Electrostatic spray deposition of $Ca_3Co_4O_{9+\delta}$ layers to be used as cathode materials for IT-SOFC

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ABSTRACT

In this paper, the deposition of $Ca_3Co_4O_{9+\delta}$ layers on CGO substrates using electrostatic spray deposition (ESD) technique, starting from calcium and cobalt nitrates as precursor salts, is reported. The microstructure was investigated as a function of process parameters such as nozzle-to-substrate distance, solvent composition, substrate temperature, flow rate and deposition time, based on an upper and a lower value. Films with controlled microstructures were obtained after annealing at 880 °C for 2 h in air. The formation of $Ca_3Co_4O_{9+\delta}$ was confirmed by X-ray diffraction, which also showed evidence of Co_3O_4 traces. As shown by *in-situ* X-ray diffraction, $Ca_3Co_4O_{9+\delta}$ starts to form at 625 °C and decomposes at 950 °C, but the transformation is reversible. Interestingly, the initial morphology of the films was maintained after annealing at either 700 or 880 °C, with the appearance of faceted crystals forming a gypsum flower-like microstructure. AC impedance spectroscopy was carried out at intermediate temperatures (600–800 °C) under air on 2 batches of symmetrical cells based on ESD and screen-printed electrodes, respectively. This work confirmed the beneficial impact of the ESD technique. The area-specific resistance was improved by at least 23% at 600 °C and 40% at 800 °C for the sample prepared by ESD compared to the reference one prepared by screen printing. This improvement was explained by a better interface between the electrode and the electrolyte.

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1. Introduction

Mixed conductors, possessing both ionic and electronic conduction properties (mixed ionic electronic conductors, MIEC), find many applications in key technological domains, such as solid oxide cells which are electrochemical devices for energy conversion (solid oxide fuel cell, SOFC) and hydrogen production at high temperature (solid oxide electrolysis cell, SOEC). In this context, good electrochemical performances were recently evidenced for the well-known thermoelectric $Ca_3Co_4O_{9+\delta}$ compound, which has been proposed as a good candidate as a potential MIEC SOFC cathode [1–3]. With an electrical conductivity higher than 200 S.cm^{-1} at 750 °C, this compound is a good electronic conductor [4]. It also exhibits high kinetics toward the oxygen reduction reaction with a surface exchange coefficient of 1.6×10^{-7} cm.s^{-1} [5] at 700 °C which increases to 4×10^{-6} cm.s^{-1} for strontium doped samples [4], leading to values in the same order of magnitude as those measured for the well-known $La_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) cathode material (5.1×10^{-6} cm.s^{-1} at 700 °C), which is now a reference in the field [6]. In contrast, oxygen diffusion in $Ca_3Co_4O_{9+\delta}$ is slow with a diffusion

coefficient of only 2.7×10^{-10} cm^2.s^{-1} at 700 °C [5] in comparison to 4.2×10^{-8} cm^2.s^{-1} for LSCF [6]. However, one advantage of $Ca_3Co_4O_{9+\delta}$ is its low thermal expansion coefficient of $9–10 \times 10^{-6}$ K^{-1} which is in good agreement with the commonly used electrolytes in SOFC applications. In contrast to LSCF, which structure is isotropic, $Ca_3Co_4O_{9+\delta}$ exhibits a layered structure formed by alternate CoO_2 hexagonal layers (CdI$_2$-type) and $Ca_2CoO_{3-\delta}$ oxygen deficient rock-salt type layers, which confer to the material anisotropic oxide ion transport properties, with a diffusion coefficient which is one order of magnitude higher along the layers than in the perpendicular direction [7]. It is therefore expected that the electrode microstructure may affect the electrochemical performance with respect to the 2D feature of the structure.

The performances of solid oxide cells are actually considerably affected by the microstructure of the electrode itself. It is known that porosity allows the permeation of gaseous species to and from reactive sites, while its geometry controls the surface area available for the oxygen reduction reaction to occur. For instance, in the case of LSCF cathodes, a strong correlation of the microstructure and the electrochemical properties of LSCF thin films was recently shown by Marinha *et al.* [8–12] with an ASR value of 0.13 Ω.cm^2 determined by a.c. impedance spectroscopy at 603 °C for a sample prepared by electrostatic spray deposition (ESD), which is among the best results in the

literature at the moment. This value is considerably lower than those reported for cathodes with similar $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ composition [13] and emphasizes the role of micro- and nanostructure on the electrochemical behavior of such thin electrodes.

ESD is a low-cost process for the deposition of SOFC electrodes, in which the gas/solid interface area is crucial. It allows obtaining a large array of different microstructures, some of which are quite original [8]. ESD is based on electrohydrodynamics laws where a precursor solution is pumped through a metallic nozzle at a controlled flow rate. The solution is then atomized by applying a high voltage that generates an electrical field between the nozzle and the substrate. The electrical field generates the aerosol and directs it toward the substrate where the droplets spread, dry, and decompose to form the film. The mechanism of film formation and the resulting microstructure depend mainly on the size of the droplets impacting the hot substrate. The droplet size can be controlled by the technical deposition parameters (nozzle–substrate distance, temperature, flow rate) and by the physicochemical parameters of the precursor solution, such as its surface tension, viscosity, boiling point, and conductivity. In this regard, relatively low surface tension and viscosity are required and conductivity values of the solution may vary between 10^{-8} and 10^{-1} S.cm^{-1}. One fundamental characteristic which influences the possible film morphologies is the boiling point [14]. Ethanol, with a boiling point of 78 °C, is very commonly used in combination with butyl carbitol with a higher boiling

point of 231 °C. By mixing the solvents in different ratios, an intermediate boiling point between these extremes may be easily achieved. Depending on the experimental set-up, the droplet size in the aerosol can vary from ~10 to 100 μm [15]. Several studies have modeled how the solution properties and the deposition parameters determine the droplet size formed at the nozzle [16–18] but the most consensual is probably the Gañan-Calvo's relationship [17], as the following:

$$d \sim \left(\frac{\rho \varepsilon_0 Q^{\alpha}}{\gamma K} \right)^{1/6}, \tag{1}$$

which correlates droplet size, d, with density ρ, vacuum permeability ε_0, flow rate Q, surface tension, γ and electrical conductivity of the solution K. Ultimately, it is the size of the droplet at the moment of impact with the heated substrate and the combined effects of relative spreading and drying rates that determine the film morphology.

In this paper, with the aim of improving the electrochemical performance, the fabrication conditions of $Ca_3Co_4O_{9+\delta}$ layers prepared by ESD on ceria doped gadolinium oxide (CGO) substrates were optimized. The microstructure was investigated as a function of the process parameters, such as nozzle-to-substrate distance, solvent composition, substrate temperature, flow rate, and deposition time, based on an upper and a lower value. To get new insights in the crystal growth of $Ca_3Co_4O_{9+\delta}$, an in-situ X-ray diffraction study was also carried out on

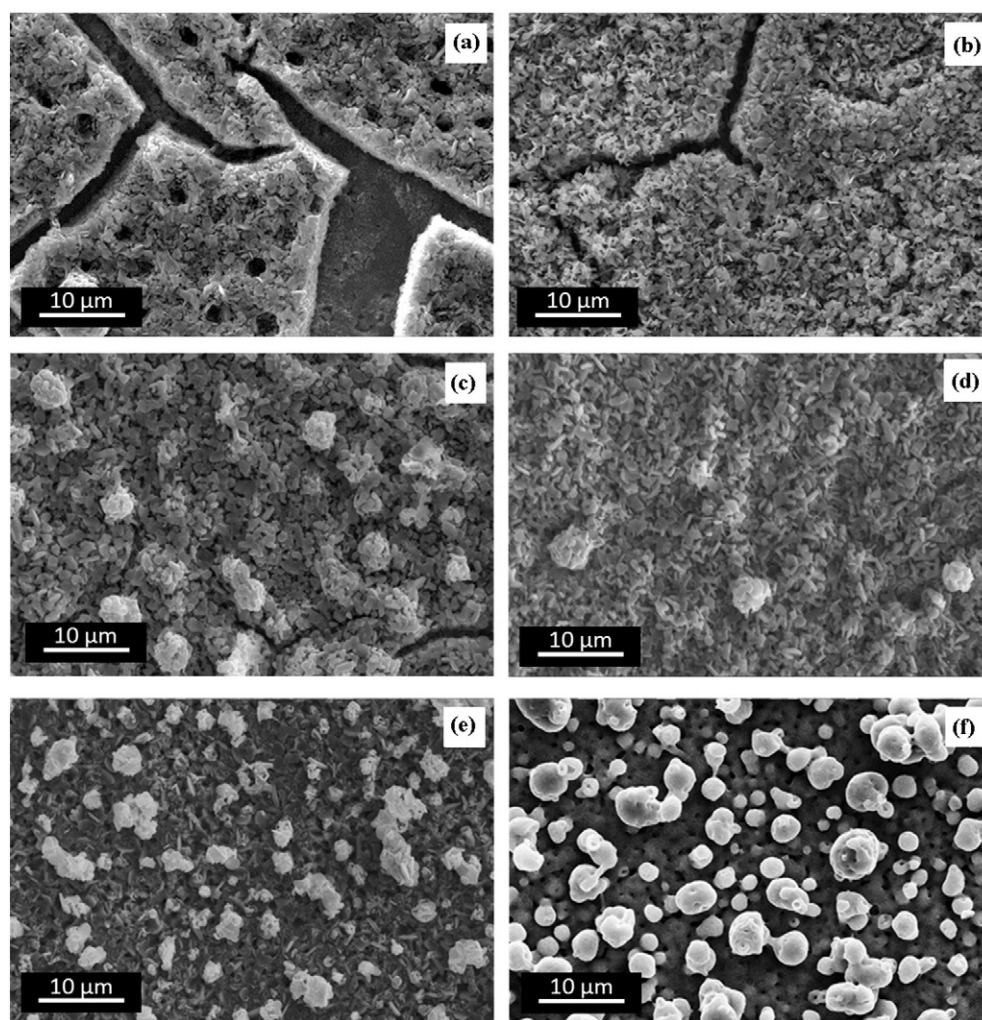**Fig. 1.** SEM micrographs of ESD films deposited on CGO substrate starting from $Ca(NO_3)_2$ and $Co(NO_3)_2$, 0.02 M, 1 mL/h, 60 min, (a) in EtOH:BC, 33:67 vol.% at 300 °C for 30 mm (b) in EtOH:BC, 33:67 vol.% at 300 °C for 50 mm (c) in EtOH:BC, 50:50 vol.% at 300 °C for 50 mm (d) in EtOH:BC, 33:67 vol.% at 350 °C for 50 mm (e) in EtOH:BC, 33:67 vol.% at 400 °C for 50 mm (f) in EtOH:BC, 33:67 vol.% at 450 °C for 50 mm.