



# Rational design of hierarchically nanostructured electrodes for solid oxide fuel cells



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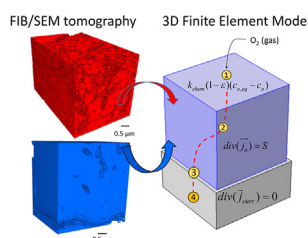
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## HIGHLIGHTS

- Films of hierarchical porosity from nano-to macro-range are fabricated.
- A numerical 3D Finite Element Method (FEM) model is developed.
- Micro/nanostructural parameters from 3D reconstructions are introduced in the model.
- The model links intrinsic properties of electrode components to microstructure.
- The model can be extended to larger, regular and heterogeneous microstructures.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Understanding, controlling and optimizing the mechanisms of electrode reactions need to be addressed for high performance energy and storage conversion devices. Hierarchically structured porous films of mixed ionic electronic conductors (MIECs) and their composites with ionic conductors offer unique properties. However, correlating the intrinsic properties of electrode components to microstructural features remains a challenging task. Here,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}:\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$  (LSCF:CGO) composite cathodes with hierarchical porosity from nano to micro range are fabricated. The LSCF film exhibits exceptional electrode performance with area specific resistance values of 0.021 and 0.065  $\Omega \text{ cm}^2$  at 650 and 600 °C respectively, whereas LSCF:CGO composite is only slightly superior than pure LSCF below 450 °C. We report for the first time a numerical 3D Finite Element Model (FEM) comprising real micro/nanostructural parameters from 3D reconstructions into a simple geometry similar to experimentally observed columnar features. The model demonstrates that heterogeneities in porosity within the film thickness and percolation of the ionically conducting phase significantly impact bulk transport at low temperatures. Design guidelines relating performance to microstructure and bulk material properties in relation to experimental results are proposed. Our model has potential to be extended for rational design of larger, regular and heterogeneous microstructures.

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## 1. Introduction

Solid oxide fuel cells (SOFC) have attracted much interest as clean, efficient and cost effective systems that can directly convert

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chemical energy into electrical energy. The improvement of the efficiency and of the stability of the cell still remains a major issue after several decades of research. While high operating temperatures provide fast electrochemical kinetics in the components of a SOFC, lower operating temperatures reduce its theoretical efficiency, even though the stability and chemical compatibility issues of the interconnect and cell materials are improved [1]. For these reasons, high performance SOFC cathodes operating as low as 400–650 °C are sought by academic and industrial research teams. Since the kinetics of the oxygen reduction reactions (ORR) in the cathode remains the main limiting factor [2], the strategy to reach this goal relies both on the cathode material choice and on the micro/nanostructure design of the cathode [3–5]. Cobalt-based perovskites, such as  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF), exhibiting simultaneous electronic and ionic conductivity (the so-called mixed ionic-electronic conductors-MIECs) take the lead in the material choice [6,7]. The introduction of ionic transport extends the ORR path from triple phase boundary (tpb) points to the gas-MIEC double-phase boundary (dpb), thus providing optimal kinetics [8]. Also, it has been demonstrated that the addition of a second phase with high ionic conductivity in the MIEC matrix, typically the same as the electrolyte material, allows the electrode performance to be dramatically improved [9–15]. Typically,  $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$  is used as the secondary cathode component, for its good chemical compatibility with LSCF, its availability and affordability. Dusastre et al. reported a fourfold performance improvement by the introduction of 36 vol % CGO in LSCF [9] and Murray et al. measured a tenfold decrease in cathode polarization resistance with 50 wt. % CGO [11]. Similarly, with a 60 wt. % CGO composite Leng et al. recorded a cathode polarization resistance of  $0.17 \Omega \text{ cm}^2$  at 600 °C, about seven times lower than pure LSCF [14]. All these studies point to the conclusion that CGO addition always leads to a lowering of the area specific resistance (ASR). However a rational guideline for choosing the optimal CGO content, in relation with other important microstructural parameters (e.g. porosity, surface area), is still missing.

Hierarchically structured porous materials are of growing interest owing to their high performance in many applications for energy conversion and storage [16,17]. It has been shown that while macro-pore channels facilitates mass transport, nano porous network enhances electrochemical reactions in the SOFC electrodes [18]. Nevertheless, hierarchical porosity should be well tailored according to the percolation of electronic and ionic phases. All these factors play a key role on the polarization resistance of SOFC electrodes [19–21]. Theoretical calculations and models are therefore essential tools to understand the relations between performance and pertinent microstructural parameters and to suggest novel ways to optimize these parameters. Numerous aspects of parameter-performance relationships have been discussed theoretically, from 1D physicochemical models [22–24] to highly detailed elementary reaction kinetics [25,26] by means of several modelling tools (e.g., finite element method, resistor network analyses, analytical calculations). Other modelling approaches incorporating 2D or 3D finite element method (FEM) into a representative geometry [27–29] or into real microstructures extracted from 3D imaging have also been proposed [30–32]. Only FEM models can potentially account for the heterogeneous nature of an electrode microstructure. However, to the best of our knowledge no 3D FEM modelling on composite cathodes and/or on hierarchical structures has been reported until now.

In this contribution, we have deposited 100 vol %  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (denoted 100 LSCF hereafter) and 60:40 vol % LSCF:CGO ( $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ , denoted 60:40 LSCF:CGO) composite cathodes by Electrostatic Spray Deposition technique (ESD) to study the influence of CGO addition on the electrochemical

performance. The films are characterized by means of scanning electron microscope (SEM), focused ion beam scanning electron microscope (FIB-SEM) tomography and X-ray diffraction (XRD). The electrochemical performance of these cathodes is assessed by electrochemical impedance spectroscopy (EIS). In the second part, a revised version of a stationary FEM model proposed by Ruger et al. [28], is used to simulate LSCF and LSCF:CGO composite cathodes with a columnar microstructure. The micro/nanostructural parameters of the cathode films obtained from the FIB-SEM 3D reconstruction are used as inputs for the modelling. The oxygen transport coefficients are deduced from EIS measurements. Finally, the influence of CGO addition and of the micro/nanostructure on the bulk diffusion, surface exchange and resulting ASR values are discussed in light of simulation results.

## 2. Experimental section

### 2.1. Fabrication of the cathode films

1 mm thick, dense  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$  (CGO) substrates, were prepared by pressing CGO powder (Praxair, 99.9%,  $20.5 \text{ m}^2/\text{g}$ ) isostatically at 300 MPa, followed by sintering at 1200 °C for 2 h in air. The substrates were grinded and polished to obtain a flat and uniform surface. 100 vol.% LSCF, 60:40 vol.% LSCF:CGO films were deposited on a CGO substrate using a vertical ESD setup [33] starting from precursor salts solutions.  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  was prepared by dissolving  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Prolabo, 99.99%),  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  (Strem Chemicals, 99%),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich, 99.999%) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Sigma-Aldrich, 99.99%) salts in adequate amounts to ensure the desired stoichiometry. These salts were mixed in absolute ethanol ( $\text{C}_2\text{H}_5\text{OH}$ , 99.9%; Prolabo) and butyl carbitol ( $\text{CH}_3(\text{CH}_2)_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ , 99+%; Acros Organics 99+%) with a 1:2 vol ratio and a total salt concentration of  $0.02 \text{ mol L}^{-1}$ . Similarly, the CGO solution was prepared by mixing powders of cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , Rectapur Prolabo, 99.5%) and gadolinium nitrate ( $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , Aldrich, 99.99%). These precursors were also mixed in ethanol and butyl carbitol with a 1:4 vol ratio and a total salt concentration of  $0.02 \text{ mol L}^{-1}$ . The ESD deposition was operated by controlling the substrate holder motion in x and y directions with a  $1 \text{ mm s}^{-1}$  speed. LSCF and CGO solutions were atomized at the same time using high voltage (5–6 kV), which maintains a cone-jet atomization regime for 3 h at a substrate temperature of 300 °C, a nozzle to substrate distance of 15 mm and a flow rate of  $0.75 \text{ mL h}^{-1}$  for each solution. All samples were sintered at 800 °C for 2 h with a  $2 \text{ }^\circ\text{C min}^{-1}$  heating rate and a  $3 \text{ }^\circ\text{C min}^{-1}$  cooling rate. A  $\text{La}_{0.62}\text{Sr}_{0.38}\text{Co}_{0.19}\text{Fe}_{0.8}\text{O}_{3-\delta}$  ink (obtained from Marion Tech.  $d_{50} = 0.27 \mu\text{m}$ ) was screen printed (SP) symmetrically onto ESD deposited films to serve as a current collector. This technique ensures a good contact between the surface of the cathode and the current collecting Pt grid. A  $0.5 \text{ }^\circ\text{C min}^{-1}$  ramp from room temperature to 160 °C for 5 h then to 350 °C for another 5 h was used to burn out binders and ink solvents. Finally, the temperature was increased to 700 °C with  $2 \text{ }^\circ\text{C min}^{-1}$  rate, followed by a fast cooling down to room temperature at  $10 \text{ }^\circ\text{C min}^{-1}$  rate. Although well below the sintering temperature, a 700 °C temperature was found high enough to generate some necking between particles.

### 2.2. Scanning electron microscopy and X-ray diffraction characterization

The morphology of the films was investigated by SEM with a field emission gun, FEG-SEM, (ZEISS Ultra 55) operating at a 3 kV voltage and a 7 mm working distance. The samples were coated with Pt to avoid electrons charging. X-ray powder diffraction (XRD)

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