

† Electronic Supplementary Information (ESI) available: [Determination of oxygen adsorption-desorption rates and diffusion rate coefficients in perovskites at different oxygen partial pressures by a microkinetic approach..]. See DOI: 10.1039/b000000x/

1) XRD after crushing of the sample

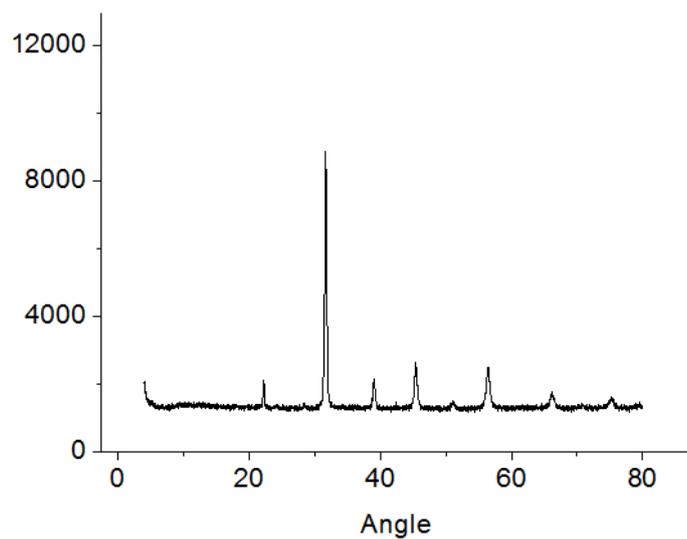


Figure S- 1 XRD analysis on BSCF before analysis

2) Solid density

$$\rho = \frac{M_i}{N_a \times V_c}$$

M_i is the molar weight of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ in $\text{g}\cdot\text{mol}^{-1}$, with δ measured by iodometric titration at room temperature, N_a is the Avogadro constant in mol^{-1} , and V_c is the volume of an elementary cell.

3) SSITKA experimental bench

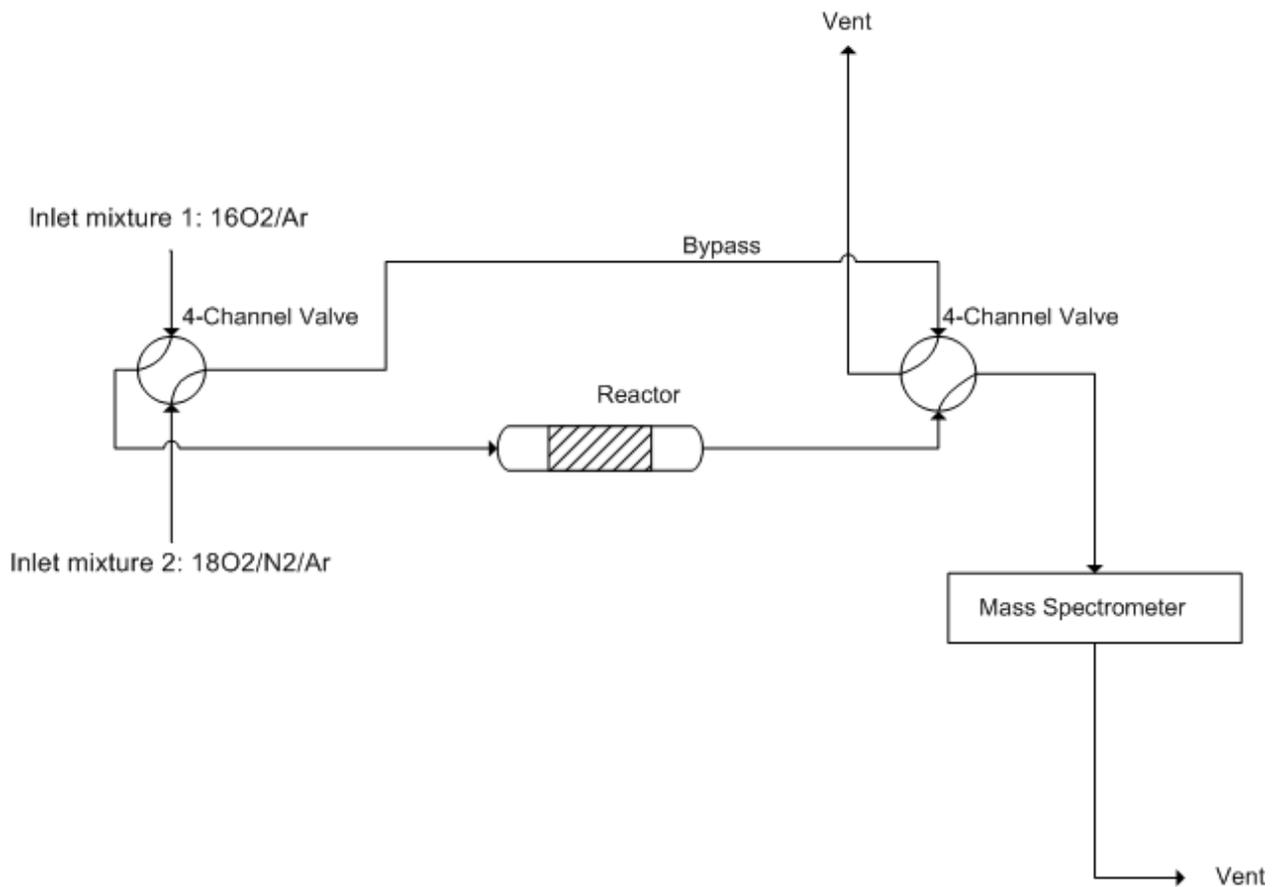
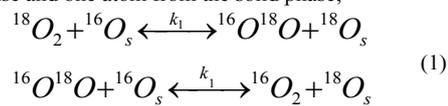


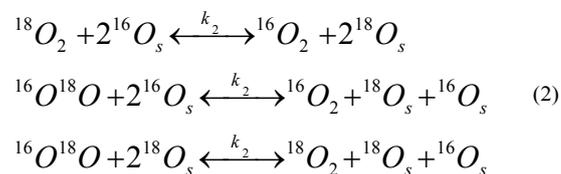
Figure S- 2 SSITKA experimental bench

4) Determination of the type of oxygen isotopic exchange

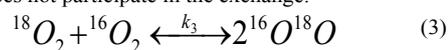
Oxygen exchange can be classified into three main types. Several isotopic exchange equations are possible: (1) simple hetero-exchange, which occurs between an oxygen molecule from the gas phase and one atom from the solid phase;



(2) double hetero-exchange, which occurs between one molecule from the gas phase and two atoms from the oxide;



and (3) homo-exchange, in which the oxide does not participate in the exchange.



The rate equations are defined as follows. For each equation, the forward and the backward kinetic parameter are considered equal, thus k_x is equal to k_{-x} . For simple hetero-exchange, the reaction rates are:

$$\begin{aligned} r_1 &= k_1 P_{^{18}O_2} \theta_{^{16}O} - 1/2 k_1 P_{^{18}O^{16}O} \theta_{^{18}O} \quad (4) \\ r_2 &= 1/2 k_1 P_{^{18}O^{16}O} \theta_{^{16}O} - k_1 P_{^{16}O_2} \theta_{^{18}O} \end{aligned}$$

For double hetero-exchange:

$$\begin{aligned} r_3 &= k_2 P_{^{18}O_2} \theta_{^{16}O} \theta_{^{16}O} - k_2 P_{^{16}O_2} \theta_{^{18}O} \theta_{^{18}O} \quad (5) \\ r_4 &= k_2 P_{^{18}O^{16}O} \theta_{^{16}O} \theta_{^{16}O} - 2k_2 P_{^{16}O_2} \theta_{^{18}O} \theta_{^{16}O} \\ r_5 &= k_2 P_{^{18}O^{16}O} \theta_{^{16}O} - 2k_2 P_{^{18}O_2} \theta_{^{18}O} \theta_{^{16}O} \end{aligned}$$

And for the homo-exchange:

$$r_6 = k_3 P_{^{18}O_2} P_{^{16}O_2} - 1/4 k_3 P_{^{18}O^{16}O} P_{^{18}O^{16}O} \quad (6)$$

For the homo-exchange, when the mixture is changed from $^{16}O_2$ to $^{18}O_2$, the gas phase is directly changed. No $^{16}O^{18}O$ species are formed. **Figure S- 2** shows the evolution of the $^{16}O^{18}O$ ratio depending on the type of hetero-exchange (simple or double).

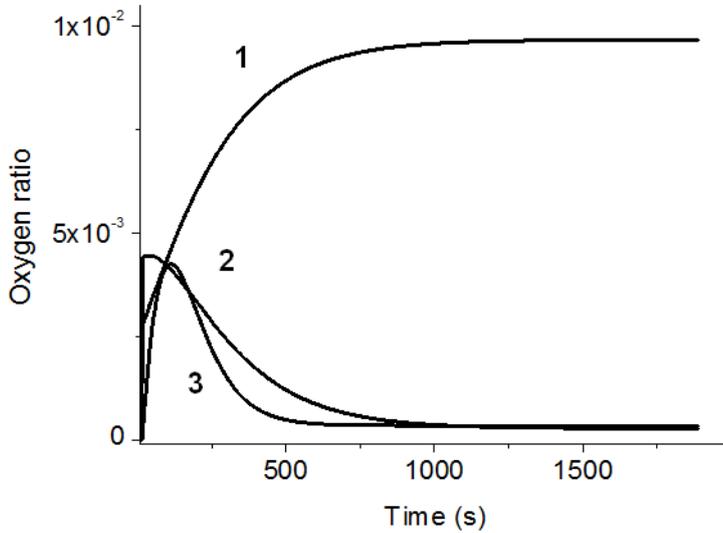


Figure S- 3 Oxygen ratio calculated, 1: $^{18}O_2(g)$, 2: $^{18}O^{16}O(g)$ (simple hetero-exchange), 3: $^{18}O^{16}O(g)$ (double hetero-exchange) with $k \gg D/r^2$

In this work, the profiles presented the shape of curve 3 in **Figure S- 2**. We therefore assume that there was double hetero-exchange.

5) Determination of the variation of the quantity of vacancies from TGA experiments:

$$\Delta\delta = \frac{\Delta m}{m_0} \times \frac{M_i}{M_O}$$

Δm is the variation of the weight measured by TGA analysis, m_0 is the initial quantity of perovskite introduced in the crucible, M_O the molar weight of oxygen (16 g mol^{-1}) and M_i the initial molar weight of the perovskite calculated by:

LSCF $M_i = 0.6M_{La} + 0.4M_{Sr} + 0.2M_{Co} + 0.8M_{Fe} + (3 - \delta_i)M_O$

BSCF $M_i = 0.5M_{Ba} + 0.5M_{Sr} + 0.8M_{Co} + 0.2M_{Fe} + (3 - \delta_i)M_O$

With δ_i determined by iodometric titration.

6) Impact of a dwell on the TGA signal

Table S- 1 TGA of LSCF powder under O₂/N₂ flow, with P_{O₂}=21kPa: and 1073, 1123,1173 K: before dwell and after one hour at the same temperature

Temperature	3-δ (ramp 5K min ⁻¹)	3-δ (after 1 hour dwell)
1073	2.95	2.95
1123	2.94	2.94
1173	2.92	2.92

Table S- 2 TGA of BSCF powder under O₂/N₂ flow, with P_{O₂}=21kPa: and 1073, 1123,1173 K: before dwell and after one hour at the same temperature

Temperature	3-δ (ramp 5K min ⁻¹)	3-δ (after 1 hour dwell)
1073	2.45	2.45
1123	2.44	2.44
1173	2.43	2.43

7) Stability of the perovskite before and after TGA

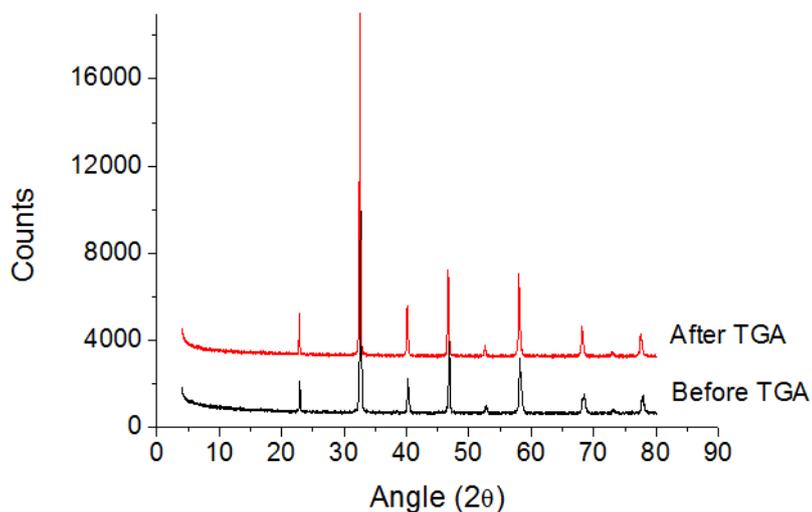


Figure S- 4 XRD analysis of the different samples: LSCF before analysis (black line), LSCF after TGA under P_{O₂}=0.21 bar (red line).

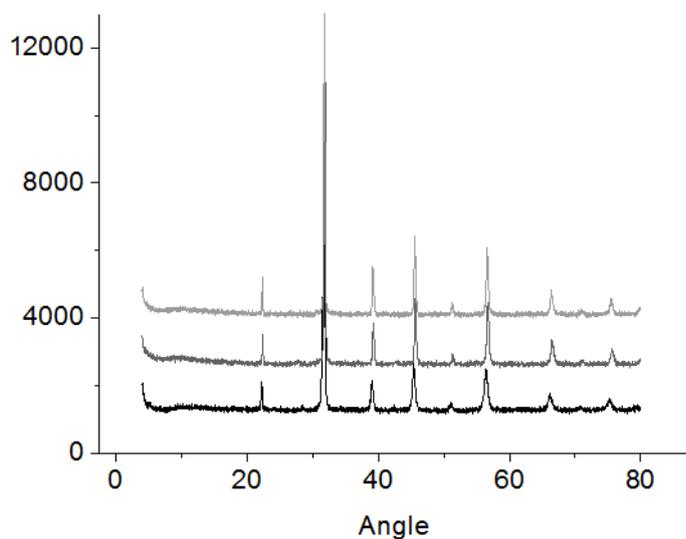


Figure S- 5 XRD analysis of the different samples: BSCF before analysis (black line), BSCF after TGA under $P_{O_2}=0.21$ bar (grey line), BSCF after TGA under $P_{O_2}=0.01$ bar (light grey line)

Table S- 3 Mesh parameter of LSCF before and after experiment

LSCF	Under 21% O ₂ in N ₂	Under 1% O ₂ in N ₂
	Mesh (error)	Mesh (error)
	Å	Å
Before experiment	3.9251(2)	3.925(1)
After experiment	3.9253(6)	3.924(1)

Table S- 4 Mesh parameter of BSCF before and after experiment

BCSF (Cubic structure)	Under 21% O ₂ in N ₂	Under 1% O ₂ in N ₂
	Mesh (error)	Mesh (error)
	Å	Å
Before experiment	3.9791(2)	3.979(1)
After experiment	3.9781(6)	3.977(1)

8) Determination of the Langmuir parameters

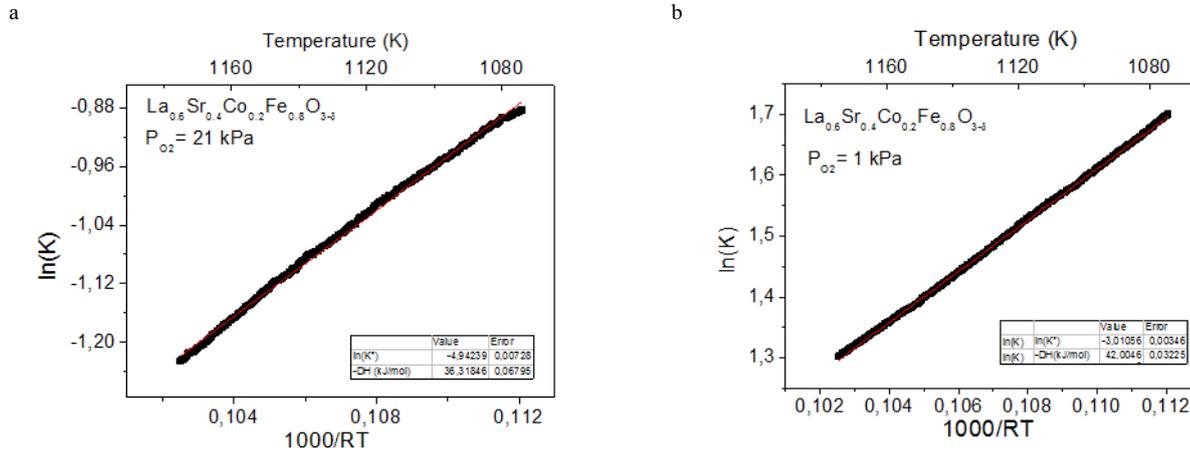


Figure S- 6 Determination of ΔH from TGA experiments for LSCF at $P_{\text{O}_2}=21 \text{ kPa}$ (a) and $P_{\text{O}_2}=1 \text{ kPa}$ (b)

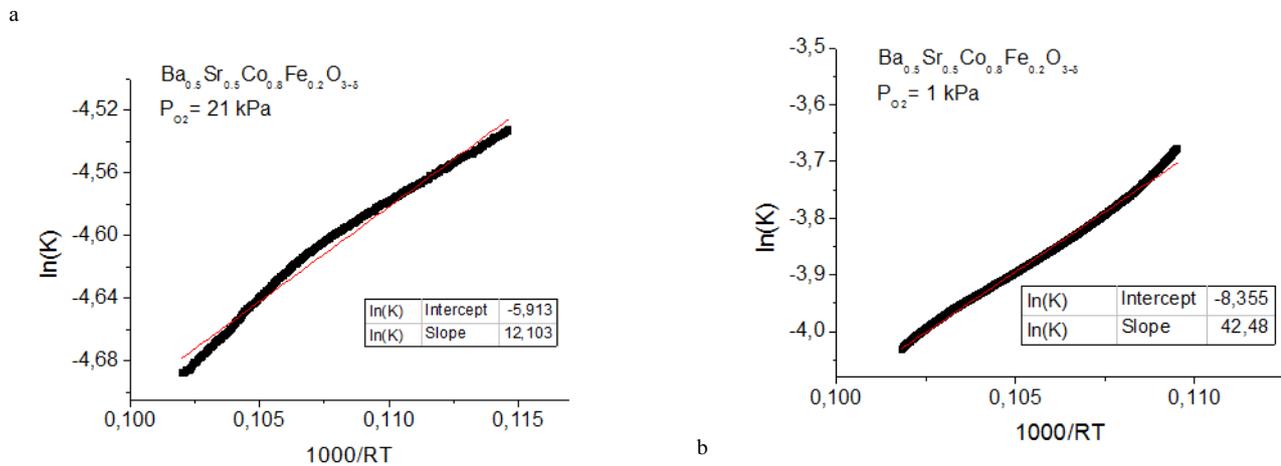


Figure S- 7 Determination of ΔH from TGA experiments for BSCF at $P_{\text{O}_2}=21 \text{ kPa}$ (a) and $P_{\text{O}_2}=1 \text{ kPa}$ (b)

9) Correlation of the parameters:

Table S- 4 Binary correlation coefficient between desorption kinetic parameter (k_f), the oxygen self diffusion parameter (D^*) and occupied oxygen sites (Sites) for LSCF for $P_{\text{O}_2}=21 \text{ kPa}$

	k_f	D^*	Sites
k_f	1	0.163	-0.342
D^*	0.163	1	-0.022
Sites	-0.342	-0.022	1

Table S- 5 Binary correlation coefficient between k_f desorption kinetic parameter (k_f), the oxygen self diffusion parameter (D^*) and occupied oxygen sites (Sites) for LSCF for $P_{\text{O}_2}=1 \text{ kPa}$

	k_f	D^*	Sites
k_f	1	-0.79	0.49
D^*	-0.79	1	-0.278
Sites	0.49	-0.278	1

Table S- 6 Binary correlation coefficient between desorption kinetic parameter (k_r), the oxygen self diffusion parameter (D^*) and occupied oxygen sites (Sites) for BSCF for $P_{O_2}=21$ kPa

	k_r	D^*	Sites
k_r	1	-0.83	0.609
D^*	-0.83	1	-0.719
Sites	0.609	-0.719	1

Table S- 7 Binary correlation coefficient between desorption kinetic parameter (k_r), the oxygen self diffusion parameter (D^*) and occupied oxygen sites (Sites) for BSCF for $P_{O_2}=1$ kPa

	k_r	D^*	Sites
k_r	1	-0.48	0.485
D^*	-0.48	1	-0.136
Sites	0.485	-0.136	1

10) V_m calculation from mesh parameter obtained through *in situ* XRD experiments

XRD was performed on a Panalytical X'Pert Pro MPD diffractometer (Bragg–Brentano para-focusing geometry, reflection mode, Cu K_{α} radiation ($\lambda=0.154184$ nm), diffracted beam graphite monochromator) equipped with a one-dimensional multistrip detector (X'Celerator, 127 channels on 2.118°) for *in situ* measurements. This apparatus enables the collection of X-ray powder patterns of samples at controlled temperature and under different gases.

The samples were mounted in an atmosphere-controlled Anton Paar XRK 900 reactor chamber. The temperature-regulated glass-ceramic sample holder was open to allow the gas to flow through the sample. Samples were heated by steps up to 1073 K at a rate of 2 K min^{-1} under a 20 mL min^{-1} flow rate of 1% O_2 in argon or under synthetic air (gas mixture consisting of N_2 : 20 mL min^{-1} and O_2 : 5 mL min^{-1}). The diffractograms were collected under isothermal conditions from 6 to 95° (2θ) with 0.0334° step and 250 s per step (90 min per scan) after a stabilization time of 1 h between each temperature modification.

Phase identification was performed using DiffracSuite Eva software (Bruker) and the ICDD-PDF4+ database. The lattice parameters were calculated with TOPAS software. The results are recorded in Table S-3.

Table S- 9 Mesh parameter calculated with TOPAS software for two PO_2 : 21 kPa and 1 kPa

BCSF (Cubic structure)	Under 21% O_2 in N_2	Under 1% O_2 in Ar
Temperature	Mesh (error)	Mesh (error)
K	Å	Å
293	3.9791(2)	3.979(1)
873	4.0154(2)	4.019(1)
923	4.0196(2)	4.023(1)
973	4.0245(2)	4.028(1)
1023	4.0294(4)	4.032(1)
1073	4.0321(7)	4.036(1)
Initial condition	3.9718(6)	3.976(1)

According to these mesh parameters, the molar volume was calculated for each condition, as shown below.

Table S- 10 Molar volume calculated at different temperatures for two P_{O_2} : 21 kPa and 1 kPa

BSCF (Cubic structure)	Under 21% O_2 in N_2	Under 1% O_2 in Ar
Temperature	V_m	V_m
K	cm^3	cm^3
293	37.94	37.94
873	38.99	39.09
923	39.11	39.21
973	39.25	39.36
1023	39.40	39.47
1073	39.48	39.59