## **Electronic Supplementary Information**

# Improvement on the electrochemical performance by morphology control of nanostructured $La_{0.6}Sr_{0.4}CoO_{3-\delta}-Ce_{0.9}Gd_{0.1}O_{1.95}$ cathodes for IT-SOFC

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#### I. XANES

X-ray Absorption Spectroscopy (XAS) is a chemical selective probe to study amorphous or crystalline materials in solid or liquid phase. This means that we can study the chemical and local order properties of a selected element in a given material. The outstanding feature of XAS experiments is that they are nondestructive and can be performed under controlled conditions of temperature, pressure or gas composition. This is a very important issue in materials with electrochemical or catalytic activity due to the sensibility they may exhibit to environment changes. This represents a significant difference with other related techniques, such as XPS (X-ray Photoelectron Spectroscopy), EELS (Electron Energy Loss Spectroscopy) or coulometric titration, where very special experimental conditions must be satisfied to warranty reliable results. In the latter case, it can only be obtained an average oxidation state of all the cations in the sample. This may be of little help when the material is composed of two or more polyvalent cations, because the activity of each one of them and the influence that they have on the observed properties of the material will remain concealed. The same applies to the case of LSC, where cobalt atoms can be found in +2, +3 or +4 oxidation state.

XAS spectrum can be divided into two regions that provide different information. XANES region (X-ray absorption Near Edge Structure) contains information about electronic orbital configuration, oxidation state and chemical coordination of the selected element in the sample. EXAFS region (Extended X-ray Absorption Fine Structure), on the other hand, brings information about the local order of the atom (coordination number, bondlength and thermal and structural disorder).Therefore, in this work it was possible to study the speciation of cobalt atoms in nanostructured LSC, under controlled environment conditions very similar to the working conditions of IT-SOFC's cathodes. Also, it was tested the sensitivity of Co speciation to changes in the oxygen concentration in the atmosphere. The key feature of this work relies on counting with the three reference standards of Co(II), Co(III) and Co(IV) (the three possible cobalt's oxidation states), needed to address the speciation study by means of the Linear Combination Fitting (LCF) method. As far as we know, the rest of the published works on this topic lack of a reliable Co(IV) reference standard and only offer a qualitative analysis on this topic.

#### II. XANES analysis procedure

Cobalt speciation was studied by means of the analysis of Co-K edge XANES in the temperature range of 20 - 700 °C and under 20 and  $5\%O_2/N_2$  atmosphere (50 mL.min<sup>-1</sup>). The analysis of the XANES spectra was performed by the linear combination fitting of standards of Co(II, III, IV), following the guidelines given by Kelly, Hesterberg and Ravel.<sup>1</sup> XAS spectra of samples and standards were recorded using the same acquisition program and raw data was normalized following the same procedure and using the same parameters in all the cases. Pre-edge background was removed with a linear function applied between 7650 and 7700 eV. Normalization was performed using a 2<sup>nd</sup> degree polynomial applied from 7732 to 8700 eV. All the sample's spectra were analyzed using the same standards and the same fitting window, i.e., from 7700 to 7732 eV, what warrantee us to cover all the spectral fraction with relevant information about cobalt's speciation and leaving out the low energy oscillations coming from the multiple-scattering of the low energy photoelectrons. The reliability of the results was tested using slightly broader (7700 -7733 eV) or narrower (7700 - 7728 eV) fitting windows. Linear Combination Fitting (LCF) was performed by fixing EO-shift parameter (the correction to the edge energy of each reference standard) to zero. No constrains or correlations were made on the sum of the relative weight of each standard spectrum. This allowed us to have an estimation of the systematic error introduced during the normalization procedure of the spectra. This value was always smaller than 3%. It is important to highlight that the results obtained with this analysis are relative to the standards and that the specific values of the speciation may be different if another set of standards is employed. Nevertheless, the evolution of the parameters with controlled changes in the experimental conditions should lead to the same qualitative behaviour of the element in the sample when proper standards are used.<sup>1,2</sup>

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Figure S1.a) Co-K edge XANES of CoO, LaCoO<sub>3</sub> and BaCoO<sub>2</sub> taken as reference standards of Co(II), Co(III) and Co(IV), respectively. b) Second derivative of the absorption coefficient  $\mu(E)$  of the standards ina). Vertical dashed lines indicate the edge energy  $E_0$  associated to each oxidation state of Co atoms. c) Detail of the second derivative of  $\mu(E)$  in the region of the pre-edge energy peak.



Figure S2. a) Co-K edge XANES of LSC powder at different temperatures under synthetic air flow. b) Second derivative of  $\mu(E)$  in the XANES region. The inset shows the shift of the absorption edge to lower energies with increasing temperature. c)Detail of the second derivative of  $\mu(E)$  in the region of the pre-edge peak. Arrows indicate the extent of the  $t_{2g}$  and  $e_g$  energy bands at room temperature or below.<sup>3,4</sup> G1-G4 indicate the energy position at room temperature of Gaussians functions according to the analysis in reference [10].

#### **III. XANES analysis**

Figure S1 shows the Co-K edge XANES spectra of CoO, LaCoO<sub>3</sub> and BaCoO<sub>3</sub>, used as reference standards of Co(II), Co(III) and Co(IV), respectively. The results of the LCF using these standards have shown a mixture of  $Co^{3+}$  and  $Co^{4+}$  at room temperature but, with increasing temperature, vacancy creation leads to the decrease of  $Co^{4+}$  population and  $Co^{3+}$  increase, along with the appearance of Co<sup>2+</sup> species. Figure S1.b shows the second derivative of the absorption coefficient respect the incident photon's energy  $(d^2\mu/dE^2)$ . The inserted lines mark the zero of  $d^2\mu/dE^2$ , which was taken by definition as the edge energy,  $E_0$ , and represents the inflection point in the absorption edge. Figure S1.c shows in detail the  $d^2\mu/dE^2$  in the pre-edge-energy interval. As explained in the main text, the profile's shape of Co(II), Co(III) and Co(IV) standards in this energy window, recorded at room temperature, is associated to high, intermediate of low spin (HS, IS or LS) states, respectively.

**Figure S2** shows the Co-K edge XANES spectra of nanostructured LSC at different temperatures (20 - 700 °C) in air. Inset in **Figure S2.b** shows the subtle shift of  $E_0$  of ~1 eV towards lower energy, indicating the overall reduction of the sample. The final value at

700 °C of  $E_0 = 7723.3$  eV coincides with that of LaCoO<sub>3</sub> standard, which would lead to the wrong conclusion that all Co atoms in LSC are in +3 oxidation state. Nevertheless, the LCF of the standards in **Figure S1** shows a more complex scenario, where a mixture of the three species evolves with temperature and O<sub>2</sub> concentration in the atmosphere. These results are one of the original contributions of the present work. It has to be mentioned that previous works found in the literature on this topic were not able to asses cobalt's speciation in LSC powders because of the lack of a proper Co(IV) reference.

The following discussion in this section is qualitative and has minor relevance in the context of the present work. It is about the relation of the metallic behaviour of LSC, regarding electronic conduction (a complementary aspect in MIECs), with the electronic configuration and spin state of cobalt atoms, information that can be obtained from the analysis of the pre-edge-energy peak.

The coexistence of the three species in LSC at high temperatures makes the qualitative analysis of the low intensity peak in **Figure S2.c** very difficult.<sup>5</sup> Simple comparison of LSC with reference patterns (**Figure S3**) would lead to the conclusion that Co atoms has in average a low spin state (LS) in both Po<sub>2</sub> conditions at 700 °C, as they are similar to BaCoO<sub>3</sub> pre-edge-energy peak (the Co(IV)

standard) and it is supposed that Co(IV) ions are in LS state at room temperature.<sup>6,7</sup> Nevertheless, it is expected that, with increasing temperature, a transition from the lower to the higher spin states take place. This is possible because, as the Co-O bond length increases with temperature, the crystal field intensity decreases, lowering the splitting between  $t_{2g}$  and  $e_g$  orbitals.<sup>6,8</sup> This explains the evolution of this pre-edge peak as function of temperature (**Figure S2.c**). At room temperature it is possible to observe two peaks at 7710.2 and 7711.4 eV, which is consistent with  $t_{2g} - e_g$  splitting. The splitting is not resolved at 300 °C, but at higher temperatures it is possible to observe a very weak peak near 7711.8 eV along with the main one at 7709.6 eV.

Then, at high temperature, the pre-edge peak shape is consistent with the expected HS or IS configuration, or a mixture of them. Electrons in these states are expected to be delocalized, which prompts electronic conduction.<sup>9</sup> According to the analysis of Itoh *et al.*, the evolution of the pre-edge energy peak (**Figure S2.c**), is consistent with a transition from IS to HS state.<sup>10</sup>



Figure S3. Second derivative of the pre-edge-energy peak in the Co-K edge XANES of a) LSC at 700 °C under synthetic air and 5%  $O_2/N_2$  flow; b) CoO; c) LaCoO<sub>3</sub> and d) BaCoO<sub>3</sub>. This reference data was recorded at room temperature in air.

Even though Itoh *et al.*, and Kozuka*et al.*, related the metallic conduction in LSC to the contraction in the Co-O bond length with increasing Sr content at room temperature, Petrov *et al.*, identified Sr doping in LaCoO<sub>3</sub> with Co<sup>4+</sup> creation, which means hole doping that obviously favours electronic conduction.<sup>9–11</sup> In addition, as mentioned before, it is possible that at high temperatures the lower crystal field strength favours the electronic conductivity through a decrease in the  $t_{2g}$ - $e_g$  splitting.<sup>6,8</sup> All these previous evidences may point out that there is not a unique source for the electronic conductivity in LSC and the mechanisms that give origin to it may vary (or have different weights) according to the environment conditions (temperature, pressure, oxygen content and others).

#### **IV. SEM Analysis**

LSC powder calcined at 900 °C 5H consists of connected submicrometer particles forming porous grains with size in the order of the microns (**Figure S4**).



Figure S4. LSC powder after thermal treatment at 900 °C 5H



Figure S5. GDC<sub>MW</sub> powder consisting of spheres of diameter 200 nm.

#### **IV. XRD Analysis**

The lattice parameters *a* and *c* of LSC phase in LSC nanopowder and LSC-GDC composite cathodes were calculated using the Rietveld refinement method and assuming the rhombohedral phase (**Table S1**). The crystal structure was refined using the  $R\overline{3}c$  space group (space group number SG#167 of the International Tables of Crystallography-ITT). No relevant variation in *a* or *c* parameters are observed between the as prepared LSC nanopowder and LSC-GDC cathodes. In addition, there is no significant change in their values after the 101 H stability test.

For the analysis of the GDC phase in GDC nanopowders and LSC-GDC composites, the refinement was performed assuming the fluorite-like phase and employing the  $Fm\overline{3}m$  space group (ITT SG#225) (**Table S2**). In this case, lattice parameter *a* remained essentially constant throughout the cathode fabrication process and after the 101 H stability test, indicating excellent chemical compatibility between the GDC and LSC phase and stability in time of the LSC-GDC composite cathode.

**Table S1.** Lattice parameters a and c of the perovskite-like structure of LSC powder and LSC in LSC-GDC composite cathodes, fresh and after 101 H long term stability test, obtained by means of the Rietveld refinement method, along with reliability factors.

Sample	a (Å)	c (Å)	R <sub>p</sub>	$R_{wp}$	R <sub>e</sub>	χ²
LSC	5.4325(5)	13.20788(9)	24.7	13.1	9.47	1.9
LSC75- GDC <sub>cc</sub> 25	5.4327(3)	13.21164(7)	18.2	10.9	8.22	1.8
LSC75- GDC <sub>MW</sub> 25	5.4328(4)	13.20901(7)	19.1	11.2	8.10	1.9
LSC75- GDC <sub>MW</sub> 25 after 100 H	5.4328(4)	13.20988(7)	19.1	11.3	8.17	1.9

**Table S2.** Lattice parameter a of the fluorite-like structure of GDC powders and GDC in LSC-GDC composite cathodes, fresh and after 101 H long term stability test, obtained by means of the Rietveld refinement method, along with reliability factors.

Sample	a (Å)	$R_p$	R <sub>wp</sub>	R <sub>e</sub>	χ²
GDC <sub>cc</sub> powder	5.42(3)	8.56	8.22	7.03	1.4
$GDC_{MW}$ powder	5.42(4)	8.61	8.26	7.09	1.5
LSC75-GDC <sub>cc</sub> 25	5.42(2)	18.2	10.9	8.22	1.8
LSC75-GDC <sub>MW</sub> 25	5.42(2)	19.1	11.2	8.10	1.9
LSC75-GDC <sub>MW</sub> 25 after 101 H	5.42(2)	19.1	11.3	8.17	1.9

In the same vein, the XRD patterns of the fresh LSC75-GDC<sub>MW</sub>25 composite cathode and after the 101 H stability test do not exhibit any difference or secondary phase that would indicate cation segregation or reaction between phases (**Figure S6**).

Comparison of the lattice parameters *a* and *c* of LSC in LSC nanopowders and in LSC75-GDC<sub>MW</sub>25 composite cathode with reference data found in the literature shows very good agreement (**Table S3**). The same holds for the lattice parameter of GDC phase in GDC powders and in LSC75-GDC<sub>MW</sub>25 composite (**Table S4**).

**Table S3.** Comparison of lattice parameters a and c ( $R\overline{3}c$  space group) of LSC in powders and in composite cathode with reference values found in the literature.

Material	<i>a</i> (Å)	<i>c</i> (Å)	Reference
LSC	5.4325(5)	13.20788(9)	This work
LSC75-GDC <sub>MW</sub> 25	5.4328(4)	13.20901(7)	This work
LSC	5.4437(1)	13.2085(5)	12
LSC	5.43576(5)	13.21706(8)	10
LSC	5.435	13.229	13

**Table S4.** Lattice parameter *a* ( $Fm\overline{3}m$  space group) of GDC<sub>CC</sub> (powder), GDC<sub>MW</sub> (spheres), and in LSC75-GDC<sub>MW</sub>25 composite cathode and reference values found in the literature.

Sample	a (Å)	Reference
GDC <sub>cc</sub>	5.42(3)	This work
GDC <sub>MW</sub>	5.42(2)	This work
LSC75-GDC <sub>MW</sub> 25	5.42(2)	This work
GDC	5.411	14
GDC	5.415	15
CeO <sub>2</sub> (2.0 nm)	5.456(3)	16
CeO <sub>2</sub> (8.4 nm)	5.413(2)	16



Figure S6. XRD pattern of LSC75-GDC\_{MW}25 cathode on SDC electrolyte after 101 H long term stability test, compared to the XRD pattern of the fresh sample.

#### V. Electrochemical Impedance Spectroscopy (EIS)

To optimize the electrical contact between the particles that compose the electrode and between the electrode itself and the electrolyte, several identical symmetrical cells, with the same LSC:GDC weight ratio, were prepared and sintered at different temperatures between 825 and 950 °C with a difference of 25 °C (Figure S7). Three different LSC:GDC weight ratios (75:25, 50:50 and 25:75) were tested in this temperature interval. Those series corresponding to composite cathodes made of  $\mathsf{GDC}_{\mathsf{MW}}$  exhibited the lowest values of ASR<sub>TOTAL</sub>. LSC75-GDC<sub>MW</sub>25 sintered at 850 °C exhibited the lowest value of ASR<sub>TOTAL</sub>. LSC75-GDC<sub>cc</sub>25 series exhibited almost the same curve than LSC50-GDC<sub>cc</sub>50 series, but shifted to lower sintering temperature. In order to make the analysis as clear as possible, we chose to compare LSC75-GDC\_{MW}25 with LSC75-GDC<sub>cc</sub>25, both sintered at 850  $^\circ\text{C}.$  The optimum sintering temperature increases with increasing GDC load. This optimum higher temperature has less negative impact on ASR<sub>TOTAL</sub> of LSC-GDC<sub>MW</sub> composite cathodes than that of LSC-GDC<sub>CC</sub>.



Figure S7. ASR<sub>TOTAL</sub> of composite cathodes as function of sintering temperature. Three different LSC:GDC weight ratios are compared. Every value corresponds to measurements recorded at T = 700  $^{\circ}$ C under synthetic air flow.

Table S5. Comparison of the ASR<sub>TOTAL</sub> of LSC and LSC75-GDC<sub>MW</sub>25 cathodes obtained in this work with some relevant recent results found in the literature. SP: screen printing; PLD: pulsed laser deposition; YSZ: ytria stabilized zirconia.

Cathode	Thickness	Electrolyte	Deposition Technique	T (°C)	ASR (mΩ.cm <sup>2</sup> )	Reference
LSC	75 μm	SDC	SP	700	41(2)	This Work
(La <sub>0.6</sub> Sr <sub>0.4</sub> ) <sub>0.99</sub> CoO <sub>3−δ</sub>	25 μm	GDC	Spray deposition	700	56	17
LSC	-	$BaCe_{0.54}Zr_{0.36}Y_{0.1}O_{2.95}$	SP	700	480	18
LSC thin film	0.150 - 0.200	GDC	Dip-coating	600	23	19
LSC75-GDC <sub>MW</sub> 25	75 μm	SDC	SP	700	18.4(2)	This Work
LSC70-GDC30	20µm	GDC	Spray deposition	700	110	20
multilayered thin films LSC/GDC + LSC Thick film	30 µm	YSZ	PLD + SP	700	30	21
multilayered thin films LSC/GDC + LSC Thick film	-	GDC	PLD + SP	700	60	22
LSC75-GDC <sub>MW</sub> 25	75 μm	SDC	SP	650	29.2(1)	This Work
LSC-GDC	30 µm	GDC	SP	650	35	23
LSC70-GDC30	10 µm	GDC	SP	650	890	24
LSC50-GDC50	20 µm	GDC	SP	650	75	25



Figure S8. Po<sub>2</sub> dependence of the HF, MF and LF arcs of LSC, LSC75-GDC<sub>cc</sub>25 and LSC75-GDC<sub>MW</sub>25 cathodes at 700 °C. Solid lines represent the linear fit to the data, and the numbers next to them, the corresponding slope. The dashed line in b) represents the extrapolation of the value that the MF arc of LSC75-GDC<sub>MW</sub>25 cathode would take at 20%  $O_2/N_2$ .



Figure S9. Long-term stability study on LSC\*75-GDC<sub>MW</sub>25. a) Nyquist plots and b) Bodephase plots of EIS spectra recorded at 700 °C under synthetic air flow. Arrows in the Bode-phase plot (b) spot the increment of the phase between 100 Hz and 30 kHz.

The dependence of the HF, MF and LF arcs on O<sub>2</sub> concentration in the atmosphere is analyzed and compared between LSC, LSC75-GDC<sub>CC</sub>25 and LSC75-GDC<sub>MW</sub>25 cathodes (**Figure S8**). The dashed line in **Figure S8.b** represents the extrapolation of the evolution of the MF arc corresponding to LSC75-GDC<sub>MW</sub>25 cathode under increasing O<sub>2</sub> content up to 20% O<sub>2</sub>/N<sub>2</sub>. The extrapolated value of ASR<sub>MF</sub> is less than 1 mΩ.cm<sup>2</sup>. This value is consistent with the impossibility to observe this MF arc under 20% O<sub>2</sub>/N<sub>2</sub> concentration, which seems to be veiled by the statistical errors. These results are summarized in **Table III** and analyzed in the main text of this work.

The experimental data recorded during the long-term stability study of the LSC75-GDC<sub>MW</sub>25 composite cathode in the symmetrical cell configuration was analyzed of by means of equivalent circuit method. The study shows that the increase in height of the curve in the Bode-phase plot between 100 Hz and 30 kHz is exclusively due to the HF (CT) process (Figure S9).

### VI. Morphology, Chemical Speciation and Electrochemical Performance.

XANES results probed the sensitivity of cobalt atoms in LSC nanopowders to changes in oxygen concentration in the gas phase. This result can be extrapolated to LSC under the conditions that can be found in the composite cathode. Under these conditions, LSC particles are in contact with other particles of LSC or GDC. Standard particles resemble cubic bodies with flat faces (Scheme S1). Two of these particles may share a relatively large contact surface. In the case of LSC, this means that that surface is not



Scheme S1. a) Standard composite LSC-GDC cathode made of powders. b) Composite cathode made of GDC spheres. Particles in a) may share large surface contact area, which hinders the interaction between LSC and the gas phase. On the other hand, in b), the contact area between LSC and GDC spheres is smaller. This fact may affect the chemical speciation of cobalt atoms, prompting in the latter case a better ionic conduction.

available (blocked) for the surface reactions with the gas phase. This will, obviously, affect its performance in a negative way. But, in addition, the LSC performance will be affected by effects at the atomic scale, driven by the contact with the GDC phase. The ionic conductivity property of GDC is based on the existence of oxygen vacancies in its lattice when the material is under working conditions. The lack of oxygen in the GDC lattice can be compared to the lower density of oxygen in the gas phase during the XANES experiment with LSC under low Po2 condition. Under that condition, the amount of  $Co^{3+}$  species was higher than under synthetic air flow. Hence, it is possible that LSC particles in contact with GDC particles of irregular shape (powders) exhibit more Co<sup>3+</sup> than when they are surrounded by GDC spheres. It has to be remembered here that XANES results show that the amount of Co<sup>2+</sup> and Co<sup>4+</sup> are higher when LSC is under synthetic air flow. Consequently, a lower superficial contact area between LSC and GDC spheres will contribute to a larger LSC surface exposed to the gas phase. In this case, it is possible that LSC chemical speciation resembles that observed with XANES under synthetic air flow.

This is a very important issue. The exposed mechanism explains how GDC morphology may affect LSC at the atomic scale, indirectly modifying its chemical speciation. The existence of  $Co^{2+}$ ,  $Co^{3+}$  and  $Co^{4+}$  in the LSC lattice, along with the possibility of locally changing every cobalt atom its oxidation state, creates a "breathing structure" that favours the anionic conduction.

It has to be mentioned that a large surface exposed to the gas phase does not ensure by its own the better performance, as this feature needs to be accompanied by good ionic conductivity (among other features), to avoid the saturation of the *ers* with oxygen species. In the present study, the cycle is completed by the excellent ionic conduction of the GDC phase, along with the better connectivity observed between the GDC spheres. These features together would contribute to deplete and keep active the *ers* on the LSC particle's surface and are the key concept behind the enhanced performance of the LSC-GDC composite cathode.

#### **Notes and references**

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