## Electronic Supplementary Information (ESI)

# Surface Strontium Enrichment on Highly Active Perovskites for Oxygen Electrocatalysis in Solid Oxide Fuel Cells

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#### **Supplementary Methods**

Synthesis of the pulsed laser deposition (PLD) target.<sup>1-3</sup> La<sub>0.8</sub>Sr<sub>0.2</sub>CoO<sub>3- $\delta$ </sub> (LSC) powder for the PLD target was synthesized using solid state reaction from stoichiometric mixtures of La<sub>2</sub>O<sub>3</sub>, SrCO<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub> (Alfa Aeser, USA) and calcined at 1,000 °C in air for 12 hours. The Gd<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2- $\delta$ </sub> (GDC) powder was synthesized via Pechini method using Gd(NO<sub>3</sub>)<sub>3</sub> and Ce(NO<sub>3</sub>)<sub>3</sub>, which were dissolved in a mixture of ethylene glycol and citric acid (Sigma-Aldrich, USA) in de-ionized water. After esterification at ~100 °C, the resin was charred at 400 °C and then calcined at 800 °C in air for 1 hour. Phase purity was confirmed using X-ray powder diffraction (XRD) (Panalytical). Subsequently PLD targets of 25 mm in diameter were formed by uniaxial pressing at ~50 MPa and sintered at 1350 °C in air for 20 hours.

Synthesis of the pellet sample for in situ APXPS. The La<sub>0.8</sub>Sr<sub>0.2</sub>CoO<sub>3- $\delta$ </sub> (LSC) pellet for *in* situ APXPS was synthesised via the Pechini method using La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Sr(NO<sub>3</sub>)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Alfa Aesar) which were dissolved into a mixture of de-ionized water, ethylene glycol, and citric acid (Sigma-Aldrich, USA), followed by esterification at 100 °C, charring the resin at 400 °C and a final calcinations step at 800 °C in air for 1 hour. Phase purity was confirmed using powder XRD (Rigaku). Then, a pellet (25 mm diameter) was prepared by uniaxial pressing at ~50 MPa and sintered at 800 °C in air for 20 hours. Prior to introducing the pellet sample into the APXPS chamber, the pellet was cleaved and the freshly prepared surface was investigated.

*Epitaxial thin film synthesis.* (001)-oriented single crystals of 9.5% mol Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> (YSZ), one-side polished (surface roughness < 1nm) and with the dimensions of 10 mm x 5 mm x 0.5 mm (Princeton Scientific, USA) were used as electrolyte and substrates for the pulsed laser deposition (PLD). The gadolinium-doped ceria (GDC) electrolytic protection layer (for avoiding reaction of YSZ with LSC at high temperature) and the LSC thin films were deposited by PLD using a KrF excimer laser with a wave length,  $\lambda$ , of 248 nm, a pulse frequency, *f*, of 10 Hz, and a pulse energy, *E*, of ~ 50 mJ (measured close to the substrate surface) under and oxygen partial pressure, *p*(O<sub>2</sub>), of 50 mTorr with 500 pulses of GDC (~5 nm, estimated using scanning transmission electron microscopy) at a substrate temperature of ~450 °C, followed by 15,000 pulses of LSC (~85 nm, estimated using atomic force microscopy (AFM, Vecco, USA)) at ~550 °C. Reflection high-energy electron diffraction was utilized to provide *in situ* monitoring of the epitaxial growth of the oxide films.

*Sample Roughness.* AFM was used to visualise the surface morphology of the film after PLD preparation (Fig. S2) and to determine the RMS surface roughness of < 0.5 nm.

*Experimental details of in situ HRXRD. In situ* high resolution XRD was conducted on a four-circle diffractometer (Panalytical) equipped with a controlled temperature stage (DHS 900, Anton Paar) in an oxygen partial pressure,  $p(O_2)$ , of 1 atm (flux ~2 sccm). Silver paste was used to adhere the thin film sample with the YSZ single crystal to the heating plate. Starting at 25 °C, a heating rate of ~10 °C/min was chosen and after

increasing the temperature (temperature steps: 25 °C, 150 °C, 250 °C, 350 °C, 450 °C, and 550 °C) the temperature was always held constant for 20 minutes to reach thermal equilibrium before XRD data were collected. Sample realignment was conducted after each temperature step to optimize the intensity of the YSZ(004) and YSZ(202) peaks for all normal and off-normal scans, respectively. This procedure included the correction of slight de-adjustments due to the thermal expansion of the sample (height offset and angles). After alignment of the YSZ(004), a full range ( $\theta$ -2 $\theta$  = 10° - 120°) *theta*-2*theta* normal scan (0.04 °/step, 2 s/step) was collected first. Subsequently, *theta*-2*theta* normal scans of LSC(002) (0.01 °/step, 3 s/step) and YSZ(202) peak, the off-normal scans of LSC(101) (0.02 °/step, 5 s/step) and YSZ(202) (0.004 °/step, 1 s/step) peaks were obtained. The collection time for the entire sequence was ~4 hours at each temperature. As the thermocouple for this experiment was placed inside the heating stage, a small difference between measured and actual temperatures on the sample surface cannot be ruled out.

Relaxed lattice parameter determination by in situ HRXRD. The Relaxed lattice parameter  $\hat{a}$  is derived from the following equation (where  $\hat{a}$  is the pseudocubic lattice parameter for the film in an unstrained state),<sup>1,4</sup>  $\frac{(c-\hat{c})}{\hat{c}} = \frac{-2v}{1-v}\frac{(a-\hat{a})}{\hat{a}}$ , assuming  $\hat{a} = \hat{c}$  and v = 0.25.<sup>4</sup> The in-plane strain is given by:  $\varepsilon_{aa} = \frac{(a-\hat{a})}{\hat{a}}$  and the out-of-plane strain by:  $\varepsilon_{cc} = \frac{(c-\hat{c})}{\hat{c}}$ , assuming  $\hat{a} = \hat{c}$ .

*Temperature induced peak shift in in situ HRXRD:* Based on Bragg's Law, a shift towards smaller 2 $\theta$ -values with increasing temperature is expected for materials having a positive thermal expansion coefficients, such as LSC, GDC, and YSZ (with increasing temperature the spacing between the planes increases  $(d_{T=25^{\circ}C} < d_{T=520^{\circ}C})$  and thus  $\theta_{T=25^{\circ}C} > \theta_{T=520^{\circ}C}$ ).

Unit cell volume calculation using in situ HRXRD data. The temperature dependence of the LSC and YSZ unit cell volume are shown in Fig. S4. Based on the Y-doping concentration of the used  $ZrO_2$  single crystals (YSZ) their crystal structure is cubic (lattice parameter a = b = c), and thus the lattice parameter, a, can directly be determined from the YSZ (202) reflection. Once a is known, the unit cell volume of YSZ can be calculated as  $a^3$ . LSC is pseudo cubic, where the c-axis lattice parameter can be determined from the LSC (002) reflection, and assuming a- and b-axis lattice parameters are equivalent, they can be determined from the geometrical relationship between the c axis and the LSC (101) reflection. Once c and a = b are determined, the unit cell volume can be obtained by  $c \cdot a^2$ .

The volumetric thermal expansion coefficients (TEC) of the LSC(001) thin film  $(14.9 \cdot 10^{-6} \text{ K}^{-1})$  and of the YSZ substrate  $(8.8 \cdot 10^{-6} \text{ K}^{-1})$  found in this study were in agreement with those reported in literature  $(16.5 \cdot 10^{-6} \text{ K}^{-1})$  for bulk LSC<sup>5</sup> and  $8.5 - 10.8 \cdot 10^{-6} \text{ K}^{-1}$  for

YSZ<sup>6</sup>). Using systematic shifts of LSC (00*l*)<sub>pc</sub> and YSZ (00*l*')<sub>cubic</sub> (*l* = 1, 2, 4 and *l*' = 2, 4) with increasing temperature (Fig. 2b), the out-of-plane lattice parameter of LSC and the cubic YSZ substrate were found, respectively. Considering that off-normal XRD data of LSC(101)<sub>pc</sub> (Fig. S3) allowed the determination of in-plane lattice parameters (assuming *a* = *b*), the LSC unit cell volume and the volumetric thermal expansion were obtained (Fig. S4). It is worth mentioning that the in-plane ( $8.6 \cdot 10^{-6} \text{ K}^{-1}$ ) and out-of-plane ( $27.1 \cdot 10^{-6} \text{ K}^{-1}$ ) TECs of the LSC thin film are considerably different from those of polycrystalline LSC bulk reported in literature,<sup>5</sup> which may be attributed to the presence of strains in the LSC films induced by its mechanical constrain to the YSZ substrate in comparison to nominally strain-free LSC powder.<sup>5</sup>

Experimental details of in situ APXPS. Ambient pressure and high temperature XPS data of the LSC(001) film and the LSC pellet were collected at the Beamlines 9.3.2 and 11.0.2 at Lawrence Berkeley National Laboratory's (LBNL) Advanced Light Source (ALS). The pellet and thin film samples were separately investigated and placed directly onto a ceramic heater, which was held in place by spring loaded Au-Pd coated tungsten tips.<sup>7</sup> The pellet was cleaved before mounting on the sample holder to investigate a freshly prepared surface. No other pre-cleaning (e.g. sputtering the surface) was carried out. A thermocouple was placed directly onto the sample surface for accurate surface temperature measurements. A piece of Au foil was placed on top of part of the sample for binding energy calibration. All binding energies are referenced to the Au 4f at 84.0 eV. The spectra were collected in the following sequence (collection time about 2 h per sequence): low resolution survey (BE = -10 - 595 eV), high resolution O 1s and Au 4f at a photon energy of 700 eV, and C 1s, La 4d, Sr 3d, Co 3p and Au 4f, at a photon energy of 390 eV. These spectra were collected at the following conditions:  $p(O_2) = 6.6 \cdot 10^{-9}$ atm at T = 25 °C,  $p(O_2) = 1 \cdot 10^{-3}$  atm at T = 25 °C,  $p(O_2) = 1 \cdot 10^{-3}$  atm at T = 220 °C,  $p(O_2) = 1 \cdot 10^{-3}$  atm at T = 370 °C,  $p(O_2) = 1 \cdot 10^{-3}$  atm at T = 520 °C,  $p(O_2) = 1 \cdot 10^{-5}$  atm at T = 520 °C,  $p(O_2) = 1 \cdot 10^{-7}$  atm at T = 520 °C. The heating rate was about 10 °C/min and the temperature was held constant for 20 min before beginning to collect data at each temperature. Due to a problem with the beamline intensity while studying the LSC pellet at  $p(O_2) = 1 \cdot 10^{-3}$  atm at T = 370 °C the data was not included.

In situ APXPS: calibration of the binding energy (BE) of the spectra. The BE for the spectra collected at room temperature was calibrated to the C 1s photoemission peak of adventitious hydrocarbons at 285.0 eV. A piece of gold foil was placed on part of the sample surface to assist BE calibration (Au 4f 7/2 = 84.0 eV) when carbon was removed from the surface at elevated temperatures.

In situ APXPS: Determination of the Inelastic-Mean-Free-Path (IMFP). The IMFP was calculated using the NIST Standard Reference Database 71 "NIST Electron Inelastic-Mean-Free-Path Database" version 1.2. The software program provides the ability to predict the IMFP for inorganic compounds supplying the stoichiometric composition of La (0.8), Sr (0.2), Co (1), O (3), the number of valence electrons per molecule (assumed to be 24), the density (6.931 g/cm<sup>3</sup>) and a band gap energy (for which we are assuming 0 eV as LSC is metallic like at high temperatures; additionally when assuming a band gap of an insulator 5 eV, the IMFP increases by ~0.03 nm). For incident photon beam

energies ranging from 300 eV to 1140 eV the IMFP was estimated to be  $\sim$ 0.75 nm to 1.91 nm, respectively.

*Curve fitting of in situ APXPS spectra.* Analysis of the photoemission lines was done after subtracting a Shirley-type background using a combined Gaussian-Lorentzian line shape, and except for Sr 3d and Co 3p symmetric line shape were used for fitting. Additional constraints for fitting the Sr 3d spectra include the Sr  $3d_{5/2}$  and  $3d_{3/2}$  doublet with an energy separation of 1.8 eV and a branching ratio of 1.5. The integrated areas (Casa XPS) for each component were then utilized for the analysis. The *BE*, full-width-half-maximum (FWHM), and integrated area for each component is provided in Table S1. Details about Co 3s peak intensity fitting: The intensity of the Co 3s peak which is overlapping with the La 4d region, is only a fraction of the overall intensity in this region and has been considered by taking the atomic subshell photoionization cross-sections<sup>8</sup> for Co 3s and La 4d into account (*Intensity*<sub>Co 3s</sub> ~  $0.1 \times Intensity$ <sub>La 4d</sub>).

In situ APXPS normalization procedure. Governed by the ideal gas law (pV = nRT with p = pressure, V = volume, n = molar number of molecules, R = ideal gas constant, T = temperature), the amount of gas molecules within the chamber is coupled to both temperature and gas pressure. Therefore as the temperature is elevated, the number of gas molecules needs to be decreased in order to maintain a constant pressure within the APXPS chamber. The reduction in the number of gas molecules will inherently increase the intensity of the X-ray beam and the ejected photoelectrons from the sample surface. In order to remove this artificial intensity increase, a normalization procedure shown in Fig. S10 is utilized. The integrated intensity of the entire elemental region (or the components, respectively) is extracted from the fitting (value shown in Table S2 and S3). To demonstrate the normalization procedure, the raw intensity values for the LSC thin film are plotted versus temperature on the left side of Fig. S10. The integrated intensity areas for each element are divided by the sum of the integrated areas of all elements at the given condition. After obtaining this ratio at each condition, the final normalization step divides the ratio by its respective normalized value at T = 220 °C and  $p(O_2) = 1 \times 10^{-3}$ atm or T = 520 °C and  $p(O_2) = 1 \cdot 10^{-3}$  atm for the temperature and pressure dependant data, respectively. This procedure yields the normalized intensity values shown on the right side of Fig. S10 (which is the same data shown in Fig. 5).

In situ APXPS error analysis: The error bars ( $\Delta I_N$ ) of the normalized area intensities,  $I_N$ , shown in Fig. 4, 5, S9, S10, and S11 were estimated by assuming a standard deviation, *SD*, of 10% for the intensities of as-collected XPS data and fitted components. No error was considered for the XPS photoionization cross-sections,  $\sigma$ . This estimation results in an error of about 14 % for the changes of the individual component of Sr or O relative to that component at 220 °C (Fig. 4 and S9), and an error of about 25 % for the changes in the Sr concentration relative to the combined Sr and O in the perovskite structure (Fig. 5, S10, S11), as shown below.

$$\Delta I_{\rm N} = \sqrt{\left(SD_{\rm Sr \, or \, O}\right)^2 + \left(SD_{\rm Sr \, or \, O(220^\circ \, C)}\right)^2} \approx \pm 14.1\%$$
  
$$\Delta I_{\rm N} = \sqrt{\left(SD_{\rm Sr \, or \, O}\right)^2 + \left(SD_{\rm Sr}\right)^2 + \left(SD_{\rm O}\right)^2 + \left(SD_{\rm Sr \, or \, O(220^\circ \, C)}\right)^2 + \left(SD_{\rm Sr(220^\circ \, C)}\right)^2 + \left(SD_{\rm O(220^\circ \, C)}\right)^2 \approx \pm 24.5\%$$

Thermodynamic Model For Surface Segregation/Enrichment in  $(La,Sr)CoO_{3-\delta}$  (LSC). This model is an extension of the bulk defect model first developed by Lankhorst to describe LSC.<sup>9</sup> Here, we describe the basic bulk (or equivalently, an epitaxial film model) as well as its extension to model surface segregation/enrichment. Finally, we briefly discuss how we obtain the model parameters.

Bulk LSC defect model. The chemical potential of oxygen in the LSC bulk is defined as<sup>9-</sup>

$$\mu_{o}(bulk) - \mu_{o}^{\circ}(bulk) = [h_{o}(bulk) - T \cdot s_{o}(bulk)] - [h_{o}^{\circ}(bulk) - T \cdot s_{o}^{\circ}(bulk)]$$
$$= [h_{o}(bulk) - h_{o}^{\circ}(bulk)] - T [s_{o}(bulk) - s_{o}^{\circ}(bulk)] \dots \dots \dots (1)$$

where *T* is temperature,  $h_o$  and  $s_o$  are the partial molar enthalpy and entropy of O, respectively, and  $h_o^{\circ}$  and  $s_o^{\circ}$  are reference state values for these quantities. Following Lankhorst,<sup>9</sup> the partial molar enthalpy,  $h_o(bulk) - h_o^{\circ}(bulk)$ , and the partial molar entropy of oxygen,  $s_o(bulk) - s_o^{\circ}(bulk)$ , in the LSC bulk can be defined as the following

Where  $k_b$  is the Boltzmann constant,  $\delta^{bulk}$  is the bulk oxygen vacancy content in the perovskite lattice (per 3 oxygen sites),  $x_{Sr}^{bulk}$  is the bulk Sr concentration, and  $g_{bulk}(\varepsilon)$  is the density of states at the Fermi level of the bulk.

At equilibrium between the oxygen gas phase and the LSC solid phase, the chemical potential of the oxygen gas phase is equal to the oxygen chemical potential of the LSC bulk, which yields

$$\frac{1}{2}(\mu_{O_2}(gas) - \mu_{O_2}^{\circ}(gas)) = \mu_O(bulk) - \mu_O^{\circ}(bulk)$$
  

$$\Rightarrow \frac{k_b T}{2} \cdot \ln(P_{O_2}) - \frac{T}{2} \cdot \Delta s_{O_2}^{vib}(gas)$$
  

$$= \Delta h_O^{\circ}(bulk) - 2 \cdot (\frac{2\delta^{bulk} - x_{Sr}^{bulk}}{g_{bulk}(\varepsilon)}) - T\left(k_b \cdot \ln(\frac{\delta_{bulk}}{3 - \delta_{bulk}}) + \Delta s_O^{vib}(solid)\right)....(2)$$

By moving the last term on the left hand side to the right hand side and combining both the solid and gas phase vibrational entropy terms into a new term  $\Delta s_{o}^{\circ} (\Delta s_{o}^{\circ} = \Delta s_{o}^{vib} (solid) - \frac{\Delta s_{o}^{vib} (gas)}{2}), \text{ we obtain}$  $\frac{k_{b}T}{2} \cdot \ln(P_{O_{2}}) = \Delta h_{o}^{\circ} (bulk) - 2 \cdot (\frac{2\delta^{bulk} - x_{Sr}^{bulk}}{g_{bulk} (\varepsilon)}) - T\left(k_{b} \cdot \ln(\frac{\delta_{bulk}}{3 - \delta_{bulk}}) + \Delta s_{o}^{\circ}\right) \dots (3)$ 

*Oxygen vacancy surface segregation.* To model the oxygen surface segregation we write an equivalent to Eqn. (3) for the LSC surface as follows:

$$\frac{1}{2}(\mu_{0_2}(gas) - \mu_{0_2}^{\circ}(gas)) = \mu_0(surf) - \mu_0^{\circ}(surf) = [h_0(surf) - h_0^{\circ}(surf)] - T[s_0(surf) - s_0^{\circ}(surf)]$$

$$\Rightarrow \frac{k_b T}{2} \cdot \ln(P_{O_2}) - \frac{T}{2} \cdot \Delta s_{O_2}^{vib}(gas) = \Delta h_O^{\circ}(surf) - 2 \cdot \left(\frac{2\delta^{surf} - x_{Sr}^{surf}}{g_{surf}(\varepsilon)}\right) - T\left(k_b \cdot \ln(\frac{\delta_{surf}}{3 - \delta_{surf}}) + \Delta s_O^{vib}(solid)\right)$$

$$\Rightarrow \Delta h_{O}^{\circ}(surf) - 2 \cdot \left(\frac{2\delta^{surf} - x_{Sr}^{surf}}{g_{surf}(\varepsilon)}\right) - T\left(k_{b} \cdot \ln\left(\frac{\delta_{surf}}{3 - \delta_{surf}}\right) + \Delta s_{O}^{\circ}\right) = \frac{k_{b}T}{2} \cdot \ln(P_{O_{2}}) \quad \dots (4)$$

Where  $\delta^{surf}$  is the surface oxygen vacancy content in the perovskite lattice,  $x_{Sr}^{surf}$  is the surface Sr concentration,  $g_{surf}(\varepsilon)$  is the density of states at the Fermi level of the surface. The driving force for the O vacancy surface segregation can be obtained by subtracting Eqn.(3) from Eqn.(4), and the following equation describes the O vacancy surface segregation:

$$k_{b}T \cdot \ln(\frac{3-\delta_{bulk}}{\delta_{bulk}} \cdot \frac{\delta_{surf}}{3-\delta_{surf}}) = -\Delta E_{O_{vac}}^{seg} - 2 \cdot (\frac{2\delta_{surf} - x_{Sr}^{surf}}{g_{surf}(\varepsilon)} - \frac{2\delta_{bulk} - x_{Sr}^{bulk}}{g_{bulk}(\varepsilon)}) \quad \dots \quad (5)$$
  
Where  $\Delta E_{O_{vac}}^{seg} = \Delta h_{O}^{\circ}(surf) - \Delta h_{O}^{\circ}(bulk)$ . Note that it is the value of  $\Delta E_{O_{vac}}^{seg} = \Delta h_{O}^{\circ}(surf) - \Delta h_{O}^{\circ}(bulk)$  that will drive the surface segregation. Also, for clarity, note that the  $a(x)$  term in Lankhorst<sup>9</sup> is equal to  $4/g_{bulk}(\varepsilon)$ 

*Sr surface segregation/enrichment.* The chemical potential of Sr in the LSC bulk can be written as

$$\mu_{\rm Sr}(bulk) - \mu_{\rm Sr}^{\circ}(bulk) = \Delta \mu_{\rm Sr}^{\circ}(bulk) = \Delta h_{\rm Sr}^{\circ}(bulk) + h_{\rm Sr}^{\rm nonideal}(bulk) + k_b T \cdot \ln(\frac{x_{\rm Sr}^{\rm outk}}{1 - x_{\rm Sr}^{\rm bulk}}) \quad \dots (6)$$

where  $h_{\text{Sr}}^{\text{nonideal}}(bulk) = \frac{(x_{\text{Sr}}^{bulk} - 2\delta_{bulk})}{g_{bulk}(\varepsilon)}$ . Similarly, for the chemical potential of Sr at the

LSC surface can be written as

$$\mu_{\rm Sr}^{\rm surf} = \Delta h_{\rm Sr}^{\circ}(surf) + h_{\rm Sr}^{\rm nonideal}(surf) + k_b T \cdot \ln(\frac{x_{\rm Sr}^{\rm surf}}{1 - x_{\rm Sr}^{\rm surf}}) \dots (7)$$

where  $h_{Sr}^{nonideal}(surf) = \frac{(x_{Sr}^{surf} - 2\delta_{surf})}{g_{surf}(\varepsilon)}$ . Note here we assume the difference of the

vibrational contribution in the Sr chemical potential between the LSC bulk and surfaces very small so that the vibrational contribution can be neglected in the Sr segregation reaction. The driving force for the Sr surface segregation can be obtained by subtracting Eqn.(6) from Eqn.(7), and the following equation describes the Sr surface segregation

$$k_{b}T \cdot \ln(\frac{x_{Sr}^{bulk}}{1-x_{Sr}^{bulk}} \cdot \frac{1-x_{Sr}^{surf}}{x_{Sr}^{surf}}) = \Delta E_{Sr}^{seg} - (\frac{2\delta_{surf} - x_{Sr}^{surf}}{g_{surf}(\varepsilon)} - \frac{2\delta_{bulk} - x_{Sr}^{bulk}}{g_{bulk}(\varepsilon)}).....(8)$$
  
where  $\Delta E_{Sr}^{seg} = \Delta h_{Sr}^{\circ}(surf) - \Delta h_{Sr}^{\circ}(bulk)$ .

Obtaining model parameters. Combining Eqn.(5) and Eqn.(8), one can solve for the surface oxygen vacancy,  $\delta_{surf}$ , and surface Sr concentration,  $x_{Sr}^{surf}$  as a function of parameters of  $\Delta E_{O_vac}^{seg}$ ,  $\Delta E_{Sr}^{seg}$ ,  $g_{bulk}(\varepsilon)$ ,  $g_{surf}(\varepsilon)$ ,  $x_{Sr}^{bulk}$  and  $\delta_{bulk}$  for a given T and  $p(O_2)$ . The model parameters of the LSC bulk<sup>9-11</sup> and epitaxial films<sup>2</sup> have been reported in the literature and are used in our model, and we assumed  $g_{surf}(\varepsilon) = g_{bulk}(\varepsilon)$ . This leaves two undetermined variables,  $\Delta E_{O_vac}^{seg}$  and  $\Delta E_{Sr}^{seg}$  which are used to fit with the experimental data for the epitaxial LSC thin film (Fig. S11). Our fit to the data yielded the fitted values:  $\Delta E_{O_vac}^{seg} = -1.28 \text{ eV}$ , and  $\Delta E_{Sr}^{seg} = 0.35 \text{ eV}$ .

Temperature	Constrained in-plane lattice parameter <i>a</i> (Å)	Constrained out-of-plane lattice parameter c (Å)	Relaxed film lattice parameter â (Å)	In-plane strain $\varepsilon_{aa} = \frac{(a-\hat{a})}{\hat{a}}$	Out-of-plane strain $\varepsilon_{cc} = \frac{(c-\hat{c})}{\hat{c}}$
25 °C	3.871	3.852	3.860	0.30 %	-0.20 %
250 °C	3.878	3.875	3.876	0.06 %	-0.04 %
350 °C	3.882	3.886	3.884	-0.06 %	0.04 %
450 °C	3.886	3.897	3.892	-0.17 %	0.12 %
550 °C	3.889	3.907	3.900	-0.29 %	0.19 %

# **Table S1.** Constrained and relaxed lattice parameters of the LSC film extracted from normal and off-normal HRXRD data as temperature was increased from 25 °C to 550 °C.

Photon Energy	Name	LSC Film					
		BE (eV)	FWHM (eV)	Area			
300 eV	Sr 3d 5/2 - Surface	133.7	1.6	19373.7			
	Sr 3d 3/2 - Surface	135.5	1.5	12915.8			
	Sr 3d 5/2 - Lattice	132.3	1.4	3274.3			
	Sr 3d 3/2 - Lattice	134.1	1.4	2180.6			
480 eV	Sr 3d 5/2 - Surface	133.8	1.5	32394.5			
	Sr 3d 3/2 - Surface	135.6	1.6	21596.3			
	Sr 3d 5/2 - Lattice	132.3	1.5	12000.0			
	Sr 3d 3/2 - Lattice	134.1	1.6	7991.9			
740 eV	Sr 3d 5/2 - Surface	134.0	1.6	12315.2			
	Sr 3d 3/2 - Surface	135.8	1.5	8210.2			
	Sr 3d 5/2 - Lattice	132.3	1.4	5500.0			
	Sr 3d 3/2 - Lattice	134.1	1.5	3662.9			
700 eV	O 1s - Surface	531.8	1.8	25124.4			
	O 1s - Surface (M-O)	530.2	1.3	11491.0			
	O 1s - Lattice	528.9	1.3	13168.3			
880 eV	O 1s - Surface	531.8	1.8	13400.8			
	O 1s - Surface (M-O)	530.2	1.3	7763.4			
	O 1s - Lattice	528.9	1.2	11069.6			
1140 eV	O 1s - Surface	531.9	1.8	2951.0			
	O 1s - Surface (M-O)	530.2	1.4	1786.6			
	O 1s - Lattice	529.0	1.4	3839.2			

 Table S2. Detailed photon energy depth resolved XPS peak positions and information on the fitting parameters

	Nama	LSC Pellet			LSC Film		
	ivanic	BE (eV)	FWHM (eV)	Area	BE (eV)	FWHM (eV)	Area
$T = 220 \text{ °C}, p(O_2) = 1 \cdot 10^{-3} \text{ atm}$	O 1s - Surface	531.6	1.8	415.7	531.5	1.7	1699.1
	O 1s - Surface (M-O)	530.3	1.8	50.3	530.2	1.4	120.3
	O 1s - Lattice	528.6	1.5	145.5	528.6	1.5	1165.2
	C 1s - Carbonates, O-C=O	289.4	2.0	15.9	289.1	2.0	39.0
	C 1s - C-O	287.2	2.0	13.9	286.8	2.0	24.5
	C 1s - Adventitious	285.0	1.8	12.9	284.9	1.7	8.5
	La 4d	-	-	205.3	-	-	2999.4
	Co 3s	102.9	2.5	25.0	102.9	2.2	140.0
	Sr 3d 5/2 - Surface	133.6	1.7	539.9	133.6	1.7	1763.5
	Sr 3d 3/2 - Surface	135.4	1.8	360.0	135.4	1.7	1175.7
	Sr 3d 5/2 - Lattice	132.3	1.3	211.0	131.9	1.3	569.9
	Sr 3d 3/2 - Lattice	134.1	1.5	140.5	133.7	1.4	379.5
	Co 3p	-	-	90.5	-	-	553.1
	Na 2s	-	-	11.5	-	-	12.3
$T = 370 \text{ °C}, p(O_2) = 1 \cdot 10^{-3} \text{ atm}$	O 1s - Surface	NA	NA	NA	531.7	1.8	1758.3
	O 1s - Surface (M-O)	NA	NA	NA	530.2	1.4	205.3
	O 1s - Lattice	NA	NA	NA	528.7	1.5	1542.6
	C 1s - Carbonates, O-C=O	NA	NA	NA	288.6	2.0	18.6
	C 1s - C-O	NA	NA	NA	286.8	2.0	27.7
	C 1s - Adventitious	NA	NA	NA	284.9	1.8	17.6
	La 4d	NA	NA	NA	-	-	3474.1
	Co 3s	NA	NA	NA	102.9	2.5	175.0
	Sr 3d 5/2 - Surface	NA	NA	NA	133.6	1.9	1621.2
	Sr 3d 3/2 - Surface	NA	NA	NA	135.4	1.9	1080.8
	Sr 3d 5/2 - Lattice	NA	NA	NA	132.4	1.5	994.8
	Sr 3d 3/2 - Lattice	NA	NA	NA	134.2	1.5	662.6
	Co 3p	NA	NA	NA	-	-	631.7
	Na 2s	NA	NA	NA	-	-	78.0
$T = 520 \text{ °C}, p(O_2) = 1 \cdot 10^{-3} \text{ atm}$	O 1s - Surface	531.8	2.2	539.3	531.7	1.0	58.7
	O 1s - Surface (M-O)	530.2	1.4	143.1	530.1	1.5	706.0
	O 1s - Lattice	528.9	1.7	335.8	528.8	1.5	2305.9
	C 1s - Carbonates, O-C=O	289.5	2.0	33.0	288.8	1.0	2.8
	C 1s - C-O	287.2	2.0	22.3	286.7	2.0	27.8
	C 1s - Adventitious	285.3	2.0	10.7	284.9	2.0	35.5
	La 4d	-	-	336.4	-	-	3453.1
	Co 3s	102.9	2.5	27.0	102.9	2.5	147.0
	Sr 3d 5/2 - Surface	133.8	1.8	1080.4	133.5	1.3	1085.5
	Sr 3d 3/2 - Surface	135.6	1.9	720.3	135.3	1.4	723.7
	Sr 3d 5/2 - Lattice	132.6	1.3	470.1	132.4	1.5	2230.8
	Sr 3d 3/2 - Lattice	134.4	1.4	313.1	134.2	1.4	1485.7
	Co 3p	-	-	112.7	-	-	569.7
	Na 2s	-	-	1.7	-	-	18.1
$T = 520 ^{\circ}\text{C}, p(\text{O}_2) = 1 \cdot 10^{-5}  \text{atm}$	O 1s - Surface	531.8	2.2	875.2	531.4	1.9	481.1
	O 1s - Surface (M-O)	530.3	1.4	285.9	530.2	1.4	1311.7
	O 1s - Lattice	528.8	1.7	646.2	528.8	1.6	5045.0
	C 1s - Carbonates, O-C=O	289.4	2.0	60.6	288.9	2.0	146.2

## Table S3. Detailed XPS peak positions and information on the fitting parameters

	C 1s - C-O	287.2	2.0	50.7	286.8	2.0	166.8
	C 1s - Adventitious	285.3	1.8	20.1	284.8	2.0	97.2
	La 4d	-	-	483.6	-	-	7037.2
	Co 3s	102.9	2.5	47.0	102.9	2.5	290.0
	Sr 3d 5/2 - Surface	133.6	1.8	1936.2	133.6	1.7	4719.3
	Sr 3d 3/2 - Surface	135.4	1.9	1290.8	135.3	1.8	3146.2
	Sr 3d 5/2 - Lattice	132.6	1.2	617.5	132.6	1.5	3009.2
	Sr 3d 3/2 - Lattice	134.4	1.1	411.3	134.4	1.4	2004.2
	Co 3p	-	-	185.3	-	-	1141.0
	Na 2s	-	-	2.9	-	-	25.0
$T = 520 \text{ °C}, p(O_2) = 1 \cdot 10^{-7} \text{ atm}$	O 1s - Surface	531.9	2.2	733.6	531.4	1.8	346.9
	O 1s - Surface (M-O)	530.4	1.4	303.4	530.2	1.3	1199.0
	O 1s - Lattice	528.9	1.7	721.6	528.8	1.6	5310.1
	C 1s - Carbonates, O-C=O	289.5	2.0	65.9	288.9	2.0	171.3
	C 1s - C-O	287.2	2.0	53.6	286.8	2.0	190.4
	C 1s - Adventitious	285.3	1.7	19.9	284.9	2.0	100.5
	La 4d	-	-	520.9	-	-	6923.9
	Co 3s	102.9	2.5	50.0	102.9	2.5	300.0
	Sr 3d 5/2 - Surface	133.7	1.8	1915.3	133.4	1.7	5252.1
	Sr 3d 3/2 - Surface	135.4	1.9	1276.9	135.1	1.8	3501.4
	Sr 3d 5/2 - Lattice	134.5	1.1	377.2	132.5	1.5	3144.1
	Sr 3d 3/2 - Lattice	132.7	1.3	566.3	134.3	1.4	2093.9
	Co 3p	-	-	198.3	-	-	1183.2
	Na 2s	-	-	3.0	-	-	30.6



**Fig. S1:** Schematic of the in-plane crystallographic relationship between the  $LSC(001)_{pc}$ , GDC(001)<sub>cubic</sub>, and YSZ(001)<sub>cubic</sub>: a cube-on-cube alignment of YSZ and GDC and a 45° rotation of GDC and LSC along the (001) axis. This rotational relationship has been determined by off-normal *phi*-scans (HRXRD).<sup>1</sup>



**Fig. S2:** Atomic force microscopy (AFM) image of the as-prepared LSC(001) thin film surface revealing a surface roughness <0.5 nm. The maximum height of this image (dark colour to white) is 20 nm.



**Fig. S3:** *In situ* HRXRD data of the off-normal LSC(101)<sub>pc</sub> as a function of temperature in a  $p(O_2)$  of 1 atm. Here, we observe the peak shifts towards lower angle in the *theta*-2*theta* with increasing temperature from 25 °C to 550 °C.



**Fig. S4:** In situ HRXRD data of the unit cell volume of the epitaxial  $(001)_{pc}$ -LSC thin film and the single crystalline  $(001)_{cubic}$ -YSZ substrate as a function of temperature in a  $p(O_2)$  of 1 atm. The "LSC measured" curve represents the *a* and *c*-lattice parameters directly measured from the HRXRD, while the "LSC relaxed" curve uses Poisson's ratio to extrapolate an unstrained (relaxed) unit cell volume. As a reference, an extrapolated unit cell volume for LSC powder as a function of temperature is provided utilizing a room temperature pseudo cubic lattice parameter of  $a_{pc} = 3.837$  Å<sup>12</sup> and thermal expansion coefficient of  $16.5 \cdot 10^{-6}$  K<sup>-1</sup>.<sup>5</sup>



**Fig. S5:** Schematic detailing the "surface" and "lattice" of LSC. The term "surface" (marked in green) includes secondary phases on the surface, such as oxides and hydroxides of the cations La, Sr, and Co or other non-perovskite  $La_vSr_wCo_xO_yH_z$  phases, and the termination layer of LSC. The term "lattice" is used for regular bonded atoms in the perovskite structure (marked in red). The probed "lattice" is a surface near region of about 2 nm in depth. This distinction between "surface" and "lattice" is based on the ability of XPS to separate between these two components based on different binding energies (*BE*).



**Fig. S6:** In situ APXPS data of the C 1s region ( $E_{photon}$ = 390 eV) as a function of oxygen partial pressure and temperature. Increasing the oxygen partial pressure from UHV (~1·10<sup>-9</sup> atm) to 1·10<sup>-3</sup> atm, the amount of carbon on the surface of (a) the LSC thin film and (b) the LSC pellet are slightly reduced. By elevating the temperature from 25 °C to 220 °C at this pressure (1·10<sup>-3</sup> atm) both surfaces are nearly carbon free. The component at lowest binding energy (*BE*) correlates to adventitious carbon (orange, 285.0 eV), the highest *BE* component is assigned to carbonates (purple), the component at about 286 eV is assigned to C-O species (green), (white circles: measured data, blue line: sum of fits, grey dotted line: background).



**Fig. S7:** In situ APXPS data of the LSC film and pellet as a function of temperature. (a) Film La 4d ( $E_{photon}$ = 390 eV) and (b) Co 3p ( $E_{photon}$ = 390 eV), (c) pellet La 4d and (d) Co 3p at 220 °C, 370 °C (film only), and 520 °C in  $p(O_2) = 1 \cdot 10^{-3}$  atm (white circles: measured data, grey dotted line: background). It is interesting to note that a small feature at ~64.5 eV appeared for the thin film and pellet at 370 °C and 220 °C, respectively, which disappeared upon further heating to 520 °C. Understanding the physical origin of this feature requires further studies, which could be related to a change in the oxidation state of cobalt and/or the (dis)appearance of a sodium impurity (Na 2s at ~ 64.2 eV).<sup>13</sup>



**Fig. S8a-d:** In situ APXPS data of the LSC thin film oxygen partial pressure dependency at T = 520 °C: (a) La 4d ( $E_{photon} = 390$  eV), (b) Sr 3d ( $E_{photon} = 390$  eV), (c) Co 3p ( $E_{photon} = 390$  eV), and (d) O 1s ( $E_{photon} = 700$  eV). For the Sr 3d and O 1s the "lattice" component of the perovskite is shown in red, while the "surface" component (secondary phases on the surface and LSC's termination layer) is shown in green. (White circles: measured data, blue line for O1s: sum of fits, grey dotted line: background).



**Fig. S8e-h:** In situ APXPS data of the LSC pellet oxygen partial pressure dependency at T = 520 °C: (e) La 4d ( $E_{photon} = 390 \text{ eV}$ ), (f) Sr 3d ( $E_{photon} = 390 \text{ eV}$ ), (g) Co 3p ( $E_{photon} = 390 \text{ eV}$ ), and (h) O 1s ( $E_{photon} = 700 \text{ eV}$ ). For the Sr 3d and O 1s, the "lattice" component of the perovskite is shown in red, while the "surface" component (secondary phases on the surface and LSC's termination layer) is shown in green. (White circles: measured data, blue line for Sr 3d: sum of fits, grey dotted line: background).



**Fig. S9:** *In situ* APXPS data of the LSC film and pellet as a function of oxygen partial pressure. Normalized\* change in the Sr and O intensity (lattice: red, surface: green) with decreasing  $p(O_2)$  for (a) the film and (b) the pellet. The error bars have been estimated by assuming a standard deviation of the raw intensity of 10 %. (\* Normalization procedure: first, the raw intensities of the Sr and O "lattice" (or "surface" component, respectively) are divided by the photo-ionization cross sections of Sr or O, respectively. Second, the obtained values are normalized by the initial value, *i.e.* divided by the obtained value at  $p(O_2) = 1 \cdot 10^{-3}$  atm and T = 520 °C).



<u>Definitions</u> (X<sub>i</sub> =n<sub>intensity</sub> / y<sub>xps-cross-section</sub>)

**Fig. S10a:** Procedure to convert the raw data (shown on the left hand side) into the normalized data (shown on the right hand side) for the LSC thin film. As shown in the equations, first the raw intensities, *I*, are divided by the photo-ionization cross sections,  $\sigma$ , of the respective elements. Second, these cross-section-normalized intensity,  $I_{\sigma}$ , values are divided by the sum of all depicted values in each graph at each temperature. Third, the obtained values,  $I_{N,\sigma}$ , are normalized to the first condition, i.e. to the value at T = 220 °C and  $p(O_2) = 1 \cdot 10^{-3}$  atm. This procedure is utilized for the total elemental regions (La 4d–Co 3s, Sr 3d, Co 3p, O 1s, depicted in the first line), for the Sr and O "lattice" component (second line), and for the Sr and O "surface" component (third line).



**Fig. S10b:** Procedure to convert the raw data (shown on the left hand side) into the normalized data (shown on the right hand side) for the LSC pellet, which is identical to the procedure used for the film (**Fig. S10a**). As shown in the equations, first the raw intensities, *I*, are divided by the photo-ionization cross sections of the respective elements. Second, these cross-section-normalized intensity values,  $I_{\sigma}$ , are divided by the sum of all depicted values in each graph. Third, the obtained values are normalized,  $I_{N,\sigma}$ , to the first condition, i.e. to the value at T = 220 °C and  $p(O_2) = 1 \cdot 10^{-3}$  atm. This procedure is utilized for the total elemental regions (La 4d–Co 3s, Sr 3d, Co 3p, O 1s, depicted in the first line), for the Sr and O "lattice" component (second line), and for the Sr and O "surface" component (third line).



**Fig. S11:** Normalized "lattice" Sr and O (red) with increasing temperature at  $p(O_2) = 1 \cdot 10^{-3}$  atm for the epitaxial thin film (as shown in Fig. 5) with corresponding predicted values by the modified canonical Lankhorst model<sup>9</sup> (black). (\* Data normalization procedure: first, the raw intensities of the Sr and O "lattice" are divided by the photo-ionization cross sections of Sr or O, respectively. Second, these cross-section-normalized intensity values for Sr or O "lattice" are divided by the sum of these values (Sr + O "lattice") at each  $p(O_2)$  condition. Third, the obtained values are normalized by the initial value, i.e. divided by the obtained value at  $p(O_2) = 1 \cdot 10^{-3}$  atm and T = 220 °C. Model normalization procedure: the obtained value are normalized by the initial value, *i.e.* divided by the obtained value at  $p(O_2) = 1 \cdot 10^{-3}$  atm and T = 220 °C.



Fig. S12: Schematic showing the influence of the amount of Sr-rich secondary phases on the LSC surface on the ORR activity. For a full coverage with an insulating Sr-rich surface phase no ORR activity is expected.<sup>3</sup> A hypothetically secondary free LSC surface has a certain, higher ORR activity. For partial coverages two cases are possible and have been reported in literature: (I) a different ORR mechanism occurs for partial coverage leading to a higher ORR activity than for a film without coverage,<sup>3</sup> (II) the part of the surface covered with secondary phases is blocked for oxygen exchange, while the particle-free surface contributes to the oxygen exchange leading to an ORR activity between full and no coverage.<sup>16</sup> Depending on the present phase or the specific mixture of phases  $(SrO/Sr(OH)_2/SrCO_3/Sr_xX_yO)$  and potential solid state reactions forming new phases (e.g. La,Sr)\_2CoO<sub>4</sub><sup>2,3</sup> both cases can occur in this system.<sup>2, 3, 16</sup> A possible location of the pellet (grey) and the film (yellow) investigated in this study is marked: based on previous ORR measurements we can exclude a full coverage, and XPS exhibited that both samples have a certain amount of coverage. Compared to the pellet, the film showed lower coverage and higher ORR activity. As reported previously,<sup>3</sup> a certain Sr-rich surface decoration is more ORR active than the unmodified LSC film surface, therefore the film is not located at the maximum of the ORR-coverage curve.

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