, a functional layer of composite cathode consisting of LSM and YSZ is conformed between the cathode and the electrolyte [4,5].

The characteristics such as enough porosity for the gases transport, raised electronic and ionic conductivities, stability in oxidant atmospheres, compatibility with the electrolyte and raised catalytic activity for oxygen reduction for LSM cathode and LSM/YSZ composite cathode are necessary and, the YSZ electrolyte, in turn, must be dense, solid, present high ionic conductivity and excellent stability in oxidant and reducing environments [1,2,6].

In this context, the present work emphasizes the forming of the cathode/electrolyte solid oxide half-cells, characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) techniques.

The forming techniques for the manufacture of the half-cells formed by LSM and LSM/YSZ ceramic films have been wet powder spraying [7] and, YSZ substrates by uniaxial pressing.

Materials and Methods

The cathode/electrolyte solid oxide half-cells forming have been prepared by commercial YSZ powders (Tosoh Corporation, Tokyo, Japan), LSM powders synthesized by the citrate technique [8] and, LSM/YSZ powders in the mass ratios of 50% LSM and 50% YSZ synthesized by the solid mixture technique [9].

The manufacture of YSZ electrolyte substrate were formed in cylindrical pellets using a uniaxial hydraulic press (SOMAR), and sintered at temperature of 1500 °C for 1 hour. The surfaces of the sintered cylindrical pellets were sandpapered for a better adherence of the LSM and LSM/YSZ ceramic thin films.

The LSM and LSM/YSZ suspensions for formation of the ceramic thin films were prepared with its respective synthesized powders, ethanol as solvent and ethylcellulose as binder [10,11,12]. The suspensions were sprayed using manual airbrush (LINCE - AL3) with compressed air, on sintered and sandpapered YSZ substrates. These formed thin films were sintered at temperature of 1200 ºC for 2 hours.

Therefore, two half-cells have been obtained, one constituted of YSZ electrolyte substrate with LSM cathode thin film (LSM - YSZ half-cell), and another constituted of YSZ electrolyte substrate with LSM/YSZ composite cathode and LSM cathode thin films (half-cell LSM - LSM/YSZ - YSZ).

The half-cells were characterized by X-ray diffractometry - XRD (RIGAKU - Multiflex) for verification of the characteristic peaks of the formed present phases, scanning electron microscopy - SEM (PHILIPS - XL 30) and energy dispersive X-ray spectroscopy - EDS (EDAX - XL 30) for observation and identification of the chemical elements in the microstructure of the half-cells.

The involved stages in the ceramic processing for the forming of the half-cells are presented in Figure 1.

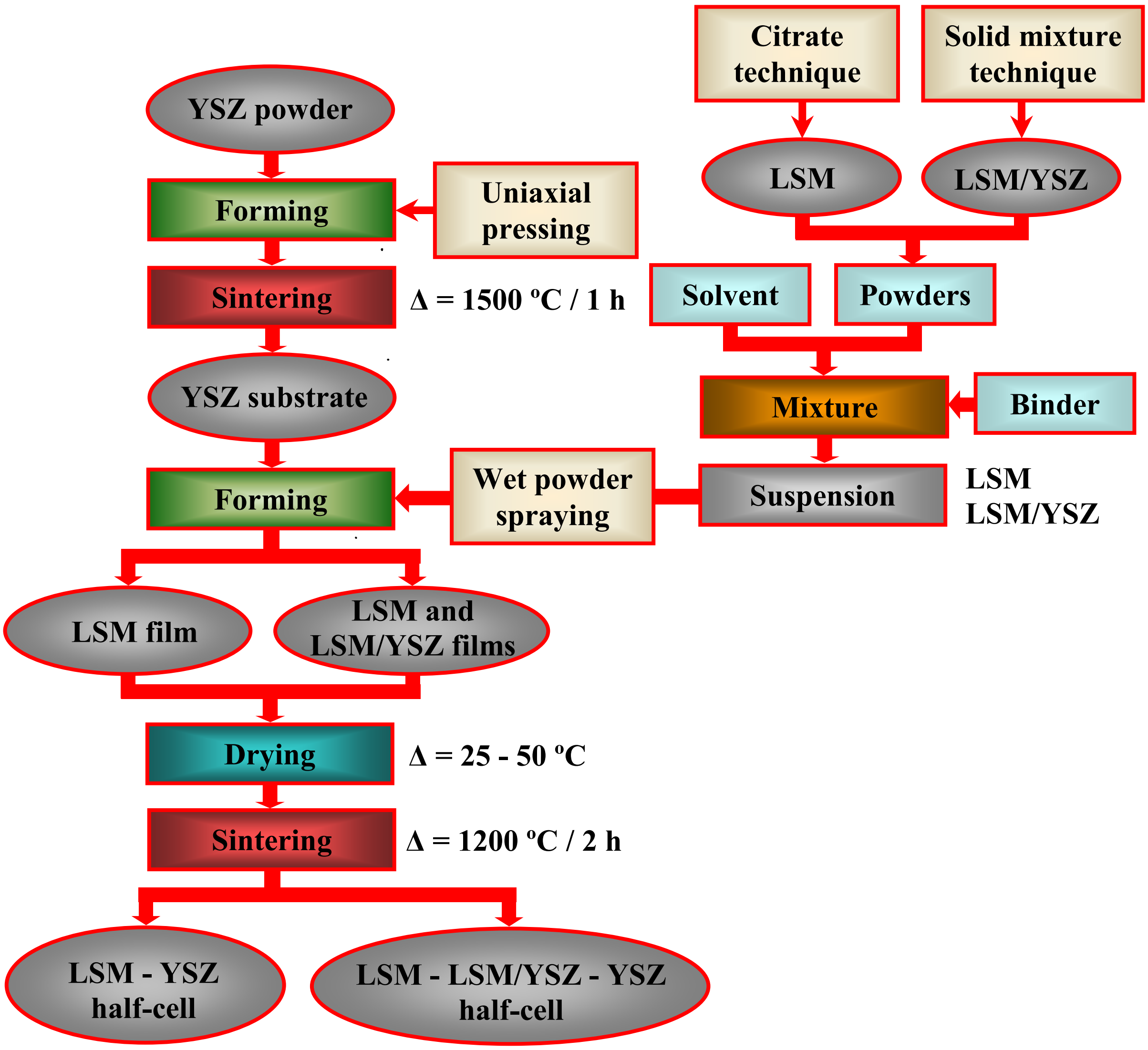


Figure 1 - Ceramic processing for the half-cells forming.

Results and Discussion

The YSZ substrate formed by uniaxial pressing and the LSM and LSM/YSZ thin films by wet powder spraying forming the YSZ - LSM and YSZ - LSM/YSZ - LSM half-cells were characterized by XRD, SEM and EDS.

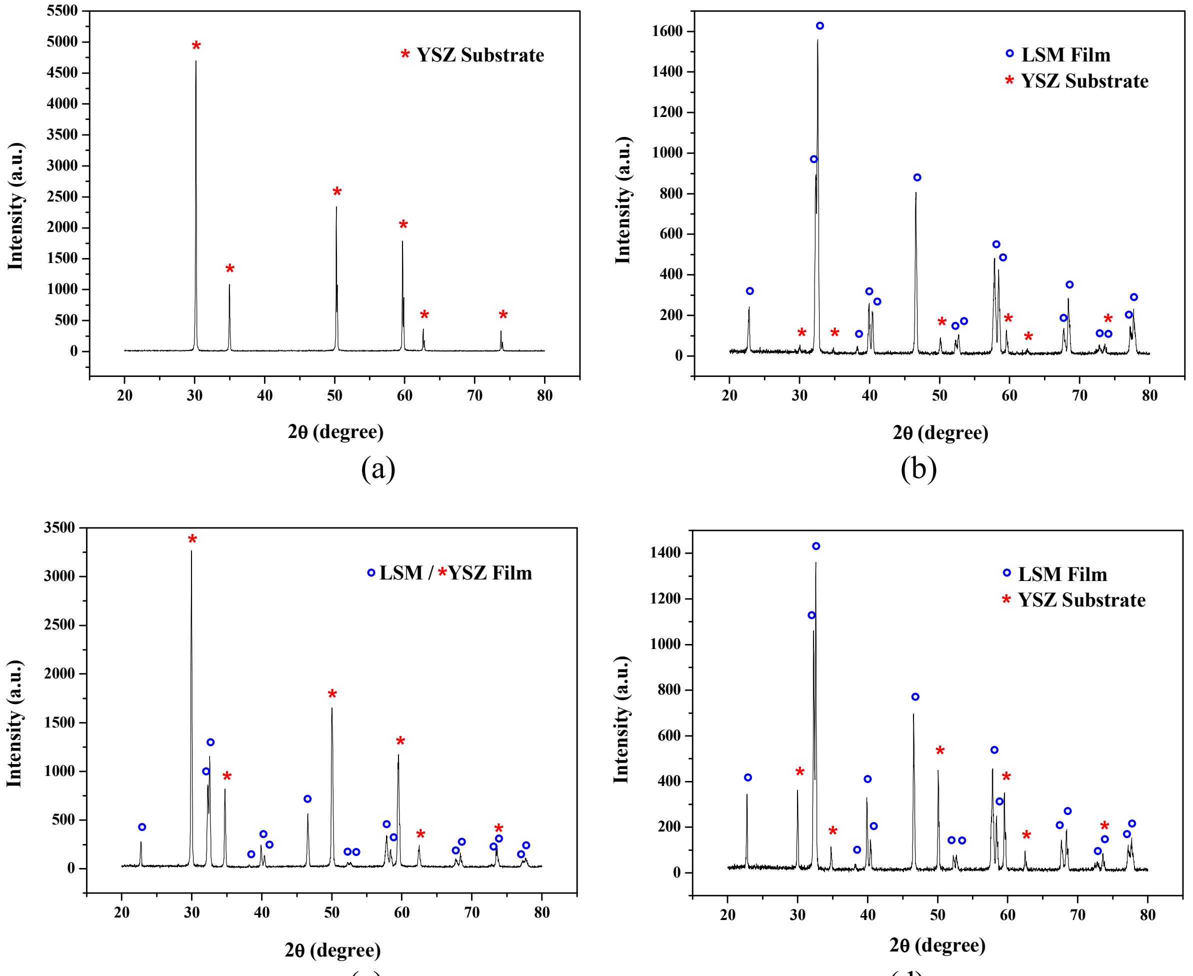
The Figure 2 show the X-ray diffractograms of YSZ substrate (a), LSM thin film on YSZ substrate (b), LSM/YSZ thin film on YSZ substrate (c) and LSM thin film on LSM/YSZ thin film and YSZ substrate (d) obtained by XRD.

The presence of YSZ single phase was confirmed in the substrate, as observed in Figure 2(a). In Figure 2(b) confirm the presence of the LSM phase with peaks of lesser intensity of YSZ phase, which the analysis realized for all the half-cell of electrolyte and cathode (YSZ - LSM).

The LSM and YSZ phases were confirmed in the half-cell constituted of electrolyte and composite cathode (YSZ - LSM/YSZ) as show Figure 2(c). In Figure 2(c), the peaks of YSZ phase with bigger intensity are identified, evidencing that the analysis was effected for all the half-cell of YSZ - LSM/YSZ.

In Figure 2(d), the diffractogram shows the formation of two phases, a LSM phase of interest and another of YSZ. The YSZ phase presence if must to the fact of the XRD analysis realized in the half-cell constituted of electrolyte, composite cathode and cathode (YSZ - LSM/YSZ - LSM).

The crystalline structure of phase LSM is hexagonal and for YSZ phase is cubic, in according to data base JCPDS N°89-648 and JCPDS N°81-1551, respectively.



(a) (b)

(c) (d)

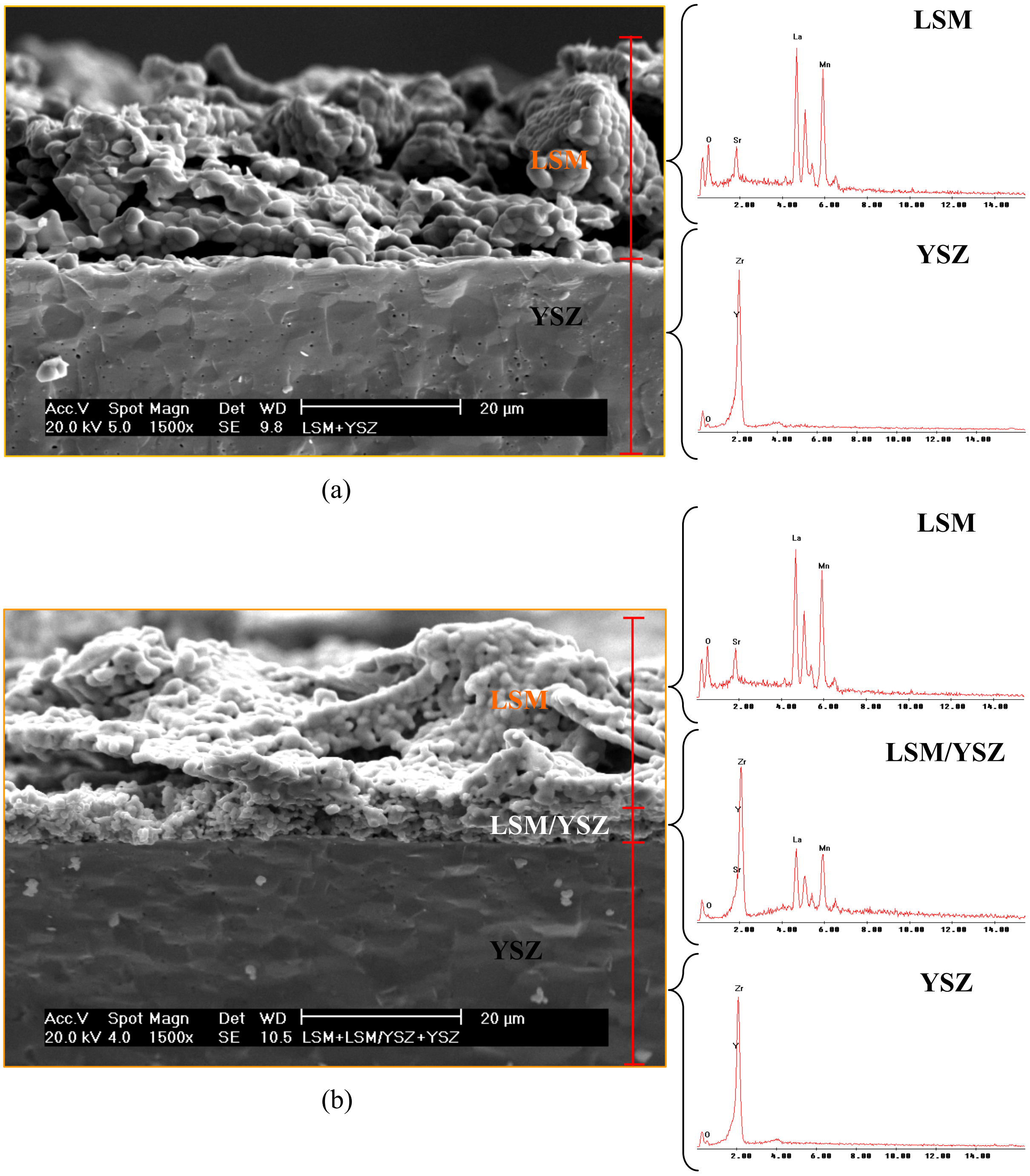
Figure 2 - Diffractograms of the YSZ substrate (a), LSM thin film on YSZ substrate (b), LSM/YSZ thin film on YSZ substrate (c) and LSM thin film on LSM/YSZ thin film and YSZ substrate (d) obtained by XRD.

The micrographs observed by SEM, shows the cross sections of the sintered and fractured half-cells of the thin films of LSM and LSM + LSM/YSZ on YSZ substrates, with its respective characteristic peaks of the chemical elements of each film and substrate obtained by EDS, as presented in Figure 3.

A qualitative analysis of the half-cells allows verify that YSZ substrate observed by SEM is dense, enough to be used as solid electrolyte, and the LSM and LSM/YSZ thin films present porous with good adherence between the cathode and electrolyte. The morphology of the LSM and LSM/YSZ ceramic films is similar that one observed for Piao *et al* [13], whose films were formed by the screen printing technique.

The characteristic peaks of the LSM and LSM/YSZ films and YSZ substrate, obtained by EDS, confirm the presence of the chemical elements.

The LSM and LSM/YSZ ceramic films had presented thickness of approximately 30 μm and 4μm, respectively. For the LSM/YSZ film, 2 layers were deposited for formation of the thin film, whereas for LSM film, 15 layers were deposited. Each layer was formed realizing the deposition in 4 different directions with intermediate stages of drying in air for the attainment of the desired thickness.



(a)

(b)

Figure 3 - Micrographs of the cross sections of the LSM (a) and LSM + LSM/YSZ (b) thin films on YSZ substrate obtained by SEM and energy spectra of each film and substrate obtained by EDS.

Conclusions

The diffractograms of the LSM and LSM/YSZ thin films and of the YSZ substrates confirm the presence of the formed phases of hexagonal (LSM) and cubic (YSZ) crystalline structures.

The micrographs of the LSM and LSM/YSZ films, confirm porous microstructures. For YSZ substrates, dense microstructures were observed. The presences of the chemical elements in the half-cells have been confirmed by EDS.

The uniaxial pressing and wet powder spraying forming techniques had shown to be possible the manufacture of LSM porous thin films adherent on YSZ dense substrates, as well as adequate for the study of the cathode/electrolyte solid oxide half-cells.

Acknowledgements

The authors thanks to the *CNPq-Conselho Nacional de Desenvolvimento Científico e Tecnológico* for the financial support and *CCTM-Centro de Ciência e Tecnologia de Materiais/IPEN-Instituto de Pesquisas Energéticas e Nucleares* (Celso V. de Morais, Glauson A. F. Machado, Nildemar A. M. Ferreira and Rene R. Oliveira) for the analysis and contribution contained in this work.

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Advanced Powder Technology VII

doi:10.4028/www.scientific.net/MSF.660-661

Crystalline Structure and Microstructural Characteristics of the Cathode/Electrolyte Solid Oxide Half-Cells

doi:10.4028/www.scientific.net/MSF.660-661.746