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Low temperature synthesis by spray pyrolysis of $La_{0.9}Sr_{0.1}Co_{0.2}Fe_{0.8}O_3$ thin films using ethanol and water as a solvent and their microstructural characterization

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Abstract

The synthesis via spray pyrolysis was investigated of lanthanum ferrite films doped with strontium and cobalt (LSCF) on silicon substrates for application as cathodes in solid oxide fuel cells (SOFCs). The following precursors were utilized: $La(NO_3)_3 \cdot 6H_2O$, $SrCl_2 \cdot 6H_2O$, $CO(NO_3)_2 \cdot 6H_2O$, and $Fe(NO_3)_3 \cdot 9H_2O$, with La:Sr:Co:Fe (9:1:2:8) stoichiometry. A solution of water and ethanol (1:3 proportion) was used. The relation among the morphology of the films, i) the temperature of the substrate and ii) the distance of deposition was investigated. The results indicate that it is possible to obtain the LSCF film with a porous morphology at 200 °C and at a distance of deposition of 120 mm. This morphology is adequate for applications of LSCF as a cathode for use in solid oxide fuel cells.

Keywords: LSCF; Spray pyrolysis; Thin films; SOFC cathodes

1. Introduction

Thin films have numerous technological applications. Thin films are present in electronic materials [1], solar cells [2], sensors, coatings, superconductors [3,4], semiconductors [4,5], and fuel cells [6–8]. The use and application of thin films makes the work with low weight equipment possible, providing a higher return in the manufacturing process. This technology has attracted considerable attention from industries due to its efficient conversion and lower pollutant emissions in comparison with non-renewable fossil fuel-based energy sources [9]. In this context, solid oxide fuel cells (SOFCs) become an interesting alternative energy source.

Several physical and chemical processes have been used to prepare the thin films, including pulsed laser ablation [10], molecular beam epitaxy [11,12], sol–gel [13,14], spin coating [15,16] and spray pyrolysis [17–22]. Among them, the spray pyrolysis technique was chosen because it has a number of advantages. For example, spray pyrolysis is a low cost technique, and it has a simple film deposition process, which makes it very attractive to the planar SOFC industry, considering that through this technique, it is possible to perform the deposition of a wide variety of ceramic films over large areas and to obtain good chemical homogeneity [6,8].

For this work, producing LSCF via spray pyrolysis at low temperatures was investigated, using a solution of water and ethanol as a solvent, with the aim of analyzing the influence of the substrate temperature and the distance of the deposition on the morphology of the LSCF films.

2. Experimental procedure

2.1. Thin film deposition

The silicon substrates were used with dimensions of 100 mm^2 in area and thickness of 1 mm. The substrates before spraying were cleaned with ethanol in an Ultra Cleaner 1400

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(UNIQUE) ultrasound bath to remove any particles from the surface.

The following precursors were used for the preparation of the spray solution: La $(NO_3)_3 \cdot 6H_2O$ (VETEC, 99%), $SrCl_2 \cdot 6H_2O$ (VETEC, 99%), $CO(NO_3)_2 \cdot 6H_2O$ (VETEC, 99%), and $Fe(NO_3)_3 \cdot 9H_2O$ (VETEC, 99%), with stoichiometric with La:Sr:Co:Fe (9:1:2:8). The nitrates and metal chlorates were dissolved in ethanol and distilled water (3:1) to prepare the solution with a concentration of 0.01 mol L^{-1}. The spray solution was then atomized with pressurized air to form the aerosol before impact onto the substrate. The silicon substrates were pre-heated at the following temperatures: 130 °C, 150 °C, 170 °C and 200 °C. The following parameters for the spray pyrolysis technique were kept constant: air pressure at 0.4 bar and solution volume of 40 mL.

2.2. Characterization

The thermal analysis (TGA/DTG) was performed using a Mettler-Toledo device, in synthetic air atmosphere at a heating rate of 10 °C min^{-1}. The phase identification was performed using an X-ray diffractometer (XRD-Philips X-Pert-MPD). The microstructure of the thin films was evaluated using a scanning electron microscope (SEM) (TM 3000 Top Microscope, HITACHI).

The estimative of the number of cracks present in the films was based on the count of the number of cracks per unit length. The number of intersections of cracks with an imaginary line was counted using SEM images.

3. Results and discussion

Fig. 1 shows the thermal analysis (TGA and DTG) of the obtained films. The TGA curve of the film as-deposited at 200 °C presents a total mass loss of 30% at 750 °C. It is possible to observe a mass loss of 7% associated with the removal of the adsorbed water at the surface. Three different mass loss rates between 100 °C and 450 °C are visible, probably indicating the decomposition of the nitrates. In temperatures between 400 °C and 500 °C, the mass loss corresponding to NO occurs.

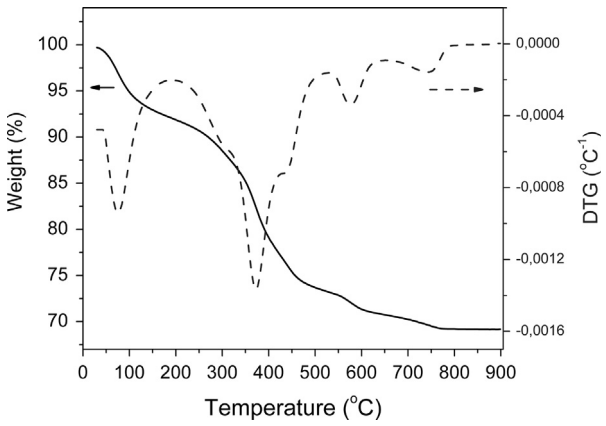

Fig. 1. Thermogravimetric analysis (TGA) and the derivative of the TGA curve (DTG) for the as-deposited LSCF film.

The DTG curve indicates the presence of four endothermic peaks at 85 °C, 371 °C, 450 °C and 575 °C. The first peak is associated with the adsorbed water. According to Hagiwara et al. [6], dehydration of the $La(NO_3)_3 \cdot 6H_2O$ occurs before 375 °C. The peaks at the temperatures between 450 °C and 575 °C can be related to the decomposition of precursor, namely ferrous nitrate, cobalt nitrate and strontium chloride [18]. At 600 °C, the mass loss is virtually stable, although an endothermic peak is present in the DTG curve regarding the formation of La_2O_3 [6]. The results of the thermal analyses enabled us to define the calcination temperature by the stability of the mass loss at the temperature of 600 °C. The thermal treatment of the film was performed at 750 °C, considering that the preliminary analyses of the X-ray diffraction revealed a considerable number of crystalline phases in comparison with the film as-deposited at 200 °C.

Fig. 2 shows the XRD of the film as-deposited at 200 °C and after the thermal treatment at 750 °C for 2 h. The as-deposited film using ethanol/water as solvent exhibits an amorphous phase. After the thermal treatment at 750 °C during 2 h, the XRD presents peaks correspond to the LSCF perovskite structure (JCPDS 89-1268). Fu et al. [23] identified diffraction peaks after calcination at 750 °C for 2 h that correspond to the perovskite phase of LSCF. The presence of three low intensity peaks is associated with the secondary phase of La_2O_3 as a result of the decomposition of La_2CO_3. The occurrence of this phase was also observed by Garcia [24] during the deposition of LSCF powders at 700 °C and by Gaudon et al. [25] and Macedo [26] in lanthanum manganites and strontium after thermal treatment at 700 °C for 2 h. It is possible occurs a hydration of La_2O_3 that promotes a decrease adhesion between cathode and electrolyte in SOFC applications [26].

3.1. Influence of the temperature

Fig. 3 presents SEM images of as-deposited LSFC films at 130 °C, 150 °C, 170 °C and 200 °C for the distance deposition

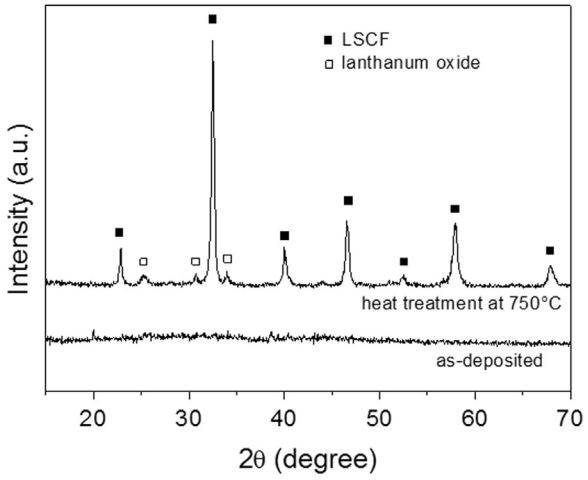

Fig. 2. X-ray diffraction of the as-deposited LSCF films at 200 °C and after the thermal treatment at 750 °C for 2 h.