

Oxygen exchange measurements on perovskites as cathode materials for solid oxide fuel cells

W. Preis, E. Bucher, W. Sitte*

Institute of Physical Chemistry, University of Leoben, Franz-Josef-Strasse 18, A-8700 Leoben, Austria

Abstract

Oxygen exchange measurements have been applied to determine simultaneously the chemical diffusion coefficient and the surface exchange coefficient of oxide perovskites. The oxygen partial pressure is changed in a step-wise manner and the relaxation of the oxide ceramics is followed as a function of time. Instead of recording the amount of exchanged oxygen, the rate of oxygen incorporation reactions is measured directly. It is shown how the kinetic parameters can be extracted from the time dependence of the oxygen flux between the sample and the surrounding gas phase. The effect of finite switching times of the reactor on the relaxing oxygen flux is investigated theoretically. The time constant of the reactor is shown to be negligibly small under the chosen experimental conditions. The oxygen exchange measurements have been performed on $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) at 725 and 825 °C as a function of the oxygen partial pressure $p(\text{O}_2)$ ranging from 10^{-4} to 10^{-3} bar. The chemical diffusion coefficient is almost independent of $p(\text{O}_2)$ at constant temperature, whereas the exchange coefficient increases significantly with increasing $p(\text{O}_2)$. Finally, the dependence of the chemical exchange coefficient on the oxygen partial pressure is interpreted in terms of different mechanisms for the surface reaction. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanum strontium cobaltite; Chemical diffusion coefficient; Surface exchange coefficient; Surface exchange kinetics; Solid oxide fuel cell (SOFC)

1. Introduction

Acceptor doped oxide perovskites play an important role as potential solid oxide fuel cell (SOFC) cathode materials [1,2]. Amongst others, a necessary requirement for the application of such oxide ceramics in SOFCs is the rapid incorporation of oxygen from the gas phase and its fast transport in the bulk of these materials to the phase boundary with the solid electrolyte. Thus, both the understanding of the mechanism of oxygen exchange reactions and the experimental determination of kinetic parameters, such as the chemical diffusion coefficient or the surface exchange coefficient, provide useful information for the selection of promising new materials.

Strontium substituted lanthanum cobaltites, $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSC), are mixed ionic–electronic conductors with a fairly high oxygen deficiency at elevated temperatures [3–5]. As trivalent lanthanum is substituted by the divalent acceptor dopant strontium, defect electrons are created which give rise to a high p-type electronic conductivity [6]. In addition, the high concentration of oxygen vacancies causes a high ionic conductivity. These large conductivities

generally favour high rates of oxygen surface exchange and diffusion, making LSC attractive for the application in high-temperature electrochemical devices.

It is the aim of this paper to present oxygen exchange measurements for the determination of chemical diffusion coefficients as well as surface exchange coefficients of oxide ceramics. In the case of conductivity relaxation experiments the variation of the amount of exchanged oxygen is recorded as a function of time. On the contrary, the technique proposed in this contribution is based on the direct measurement of the rate of oxygen exchange (oxygen flux) between the gas phase and the oxide perovskite. This method is applied to $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ in order to investigate the oxygen partial pressure dependence of the chemical diffusion coefficient as well as the exchange coefficient at constant temperature. LSC is particularly suitable for fundamental studies because of its fast exchange kinetics. Furthermore, the mechanism of the surface exchange reaction will be interpreted in terms of different rate controlling steps.

2. Theory

A sudden change of the oxygen partial pressure in the ambient atmosphere of mixed ionic–electronic conducting

* Corresponding author. Tel.: +43-3842-402-330;
fax: +43-3842-402-335.
E-mail address: w.sitte@unileoben.ac.at (W. Sitte).

oxide ceramics causes a release or uptake of oxygen of the sample until a new equilibrium (oxygen non-stoichiometry δ) is attained. The rate of oxygen exchange (oxygen flux) between the sample and the gas phase can be followed directly by the help of solid electrolyte coulometry in a constant carrier gas stream (see Section 3 of this work). The time dependence of the oxygen flux owing to the relaxation of the oxygen content of the specimen is given by the reaction rate for the oxygen exchange at the surface and the chemical diffusion of oxygen in the bulk of the sample. The chemical diffusion process is described by Fick's second law of diffusion

$$\frac{\partial c}{\partial t} = \tilde{D} \frac{\partial^2 c}{\partial x^2} \quad (1)$$

where the chemical diffusion coefficient \tilde{D} is assumed to be spatially invariant and c denotes the concentration of the diffusing component. When the surface exchange reaction obeys first-order kinetics, the conservation of fluxes at the surface leads to the boundary condition

$$\tilde{D} \frac{\partial c}{\partial x} = \pm \tilde{k}(c - c_s); \quad x = 0, L \quad (2)$$

with \tilde{k} denoting the chemical surface exchange coefficient. In this contribution the model for the sample geometry is confined to a plane sheet with two parallel surface planes a distance L apart. Since the diameter of the disc-shaped samples exceeds the thickness by far, any exchange reactions at the lateral surface can be excluded. The symbol c_s is the surface concentration of the diffusant, if the sample is in equilibrium with the gas phase. In the case of an ideal step-like change of the oxygen partial pressure the concentration c_s is constant during the relaxation experiment. When finite time is required to flush the reactor containing the specimen with gas of a new composition, the oxygen partial pressure in the gas phase as well as the concentration c_s vary gradually with time. The finite switching time can be taken into account by introducing a characteristic time constant τ for the reactor

$$c_s = c_0 + (c_\infty - c_0) \left[1 - \exp\left(-\frac{t}{\tau}\right) \right] \quad (3)$$

where c_∞ and c_0 are the final and initial concentrations of the diffusing component in the oxide ceramics, respectively.

The diffusion problem outlined above (Eqs. (1)–(3)) can be solved by means of the Laplace transform method, resulting in

$$\begin{aligned} \frac{c - c_0}{c_\infty - c_0} = & 1 - hL \sum_{n=0}^{\infty} \frac{\cos[\alpha_n(x - L/2)]}{\cos(\alpha_n L/2) (h^2 L^2/4 + hL/2 + L^2 \alpha_n^2/4)} \\ & \times \left\{ \exp(-\alpha_n^2 \tilde{D} t) - \frac{\alpha_n^2 \tilde{D}}{\alpha_n^2 \tilde{D} - 1/\tau} \right. \\ & \left. \times \left[\exp(-\alpha_n^2 \tilde{D} t) - \exp\left(-\frac{t}{\tau}\right) \right] \right\} \quad (4) \end{aligned}$$

The parameters α_n are given by the positive roots of the transcendental equation

$$\alpha_n \tan\left(\alpha_n \frac{L}{2}\right) = h \quad (5)$$

with h being the ratio between the surface exchange coefficient and the chemical diffusion coefficient $h = k/\tilde{D}$. The oxygen flux into or out of the sample J_{ex} can be written as

$$J_{\text{ex}} = \frac{n_{\text{O}}}{L} \frac{\partial}{\partial t} \int_{x=0}^L \frac{c - c_0}{c_\infty - c_0} dx \quad (6)$$

The total amount of oxygen n_{O} , exchanged with the sample during the experiment, is defined as

$$n_{\text{O}} = \int_{t=0}^{\infty} |J_{\text{ex}} - J_\infty| dt \quad (7)$$

Inserting Eq. (4) into Eq. (6) leads to the exact expression for the time dependence of the total oxygen flux J in the case of finite switching time for the reactor (non-ideal step response)

$$\begin{aligned} J = & J_0 \exp\left(-\frac{t}{\tau}\right) \\ & + 2n_{\text{O}} \tilde{D} h^2 \sum_{n=0}^{\infty} \frac{1/\tau \exp(-\alpha_n^2 \tilde{D} t) - \exp(-t/\tau)}{1/\tau - \alpha_n^2 \tilde{D} h^2 L^2/4 + hL/2 + L^2 \alpha_n^2/4} \quad (8) \end{aligned}$$

The first term at the right-hand side of Eq. (8) is a capacitive flux, $J_0 \exp(-t/\tau)$, necessary for charging the empty reactor volume. The second term corresponds to the oxygen flux J_{ex} due to the reaction of the specimen with the gas phase.

A Turbo Pascal routine was written which enables the simulation of transients of the oxygen flux. The kinetic parameters \tilde{D} and \tilde{k} are determined by applying a non-linear least squares fit of Eq. (8) to the experimental data. The application of iterative procedures [7] for the numeric calculation of the roots of transcendental equations is a well-known technique in the literature [8,9] in order to compute concentration profiles for a number of diffusion processes. With respect to the present diffusion problem usually 8–12 iteration steps were sufficient to solve the transcendental Eq. (5). In general, the iteration procedure was stopped when the relative change of the parameter α_n between two successive iteration steps was smaller than 10^{-9} . The series in Eq. (8) converged after two to three terms except at short times where up to 10–15 terms were necessary to obtain reliable solutions.

Fig. 1 shows calculated curves of the oxygen flux for various time constants τ of the reactor by using Eq. (8). In general, the time constant of the reactor can be altered by modifying the reactor volume and/or the flow rate of the gas. All lines in Fig. 1a are calculated for constant oxygen fluxes at $t = 0$, i.e. $J_0 = \text{constant}$. In this case the time constant is increased by raising the volume (capacity) of the empty reactor at a constant flow rate of the gas, which likewise

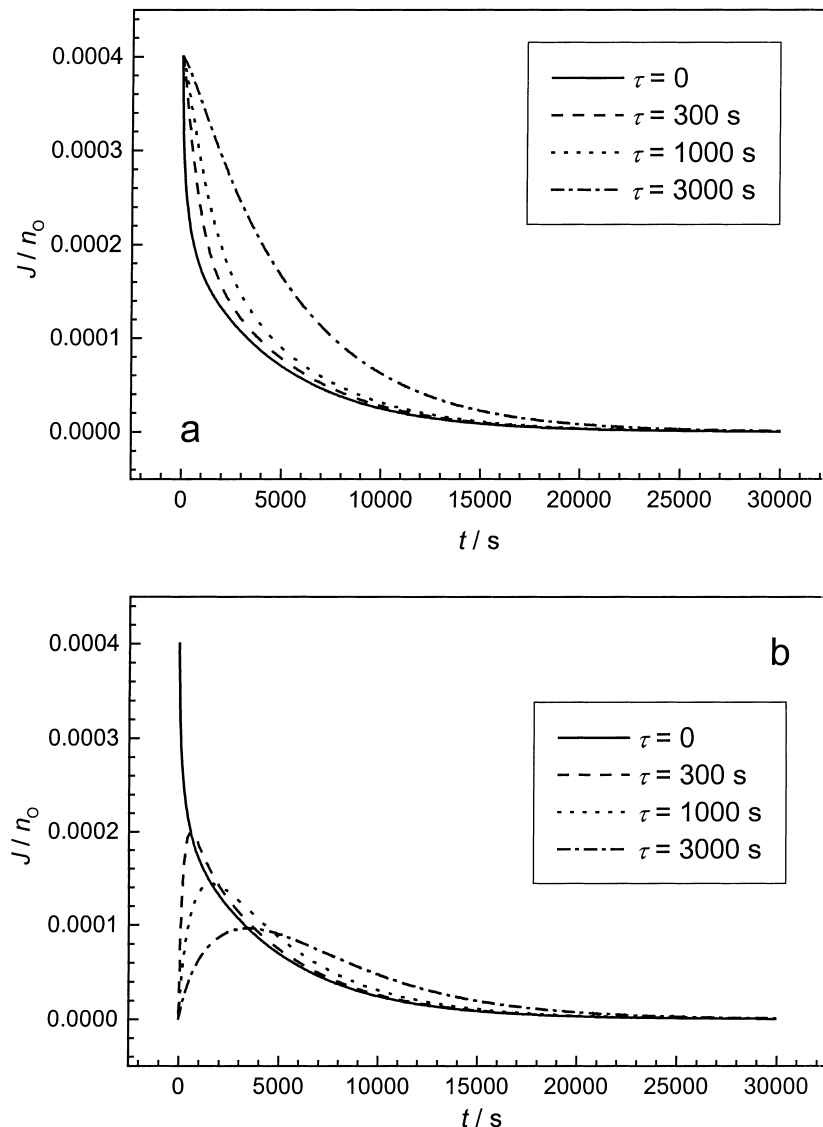


Fig. 1. Simulation of the effect of a finite switching time of the reactor on the normalized oxygen flux J/n_O into or out of a perovskite oxide. $L = 0.05$ cm; $\tilde{D} = 10^{-7}$ cm² s⁻¹; $\tilde{k} = 10^{-5}$ cm s⁻¹. (a) The time constant τ of the reactor is varied by increasing the reactor volume at a constant flow rate of the gas stream, $J_0/n_O = 4 \times 10^{-4}$ = constant. (b) The time constant τ of the reactor is varied by decreasing the flow rate of the gas stream at a constant volume of the reactor, $J_0\tau/n_O = 4 \times 10^{-4}$ = constant.

leads to increasing areas under the curves in Fig. 1a. The different time constants in Fig. 1b are obtained by varying the flow rate of the gas and fixing the capacity (volume) of the reactor, i.e. $J_0\tau = \text{constant}$. Interestingly, all curves in Fig. 1b show a maximum at their intersection with the line valid for $\tau = 0$. The increase of the oxygen flux at very short reaction times can be attributed to the increase of the reaction rate at the surface of the sample at a very early stage of the exchange process owing to the gradual change of the oxygen content in the gas phase and negligible capacitive fluxes for charging/discharging the empty reactor. Obviously, in all cases (Fig. 1a and b) the deviation from the ideal step-like response is more pronounced at higher time constants of the reactor.

3. Experimental

Experiments towards the determination of \tilde{D} and \tilde{k} were carried out using the oxygen deficient perovskite $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC). Details on the preparation of LSC samples are given elsewhere [5]. For the analysis of the oxygen flux the Oxylyt system (SensoTech, Germany) was used with which the oxygen flux J is monitored by transforming the flux into an electrical current $I = 2FJ$ (F denotes the Faraday constant) by means of appropriate electrochemical oxygen pumps. The electrochemical oxygen pumps are tubular cells consisting of stabilised zirconia operated at 700 °C. The quartz reactor containing the sample is connected to two electrochemical pumps, one of which is

used for adjusting the oxygen partial pressure in the gas stream entering the reactor by coulometric titration from pure argon (99.999%). The second pump analyses the gas stream after passing the reactor. The electrical current, necessary to keep the composition of the gas streaming out of the reactor at a constant level, corresponds directly to the relaxing oxygen flux due to oxygen exchange reactions inside the reactor. Additional details can be found in [5,10].

The oxygen exchange measurements were performed on a sintered disc-shaped sample of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ with a thickness of 0.0776 cm and a diameter of approximately 0.8 cm. Usually, the oxygen partial pressure steps were in the range $0.2 \leq \Delta \log p(\text{O}_2) \leq 0.4$. The experiments were carried out at various partial pressures of oxygen from 10^{-4} to 10^{-3} bar at 725 as well as 825 °C.

4. Results and discussion

A typical charging/discharging process of the empty reactor is depicted in Fig. 2. Usually, the time constants of the reactor were found to be in the range from 3 to 8 s. Therefore, a new composition of the gas phase can be adjusted fast enough that the resulting transients of the oxygen flux are almost indistinguishable from an ideal step response with negligible capacitive fluxes, $J_0 \exp(-t/\tau) \ll J_{\text{ex}}$. All exchange measurements were evaluated with the parameter τ arbitrarily set equal to 5 s which is lower by orders of magnitude than the relaxation times for oxidation/reduction reactions of oxide ceramics investigated in this study.

The variation of the oxygen flux with time for a typical oxygen exchange measurement on $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ at 825 °C is illustrated in Fig. 3. Examples for both an oxidation ($\log[p(\text{O}_2)/\text{bar}]$: $-3.99 \rightarrow -3.79$) and a reduction

($\log[p(\text{O}_2)/\text{bar}]$: $-3.79 \rightarrow -3.99$) experiment are presented. It can be deduced from Fig. 3 that Eq. (8) provides a perfect fit to the experimental data. The optimised parameters derived from the oxidation process ($\tilde{D} = 2.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$; $\tilde{k} = 1.4 \times 10^{-5} \text{ cm s}^{-1}$) agree reliably with those obtained from the reduction process ($\tilde{D} = 1.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$; $\tilde{k} = 1.6 \times 10^{-5} \text{ cm s}^{-1}$). The oxidation reactions seem to proceed faster than the pertinent reduction processes. Thus, oxidising the sample yields somewhat higher values for the chemical diffusion coefficient compared to the results of the reduction experiments.

The logarithm of the chemical diffusion coefficient \tilde{D} of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ measured at 725 and 825 °C is plotted as a function of $\log p(\text{O}_2)$ in Fig. 4. Intermediate values of the $p(\text{O}_2)$ intervals were used to calculate the pertinent $\log p(\text{O}_2)$ values. Fig. 4 reveals that no dependence of \tilde{D} on the partial pressure of oxygen at constant temperature can be observed. In general, the chemical diffusion coefficient is expected to increase with decreasing $p(\text{O}_2)$ because of the increase of the oxygen vacancy concentration. This effect, however, seems to be counterbalanced by the occurrence of defect ordering at low oxygen partial pressures [11–13]. A similar behaviour of the chemical diffusion coefficient was observed for $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ by Wang et al. [14]. In addition, van Doorn et al. [15] found the tracer diffusion coefficient of $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ to be independent of $p(\text{O}_2)$.

Fig. 5 shows a double-logarithmic plot of the chemical surface exchange coefficient \tilde{k} of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ as a function of the partial pressure of oxygen at 725 and 825 °C. In contrast to the chemical diffusion coefficient the surface exchange coefficient increases with increasing $p(\text{O}_2)$. The slopes of the solid lines in Fig. 5 amount to (0.37 ± 0.08) at 725 °C and (1.12 ± 0.20) at 825 °C, respectively. Wang et al. [14] report slopes of $\log \tilde{k}$ versus $\log p(\text{O}_2)$ plots to be in the range from 0.3 to 0.4 for

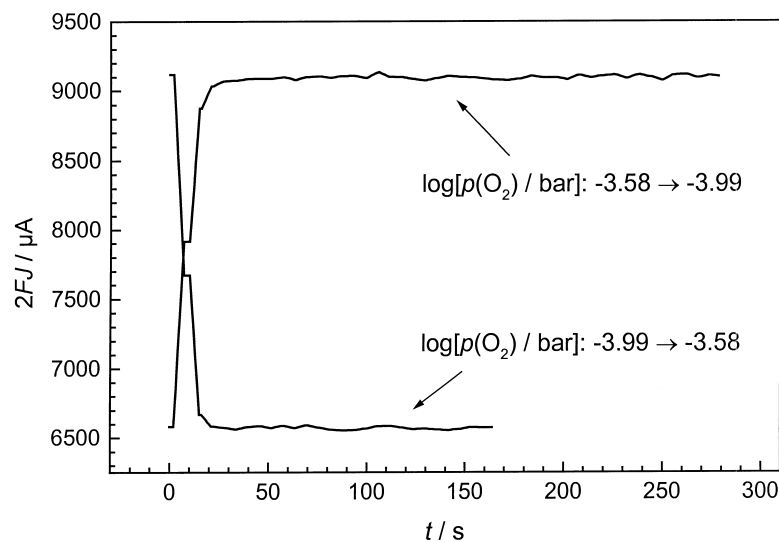


Fig. 2. Experimental determination of the time constant of the reactor with oxygen flux into or out of the empty reactor plotted against time. Oxidation step: $\log[p(\text{O}_2)/\text{bar}]$: $-3.99 \rightarrow -3.58$, $\tau = 3.0$ s. Reduction step: $\log[p(\text{O}_2)/\text{bar}]$: $-3.58 \rightarrow -3.99$, $\tau = 3.8$ s.

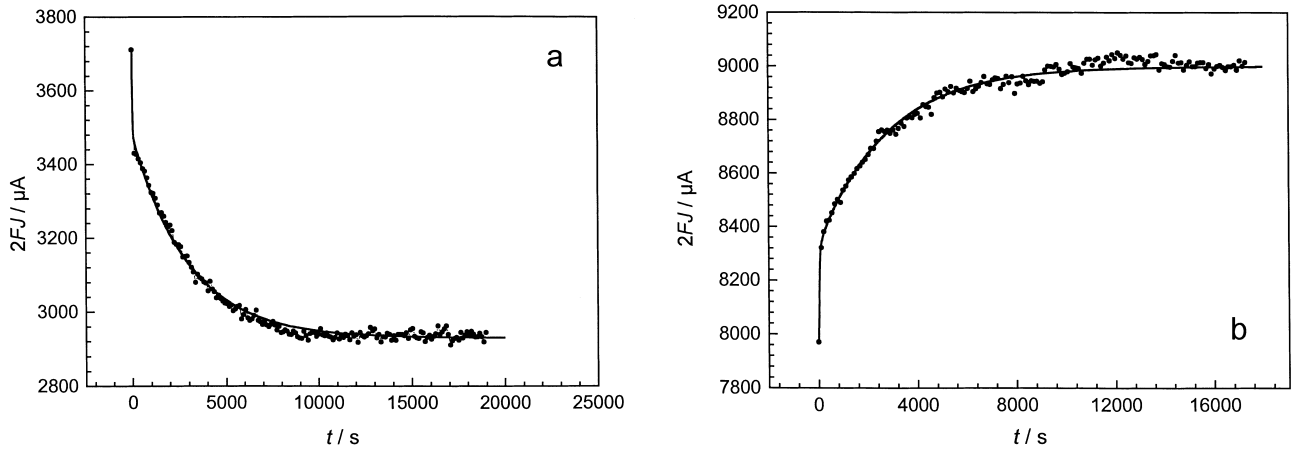


Fig. 3. Plot of the oxygen flux vs. time for typical exchange experiments on $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ at 825°C ($L = 0.0776\text{ cm}$; $\tau = 5.0\text{ s}$). (a) Oxidation step: $\log[p(\text{O}_2)]/\text{bar}$: $-3.99 \rightarrow -3.79$; $\tilde{D} = 2.5 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$; $\tilde{k} = 1.4 \times 10^{-5}\text{ cm s}^{-1}$. (b) Reduction step: $\log[p(\text{O}_2)]/\text{bar}$: $-3.79 \rightarrow -3.99$; $\tilde{D} = 1.3 \times 10^{-6}\text{ cm}^2\text{ s}^{-1}$; $\tilde{k} = 1.6 \times 10^{-5}\text{ cm s}^{-1}$. The solid lines are least squares fits of Eq. (8) to the experimental data.

$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ and van Doorn et al. [15] obtained $d \log \tilde{k}^*/d \log p(\text{O}_2) = 0.41$ for the tracer exchange coefficient of $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$.

Following the procedure outlined by Maier [16], the dependence of the chemical exchange coefficient on the partial pressure of oxygen can be written as

$$\tilde{k} = k_f p(\text{O}_2)^{1/2} \frac{\delta}{3 - \delta} \vartheta \quad (9)$$

when the rate determining step is a phase (charge) transfer reaction of adsorbed oxygen atoms $\text{O}_{\text{ad}} + \text{V}_{\text{O}}^{\bullet\bullet} \leftrightarrow \text{O}_{\text{O}}^{\times} + 2h^{\bullet}$ using Kröger–Vink notation. The symbol k_f denotes the rate constant for the forward reaction of the oxygen phase transfer, including all constants for the transformation of the concentration of adsorbed oxygen atoms into $p(\text{O}_2)^{1/2}$. The thermodynamic factor ϑ is defined as $\vartheta = 1/2[d \log p(\text{O}_2)/d \log c]$ and δ is the oxygen non-stoichiometry parameter. If the

dissociative adsorption of oxygen atoms is the rate determining step, $(1/2)\text{O}_2(\text{g}) + \text{V}_{\text{ad}} \leftrightarrow \text{O}_{\text{ad}}$, the chemical surface exchange coefficient is given by

$$\tilde{k} = k'_f p(\text{O}_2)^{1/2} \frac{V_m}{3 - \delta} \vartheta \quad (10)$$

The parameters V_m and k'_f refer to the molar volume of the oxide ceramics and the rate constant for the forward reaction of the adsorption process including the concentration of empty surface sites, respectively. According to the data for the oxygen non-stoichiometry of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ presented in [10] $\log[\vartheta/(3 - \delta)]$ is almost independent of $\log p(\text{O}_2)$, whereas $\log \delta$ varies significantly with $\log p(\text{O}_2)$. The oxygen pressure dependence of δ is estimated to be $d \log \delta/d \log p(\text{O}_2) = -0.094$ at 725°C and $d \log \delta/d \log p(\text{O}_2) = -0.11$ at 825°C . Combining these values with Eqs. (9) and (10) the slope $d \log \tilde{k}/d \log p(\text{O}_2)$ should

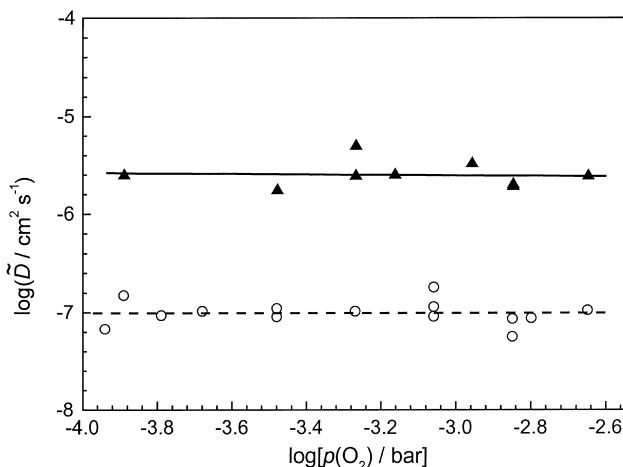


Fig. 4. Double-logarithmic plot of the chemical diffusion coefficient of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ as a function of the partial pressure of oxygen. Open circles: 725°C ; solid triangles: 825°C . The lines are linear least squares fits as a guide to the eye.

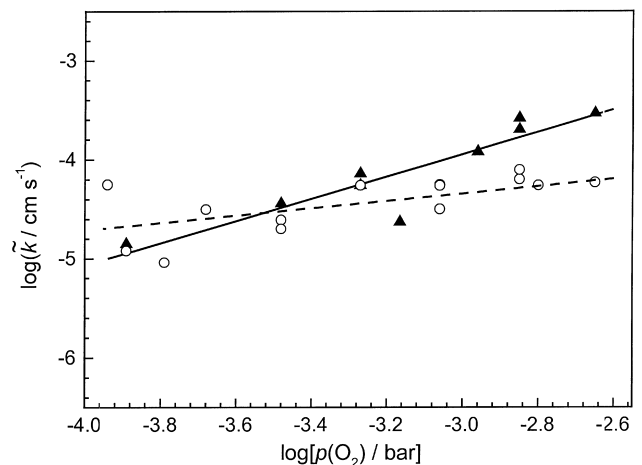


Fig. 5. Double-logarithmic plot of the chemical surface exchange coefficient vs. partial pressure of oxygen. Open circles: 725°C ; solid triangles: 825°C ; dashed line: 725°C ; slope = 0.37 ± 0.08 ; solid line: 825°C ; slope = 1.12 ± 0.20 .

amount to approximately 0.4 for phase transfer control and 0.5 for adsorption control. It can be concluded that at least at 725 °C the $p(\text{O}_2)$ dependence of \tilde{k} provides evidence for a phase transfer controlled mechanism of the surface exchange kinetics of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$. It should be noted that Wang et al. and van Doorn et al. arrived at similar conclusions. However, the $p(\text{O}_2)$ dependence of \tilde{k} at 825 °C cannot be interpreted in terms of a phase transfer or an adsorption control of the surface kinetics. It should be mentioned that in the case of $\text{La}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}$ (higher doping level of the acceptor dopant Sr) the slope of $\log \tilde{k}$ plotted versus $\log p(\text{O}_2)$ shows likewise values around 1.0 [10].

5. Conclusions

A detailed analysis of oxygen exchange measurements on $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ has been presented. The oxygen partial pressure has been changed abruptly and the rate of the oxygen exchange between the relaxing oxide ceramics and the surrounding gas phase has been determined directly. Thus, the variation of the oxygen flux with time has been monitored, alternatively to conductivity relaxation measurements where the amount of oxygen incorporated or released by the sample is followed as a function of time. A model has been developed taking into account the effect of a finite switching time of the reactor on the resulting transients of the relaxing oxygen flux. However, it has been shown experimentally that the switching times are very short ensuring an ideal step response. It has been outlined how important kinetic parameters, such as the chemical diffusion coefficient or the chemical surface exchange coefficient, can be extracted from the time dependence of the relaxation curves of the oxygen flux into or out of the sample. It should be mentioned that even if the chemical diffusion coefficient is higher by several orders of magnitude than the surface exchange coefficient, the surface reaction can dominate the oxygen exchange process in the case of thin films of the mixed conducting perovskite ($L \ll \tilde{D}/\tilde{k}$). Such thin films may become important for the application in SOFCs.

The investigation of the variation of the exchange coefficient with the partial pressure of oxygen allows to

understand the mechanism of surface exchange kinetics of mixed conducting perovskites. An analysis of different mechanisms, viz. phase (charge) transfer control and adsorption control, revealed the phase transfer reaction of adsorbed oxygen atoms to be rate limiting at least in the case of $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ at 725 °C.

Acknowledgements

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