Supplementary Information

Oxygen surface exchange kinetics of $La_{1-x}Sr_xCoO_{3-\delta}$ thin-films decorated with binary oxides: links between acidity, strontium doping, and reaction kinetics.

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Supplementary Note 1: X-Ray Diffractograms of $La_{1-x}Sr_xCoO_{3-\delta}$ targets

The measurement are carried on a Bruker D8 advance diffractometer in Bragg-Brentano geometry. The X-ray source is a copper anode source with emission wavelength of 1.5406 Å and 1.5418 Å. The detector is a LynxEye detector with a germanium monochromator selecting the 1.5406 Å wavelength of the emission.

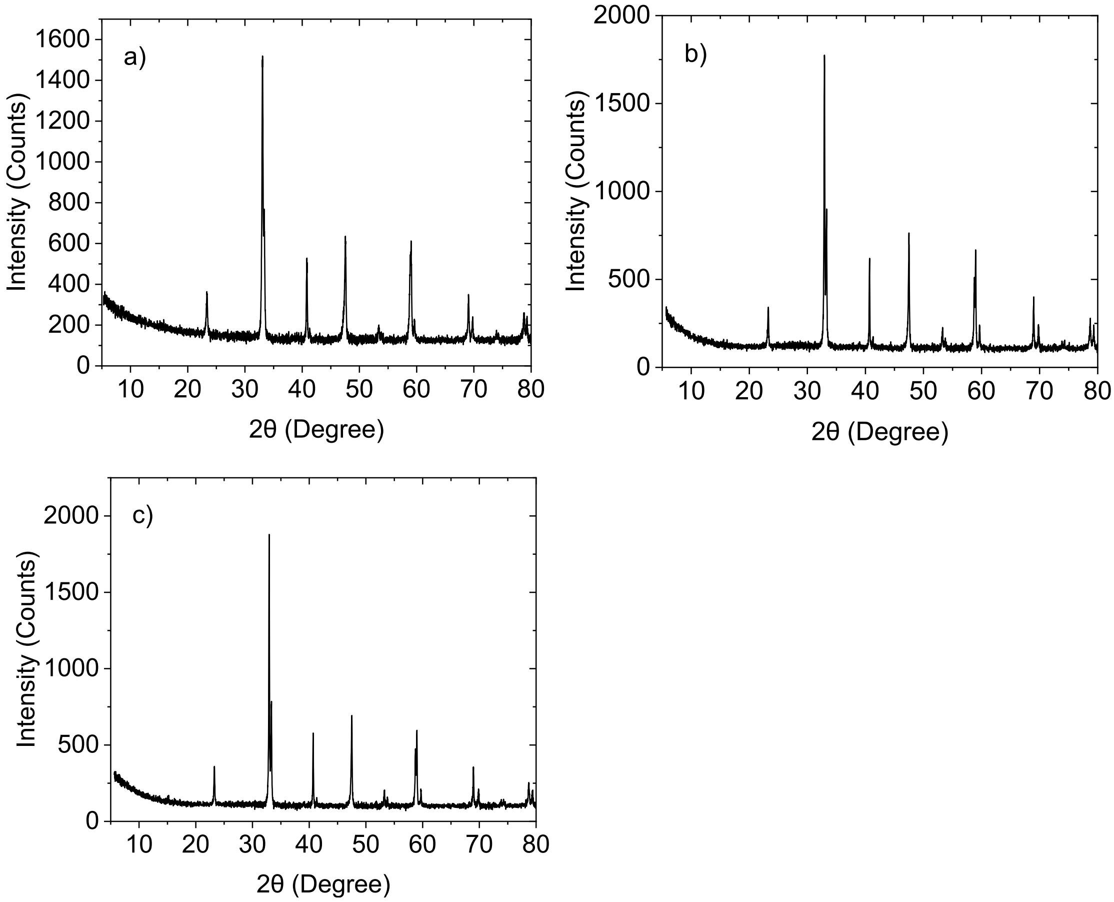

Figure S1. Diffractogram of $La_{1-x}Sr_xCoO_{3-\delta}$ compositions a) $La_{0.95}Sr_{0.05}Co_{1.00}O_{3-\delta}$ b) $La_{0.90}Sr_{0.10}Co_{1.00}O_{3-\delta}$ and c) $La_{0.80}Sr_{0.20}Co_{1.00}O_{3-\delta}$ with a 2θ from 5 to 80°.

Supplementary Note 2: Targets composition verification

The composition of the different pellets is verified by ICP-AES. The pellet is dissolved in 10 % HNO3. The concentration of Co in the solution is used as reference for Sr and La content. Controlled concentration of standard are added to the solution. The standard used are Cobalt standard solution 1000 µg/mL (Plasma HIQU), Strontium standard solution 1000 µg/mL (Plasma HIQU) and Lanthanum standard solution 1000 µg/mL (Plasma HIQU) from Chem-lab, Belgium.

Sample	Sr	La
$La_{0.95}Sr_{0.5}Co_{1.00}O_{3-\delta}$	0.049 (1)	0.950 (9)
$La_{0.9}Sr_{0.10}Co_{1.00}O_{3-\delta}$	0.100 (1)	0.899 (9)
$La_{0.80}Sr_{0.20}Co_{1.00}O_{3-\delta}$	0.199 (7)	0.800 (2)

Supplementary Note 3: Vacancies concentration variation with oxygen partial pressure and temperature evolution

The used oxygen concentrations, c_o, and vacancies concentrations, c_v, are calculated considering only the dopant effect. The variation of these concentrations with temperature and pO_2 in this part are determined. The determination of these quantities is carried out using the Equation S1 from Kawada et al.[1] for the pristine samples of $La_{0.80}Sr_{0.20}CoO_{3-\delta}$, $La_{0.9}Sr_{0.10}CoO_{3-\delta}$ and $La_{0.95}Sr_{0.05}CoO_{3-\delta}$.

$$C_v = \frac{C_{dop}}{4} - \frac{C_{chem}k_BT}{8e^2} \pm \sqrt{\frac{C_{dop}C_{chem}k_BT}{8e^2} + \left(-\frac{C_{dop}}{4} + \frac{C_{chem}k_BT}{8e^2}\right)^2} \qquad \text{S1}$$

c_v is calculated using the chemical capacitance of the thin-film, C_{chem}, the dopant concentration, C_{dop}, the temperature of the thin-film, T. The obtained results are represented in Table 1 as well as the variation calculated with for the pristine samples of the three compositions:

	Temperature dependence				
	1000/T K^{-1}	Co (C_{chem}) cm^{-3}	Cv (C_{chem}) cm^{-3}	Co variation (%)	Cv variation (%)
$La_{0.80}Sr_{0.20}CoO_{3-\delta}$ c_v (dop) = 8.59993E+20 cm^{-3} c_o (dop)= 5.07396E+22 cm^{-3}	1.13	5.07521E+22	8.725E+20	0.02	1.4
	1.19	5.07500E+22	8.704E+20	0.02	1.2
	1.21	5.07495E+22	8.699E+20	0.02	1.1
	1.29	5.07481E+22	8.685E+20	0.02	1.0
$La_{0.9}Sr_{0.10}CoO_{3-\delta}$ c_v (dop) = 4.300E+20 cm^{-3} c_o = 5.11696E+22 cm^{-3}	1.29	5.11759E+22	4.363E+20	0.01	1.5
	1.23	5.11766E+22	4.370E+20	0.01	1.6
	1.17	5.11772E+22	4.376E+20	0.01	1.8
	1.14	5.11777E+22	4.381E+20	0.02	1.9
$La_{0.95}Sr_{0.5}CoO_{3-\delta}$ c_v (dop) = 2.14998E+20 cm^{-3} c_o (dop) = 5.13846E+22 cm^{-3}	1.14	5.13933E+22	2.237E+20	0.02	4.0
	1.17	5.13927E+22	2.231E+20	0.02	3.8
	1.22	5.13920E+22	2.224E+20	0.01	3.5
	1.29	5.13916E+22	2.220E+20	0.01	3.2

Table 1. Variation of the vacancy concentration with the temperature change between 500°C and 600°C

	pO2 dependence				
	PO2 (mbar)	Co (C_{chem}) cm^{-3}	Cv (C_{chem}) cm^{-3}	Co variation (%)	Cv variation (%)
$La_{0.80}Sr_{0.20}CoO_{3-\delta}$	0.01	5.07535E+22	8.739E+20	0.03	1.6
c_v (dop) = 8.59993E+20 cm^{-3}	0.04	5.07519E+22	8.723E+20	0.02	1.4
c_o (dop)= 5.07396E+22 cm^{-3}	0.1	5.07512E+22	8.716E+20	0.02	1.3
	1	5.07493E+22	8.697E+20	0.02	1.1
	10	5.07491E+22	8.695E+20	0.02	1.1
	100	5.07434E+22	8.638E+20	0.01	0.4
$La_{0.9}Sr_{0.10}CoO_{3-\delta}$	0.01	5.11786E+22	4.390E+20	0.02	2.1
c_v (dop) = 4.300E+20 cm^{-3}	0.04	5.11779E+22	4.383E+20	0.02	1.9
c_o = 5.11696E+22 cm^{-3}	0.1	5.11776E+22	4.380E+20	0.02	1.9
	1	5.11776E+22	4.380E+20	0.02	1.9
	10	5.11749E+22	4.353E+20	0.01	1.2
	100	5.11746E+22	4.350E+20	0.01	1.2
$La_{0.95}Sr_{0.5}CoO_{3-\delta}$	0.01	5.13942E+22	2.246E+20	0.02	4.4
c_v (dop) = 2.14998E+20 cm^{-3}	0.04	5.13936E+22	2.240E+20	0.02	4.2
c_o (dop) = 5.13846E+22 cm^{-3}	0.1	5.13931E+22	2.235E+20	0.02	4.0
	1	5.13923E+22	2.227E+20	0.01	3.6
	10	5.13927E+22	2.231E+20	0.02	3.8
	100	5.13919E+22	2.223E+20	0.01	3.4

Table 2. Variation of the vacancy concentration with the oxygen partial pressure change between 0.01 mbar and 100 mbar.

Supplementary Note 4: Determination of measure deviation

Determination of standard variation of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ in the measurement setup from previous articles:

$La_{0.60}Sr_{0.40}Co_{1.00}O_{3-\delta}$ at 600C and 0.04 mbar	
Article	ASR ($\Omega.cm^2$)
Siebenhofer et al.[2]	1.35
	1.35
	1.73
Siebenhofer et al.[3]	1.53
	1.37
	1.30
	1.83
Siebenhofer et al.[4]	1.33
	1.34
	1.52
	1.58
	1.69
Siebenhofer et al.[5]	1.80
	1.30
Average ($\Omega.cm^2$)	1.50
standard deviation ($\Omega.cm^2$)	0.19
standard deviation (%)	13

References:

1. Kawada, T. *et al.* Determination of Oxygen Vacancy Concentration in a Thin Film of La0.6Sr0.4CoO3À by an Electrochemical Method. *Journal of The Electrochemical Society*.
2. Siebenhofer, M. *et al.* Engineering surface dipoles on mixed conducting oxides with ultra-thin oxide decoration layers. *Nat Commun* **15**, 1730 (2024).
3. Siebenhofer, M. *et al.* Investigating oxygen reduction pathways on pristine SOFC cathode surfaces by *in situ* PLD impedance spectroscopy. *J. Mater. Chem. A* **10**, 2305–2319 (2022).
4. Siebenhofer, M. *et al.* Improving and degrading the oxygen exchange kinetics of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ by Sr decoration. *J. Mater. Chem. A* **11**, 12827–12836 (2023).
5. Siebenhofer, M. *et al.* Surface Chemistry and Degradation Processes of Dense $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ Thin Film Electrodes. *J. Electrochem. Soc.* **170**, 014501 (2023).