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Determination of oxygen adsorption-desorption rates and diffusion rate coefficients in perovskites at different oxygen partial pressures by a microkinetic approach.

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A novel, powerful method based on a microkinetic approach is described for the estimation of the oxygen transport parameters of mixed electronic conducting materials (MIECs). This method is validated on the perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and has been applied on $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$. This approach is original and relevant in that the surface kinetic rate constants are measured using a sample in powder form. In contrast to methods previously used, such as isotope exchange depth profiling (IEDP) and electrical conductivity relaxation (ECR), which determine the global exchange kinetic parameter, our microkinetic modelling approach allows the estimation of the forward and reverse kinetic rates accounting for the oxygen vacancy concentration. Also, the self-diffusion rate coefficient has been estimated at different oxygen partial pressures. This microkinetic approach, which combines SSITKA (steady-state isotopic transient kinetic analysis) and thermogravimetric measurements under controlled oxygen partial pressure, has the potential to significantly accelerate the characterization of oxygen transport in perovskites and related materials in the future. In this study, the kinetic parameters were measured in a temperature window between 873 K and 1173 K, and at two oxygen pressure conditions (21 kPa and 1 kPa) that are appropriate for simulating the semi-permeability of oxygen in a membrane in a process of oxygen separation from air.

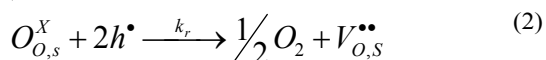
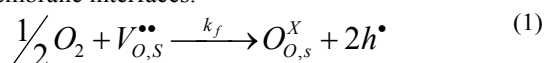
Introduction

Mixed ionic and electronic conductors (MIECs) are an important class of materials that include oxides of different structures such as perovskites, brownmillerite and fluorites. They can potentially be employed in high-temperature applications for which simultaneous reaction and separation is advantageous¹. Research using MIECs has been conducted on partial oxidation of methane to syngas²⁻³, oxidative coupling of methane⁴, and oxidative dehydrogenation of ethane to ethylene⁵. These materials are also proposed for oxygen separation applications and cathode materials for the latest SOFC technologies^{6,7,8,9,10}.

The mechanism of oxygen transport through these materials can be summarized in three major steps. The first step is the dissociative adsorption of O_2 on the surface of the perovskite, leading to the formation of anionic oxygen; the second step is oxygen diffusion by an activated hopping mechanism with oxygen vacancies ($\text{V}_{\text{O},s}^{\bullet}$); and the final step is the desorption/recombination of O_2 on the permeate side¹¹. Different experimental techniques and associated modelling approaches have been developed for the measurement and

estimation of the surface exchange parameters and diffusion parameters that govern the oxygen flux in MIEC membranes in general and perovskite membranes in particular.

Xu and Thomson¹² developed a membrane transport model that enables the determination of the forward and reverse adsorption kinetics and the diffusion parameter of membrane materials using a dataset of semi-permeability measurements. The model is based on the following assumptions: the forward and reverse parameters for the equations, k_f and k_r , are assumed to be independent of the oxygen partial pressure, and to be equal on both membrane interfaces.



The diffusion of oxygen in the bulk ($\text{O}_{\text{O},s}^{\times}$) is described by Fick's first law. Although the diffusion parameter (D_v) depends in theory on the oxygen defect lattice structure¹³, Xu and Thomson assume D_v to be constant across the membrane despite the different oxygen potential, and the number of oxygen vacancies ($\text{V}_{\text{O},s}^{\bullet}$). From the assumptions that the kinetic parameters k_r , k_f and D_v are constants regarding oxygen

potential, Xu and Thomson arrive at the following expression for the oxygen flux across a thin ceramic membrane:

$$J_{O_2} = \frac{D_v k_r (P_{O_2}^{0.5} - P_{O_2}^{\prime 0.5})}{2Lk_f (P_{O_2}^{\prime} P_{O_2}^{\prime\prime})^{0.5} + D_v (P_{O_2}^{0.5} + P_{O_2}^{\prime 0.5})} \quad (3)$$

The six parameters of expression (3) accounting for the pre-exponential factors of the diffusion, forward reaction and reverse reaction (D_v , k_f , k_r), and associated activation energy (E_d , E_f , E_r) were estimated by regression on two distinct $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ membranes of different thicknesses and using 126 different experimental conditions of oxygen partial pressure and temperature.

The measurement of oxygen semi-permeability on membranes, along with modelling using the Xu and Thomson model, is currently the only solution for the estimation of both forward and backward kinetic parameters for oxygen adsorption-desorption on MIEC materials. Other characterization techniques such as electrical conductivity relaxation (ECR)¹⁴⁻¹⁶ and isotopic exchange depth profiling (IEDP)¹⁷⁻¹⁹, which are carried out on shaped materials, give access to global kinetic rate parameters only. Hence, there is a strong incentive to develop straightforward approaches that do not involve membrane testing under relevant (steady-state) conditions for the measurement of microkinetic constants.

In this paper, we describe an original methodology based on measurements on perovskites in powder form, for the microkinetic modelling of oxygen transport under conditions applied during membrane operation. The originality of our method consists in the integration of oxygen vacancy concentration measurements by thermogravimetric analysis (TGA) with isotopic oxygen exchange experiments ($^{16}\text{O}_2/^{18}\text{O}_2$) in a microkinetic model. All necessary kinetic and transport parameters can be estimated and used as input for an oxygen membrane flux model in order to optimize the material formulation. Our novel microkinetic approach is validated on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) by comparing results obtained by the Xu/Thomson approach and then applied on $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF), which is currently of the most-studied perovskites in the domain¹⁰. The result section is divided into three parts: (i) determination of the adsorption equilibrium constant (K) and the degree of oxygen non-stoichiometry (δ) from TGA experiments, (ii) estimation of kinetic rate parameters (k_f , k_r) from oxygen isotopic exchange experiments, and (iii) estimation of the oxygen self-diffusion rate (D^*).

Experimental

Perovskite synthesis and characterization

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) was synthesized using a sol gel method. All the precursors were purchased from Sigma Aldrich (pur: 99.5%). $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (433.01 g mol⁻¹), $\text{Sr}(\text{NO}_3)_2$ (211.6 g mol⁻¹), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (404.0 g mol⁻¹) and finally $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (291.0 g mol⁻¹). These components were weighted then stirred in distilled water until total dissolution of

the components. Meanwhile, ethylenediaminetetraacetic acid (EDTA, 292.24 g mol⁻¹) and citric acid (192.1 g mol⁻¹) were mixed in distilled water. One molar equivalent of EDTA was added for each molar equivalent of total metal ion and two molar equivalent of citric acid. This mixture was stirred until total dissolution of both components. Ammonia solution was then slowly added until obtaining a transparent solution (70 mL, 6<pH<8). The solution was stirred and heated at 373K until a gel like solution was obtained. The resulting gel was heated at 473K in air for two hours and then fired for 5 hours at 1423K in order to obtain a pure perovskite phase.

$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) powder was purchased from Marion Technologies (France). The perovskite powder was processed in the same manner as for membrane preparation in order to generate an identical microstructure. The powder was dry-pressed at a pressure of 100 MPa. After sintering at 1448 K for 10 h, the relative density of the pellet was about 86-91%. The resulting sintered pellet was gently crushed and sieved at the 425-600 μm fraction for TGA, SSITKA and scanning electron microscopy (SEM) studies. The structure of a crushed powder was analyzed by X-ray diffraction (XRD) at room temperature in air using a Bruker D8 Advance A25 system in the 2θ range of 3-80°, with a step width of 0.02°, a counting time of 1 s and Cu K α 1+ α 2 radiation ($\lambda=1.54184 \text{ \AA}$) (SI-1). The solid density of LSCF and BSCF was calculated from the unit cell parameters at room temperature (SI-2). The crystallite size distribution was determined from SEM images (ImageJ software) using a spherical model on a population of 250 crystallites. Independently, the porous oxide powder is modelled using the equivalent geometry of dense sphere given by $d_{\text{crys}}=6/(\rho \cdot S_{\text{BET}})$ ^{20,21}. The specific surface areas (S_{BET}) are measured by nitrogen adsorption at 77 K.

Steady-State Isotopic Transient Kinetic Analysis (SSITKA)

The oxygen exchange experiments were carried out in a fixed-bed quartz tube reactor (i.d. 5 mm) containing 50 mg of sieved perovskite (SI-3). The reactor space before the sample was filled with quartz particles of the same sieve fraction. This lowers the dead volume, preheats the gas, and establishes a plug flow before the sample. A thermocouple was inserted directly into the sample zone to monitor the sample temperature. Experiments were carried out from 873 K to 1173 K with a step every 50 K and at a pressure between 120-160 kPa. Inlet flows were controlled with mass flow controllers. A gas mixture of 50 mL min⁻¹ of x% $^{16}\text{O}_2$ (Air Liquide, 99.999%) + (100-x)% Ar was replaced by a mixture of 50 mL min⁻¹ of x% $^{18}\text{O}_2$ (Eurisotop 98% $^{18}\text{O}_2$ and 2% $^{16}\text{O}_2$) + 5% N_2 + (95-x)% Ar, where x was either 21% or 1%. After this experiment, a back-switch was performed. The changes in the gas composition were continuously monitored by a mass spectrometer ($m/e=32, 34, 36, 40$ and 28) with an acquisition rate of approximately 1 point/s. Nitrogen was added to the feed gas as an inert tracer to measure the gas holdup of the system. The highest oxygen exchange rate was measured at 900°C and amounted to $1.5 \cdot 10^{-4}$

mol/kg/s. Under these conditions, the Carberry number, which characterizes external diffusion limitations, amounts to 2×10^{-6} . This is well below the value of 0.05 at which diffusion limitations may occur. Similarly, the Weisz modulus of 10^{-5} is well below the critical value of 0.08 for pore diffusion limitations²².

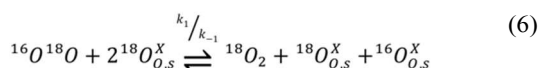
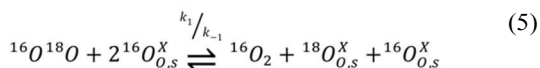
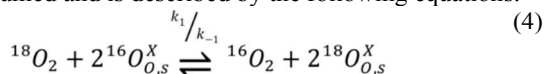
Thermogravimetric analysis (TGA)

The degree of oxygen non-stoichiometry (δ) of the perovskite was measured as a function of temperature using a Setsys Evolution 12 thermogravimetric analyzer from SETARAM. The measurements were carried out on 80 mg of sample under a total flow of 50 mL min⁻¹ consisting of argon and two different partial pressures of oxygen, $P_{O_2}=21$ kPa and 1 kPa. Two different temperature programs were carried out, a continuous ramp and step-by-step to target settings for method validation purposes. For the continuous ramp, the temperature was increased from room temperature up to 1173 K with a heating ramp of 5 K min⁻¹. The stepwise program consisted of two-hour dwells at constant temperature that allowed the sample to reach thermodynamic equilibrium. Prior to analysis, the sample was pre-treated *in situ* in an oxygen/helium mixture for two hours at 1173 K in order to remove all traces of water and carbonates. It was then cooled down to room temperature in a CO₂ - and water-free atmosphere. The structure of the perovskite was checked by XRD after TG analysis. The initial oxygen non-stoichiometry (δ) of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} and Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} were measured by iodometric titration using a state of the art method which is described elsewhere by Manthiram *et al*²³.

Isotopic oxygen exchange modelling

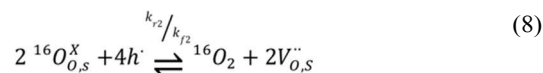
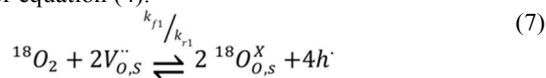
Microkinetic model

Oxygen exchange between gas-phase oxygen and solid oxides such as perovskites can occur according to three overall reactions in which zero, one, or two oxygen atoms are exchanged with the solid²⁴⁻²⁷. Based on the best fit, model discrimination was carried out in order to select the most appropriate exchange model (SI-4). A double hetero-exchange was assumed and is described by the following equations:



The proposed microkinetic model involves the integration of oxygen vacancies ($V_{O}^{\bullet}$) in the description of oxygen adsorption-desorption at the surface. Equations (7) and **Error!**

Reference source not found. are the corresponding elementary steps for equation (4).



The rate constants in equations (7) and (8) are the same because the kinetic isotope effect between ¹⁸O₂ and ¹⁶O₂ is negligible under these conditions. Therefore, $k_{f1}=k_{f2}=k_f$ and $k_{r1}=k_{r2}=k_r$. The kinetic constants k_f and k_r are expressed in the units of Pa⁻¹ s⁻¹ and s⁻¹, respectively, with E_f and E_r being the associated activation energies in kJ mol⁻¹.

$$k_r = k_r^{\circ} \exp\left(\frac{-E_r}{RT}\right) \quad (9)$$

$$k_f = k_f^{\circ} \exp\left(\frac{-E_f}{RT}\right) \quad (10)$$

The reaction rate (r) for this step according to the law of mass action then reads:

$$r = k_f P_{^{18}O_2} \theta_v^2 - k_r \theta_{^{18}O}^2 h^4 \quad (11)$$

$$r = k_r \theta_{^{16}O}^2 h^4 - k_f P_{^{16}O_2} \theta_v^2 \quad (12)$$

To complete the oxygen exchange kinetics, a third rate equation for $P_{^{16}O^{18}O}$ is necessary:

$$r = k_f P_{^{16}O^{18}O} \theta_v^2 - k_r \theta_{^{16}O} \theta_{^{18}O} h^4 \quad (13)$$

The total oxygen coverage gives $\theta_{^{16}O} + \theta_{^{18}O} + \theta_v = 1$, where $\theta_{^{16}O}$ ($\theta_{^{18}O}$) is the fraction of sites occupied by ¹⁶O (or ¹⁸O), and θ_v is the fraction of vacant sites ($V_{O,S}^{\bullet}$), and h is the fraction of electron holes ($h^{\bullet}$).

The concentrations of surface species ($V_{O,S}^{\bullet}$, ¹⁸O_{O,S}^X, ¹⁶O_{O,S}^X) are calculated by assuming a Langmuir adsorption isotherm. This implies that only one site exists (all sites are energetically equivalent and there is no interaction between the adsorbed species), with this site being either occupied or vacant, and that the oxygen surface species are in equilibrium with the gas phase. The equilibrium constant K , which can be expressed as a Van 't Hoff expression, is equal to the ratio k_f/k_r :

$$K = K^{\circ} \exp\left(\frac{-\Delta H}{RT}\right) \quad (14)$$

With $\Delta H = E_r - E_f$

$$K = \frac{(1 - \theta_v)^2}{\theta_v^2 P_{O_2}} \quad (15)$$

The oxygen non-stoichiometry (δ) is related to the fraction of vacancies through $\theta_v = \delta/3$ according to the general perovskite formula, ABO_{3- δ} .

Global mass balance:

The oxygen transport model is based on the one-dimensional pseudo-homogeneous diffusion convection equation for a fixed-bed reactor, implying the usual assumptions²⁸ coupled with the oxygen exchange kinetics at the surface and oxygen diffusion through the bulk, described by equation (16). Polarisation resistance is not taken into account in our model.

$$\varepsilon_b \frac{\partial P_i}{\partial t} = -u \frac{\partial P_i}{\partial z} - (1 - \varepsilon_b) L_t \sum_{j=1}^n v_{ij} r_j \quad (16)$$

Where P_i (Pa) is the partial pressure of oxygen in the gas phase ($i=^{18}\text{O}_2$, $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$), t (s) is time, u_s ($\text{m}^3_{\text{G}} \text{m}^{-2}_{\text{R}} \text{s}^{-1}$) is the superficial gas velocity, L_t is the number of active sites ($\text{mol m}^{-3}_{\text{S}}$), ε_b ($\text{m}^3_{\text{G}} \text{m}^{-3}_{\text{R}}$) is the inter-granular void space, D_e ($\text{m}^2_{\text{G}} \text{m}^{-1}_{\text{R}} \text{s}^{-1}$) is the effective axial diffusivity, z (m_{R}) is the axial reactor coordinate, R ($\text{J mol}^{-1} \text{K}^{-1}$) is the gas constant, T (K) is the absolute temperature, v_{ij} (-) is the stoichiometric coefficient for species i in reaction j , and r_j (s^{-1}) is the reaction rate of step j (equations (11) to (13)). Note that all four terms in equation (16) are expressed in Pa s^{-1} .

The following boundary conditions were used:

$$z=0, P_i=P_i^0$$

$$z=L, \left. \frac{\partial P_i}{\partial z} \right|_{z=L} = 0$$

The Fick's law describes a variation of the concentration of oxygen through the bulk. Assuming spherical perovskite particles with radius R_p (m), Fick's second law then reads:

$$\frac{\partial \theta_{z,r}}{\partial t} = D^* \left(\frac{\partial^2 \theta_i}{\partial r^2} + \frac{2}{r} \frac{\partial \theta_{z,r}}{\partial r} \right) \quad (17)$$

Where D^* ($\text{m}^2_{\text{S}} \text{s}^{-1}$) is the oxygen tracer diffusion coefficient, $\theta_{18\text{O},r}$ (-) is the ^{18}O fraction in the perovskite (equal to $C_{18\text{O}}/(C_{18\text{O}} + C_{16\text{O}} + C_{\text{V}})$, C_{V} ($\text{mol}/\text{m}^3_{\text{S}}$) being the oxygen vacancy concentration), and r (m_{S}) is the radial coordinate of the perovskite sphere.

Boundary conditions:

$$\text{At } r=R_p$$

$$-D^* \frac{3}{R_p} \frac{d\theta_z}{dr} = \sum_{j=1}^n v_{ij} r_j \quad (18)$$

At $r=0$

$$\left. \frac{\partial \theta_{18\text{O}}}{\partial r} \right|_{r=0} = 0 \quad (19)$$

For the initial conditions, at $t < 0$, the entire solid and the gas-phase oxygen are assumed to be composed of only ^{16}O isotope, as the perovskite has been pre-treated at the same temperature under a $^{16}\text{O}_2$ flow. ($P_i=P_{16\text{O}_2}$ and $\theta_{\text{O}}(r)=0$). Then, at $t=0$, the partial pressure of $^{18}\text{O}_2$ is defined by equation (20) with cst (s^{-1}) as a constant that depends on the four-way switching valve.

$$P_{^{18}\text{O}_2} = P_{^{18}\text{O}_2}^0 \frac{1 - \exp(-cst \times t)}{1 + \exp(-cst \times t)} \quad (20)$$

The first-order differential equations were numerically integrated using the ODEPACK library²⁹. The non-linear least square regression analysis to estimate k_r , k_f and D^* was performed by a Levenberg-Marquardt minimization algorithm^{30,31}. After regression analysis, a statistical test was performed³².

Results and discussion

Determination of equilibrium constant (K) and vacancy fraction (θ_v) by TGA

The evolution of the oxygen non-stoichiometry (δ) and thus the oxygen vacancies (θ_v) of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ with the temperature at fixed oxygen partial pressure can be followed by thermogravimetric analysis (TGA). Prior to TGA, the initial oxygen non-stoichiometry (δ) of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ at room temperature were determined by iodometric titration^{23,33}. A series of 10 repetitive measurements on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (resp. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$) gave a non-stoichiometry (δ) value equal to 0.03 ± 0.01 (resp. 0.41 ± 0.01) corresponding to a fraction of oxygen vacancies (θ_v) of 0.01 (resp. 0.137). Figure 1 shows the evolution of the fraction of vacancies as a function of temperature as calculated from the weight loss of the TGA curve (SI-5) ($\theta_v = \delta/3$) under two different fixed oxygen partial pressures for LSCF (Figure 1a) and BSCF (Figure 1b). The partial pressures of 21 kPa of O_2 (solid line) and 1 kPa of O_2 (dashed line) correspond to the conditions typically applied for air separation in a membrane process, for the oxygen-rich side (air feed) and for the oxygen-lean side (permeate side), respectively. For LSCF, the TGA profiles are characterized by a long plateau corresponding to constant fraction of vacancies till relatively high temperature. The vacancy fractions increase with a linear rate starting from 823 K under $P_{\text{O}_2}=1$ kPa and from 1050 K under $P_{\text{O}_2}=21$ kPa. Hence, we can observe an almost constant difference of oxygen vacancy concentration between the oxygen rich and lean conditions over the temperature range of interest. In contrast for BSCF, the fraction of vacancies (θ_v) is stable only until 473 K, then increases linearly with temperature in the case of $P_{\text{O}_2}=21$ kPa^{15,34,35}. For lower oxygen pressure ($P_{\text{O}_2}=1$ kPa), we can observe a pronounced oxygen loss at 550-650 K that accounts for a more thorough reduction of the solid, followed by a linear trend parallel to the former. Our data fall within the typical range of oxygen non-stoichiometry generally found for LSCF^{36,37} and are in very good agreement with the data of Kriegel *et al*³⁴ for BSCF³⁸. In order to validate dynamic TGA measurement, additional TGA measurements were carried out by maintaining the sample at a constant temperature for a longer time before ramping to the next temperature level. A dwell-type temperature program gave non-stoichiometry values (δ) that were similar to those obtained by a continuous temperature ramp (SI-6). We can therefore conclude that oxygen adsorption/desorption and transport is

more rapid and in quasi-equilibrium compared to the change in temperature.

No consensus exists in the literature regarding the stability of the BSCF material during TGA measurements. Stable behavior³⁵ and slow partial decomposition^{38–40} have been reported in separate studies. We observed that after TGA measurements, the cell parameters remained constant within measurement errors (SI-7). In addition, we did not observe the formation of a new phase. Hence, the modification of the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ material during TGA experiments, if it does occur, is at least reversible. Similar conclusions for LSCF can be drawn up.

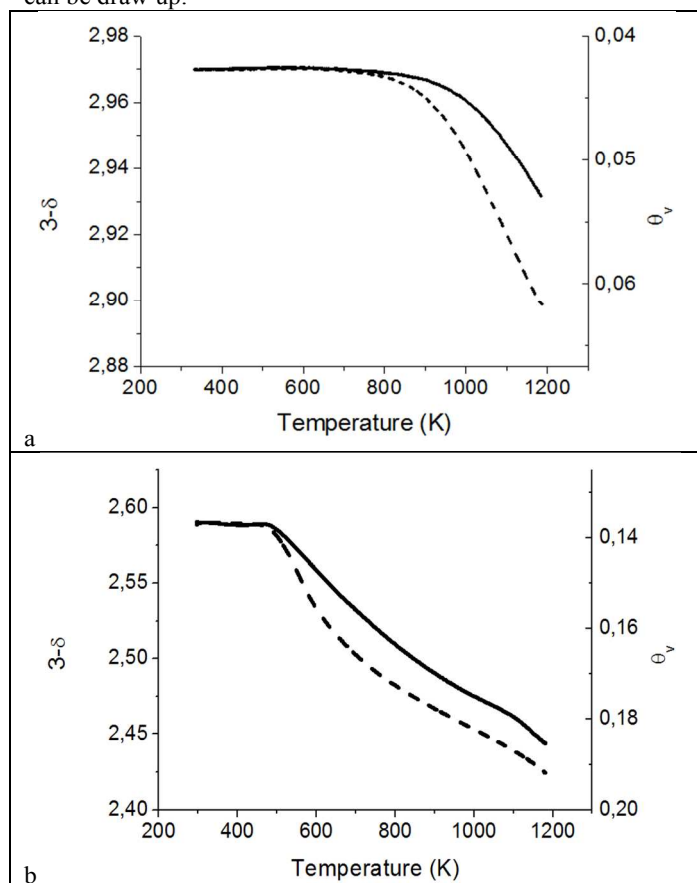


Figure 1 TGA of LSCF (a) and BSCF (b) powders under O_2/N_2 flow, with $\text{PO}_2=21$ kPa (solid line) and $\text{PO}_2=1$ kPa (dashed line).

The adsorption equilibrium constant (K) parameters were calculated for each oxygen pressure using equation (15). This is the simplest approach for describing oxygen non-stoichiometry in perovskites⁴¹. A Van't Hoff-type equation was used to describe the temperature dependence (equation (14)) (SI-8). The corresponding parameters are presented in Table 1.

Table 1 Parameter estimates of the adsorption equilibrium constant (K) by equation (15) for two oxygen partial pressures (SI-8).

Perovskite	P_{O_2} (kPa)	$K^\circ(1 \text{ Pa}^{-1})$	ΔH (kJ mol ⁻¹)
LSCF	1	$(5.0 \pm 0.07) 10^{-2}$	-41.6 ± 0.9
LSCF	21	$(7.2 \pm 0.07) 10^{-3}$	-36.3 ± 0.9
BSCF	1	$(2.4 \pm 0.05) 10^{-4}$	-42.5 ± 0.9
BSCF	21	$(2.7 \pm 0.05) 10^{-3}$	-12.1 ± 0.1

In the case of LSCF, the heat of adsorption does not significantly change under different oxygen partial pressures, meaning that the equilibrium constant varies similarly under rich and lean-oxygen atmosphere. In contrast, significantly different parameters are found for BSCF, which should reveal a structural change at the solid surface leading to different adsorption-desorption properties. The physical interpretation of these data is rather problematic. Thermodynamic models that describe the defect chemistry have been developed⁴², but no specific model for BSCF has yet been reported. The oxygen non-stoichiometry behaviour of BSCF is complex due to the presence of both cobalt and iron cations in three different valence states⁴³. The higher enthalpy at lower partial pressure of oxygen is consistent with an enthalpy that decreases with increasing oxygen vacancy concentration (or δ), as observed by Mizusaki *et al.* for $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_{3-\delta}$ ⁴².

The semi-empirical model proposed by Yang and Lin (equation (21)) did not work either for BSCF, because n varied at each temperature⁴⁴.

$$\left(\delta = \frac{3KP_{\text{O}_2}^n}{1 + KP_{\text{O}_2}^n} \right) \quad (21)$$

As we are proposing a straightforward, versatile method for the screening of perovskite powders to extract transport parameters in order to predict the oxygen semi-permeability, we have continued to use the simplified model as given by equation (15) with two sets of values: one on the air side and one on the permeate side. The development of a theoretically-based model for the full description of the defect chemistry as a function of oxygen partial pressures and temperatures is outside the scope of this study.

Modelling of oxygen isotopic exchange and estimation of surface exchange kinetic coefficients (k_r , k_f)

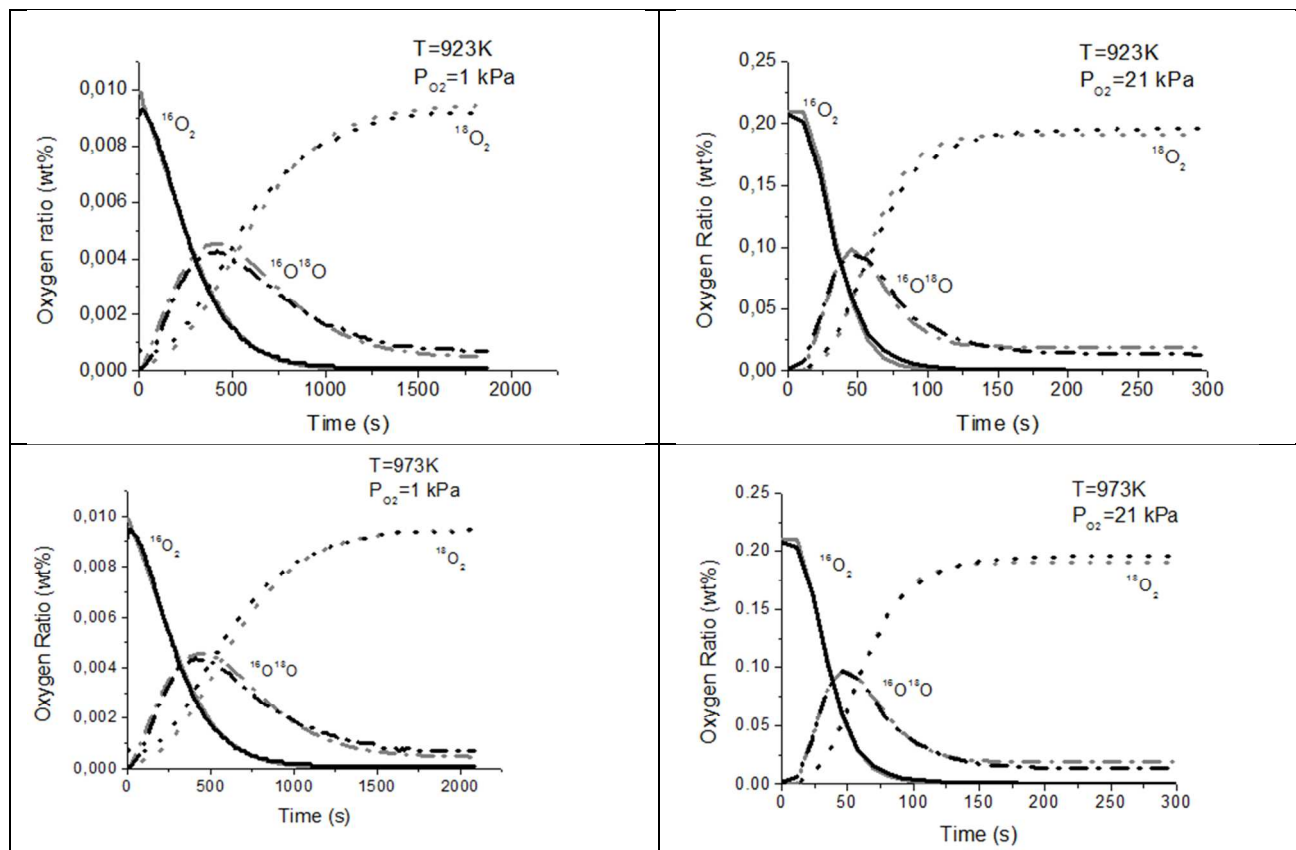
The TGA data could not be described over the entire range of oxygen pressures using a simple, one-parameter defect model. In order to avoid the need to develop a full defect model, isotopic oxygen exchange measurements were carried out at the same conditions applied for TGA measurements, namely 1 kPa and 21 kPa. By fixing the equilibrium oxygen adsorption constant at the values obtained from TGA experiments, the forward adsorption rate constant can be estimated from the isotopic oxygen exchange experiments.

Figure 2 and Figure 3 show examples of oxygen exchange experiments for two partial pressures of oxygen at three temperatures for LSCF and BSCF, respectively. The exchange took about an order of magnitude longer at $\text{P}_{\text{O}_2}=1$ kPa than at

$P_{O_2}=21$ kPa. On the other hand, the temperature initially had an effect at low temperatures, but the effect levelled out quickly above 900 K. The integration of the $0.5^*P^{32}O_2 + P^{16}O^{18}O$ signals gave the amount of exchanged oxygen. For experiments carried out at $P_{O_2}=21$ kPa and $T=973$ K, 86% and 95% of all oxygen atoms are exchanged for LSCF and BSCF, respectively. In contrast, only 50% of oxygen atoms are exchanged for both at $P_{O_2}=1$ kPa in 35 minutes. For cost reasons, the exchange curves were not recorded until the end of the exchange. It is known that structure changes of BSCF occur in the range of conditions applied here⁵. Nevertheless, we did not observe significant modifications of the exchange profiles after 1 hr of exposure in given temperature and oxygen partial pressure conditions.

The oxygen exchange curves ($P^{16}O_2$ and $P^{16}O^{18}O$) were modelled for each level of oxygen partial pressure separately, but including all temperatures simultaneously. Initial regression analysis showed that quasi-equilibrium of the exchange rates was established at the time scale of the experiment. Thus only the forward rate parameters (k_f) were estimated during the regression analysis, and the reverse rate parameters (k_r) were

calculated from the equilibrium rate constants ($K=k_f/k_r$) determined from the TGA experiments (Table 1). Using the electroneutrality condition, the electron hole concentration $[h]$ was estimated to be on the order of $2*10^{-5}$. The value of the rate constant was adjusted accordingly. In the temperature interval between 650-900°C the concentration $[h]$ varies roughly 30%, which is negligible compared to the change in the oxygen exchange rate. Thus an intrinsic activation energy can be obtained from the exchange experiments. In addition to the oxygen exchange parameters, the characteristic time constant (D/r^2) for oxygen transport was estimated from the isotopic exchange response curves. On Figure 2, the model-predicted response curves are compared to the experimental curves for LSCF. A good fit is obtained in all temperatures and pressure conditions. The surface parameter and diffusion estimates are reported in Table 2 and Table 4, respectively. Similarly, Figure 3 compares the model-predicted response curves with the experimental curves for BSCF. A good fit was obtained at both oxygen partial pressures and at all temperatures. The surface parameter and diffusion estimates are reported in Table 3 and Table 4, respectively.



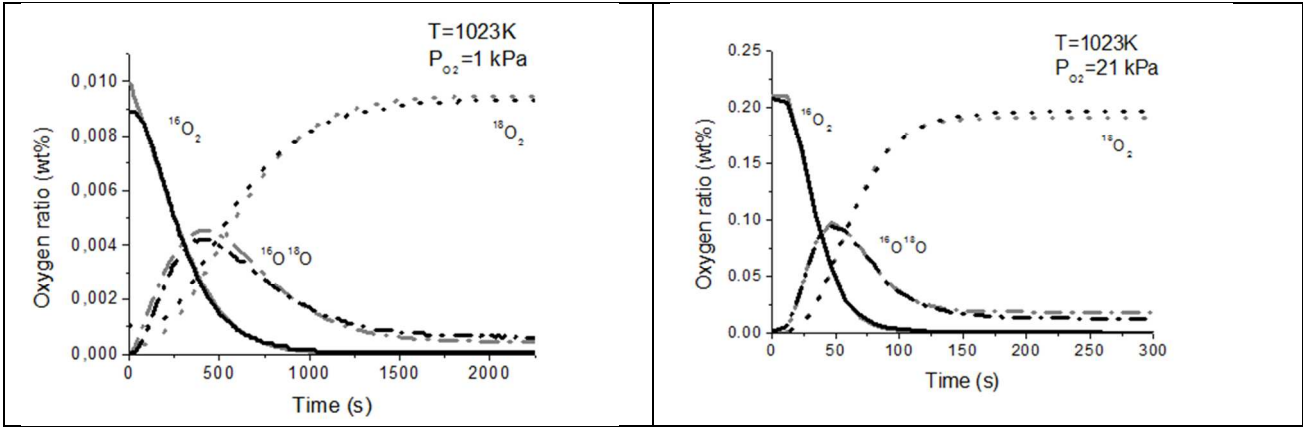
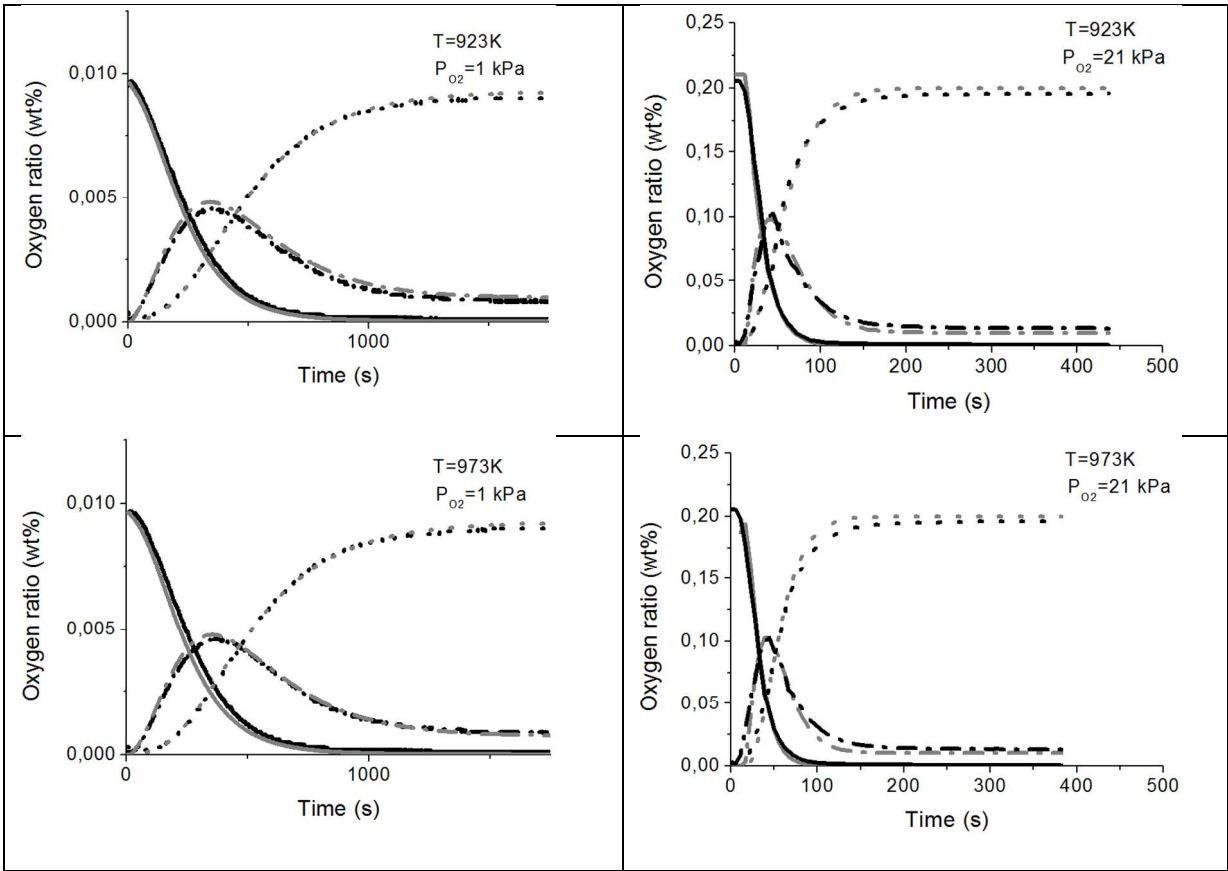


Figure 2 SSITKA experiments (black) and model curves (light grey), $^{16}\text{O}_2(\text{g})$ (solid line), $^{16}\text{O}^{18}\text{O}(\text{g})$ (dashed line), $^{18}\text{O}_2(\text{g})$ (dotted line) at different partial pressures of oxygen and different temperatures for LSCF.



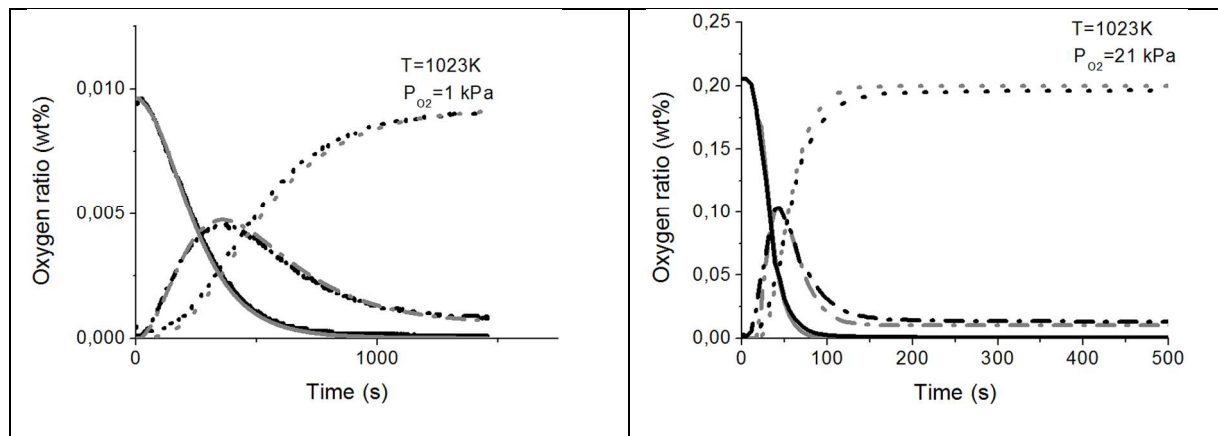


Figure 3 SSITKA experiments (black) and model curves (light grey), $^{16}\text{O}_2(\text{g})$ (solid line), $^{16}\text{O}^{18}\text{O}(\text{g})$ (dashed line), $^{18}\text{O}_2(\text{g})$ (dotted line) at different partial pressures of oxygen and different temperatures for BSCF.

Table 2 Kinetic parameters estimated from regression analysis of the isotopic oxygen exchange response curves. The confidence intervals are estimated at 95%. For comparison, the estimated parameters are reported in two different units. Results from Xu and Thomson¹² obtained on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ membrane semi-permeability data model are reported.

LSCF		Surface reverse kinetic parameter		Surface forward kinetic parameter		
Shape	P_{O_2}	k_r°	E_r	k_f°	E_f	ref
	kPa	s^{-1}	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{Pa}^{-1}\cdot\text{s}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	
Powder	21	$(2.7\pm0.07) 10^{11}$	239 ± 25	$(8.1\pm0.1) 10^7$	198 ± 16	This work
Powder	1	$(2.7\pm0.07) 10^{11}$	243 ± 25	$(4.4\pm0.05) 10^7$	207 ± 16	This work
	kPa	$\text{mol cm}^{-2}\text{s}^{-1}$	kJ mol^{-1}	$\text{cm atm}^{-0.5}\text{s}^{-1}$	kJ mol^{-1}	
Powder	21	$(5.5\pm0.15) 10^4$	239 ± 25	$(5.9\pm0.1) 10^6$	198 ± 16	This work
Powder	1	$(5.5\pm0.15) 10^4$	243 ± 25	$(3.2\pm0.03) 10^6$	207 ± 16	This work
Membrane	n.d.	$2.07 10^4$	241.3	$5.90 10^6$	226.9	¹²

n.d. not determined

We can see that pre-exponential factors (k_r° , k_f°) and activation energies (E_r , E_f) for the reverse and forward reactions estimated from the SSITKA/TGA approach match very well with the results of Xu and Thomson obtained by modelling the semi-permeability data on LSCF membrane¹². Thus, we can conclude on the validity of this novel microkinetic approach which uses a powder instead of a membrane for the estimation of reverse and forward kinetic parameters.

We can note that kinetics parameters for LSCF do not change significantly when measured at $P_{\text{O}_2}=1$ kPa and $P_{\text{O}_2}=21$ kPa.

Other experimental approaches (isotope exchange depth profiling (IEDP) and electrical conductivity relaxation (ECR)) lead to global kinetic rate parameters that do not take the oxygen vacancies into account and thus kinetic parameters cannot be directly compared. We can note, however, that Sahibzada et al.²⁰ found variations of global kinetic parameter and chemical diffusion coefficient as a function of the partial pressure of oxygen for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ for very low partial pressure of oxygen (lower the 0.1 kPa).

Table 3 Kinetic parameters estimated from regression analysis of the isotopic oxygen exchange response curves for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$. The confidence intervals are estimated at 95%.

BSCF		Surface reverse kinetic parameter		Surface forward kinetic parameter	
Shape	P_{O_2}	k_r°	E_r	k_f°	E_f
	kPa	s^{-1}	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{Pa}^{-1}\cdot\text{s}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
Powder	21	$(1.3\pm0.6) 10^{11}$	216 ± 45	$(3.1\pm1.9) 10^7$	204 ± 45
Powder	1	$(1.7\pm0.2) 10^{11}$	241 ± 20	$(1.4\pm0.2) 10^7$	199 ± 21
	kPa	$\text{mol cm}^{-2}\text{s}^{-1}$	kJ mol^{-1}	$\text{cm atm}^{-0.5}\text{s}^{-1}$	kJ mol^{-1}
Powder	21	$(1.3\pm0.6) 10^6$	216 ± 45	$(1.2\pm0.1) 10^8$	204 ± 45
Powder	1	$(1.6\pm0.2) 10^6$	241 ± 20	$(5.7\pm0.1) 10^7$	199 ± 21

In contrast, for BSCF we can observe significant larger activation energy of the reverse reaction at lean oxygen pressure, whereas for the forward reaction the activation

energies are very similar. This result is supported by DFT calculations which indicate that a simple “defect-chemical model” for BSCF is not applicable⁴⁵. As a consequence, for

BSCF the rates of desorption of oxygen is lower than for adsorption at low oxygen partial pressure which would represent the sweep side in a membrane operation. These experimental results are opposite to Xu and Thomson hypothesis¹². Unfortunately, to the best of our knowledge no data related to intrinsic kinetic parameters have been reported in the literature for BSCF materials, but only surface exchange coefficients^{46,47} which does not allow direct comparison with our data. Moreover, the values of the surface exchange coefficients in the two studies vary by two orders of magnitude^{46,47}.

Estimation of diffusion coefficients from characteristic time

Oxygen exchange experiments give access to the characteristic diffusion time, which is the ratio of the diffusion coefficient to the square of the characteristic length (D^*/r^2). This is similar to all other techniques used for the measurement of diffusion coefficients. If the diffusion measurements are carried out directly on the shaped material for the intended application, then the value of D^*/r^2 can be used directly. In our context, the method we have developed aims to predict the permeation of

membranes from kinetic modelling carried out on the corresponding powders. In this case, the characteristic length of diffusion is not the same. For the membrane application the length corresponds to the thickness of the membrane, whereas for powder it corresponds to the crystallite size. Therefore, the crystallite size for the powders used in this study needs to be determined. The crystallite diameter can be estimated directly from SEM image analysis (Figure 4). The size distribution of the crystallites was measured by counting 250 crystallites (Figure 4). The distribution is centred at 7 μm using a non-linear Gauss curve fit (Figure 5). Independently, the mean diameter of crystallite with an accessible surface was determined by N_2 adsorption measurements at 77 K. For LSCF, the BET surface area is equal to $3.2 \text{ m}^2 \text{ g}^{-1}$ and $\rho=5.89 \text{ g cm}^{-3}$ which leads to a crystallite diameter (d_{crys}) of 0.32 μm . Thus, we set the crystallite radius (r) to 0.16 μm for the estimation of the diffusion parameter (Table 4).

For BSCF, the BET surface area is equal to $150 \pm 1 \text{ m}^2 \text{ kg}^{-1}$, which leads to a crystallite diameter (d_{crys}) of 7.2 μm , in good agreement with SEM image analysis (Figure 4). The crystallite radius (r) has been set to 3.5 μm for allowing the estimation of the diffusion parameter (Table 4).

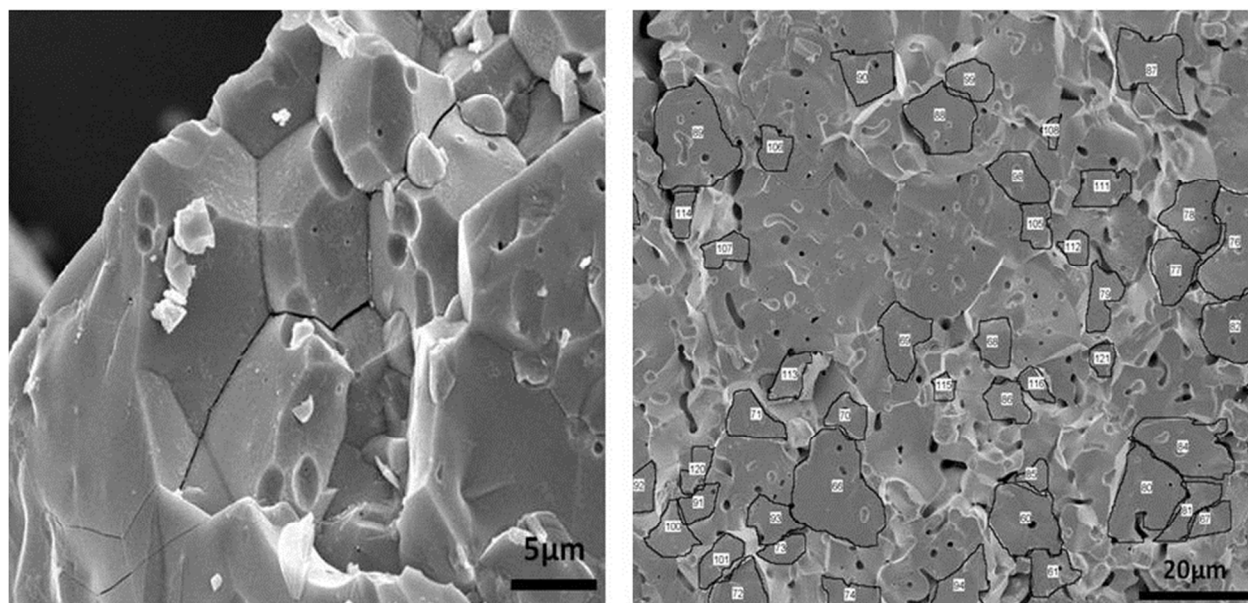


Figure 4 SEM images of a BSCF grain: surface of a grain (x4000) (left), bulk (x1000) (right). Crystallite size distribution measurement using ImageJ software

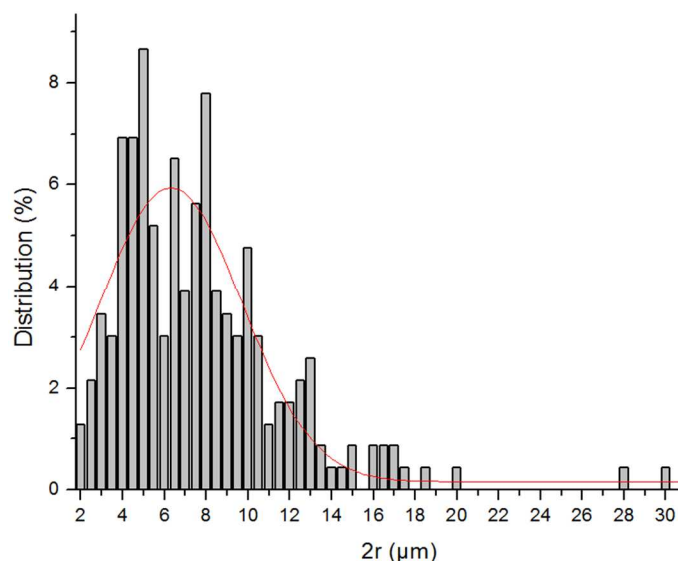


Figure 5 Distribution of the crystallite size from SEM image analysis for BSCF material

Isotopic exchange measurements were carried out on sieved powder with a mean grain size of about 500 μm . Assuming a mean crystallite radius (r) of 0.16 μm for LSCF and 3.5 μm for BSCF, a grain consists on average of 10,000,000 crystallites for LSCF and 5,000 for BSCF, respectively. The transport measurement in a grain is thus representative of the transport phenomena occurring in a continuous body such as a film or a membrane. We can also conclude that SSITKA measurements that are carried out over powders can account well for transport phenomena at the grain boundaries. In other words, the gentle crushing of the membrane into grains of 500 μm does not alter the microstructure of the solid.

From SSITKA modelling, the self-diffusion parameters (D^*) were calculated at two different oxygen partial pressures using the estimated characteristic diffusion times and the mean crystallite radius associated to each solids (Table 4). We can see major differences of the diffusion energies between LSCF and BSCF. As for the surface kinetic parameters of LSCF, the diffusion energy ($E_d = 76.9 \pm 10$) does not vary with the partial pressure. In contrast, the diffusion energy of BSCF significantly varies with the oxygen pressure, in line with results found elsewhere for $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_{3-\delta}$ ⁴². In addition, the activation energies of BSCF are much smaller ($35\text{--}48\text{ kJ mol}^{-1}$) when compare to LSCF which is in very good agreement with DFT calculations found elsewhere (43 kJ mol^{-1})⁴⁵.

Table 4 Characteristic time constants for diffusion estimates from regression analysis of the oxygen exchange response curve between 700–900°C, and self-diffusion parameter calculated using the crystallite radius (r) equal to 0.16 for LSCF and 3.5 μm for BSCF. Confidence intervals estimated at 95%.

Material	P_{O_2} kPa	D^{*0}/r^2 s^{-1}	D^{*0} $\text{cm}^2 \text{s}^{-1}$	E_d kJ mol^{-1}
LSCF	21	$(2.0 \pm 0.4)10^5$	$(5 \pm 1)10^{-5}$	76.9 ± 10
LSCF	1	$(3.0 \pm 0.6)10^5$	$(7.6 \pm 1.5)10^{-5}$	76.9 ± 10
BSCF	21	$(5.3 \pm 0.4)10^2$	$(6.5 \pm 0.4)10^{-5}$	35 ± 16
BSCF	1	$(7.4 \pm 0.9)10^3$	$(9.1 \pm 0.9)10^{-4}$	48 ± 16

The comparison of diffusion results with literature data are not straight forward since they can be obtained either in equilibrated or non equilibrated conditions. In addition, there are different types of diffusion parameters. The vacancy diffusivity, D_v , describes the rate of oxygen vacancy transport. The vacancy diffusion constant (D_v) is usually obtained from regression analysis using membrane permeation data. The self-diffusion of oxygen (D^*) and oxygen vacancy diffusion (D_v) coefficients are linked through the oxygen vacancy molar fraction θ_v by the following expression (22). The vacancy diffusion constant (D_v) of LSCF are calculated using equation (22) and compared with Xu and Thomson results in Table 5. Here again, we observe a perfect match between results obtained with the novel microkinetic approach from powder and the modelling of semi-permeability data by Xu and Thomson¹².

$$D_v = \frac{D^*(T, P_{\text{O}_2})(1 - \theta_v(T, P_{\text{O}_2}))}{f^* \theta_v(T, P_{\text{O}_2})} \quad (22)$$

Ishigaki *et al.*⁴⁸ calculated the correlation factor (f^*) of 0.69 for perovskites.

Table 5 Comparison of calculated oxygen self-diffusion rates at the given conditions with literature results for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$.

Shape	P_{O_2} kPa	D_v^0 $10^2 \text{ cm}^2 \text{s}^{-1}$	E kJ mol^{-1}	Ref
Powder	21	0.73 ± 0.1	76.9 ± 10	this work
Powder	1	1.10 ± 0.2	76.9 ± 10	this work
Membrane		1.58	73.9	¹²

The comparison of oxygen conductivity is another way to validate the diffusion data obtained by the microkinetic approach. The Nernst-Einstein equation allows the calculation of the oxygen conductivity (σ_0) from the oxygen self-diffusion (D^*) according to the formula:

$$\sigma_0 = \frac{4F^2(3 - \delta)D^*}{RTV_m} \quad (23)$$

F is the Faraday constant, R the gas constant and V_m the molar volume in mol cm^{-3} (SI-10).

For $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ with $P_{\text{O}_2} = 21$ kPa, Ullman *et al.*⁴⁹ found an oxygen conductivity of 0.007 S cm^{-1} . In this work, the oxygen conductivities calculated at 1073K, at 1 kPa and 21 kPa

are 0.003 and 0.005 S cm⁻¹ respectively in very good agreement with the literature.

The self-diffusion rates calculated at given conditions of temperature and oxygen pressure are compared with the literature results available on Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (Table 6). Good agreement is found with the values of the tracer diffusion

study, but not with those obtained by relaxation conductivity. The latter deviation is not of obvious origin, since it can arise either from a different material microstructure or from the fact that the measurement technique used is not a steady-state method.

Table 6 Comparison of calculated oxygen self-diffusion rates at the given conditions with literature results for Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ}.

Formulation	Method	T	P _{O2}	D*	Reference
		K	kPa	cm ² s ⁻¹	
Membrane	IEDP	973	50	8.0 10 ⁻⁷	Wang et al. ⁵⁰
Membrane	Conductivity relaxation	973	2.1	1.09 10 ⁻⁷	Bucher and al. ¹⁵
Membrane	Conductivity relaxation		1	3.99 10 ⁻⁸	Bucher and al. ¹⁵
Powder	SSITKA	973	21	8.3 10 ⁻⁷	Our work
Powder	SSITKA	973	1	2.4 10 ⁻⁶	Our work

General discussion

In this section, we describe the pros and cons of the different techniques and approaches for the estimation of kinetic and diffusion parameters in oxygen transport materials.

The model of Xu and Thomson was a major progress for the modelling of oxygen semi-permeability of perovskite membranes. Although a good fit with experimental data is obtained, the authors indicate that their model fails to describe the flux when the oxygen concentration is varied on the retentate side. Aside from modelling limitations, the estimation of transport coefficients from membrane testing presents practical challenges. The development of dense membranes is a very tedious process achieved mainly through trial and error⁵¹. In addition, the high temperatures required for good permeability often cause membrane breakdown during testing and/or issues with sealing. Consequently, alternative measurement methods are highly desired.

Electrical conductivity relaxation (ECR) allows the measurement of the oxygen self-diffusion parameter, D_{chem} , and the global exchange kinetic parameter, k_{chem} ^{14–16}. The measurements are carried out on sintered samples, which are then cut to obtain thin films. The electrical signal is measured under transient conditions by applying a step change in the pressure of oxygen. Unfortunately, this modifies the concentration of oxygen vacancies during the measurements and therefore introduces a bias in the estimation of adsorption and diffusion rate constants. The estimation of kinetic constants in a non-equilibrated regime usually makes the modelling and the parameter estimation quite complex. Solid electrolyte coulometry (SEC)²⁰ is an attractive alternative relaxation technique which is easier to use since measurements are carried out on powders. However, the concerns related to non steady-state measurements still remain²⁰.

Oxygen isotopic exchange techniques for which oxygen concentration steps are carried out at equilibrium conditions by replacing ¹⁶O₂ by ¹⁸O₂ are a very appropriate alternative solution. The oxygen isotopic exchange takes place under steady-state conditions, thus the oxygen partial pressure and the

concentration of oxygen vacancies are constant during the measurements. This also greatly simplifies the modelling and the parameter estimation. The technical and modelling advantages of steady-state transient methods have been described by Shannon and Goodwin⁵².

The group of Carter and Steele¹⁷ developed a steady-state isotopic ¹⁸O/¹⁶O technique called isotopic exchange depth profiling (IEDP), which allows the estimation of the global surface exchange (k^*) and diffusion (D^*) parameters^{18,19}. This technique is based on surface thin-film analysis by secondary ion mass spectrometry (SIMS), which provides a three-dimensional map of the ¹⁸O distribution^{53–55}. The assumption for the ¹⁸O transport modelling is that the rate of isotope exchange across the gas/solid interface is considered to be directly proportional to the difference in isotope concentration between the gas and the solid. Vacancy concentrations are not taken into account in the modelling. Diffusion is defined by Fick's law and is directly proportional to the exchange kinetics based on the film model.

$$-D^* \frac{\partial C}{\partial x} \Big|_{x=0} = k^* (C_s - C_g) \quad (24)$$

D^* is the self-diffusion parameter, and C_g and C_s are, respectively, the concentration in isotopic oxygen in the gas phase and in the solid phase. The IEDP technique is advantageous because it is carried out on a thin film that allows the direct application of the estimated parameters to the transport modelling of a flat membrane, due to identical geometry¹⁸. On the other hand, each experimental condition requires a new sample that must be prepared and shaped as a thin film. For this reason, sample preparation requirements make this technique tedious to use. In addition, this method usually requires a relatively high oxygen pressure (P_{O_2} =70 kPa) to obtain sufficient analytical resolution. This high oxygen partial pressure is not, however, consistent with membrane processes, which operate at much lower oxygen partial pressures, typically in the range of 1–21 kPa.

Isotopic $^{18}\text{O}_2/^{16}\text{O}_2$ exchange has also been carried out on samples in powder form for the estimation of the rate of adsorption and desorption, the concentration of oxygen on catalysts, and the surface diffusion coefficient of oxygen⁵⁶. In contrast to the IEDP technique, in which the $^{16}\text{O}/^{18}\text{O}$ gradient is measured in the solid after a given time, steady-state isotopic transient kinetic analysis (SSITKA) is a time-resolved method that analyzes the evolution of the isotope concentration in the gas phase by online mass spectrometry. The use of powders accelerates the experimental part of the work, while the use of intrinsic kinetic and transport parameters allows a coherent description of oxygen permeation through the membrane. The latter has been accomplished in this study by describing all the processes on the microkinetic scale (at the level of the elementary steps) and not, like most approaches reported in the literature so far, by lumped apparent parameters (a macrokinetic approach)^{57,58}. It might seem that carrying out the measurements over the powder-form sample could be a drawback of this approach, as this powder might not be representative of the microstructure of the membrane material. Indeed the issues of transport modelling when crystallite boundaries come into play were acknowledged to be a scientific challenge. In this study, we have clearly demonstrated that a gentle crushing of a perovskite sintered pellet preserve the microstructure of the solid, thus allowing a proper sampling for SSITKA experimentation.

We have presented a new methodology for evaluating the parameters needed to predict oxygen permeation through dense perovskite membranes. Rather than measuring the permeation flux over a membrane or a thin film, which is delicate and time-consuming to produce, measurements were carried out directly on the powder sample. The measurements consisted of a combination of TGA and isotopic oxygen exchange experiments. Both techniques are straightforward. In a TGA experiment, the sample is subjected to a temperature ramp going up or down under controlled oxygen flow. In the case study presented here, the kinetic and transport parameters for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ have been determined using this methodology. The approach retained can be used for reducible oxides that form oxygen vacancies. If necessary, more complicated oxygen non-stoichiometry thermodynamic models can be integrated into the approach, thus making it applicable to other MIECs. In a forth coming study, we will show that by combining the microkinetic model with a hydrodynamic model (*e.g.*, mass transfer) of the membrane configuration, the overall oxygen permeation can be correctly predicted in various conditions of pressure, temperature and membrane thickness.

Conclusions

We have described an original method based on a microkinetic approach for the estimation of the oxygen transport parameters from powder. This original approach has been first validated on the reference perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ and then has

been applied to $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ powder. In contrast to previous IEDP, ERC and SSITKA studies that can determine the global exchange kinetic parameter, our microkinetic modelling approach allows the estimation of the forward and reverse kinetic rate, thereby accounting for the oxygen vacancy concentration. In addition, the self-diffusion rate coefficient was estimated at different oxygen partial pressures. This microkinetic approach that combines SSITKA and TGA measurements has the potential to significantly accelerate the characterization of oxygen transport in perovskites and related materials. In this study, the kinetic parameters were measured in a temperature window between 873 K and 1173 K and at two pressure conditions (21 kPa and 1 kPa) chosen for their appropriateness for simulating the semi-permeability of oxygen in a membrane in a process of oxygen separation from air. The values of the estimated parameters for oxygen adsorption and diffusion over $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ in powder form are the same as those obtained by Xu and Thomson¹² over the same perovskite but in a membrane configuration, implying that the approach shown here allows calculating the oxygen flux through the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ dense membrane. The simulation of the oxygen flux of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membrane using the estimated parameters obtained from the corresponding powder will be reported in an upcoming study.

Acknowledgements

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Symbol	
δ	oxygen non-stoichiometry (-)
$P'_{\text{O}_2}, P''_{\text{O}_2}$	partial pressure of oxygen on the rich side and on the lean side, respectively (atm)
$\text{O}^{\times}_{\text{O},\text{s}}, \text{O}^{\times}_{\text{O},\text{b}}$	surface oxygen and bulk oxygen, respectively(-)
$\text{V}^{\times}_{\text{O},\text{s}}, \text{V}^{\times}_{\text{O},\text{b}}$	surface oxygen vacancies and bulk oxygen vacancies, respectively(-)
h°, h	electron hole, electron hole concentration(-)
$\theta_{\text{V}}, \theta_{16\text{O}}, \theta_{18\text{O}}$	vacancy coverage, ^{16}O coverage and ^{18}O coverage(-)
U	superficial velocity(cm s^{-1})
J_{O_2}	oxygen flux($\text{mol cm}^{-2} \text{s}^{-1}$)
D_{V}	diffusion of vacancies($\text{cm}^2 \text{s}^{-1}$)
D^*	self-diffusion of oxygen($\text{cm}^2 \text{s}^{-1}$)
k	surface rate coefficient(cm s^{-1})
k_{f}	forward adsorption rate coefficient($\text{Pa}^{-1} \text{s}^{-1}$)
k_{f}°	forward adsorption pre exponential factor($\text{Pa}^{-1} \text{s}^{-1}$)
k_{r}	reverse adsorption rate coefficient(s^{-1})
k_{r}°	reverse adsorption pre exponential factor(s^{-1})
K	Langmuir constant(Pa^{-1})
K°	Langmuir constant pre exponential factor(Pa^{-1})
$S_{\text{(BET)}}$	BET surface area ($\text{cm}^2 \text{g}^{-1}$)
ρ	solid density(g cm^{-3})
d_{crys}	crystallite diameter(cm)
$E_{\text{f}}, E_{\text{r}}$	activation energy associated with the adsorption or desorption, respectively(kJ mol^{-1})
ΔH	oxygen adsorption enthalpy(kJ mol^{-1})
r	crystallite radius(μm)
L_{t}	number of active sites ($\text{mol m}^{-3}_{\text{S}}$)
ϵ_{b}	inter-granular void space ($\text{m}^3_{\text{G}} \text{m}^{-3}_{\text{R}}$)
D_{e}	effective axial diffusivity($\text{m}^2 \text{s}^{-1}$)
z	axial reactor coordinate(m_{R})
R	gas constant($\text{J mol}^{-1} \text{K}^{-1}$)

T	absolute temperature(K)
v_{ij}	stoichiometric coefficient for species i in reaction j(-)
r_j	reaction rate of step j(s ⁻¹)
V _m	molar volume(mol cm ⁻³)
σ_O	oxygen conductivity(S cm ⁻¹)
F	Faraday constant(C mol ⁻¹)

Notes and references

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† Electronic Supplementary Information (ESI) available: [1] XRD after crushing; 2) Solid density; 3) SSITKA experimental bench; 4) Determination of the type of oxygen isotopic exchange; 5) Determination of the variation of the quantity of vacancies from TGA experiments; 6) Impact of a dwell on the TGA signal; 7) Stability of the perovskite before and after TGA; 8) Determination of the Langmuir parameters; 9) Correlation of the parameters; 10) V_m calculation from mesh parameter obtained through *in situ* XRD experiments]. See DOI: 10.1039/b000000x/

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