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Influence of electrospraying parameters on the microstructure of $La_{0.6}Sr_{0.4}Co_{0.2}F_{0.8}O_{3-\delta}$ films for SOFCs

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A B S T R A C T

Ceramics can play a remarkable role in the engineering of intermediate temperature solid oxide fuel cells (IT-SOFCs) capable of meeting the ambitious targets of reduced cost and improved lifetime. While mixed ionic–electronic conductors such as $La_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ are being used as volumic cathodes to increase the catalytic performance of these components, adequate microstructures are also an important requirement for optimal performance, particularly at lower operating temperatures. This work is devoted to the fabrication of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ films on $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ substrates by electrostatic spray deposition (ESD) and to the characterization of the microstructural dependence on the deposition conditions. A wide variety of microstructures ranging from dense to porous, with particular features such as reticulation and micro-porosity, were obtained by varying the ESD deposition parameters: nozzle-to-substrate distance (15, 30, 43, 45, and 58 mm), solution flow rate (0.34 and 1.5 mL/h), and substrate temperature (300, 350, 400 and 450 °C). The correlation between deposition parameters and resulting microstructures was systematically studied and put into evidence.

1. Introduction

The main goal of current research on solid oxide fuel cells is to improve the performance of solid oxide fuel cells operating at temperatures ranging from 500 to 700 °C. These so called IT-SOFCs are expected to increase useful lifespan and reduce operation costs, making them more practical and commercially more attractive. Unfortunately, detrimental phenomena such as electrolyte ohmic losses and cathode polarization increase at lower temperatures. To compensate for the efficiency reduction, alternative electrolyte and cathode materials are being evaluated as potential candidates for IT-SOFCs. $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (CGO) [1,2] is being studied as a replacement for conventional YSZ electrolytes due to its higher ionic conductivity values in the 500–700 °C range [3,4]. On the cathode side, $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ LSCF [5,6] has surfaced as a promising material due to its improved ionic conductivity relatively to LSM [7–9] and good chemical and physical compatibility with CGO [7,9]. These properties can be adjusted by changing the concentration of dopants [10–12], and a compromise between conductivity and mechanical compatibility with CGO can be attained for the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ composition.

Microstructural design of the cathode film is also an important factor when considering optimal performances [13,14]. A combination of porous microstructures and small particle size enhances the catalytic properties by improving gas intrusion and enlarging the reactive surface areas. The possibility to produce different types of microstructures using the same synthesis technique would therefore be interesting for a systematic study correlating film morphology and electrochemical properties, while limiting the amount of variables, such as compositional differences.

Unlike other deposition techniques, electrostatic spray deposition (ESD) provides the possibility to obtain a wide range of very distinct microstructures in a fairly simple way. In this technique an aerosol is created and guided by an electrical field imposed on a metallic nozzle towards a grounded substrate which is normally heated. The shape and spraying modes of the aerosol may be tuned by changing the applied voltage [15]. The most stable configuration is known as the cone-jet mode and it can be obtained in a relatively small range of applied voltages for each set of experimental conditions [16]. The chemical composition of the aerosol is strictly determined by that of a precursor solution being pumped to the nozzle, granting control over the stoichiometry of the deposited layer. A large variety of microstructures can be tailored by varying the deposition parameters. The droplet size in the aerosol can vary from ~10 [17] to 100 μm [15], according to the setup. This parameter is fundamental to understand the formation mechanism of film microstructures and is dictated by a

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combination of the chemical nature of the solution and the deposition parameters. Some studies have determined mathematical relationships that model the effect of these parameters on the resulting droplet size [16,18,19]. These studies aim to predict the droplet size that forms at the nozzle due to an electrohydrodynamic interaction. GananCalvo's [16] solution $d{\sim}(\rho\varepsilon_0 Q^3/\gamma K)^{1/6}$, which correlates droplet size d, with density ρ, vacuum permeability ε_0, flow rate Q, surface tension, γ and electrical conductivity K, of the solution, is possibly the most consensual in the literature.

A recent study from Wilhelm et al. [19] models the dynamic changes of the droplet size during its transport towards the substrate, starting from GananCalvo's model. A detailed review on the topic has been reported by Jaworeck [15]. Ultimately, the morphological features of the deposited layer are determined by the size of the droplet and its interaction with the heated substrate (impact, spreading, drying and precursor decomposition).

In conclusion, ESD is a fast and easy way to deposit pure, composite or graded oxide layers. It is less expensive than other deposition techniques, which typically require vacuum, and it is also highly flexible, allowing for a large selection of materials to be deposited. Previous studies in our laboratory have successfully used ESD to deposit YSZ [20] and LSM/YSZ composite layers [21]. Elsewhere, ESD has also been used to deposit different compositions of the LSCF family on glass and stainless steel [11,22]. This technique has also been used to deposit LSCF on CGO substrates but only one microstructure was reported [22]. This paper reports a systematic study of the influence of nozzle-to-substrate distance, solution flow rate and substrate temperature on the microstructure of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ deposited over $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ substrates for the first time. A correlation between these parameters and the resulting microstructures will be presented and discussed.

2. Experimental section

CGO substrates were prepared in the shape of disks, 19 mm in diameter and 1 mm thick. Powders (Praxair, 99.9%) were isostatically pressed at 250 MPa for 5 min and sintered at 1450 °C for 4 h in air. The surfaces of the densified pellets were machined to become parallel and then polished to guarantee uniform surface conditions.

Precursor salts solution was prepared by weighing $La(NO_3)_3.6H_2O$ (Prolabo, 99.99%), $SrCl_2.6H_2O$ (Strem Chemicals, 99%), $Co(NO_3)_2.6H_2O$ (Sigma-Aldrich, 99.999%) and $Fe(NO_3)_2.9H_2O$ (Sigma-Aldrich, 99.99%) salts in adequate amounts as to obtain the $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ stoichiometry. These were mixed in ethanol (C_2H_5OH, 99.9%; Prolabo) and diethylene glycol monobutyl ether, also known as butyl carbitol ($CH_3(CH_2)_3OCH_2$-$CH_2OCH_2CH_2OH$, 99+%; Acros Organics 99+%) with a 1:2 volume ratio and a total salt concentration of 0.02 mol/L.

The LSCF films were deposited using a vertical ESD setup (Fig. 1).

Depositions were made at different nozzle-to-substrate distances (15, 30, 43, 45 and 58 mm), and solution flow rates of 0.34 and 1.5 mL/h using a Sage™ M361 syringe pump. Deposition temperatures were of 300, 350, 400 and 450 °C. These values refer to the surface of the substrate facing the solution spray, and were obtained after temperature calibration. A positive high voltage was selected and applied between the nozzle and the hot plate, in order to generate the aerosol and the cone-jet spraying mode in each deposition. Values ranged from 5 to 12 KV. Bevelled stainless steel nozzles, 3 mm long and 0.6 mm in diameter, were used for spraying. Total deposition time remained fixed at 1 h.

Thermal decomposition of iron and cobalt nitrates, as well as of the precursor salt solution, were performed in air, from room temperature to 690 °C at a 10 °C/min heating rate, using a Netzsch simultaneous thermal analyzer STA 409 instrument. Microstructures and elemental analysis of the deposited films were studied using scanning electron microscopy (LEO S440) coupled with EDS detector (EDAX). X-ray powder diffraction was carried out on

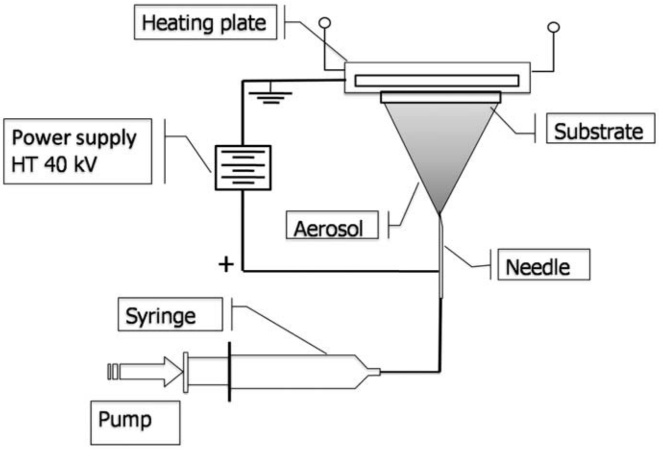

Fig. 1. Schematic drawing of the ESD setup used in sample preparation.

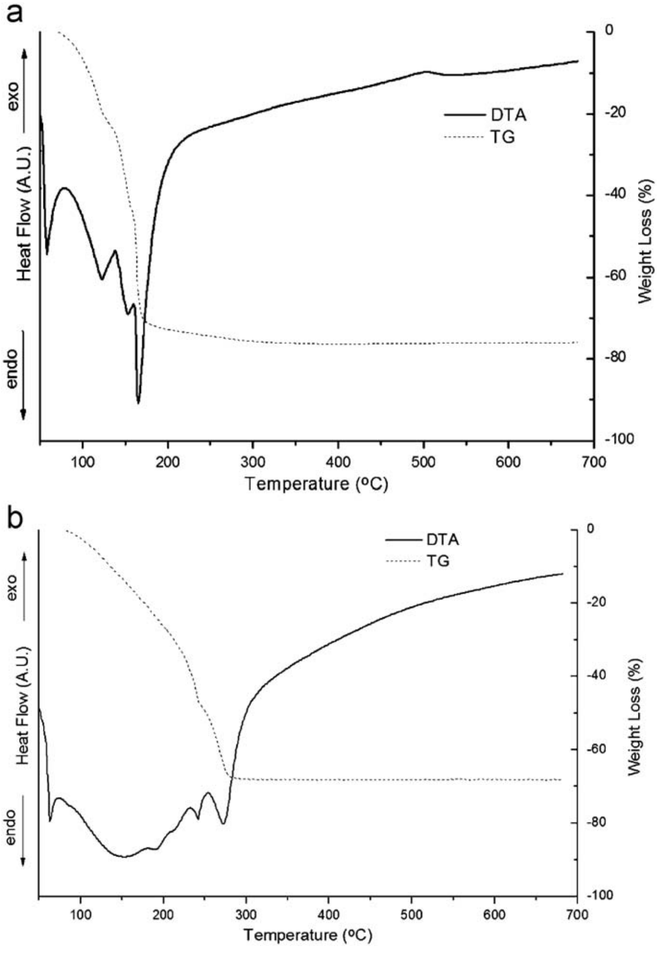

Fig. 2. TG/DTA plots of $Fe(NO_3)_2 \cdot 9H_2O$ (a) and $Co(NO_3)_2 \cdot 6H_2O$ (b) obtained at 10 °C/min in air.