

Preparation and characterization of yttria stabilized zirconia (YSZ) films deposited by dip-coating on LSM-YSZ substrate with different proportions

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ABSTRACT

In this work, sol-gel/dip-coating process for obtaining yttria stabilized zirconia (YSZ, $ZrO_2-8\% Y_2O_3$) films deposited onto LSM-YSZ (lanthanum strontium manganite (LSM, $La_{0.7}Sr_{0.3}MnO_3$) mixed with YSZ) with different proportions (20/80, 50/50, 80/20) was investigated. The films were deposited on substrate varying the number of layers deposited.

LSM powders were obtained by the combustion method using metal nitrates and urea and YSZ was commercial. LSM-YSZ composite powders were obtained by the solid state method, through ball-milling of a mixture of LSM-YSZ (mass ratio) powder for 4 h with 500 rpm using ZrO_2 balls as milling media. For LSM-YSZ substrate a study of sintering temperature was performed, where the optimum sintering temperature for each LSM-YSZ studied proportion was obtained. According to our results, it was found that 1100 °C is the optimum sintering temperature for 20/80, 950 °C is the optimum sintering temperature for 50/50 and 900 °C is the optimum sintering temperature for 80/20 because of the good phase formation.

The films were characterized by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The films showed LSM, YSZ, $SrZrO_3$ and La_2O_3 phases. Crack-free, homogeneous and well adhered films were obtained with a thickness between 3 and 38 μm . In this work, YSZ films with appropriate thickness were obtained for application as SOFC electrolyte.

Keywords: YSZ films, LSM-YSZ substrate, SOFC, Dip-coating.

1. INTRODUCTION

Fuel cells are energy-conversion devices that convert the chemical energy of a fuel gas directly to electrical energy, with high efficiency and negligible production of pollutants [1]. When compared with conventional methods of power generation, solid oxide fuel cells (SOFCs) have many advantages, such as substantially higher conversion efficiency, easy modular construction, wide range of fuel possibilities, potential for cogeneration, and low maintenance cost [1,2]. The current focus in research in SOFCs is material development and reduced-temperature operation.

The most used materials in SOFCs are Ni/YSZ cermets as anode, lanthanum manganite doped with Sr ($La_{1-x}Sr_xMnO_3$, LSM) as cathode and yttria-stabilized zirconia ($ZrO_2 - 8\% Y_2O_3$, YSZ) as the electrolyte. LSM-YSZ composites are also studied as SOFC cathode because the addition of YSZ to LSM substrate improves the electrochemical performance due to an increase of the triple phase boundary (TPB) area, extending the electrode reaction sites and significantly reducing electrode polarization and enlarging the electrolyte/electrode interface [3,4]. Moreover, there is a significant enhancement of the catalytic activity of the electrode using LSM-YSZ composites and an improved adhesion between the film and the substrate due to the intimate sintering of YSZ particles to the LSM-YSZ substrate [5,6].

In comparison to other fabrication methods, deposition of thin films by dip-coating technique is an easy, simple and inexpensive method, it offers a potential route for SOFC electrolyte preparation, and makes the process very attractive and economical for potential large-scale commercial fabrication [7]. The dip-coating can

be used to synthesize homogeneous thin films of multi-component oxides [8] and is considered as an effective and practical method to produce YSZ films [9,10].

There are no reports in the literature about the dip-coating deposition of YSZ films on LSM-YSZ substrates; only using another technique. YSZ films with a thickness of 10 μm were deposited on LSM-YSZ 50/50 using DC magnetron sputtering [6]. CHEN and LIU [5] used electrophoretic deposition (EPD) to prepare YSZ films onto LSM-YSZ 80/20 (weight ratio) and dense, crack and pinhole-free films with a thickness of about 10 μm were obtained.

In this paper, thin YSZ films were deposited on LSM-YSZ substrate by the dip-coating technique. Firstly, it was investigated the sintering temperature for preparation of LSM-YSZ composite substrates, and then YSZ films were dip-coated onto these substrates, varying the number of layers deposited. We studied YSZ films on LSM-YSZ substrates with different proportions, this is important because the adhesion between LSM-YSZ substrate and YSZ thin layer depends on YSZ content of the substrate.

2. MATERIALS AND METHODS

2.1 Material preparation

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) powder was prepared by the combustion method using metal nitrates and urea, as described by CONCEIÇÃO *et al.* [11]. LSM-YSZ composite powders were prepared through ball-milling of a mixture 20/80, 50/50, 80/20 (weight ratio) LSM/YSZ (Saint-Gobain Norpro) powders for 4 h using ZrO_2 balls as milling media, at room temperature, with speed of 500 rpm. The powders were calcined in air (60 mL/min) at 750 $^\circ\text{C}$ for 10 h at 10 $^\circ\text{C}/\text{min}$.

The LSM-YSZ powders were then pressed into pellets (13 mm diameter and 2 mm thickness) under uniaxial pressure of 200 MPa. The pellets were sintered at different temperatures between 850 $^\circ\text{C}$ and 1300 $^\circ\text{C}$, at a heating rate of 10 $^\circ\text{C}/\text{min}$ for 2 h, in order to choose the optimum sintering temperature of each substrate. The LSM-YSZ 20/80 substrate was sintered at 1000 $^\circ\text{C}$, 1100 $^\circ\text{C}$, 1200 $^\circ\text{C}$ and 1300 $^\circ\text{C}$, the LSM-YSZ 50/50 substrate was sintered at 850 $^\circ\text{C}$, 950 $^\circ\text{C}$, 1000 $^\circ\text{C}$ and 1300 $^\circ\text{C}$ and the LSM-YSZ 80/20 substrate was sintered at 850 $^\circ\text{C}$, 900 $^\circ\text{C}$, 950 $^\circ\text{C}$ and 1000 $^\circ\text{C}$. After that, the surface of the fired pellets was sanded with SiC paper (4000 mesh) and polished.

YSZ film precursors were prepared by a polymeric sol-gel process. The solution of metal salts was prepared from $\text{Zr}(\text{NO}_3)_2$ and $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ (Acros Organics) with concentration of Cs = 1 mol/L. An organic solution consisting of complexing and polymeric agents (hexamethylenetetramin (HMTA- $\text{C}_6\text{H}_{12}\text{N}_4$), acetylacetone (acac- $\text{C}_5\text{H}_8\text{O}_2$) and acetic acid (a.a.- $\text{C}_2\text{H}_4\text{O}_2$)), with Co concentration, was added to the metal salt solution to promote polyesterification and polycondensation reactions. R, defined as Co/Cs ratio, was 5. The obtained sol was refluxed at 80 $^\circ\text{C}$ on a hot plate until the desired viscosity (100 cP) was reached.

The as-obtained YSZ gel was deposited on LSM-YSZ substrate at room temperature by the dip-coating technique. The withdrawal speed was 50 mm/min and the time of deposition was of 40 s. The films were dried at 70 $^\circ\text{C}$ for 30 min and then sintered at optimum sintering temperature of each substrate with a heating rate of 2 $^\circ\text{C}/\text{min}$ for 2 h. It was deposited 1, 2 and 3 layers, with drying between successive depositions.

2.2 Characterization

The crystalline structure of material was analyzed by X-ray diffraction (XRD) using a Rigaku Miniflex II with $\text{CuK}\alpha$ radiation and 2θ range from 10 to 90 $^\circ$. The XRD patterns were analyzed using JCPDS (*Joint Committee on Powder Diffraction Standards*) database of crystal structures. The crystallite sizes (D) and microstrain (ϵ) were calculated using the equation (1) [12]:

$$\beta \cos \theta / \lambda = 1 / D + 4\epsilon \sin \theta / \lambda \quad (1)$$

where λ is the X-ray wavelength (0.154 nm), θ is the Bragg diffraction angle and β is the FWHM (full width at half maximum) of the peak.

Scanning electron microscopy (SEM) was carried out to characterize both morphology and microstructure of LSM-YSZ substrate and YSZ films, using a HITACHI TM-1000 microscopy.

3. RESULTS AND DISCUSSION

3.1 Characterization of LSM-YSZ substrate

LSM-YSZ composite was sintered at four different temperatures in order to select the optimum sintering temperature to prepare the substrate. The XRD patterns are shown in Figure 1.

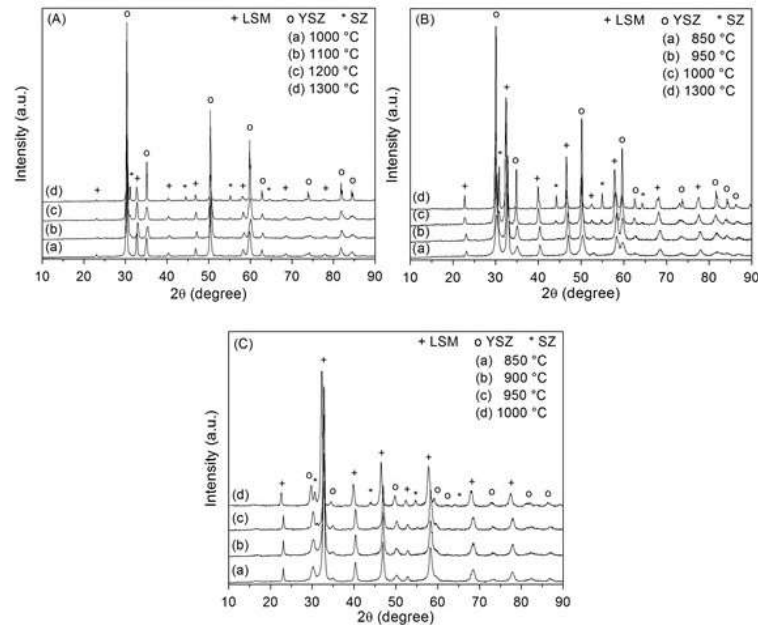


Figure 1: XRD patterns of the LSM-YSZ substrates after sintering for 2 h at 10 °C/min at different temperatures and proportions: (A) 20/80, (B) 50/50 and (C) 80/20.

When the sintering temperature was 1000 °C and 1100 °C for 20/80, 850 °C and 950 °C for 50/50 and 850 °C and 900 °C for 80/20, the diffraction peaks are identified as YSZ cubic phase (JCPDS 301468) and LSM perovskite phase (JCPDS 401100). The presence of any other phases was not detected; which indicates that YSZ and LSM do not react with each other during the synthesis process at these temperatures.

On the other hand, at sintering temperatures of 1200 °C and 1300 °C for 20/80, 1000 °C and 1300 °C for 50/50 and 950 °C and 1000 °C for 80/20, there are additional peaks corresponding to the formation of SrZrO₃ (SZ) phase (JCPDS 44161), due to the high-temperature reactions between LSM and YSZ [13,14]. The SZ phase increases with increasing the sintering temperature. The presence of SZ and/or La₂Zr₂O₇ (LZ) phases weakens the electrical contact of cathode/electrolyte because the conductivity of these zirconates is at least 2–3 orders of magnitude lower than that of YSZ electrolyte [15]. BRANT *et al.* [16] observed formation of SZ at the interface between YSZ and porous LSM after annealing over to 1200 °C. In fact, according to VAN ROOSMALEN and CORDFUNKE [17] the formation of SZ from La_{0.7}Sr_{0.3}MnO₃ and ZrO₂ is estimated to start at 1247 °C. Thus, it can be concluded that 1100 °C, 950 °C and 900 °C is the optimum sintering temperature for 20/80, 50/50 and 80/20, respectively, because of the good phase formation of the substrate without secondary phases.

Figure 2 shows the SEM micrographs of the surface of LSM-YSZ 20/80 substrate after calcination, sintering at 1100 °C and polishing with sandpaper. The calcined powder showed a porous structure with agglomeration of particles of different sizes, while in the sintered substrate the particle size is more uniform and the porosity is lower. After the polishing process, there was a significant improvement in the substrate surface, reducing the porosity and leaving a homogeneous surface. The same result was obtained in the other LSM-YSZ proportions studied.

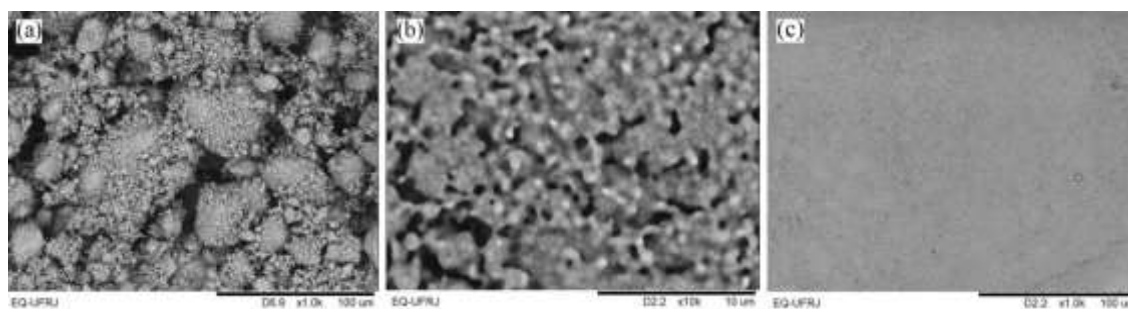


Figure 2: SEM micrographs of LSM-YSZ 20/80 substrate: (a) calcined, (b) sintered and (c) sanded.

3.2 Characterization of YSZ films

X-ray diffraction patterns of YSZ films deposited on LSM-YSZ 20/80, 50/50 and 80/20 substrates are presented in Figure 3 for different layers (1, 2 and 3), after sintering at the optimum sintering temperature for each substrate (1100 °C for 20/80, 950 °C for 50/50 and 900 °C for 80/20) for 2 h at 2 °C/min.

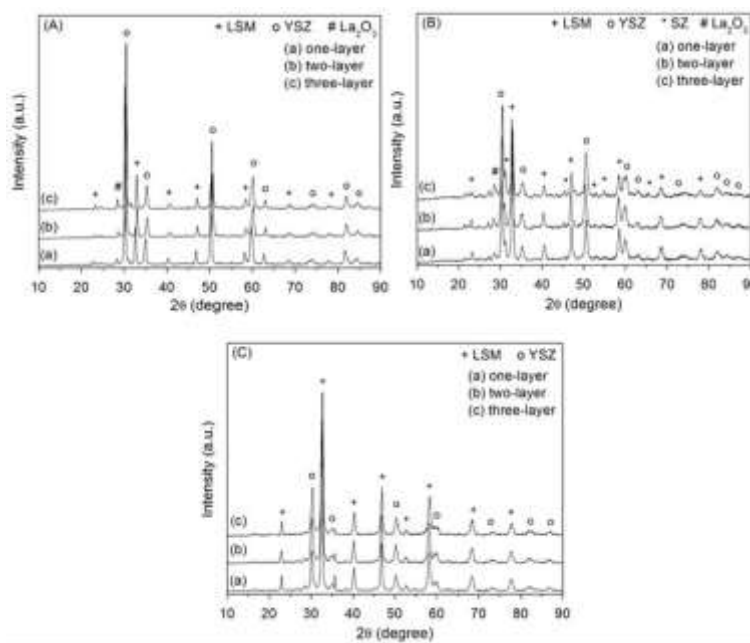


Figure 3: XRD patterns of YSZ film on LSM-YSZ substrates for one-layer, two-layers and three-layers, sintered at the optimum sintering temperature: (A) on 20/80 at 1100 °C, (B) on 50/50 at 950 °C, and (C) on 80/20 at 900 °C.

The XRD patterns are similar for all layers and all LSM-YSZ proportions, showing the cubic YSZ and LSM phases. For LSM-YSZ 20/80 and 50/50 substrates there are a small diffraction peak at 28.5°, which may be attributed to La₂O₃ (JCPDS 22641). The formation of this secondary phase is more pronounced for the three-layer sample, because the weaker interaction between the film and the substrate favors perovskite decomposition to simple oxides. The slow heating rate used for sintering after film deposition may enhance LSM decomposition to La₂O₃, however the heating rate of 2 °C/min used was due to the values of the sintering temperatures used (< 1200 °C), moreover films at higher heating rate were made and the YSZ films showed cracks. For LSM-YSZ 50/50 substrate is also the formation of SZ phase.

The average crystallite size and microstrain of the YSZ phase calculated from XRD data of films are reported in Table 1. The increase in the number of layers does not significantly affect the average crystallite size and microstrain, indicating that the crystallinity of the YSZ films does not change with the number of layers.

Table 1: Crystallite sizes and microstrain of YSZ films on LSM-YSZ substrate.

LSM-YSZ SUBSTRATE	LAYERS	CRYSTALLITE SIZES (nm)	MICROSTRAIN (%)
20/80	1	35,8	0,32
20/80	2	33,4	0,33
20/80	3	34,3	0,33
50/50	1	18,3	0,59
50/50	2	19,4	0,58
50/50	3	18,2	0,66
80/20	1	23,3	0,49
80/20	2	20,4	0,54
80/20	3	22,1	0,50

Figure 4 shows the cross-section microstructure of the YSZ film on LSM-YSZ 20/80 substrate sintered at 1100 °C, on LSM-YSZ 50/50 substrate sintered at 950 °C and on LSM-YSZ 80/20 substrate sintered at 900 °C for one-layer, two-layer and three-layer. As observed from the SEM images, dense and crack-free films, with a substrate/film interface well defined, were obtained for all layers. With increasing the number of layers, the film thickness becomes more homogeneous.

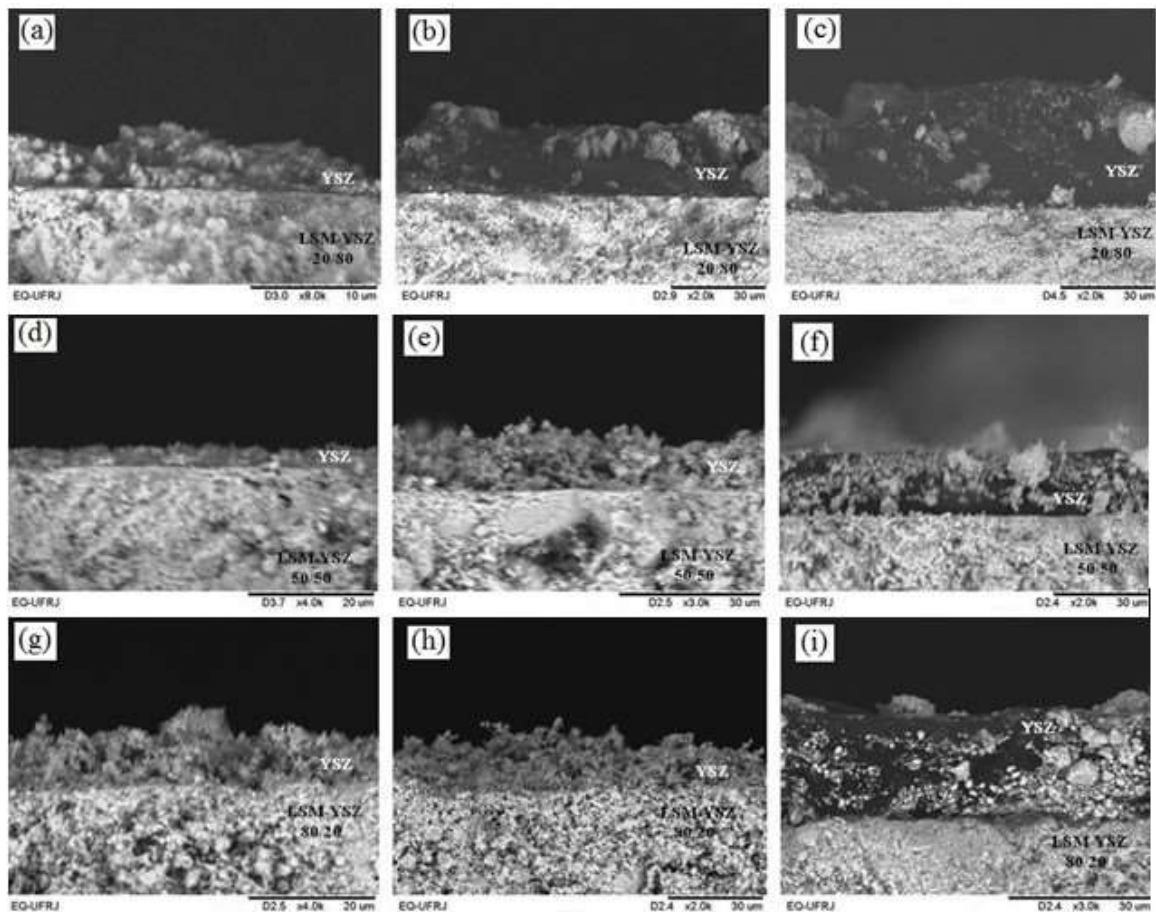


Figure 4: Cross-sectional microstructures of YSZ film on LSM-YSZ substrates sintered at the optimum sintering temperature for different layers and proportions: (a) one-layer sample on 20/80, (b) two-layer sample on 20/80, (c) three-layer sample on 20/80, (d) one-layer sample on 50/50, (e) two-layer sample on 50/50, (f) three-layer sample on 50/50, (g) one-layer sample on 80/20, (h) two-layer sample on 80/20 and (i) three-layer sample on 80/20.

The thickness of the YSZ film on LSM-YSZ 20/80, 50/50, 80/20 substrates for one-layer, two-layer and three-layer sample are reported in Table 2. For all substrates, the thickness of the YSZ films is proportional to the number of layers, as expected. Some authors have obtained similar values of YSZ film thickness, but using other substrates or other deposition techniques. YANG *et al.* [18] have reported a thickness of the YSZ film deposited on the $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ substrate using the EPD method of about 16 μm . WANG *et al.* [19] have prepared YSZ thin films on NiO-YSZ anode substrates by dip-coating with different number of layers and the film thickness of one-layer sample was about 10 μm , of two-layer sample was 16 μm , and that of three-layer sample was 21 μm . In general, YSZ films of 5-30 μm are suitable for application as SOFC electrolyte [2].

Table 2: Thickness of YSZ films on LSM-YSZ 20/80, 50/50, 80/20 substrates for one-layer, two-layer and three-layer.

LSM-YSZ SUBSTRATE	LAYERS	THICKNESS (μm)
20/80	1	3,8
20/80	2	24,6
20/80	3	38,0
50/50	1	3,5
50/50	2	12,5
50/50	3	20,4
80/20	1	10,1
80/20	2	17,7
80/20	3	23,1

4. CONCLUSIONS

A study of the sintering temperature of LSM-YSZ 20/80, 50/50, 80/20 substrates was performed, and, according to our results, 1100 °C is the optimum sintering temperature for 20/80, 950 °C is the optimum sintering temperature for 50/50 and 900 °C is the optimum sintering temperature for 80/20 because of the good phase formation. The dip-coating process was used to prepare YSZ films deposited on LSM-YSZ substrate, with one, two or three layers. XRD results of the films sintered at the optimum sintering temperature for each substrate showed: cubic YSZ and LSM perovskite phases, besides a small formation of La_2O_3 secondary phase for 20/80 substrate; YSZ, LSM, La_2O_3 and SZ phase for 50/50 substrate and YSZ and LSM phase for 80/20 substrate. Homogeneous, dense, continuous, and crack-free YSZ films were obtained with a thickness between 3 and 38 μm .

To prepare YSZ films deposited on LSM-YSZ substrate, the optimum LSM-YSZ substrate is 80/20, because for all layers: 1) the films showed LSM and YSZ phases without secondary phases, 2) the film thickness of 10-23 μm are suitable for application as SOFC electrolyte, 3) this proportion have sufficient electrical conductivity for electrode application, according to the literature.

5. ACKNOWLEDGMENTS

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