



ELSEVIER

Solid State Ionics 96 (1997) 1–7

**SOLID  
STATE  
IONICS**

## Surface oxygen exchange of $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$

René H.E. van Doorn<sup>a,\*</sup>, Ian C. Fullarton<sup>b</sup>, Roger A. de Souza<sup>b</sup>, John A. Kilner<sup>b</sup>, Henny J.M. Bouwmeester<sup>a</sup>, Anthonie J. Burggraaf<sup>a</sup>

<sup>a</sup>Laboratory for Inorganic Chemistry and Materials Science, Department of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

<sup>b</sup>Department of Materials, Imperial College of Science Technology and Medicine, London SW7 2BP, United Kingdom

Received 3 May 1996; accepted 10 December 1996

### Abstract

The surface oxygen exchange of  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$  has been studied by  $^{18}\text{O}/^{16}\text{O}$  exchange followed by dynamic SIMS analysis in the temperature region 700–900°C at a  $p_{\text{O}_2}$  of  $2.1 \times 10^4$  Pa. The activation energy for the surface exchange rate ( $k$ ) is  $28 \pm 5$  kJ mol<sup>-1</sup> and for the oxygen tracer diffusion coefficient ( $D^*$ )  $56 \pm 4$  kJ mol<sup>-1</sup>. The absolute values for both  $k$  and  $D^*$  are among the highest known in the literature. The characteristic thickness at a  $p_{\text{O}_2}$  of  $2.1 \times 10^4$  Pa is calculated to lie in the range 0.70 to 1.3 mm and is a function of temperature. The latter reflects the different activation energies for  $k$  and  $D^*$ . The surface oxygen exchange coefficient is proportional to  $p_{\text{O}_2}^n$  with  $n = 0.41 \pm 0.02$  at 800°C, which has been explained by a rate determining step involving an adsorbed oxygen species and an oxygen vacancy. No oxygen pressure dependence for the tracer diffusion coefficient was observed at this temperature.

**Keywords:**  $^{18}\text{O}/^{16}\text{O}$  exchange;  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ ; Tracer diffusion coefficient; Surface exchange; Vacancy diffusion coefficient

### 1. Introduction

Oxygen permeation through dense mixed conducting membranes comprises two different processes viz. surface exchange and (ionic) diffusion [1,2]. The ionic conductivity of phases  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  has been discussed elsewhere [1,2]. In these papers, it was found that the permeation flux through highly Sr doped  $\text{LaCoO}_{3-\delta}$  is limited by surface exchange even for a 2.0 mm thick sample.

The surface oxygen exchange of Sr-doped

$\text{LaCoO}_{3-\delta}$  has been reported in the literature only for lower doped compositions [3–9]. These results were mainly obtained at a fixed  $p_{\text{O}_2}$  and no information is available on the  $p_{\text{O}_2}$ -dependence of the surface oxygen exchange rate. Furthermore, this data has been partly obtained from experiments on single crystals [6,7] and the surface exchange on polycrystalline materials may be different, as suggested by Yasuda et al. [10]. The latter study has, however, been performed on  $\text{La}_{1-x}\text{Ca}_x\text{CrO}_3$  a material with a considerably lower ionic conductivity and hence a far more important contribution of the grain boundaries to the ionic conductivity. In the highly doped materials investigated in this study, the bulk

\*Corresponding author. Present address: Air Products and Chemicals, 7201 Hamilton Boulevard, Allentown, PA 18195-1501, USA. Fax: (1-610) 481-6517; e-mail: vandoorh@apci.com

ionic diffusivity and contributions due to grain boundaries will be negligible or even blocking.

In the study by Ishigaki et al. [6] on single crystal  $\text{LaCoO}_{3-\delta}$ , no  $p_{\text{O}_2}$ -dependence of  $k$  could be detected. The tracer diffusion coefficient, however, showed a  $p_{\text{O}_2}^{-0.35}$  dependence in the  $p_{\text{O}_2}$  range of  $2.0 \times 10^3$  to  $1.0 \times 10^4$  Pa at  $950^\circ\text{C}$ .

Results of cathodic polarisation measurements on  $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{B}'_y\text{O}_{3-\delta}$  ( $\text{B}' = \text{Co}, \text{Ni}, \text{Fe}, \text{Mn}$  or  $\text{Cu}$ ) of Inou et al. [11–13] suggest high surface exchange coefficients for these materials. The results further suggest a correlation between the lowest temperature at which theoretical Nernst behaviour is attained and the vacancy concentration of the material. Results of cathodic polarisation measurements by Takeda et al. on  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $0 \leq x \leq 0.7$ ) also indicate high surface exchange rates [14]. An increase in exchange rate with Sr-doping level was observed. These authors further concluded that the charge transfer reaction probably is the rate limiting step in the surface exchange reaction.

It is noted that, although surface oxygen exchange properties have been reported in the literature on  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  materials, it is not certain that under actual oxygen permeation conditions this is the phase present at the surface [15]. This point is further discussed in Section 4.

In a recent paper by Kilner [16] it was suggested that the surface exchange is proportional to the square root of the tracer diffusion coefficient for the type of perovskites employed in this study. He also suggested a maximum value of 100 for the ratio between  $k$  and  $D^*$ .

Although the data showed considerable scattering, results of Fullarton et al. [17] on  $\text{Sm}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  ( $0 \leq x \leq 0.6$ ) indicate an increase in the surface exchange rate with Sr doping level, which may be due to the increased number of oxygen vacancies present at an increased Sr-doping level [17].

In this paper a study of the rate of the oxygen exchange on dense samples of  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$  is reported in the temperature range  $700\text{--}1000^\circ\text{C}$  at a  $p_{\text{O}_2}$  of  $2.1 \times 10^4$  Pa. The  $p_{\text{O}_2}$ -dependence was measured in the  $p_{\text{O}_2}$  range  $4.0 \times 10^2\text{--}1.0 \times 10^5$  Pa at  $800^\circ\text{C}$ . Experiments were performed by annealing disks under a controlled  $^{18}\text{O}_2$  atmosphere, followed by quenching and measurement of the  $^{18}\text{O}/^{16}\text{O}$  depth profile by SIMS. This profile was subsequently

fitted to a solution of Fick's second diffusion law, from which values of  $k$  and  $D^*$  were obtained.

## 2. Theory

By annealing a dense sample of a mixed ionic electronic conducting material in an  $^{18}\text{O}_2$  containing atmosphere, the diffusion of the  $^{18}\text{O}$  into the sample can be described by the solution of Fick's second law [given by Eq. (1)]. Using the following assumptions:

1. The exchange flux is proportional to the difference between the  $^{18}\text{O}$  fraction in the gas phase ( $c_g$ ) and the corresponding concentration at the surface ( $c_s$ ).
2.  $c_g$  is constant during the experiment.
3. The anneal time is short enough and the sample dimensions are chosen such that only one dimensional diffusion occurs.

The solution to Fick's second law for a semi-infinite medium is given by [18]:

$$\begin{aligned} c'_x &= \frac{c_x - c_{\text{na}}}{c_g - c_{\text{na}}} \\ &= \text{erfc} \left[ \frac{x}{2\sqrt{D^*t}} \right] \\ &\quad - [\exp(hx + h^2D^*t)] \text{erfc} \left[ \frac{x}{2\sqrt{D^*t}} + h\sqrt{D^*t} \right] \end{aligned} \quad (1)$$

with  $h = k/D^*$  and  $c'_x$  the normalised isotopic fraction at depth  $x$  (cm) from the surface,  $c_x$  the concentration of  $^{18}\text{O}$  at a distance  $x$ ,  $c_{\text{na}}$  the natural abundance of  $^{18}\text{O}_2$  (0.204%),  $D^*$  is the tracer diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ) and  $t$  the anneal time (s). The constant of proportionality between  $h$  and  $D^*$  in the above equation is the surface exchange coefficient ( $k$ ,  $\text{cm}^2 \text{s}^{-1}$ ), which follows from the boundary condition:

$$-D^* \left[ \frac{dc}{dx} \right]_{x=0} = k(c_g - c_s). \quad (2)$$

For materials exhibiting an electronic transference number close to unity, the parameter  $h$  ( $\text{cm}^{-1}$ ) in Eq. (1) is related to the so called characteristic thickness

$L_c$  (cm), at which the surface oxygen exchange and the bulk diffusion through the material are equally important during oxygen permeation [4,19]. The relation between  $h$  and  $L_c$  is given by:

$$L_c = \frac{D_i}{k} = \frac{fD^*}{k} \approx \frac{1}{h} \quad (3)$$

with  $f$  the correlation factor, which is 0.69 for a cubic perovskite lattice [6]. Although strictly speaking the correlation factor should be included, as done in Eq. (3), we will use the widely used literature simplification  $L_c = 1/h$  (i.e. taking  $f=1.0$ ). Since  $k$  and  $D^*$  are not necessarily the same function of  $T$  and  $p_{O_2}$ ,  $L_c$  is both a function of  $T$  and  $p_{O_2}$ .

### 3. Experimental

Rod shaped samples with composition  $x=0.7$  were made by thermal decomposition of metal–EDTA complexes followed by calcination at 900°C, shaping, sintering and machining as described elsewhere [20]. The density of these rods was determined by the Archimedes method using mercury, and was found to be larger than 94% of the theoretical value. The rods were sliced into disks with a diameter of 12 mm and a thickness of 2 mm.

For the subsequent sample preparation we refer to Fig. 1. One side of the disks was polished down to 0.25  $\mu\text{m}$  using diamond paste, after which it was diametrically sliced (A). One of these slices was used during a complete exchange run. The slice was treated at an absolute pressure less than  $5.0 \times 10^{-6}$  Pa at ambient temperature. Hereafter, the slice was annealed under dry ( $<1$  ppm  $\text{H}_2\text{O}$ ) research-grade

Table 1  
Experimental conditions for the exchange measurements

$T$ (°C)	$p_{O_2}$ (Pa)	$t_{\text{anneal}}^{18\text{O}}$ (s)	Line scan length ( $\mu\text{m}$ )
699	$2.1 \times 10^4$	3787	1280
743	$2.1 \times 10^4$	2133	1280
798	$4.0 \times 10^2$	462	2000
799	$4.0 \times 10^3$	810	1275
798	$2.1 \times 10^4$	1411	1280
799	$1.0 \times 10^3$	1443	1024
888	$2.1 \times 10^4$	624	1280
998	$2.1 \times 10^4$	309	1280

$^{16}\text{O}_2$  gas (British Oxygen Corporation) at a temperature and pressure specified in Table 1, for times in excess of at least 10 times the  $^{18}\text{O}$  anneal times  $t_{\text{anneal}}^{18\text{O}}$ . After the anneal the sample was quenched to room temperature and again evacuated to a pressure less than  $5.0 \times 10^{-6}$  Pa followed by  $^{18}\text{O}_2$  gas (93%) exchange at a temperature, pressure and time given in Table 1. Following this exchange, the sample was again quenched to room temperature. From the quenched sample, a bar was cut out of the centre with a thickness of approximately 1.5 mm (B). One cutting edge of the rod was polished down to 0.25  $\mu\text{m}$  using diamond spray (C). SIMS line scans were recorded along this polished edge in a direction perpendicular to the flat surface exposed to the  $^{18}\text{O}_2$  (D).

Line scans were recorded using an Atomika 6500 SIMS with  $\text{Xe}^+$ -ions (15 keV), analysing the negative ions with  $m/e$  ratios 16 ( $^{16}\text{O}^-$ ), 17 ( $^{17}\text{O}^-$ ,  $^{16}\text{OH}^-$ ), 18 ( $^{18}\text{O}^-$ ,  $^{17}\text{OH}^-$ ) and 19 ( $^{18}\text{OH}^-$ ,  $^{19}\text{F}^-$ ). Apart from the line scans, sputter depth profiling on the polished surface exposed to the  $^{18}\text{O}_2$  was also performed. The sputter profiles were used for the exact determination of the surface concentration  $^{18}\text{O}$  in the sample. For the calculation of the surface oxygen exchange as well as the tracer diffusion coefficient, the line scan profiles have been used. For this purpose, experimental data were fitted to Eq. (1), using a specially written MAPLE V computer program checking for local minima.

The sample annealed and exchanged at 1000°C, showed considerable cracking after removal from the exchange reactor. This cracking causes scatter in the line scan and consequently inaccuracy in the  $k$  and  $D^*$ -values obtained from this line scan.

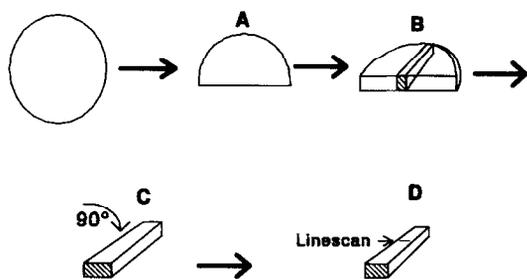


Fig. 1. Sample preparation for the  $^{18}\text{O}_2$ -anneal and SIMS line scan.

Apart from the  $m/e$  ratios 16–19 (O) the  $m/e$  ratio 87 (Sr) was also measured, to check for any Sr segregation towards the surface, which was not observed.

#### 4. Results and discussion

In Fig. 2 the  $^{18}\text{O}$ -normalised isotope fraction from line scan data of the sample annealed at  $743^\circ\text{C}$  is shown. Included in this figure is the best fit of the solution of Eq. (1). The region close to the surface is well described by this solution. The tail of the diffusion profile is, however, slightly underestimated. This underestimation might be due to the small amount of cracking observed or to some rest porosity present in these samples.

The results obtained from the exchange measurements are given in Table 2. The Arrhenius plots for the surface exchange and tracer diffusion coefficient are given in Fig. 3 and Fig. 4, respectively. As is evident from these figures the sample exchanged at  $1000^\circ\text{C}$  shows a large scatter. This is probably due to considerable cracking, induced by the quenching of the sample which causes scatter in the  $^{18}\text{O}/(^{18}\text{O}+^{16}\text{O})$  line profile. For this reason, the value obtained

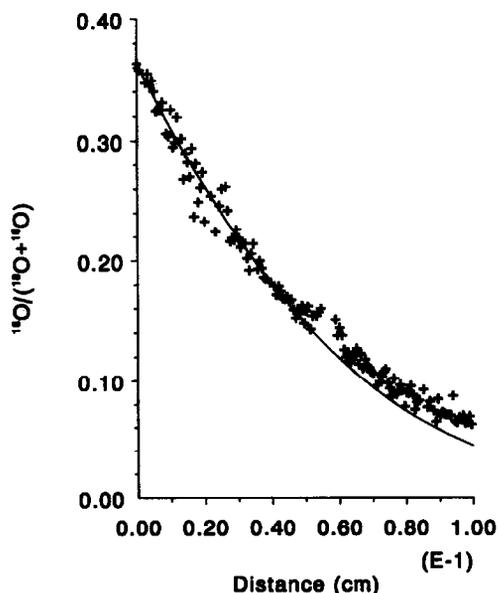


Fig. 2.  $^{18}\text{O}$ -normalised and fit to semi-infinite diffusion [ Eq. (1)] for the sample exchanged at  $743^\circ\text{C}$ .

Table 2  
Results of the  $^{18}\text{O}/^{16}\text{O}$  exchange measurements

$T$ ( $^\circ\text{C}$ )	$p_{\text{O}_2}$ (Pa)	$D^*$ <sup>a</sup> ( $\text{cm}^2 \text{s}^{-1}$ )	$k$ <sup>a</sup> ( $\text{cm s}^{-1}$ )	$L_c$ <sup>b</sup> (cm)
699	$2.1 \times 10^4$	$8.43 \times 10^{-7}$	$1.21 \times 10^{-5}$	0.070
743	$2.1 \times 10^4$	$1.31 \times 10^{-6}$	$1.26 \times 10^{-5}$	0.104
798	$4.0 \times 10^2$ <sup>c</sup>	$2.04 \times 10^{-6}$	$3.04 \times 10^{-6}$	0.671
799	$4.0 \times 10^3$	$9.20 \times 10^{-7}$	$7.77 \times 10^{-6}$	0.118
798	$2.1 \times 10^4$	$1.66 \times 10^{-6}$	$1.48 \times 10^{-5}$	0.112
799	$1.0 \times 10^5$	$1.47 \times 10^{-6}$	$2.76 \times 10^{-5}$	0.053
888	$2.1 \times 10^4$	$2.73 \times 10^{-6}$	$2.13 \times 10^{-5}$	0.128
998	$2.1 \times 10^4$	$1.43 \times 10^{-6}$	$1.73 \times 10^{-5}$	0.083

<sup>a</sup> Determined using semi-infinite diffusion [ Eq. (1)].

<sup>b</sup> Calculated using Eq. (3).

<sup>c</sup> This data point might have suffered from a lower actual  $^{18}\text{O}_2$  partial pressure, due to some depletion of the gas phase.

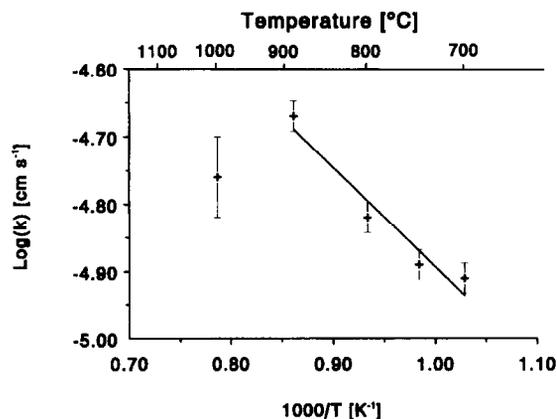


Fig. 3. Arrhenius plot for the surface oxygen exchange coefficient of  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-8}$  at  $p_{\text{O}_2} = 2.1 \times 10^4$  Pa.

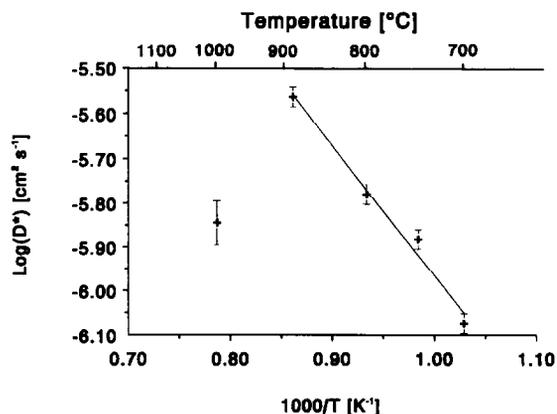


Fig. 4. Arrhenius plot for the tracer diffusion coefficient at  $p_{\text{O}_2} = 2.1 \times 10^4$  Pa.

at 1000°C has been excluded from further data analysis.

The activation energy for the surface exchange at a  $p_{O_2}$  of  $2.1 \times 10^4$  Pa is  $28 \pm 5$  kJ mol<sup>-1</sup> and that for the tracer diffusion coefficient  $56 \pm 4$  kJ mol<sup>-1</sup>.

The anomaly reported in the Arrhenius plot of the chemical diffusion coefficient between 750 and 775°C [1,2,22] is not observed in the Arrhenius plot of the tracer diffusion coefficient. Using the non-stoichiometry data reported in literature [2,21] and the relations:

$$D_v = \frac{D^* c_i}{f c_v}, \quad (4)$$

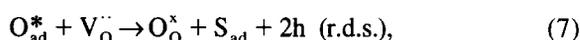
$$D^* = f D_i, \quad (5)$$

with  $c_i$  and  $c_v$  the concentration of oxygen anions, the vacancy diffusion coefficients given in Table 3 were calculated. The vacancy diffusion coefficient at 888°C is about 1.5 times higher than that determined from oxygen permeation at 900°C ( $2.5 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup> [2,22]). The activation energy for the vacancy diffusion coefficient is  $40 \pm 3$  kJ mol<sup>-1</sup>, which is in reasonable agreement with the value reported in Ref. [2] ( $56 \pm 5$  kJ mol<sup>-1</sup>). The activation energy for the tracer diffusion coefficient is in excellent agreement with the activation energy for the self diffusion coefficient determined from computer simulations on LaCoO<sub>3-δ</sub> by Cherry et al. [23].

Contrary to the results of Ishigaki et al. [6] on single crystals LaCoO<sub>3-δ</sub>, no  $p_{O_2}$ -dependence of  $D^*$  could be observed. Assuming the oxygen vacancies to be randomly distributed,  $D_i$  is proportional to their concentration. Therefore,  $D^*$  should have the same  $p_{O_2}$ -dependence as  $D_i$ . The oxygen non-stoichiometry as a function of  $p_{O_2}$  for the non-acceptor doped LaCoO<sub>3-δ</sub> can be described by a power law in  $p_{O_2}$  with a power of  $-0.50$  at 900°C [21]. The oxygen non-stoichiometry of the highly acceptor doped

La<sub>0.3</sub>Sr<sub>0.7</sub>CoO<sub>3-δ</sub> is, however, only slightly dependent on  $p_{O_2}$  [2,21]. This difference in  $p_{O_2}$ -dependence of the non-stoichiometry might explain the observed difference in  $p_{O_2}$ -dependence of  $D^*$  for the different compositions.

The result of the  $p_{O_2}$ -dependence of the surface exchange coefficient is given in Fig. 5. It can be described as a power law in  $p_{O_2}$  with a power of  $+0.41 \pm 0.02$ . As a possible explanation for this power law the following reaction path for the incorporation of oxygen is proposed:



in which  $O_{ad}^*$  is an adsorbed oxygen species and  $S_{ad}$  a surface adsorption site. The exact nature of this adsorbed species and adsorption site are unknown. It will be clear that the previous two reaction steps are a lumped sum of different, more elementary, steps. The associated equilibrium constants for these reactions are given by:

$$K_{(6)} = \frac{[O_{ad}^*]^2}{p_{O_2} [S_{ad}]^2}, \quad (8)$$

$$K_{(7)} = \frac{[O_O^x][S_{ad}]p^2}{[O_{ad}^*][V_O^{\bullet\bullet}]}, \quad (9)$$

where square brackets denote concentrations and  $p$  is the concentration of electron holes. It follows from Eq. (8) that the concentration of adsorbed oxygen

Table 3  
Vacancy diffusion coefficients calculated from tracer diffusion

$T$ (°C)	$D_v$ (cm <sup>2</sup> s <sup>-1</sup> )	$\delta$ ( $=c_v/V_M$ )
699	$2.0 \times 10^{-5}$	0.17
743	$2.8 \times 10^{-5}$	0.19
798	$3.2 \times 10^{-5}$	0.21
888	$4.5 \times 10^{-5}$	0.24

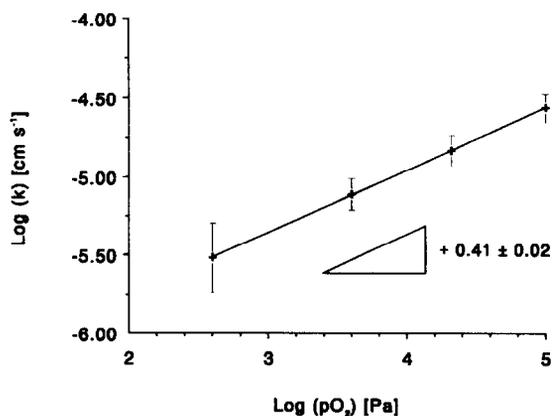


Fig. 5.  $p_{O_2}$ -dependence of  $k$  at 800°C.

species shows a square root dependence on the  $p_{\text{O}_2}$ . So, if the dissociative adsorption of oxygen were the rate determining step, a  $p_{\text{O}_2}$ -dependence of 0.5 should be observed.

If, on the contrary, Eq. (7) is the rate determining step as proposed by Takeda et al. [14], the surface exchange is proportional to the concentration of adsorbed oxygen species and oxygen vacancies. The oxygen vacancy concentration of  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$  at 800°C shows a  $p_{\text{O}_2}$ -dependence of  $-0.07 \pm 0.002$  [2,21]. As follows from Eq. (8) the concentration of  $\text{O}_{\text{ad}}^*$  is proportional to the square root of  $p_{\text{O}_2}$ . This reaction mechanism thus gives an overall order of +0.43, which agrees with the measured value of  $+0.41 \pm 0.02$ . A similar type of rate limiting step has recently been proposed by Kilner for fluorite type oxides [16].

A comparison of the results obtained in this study with those of Fullerton et al. [17] on  $\text{Sm}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}$  at a  $p_{\text{O}_2}$  of  $1.0 \times 10^5$  Pa shows that  $D^*$  for  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$  is higher by a factor of about 3–5 over the whole temperature region as employed in this study, whereas  $k$  is almost the same.  $D^*$  and  $k$ -values of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-\delta}$  measured by Carter et al. [8] are about an order of magnitude below the corresponding values of  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ . Results of Ishigaki et al. on  $\text{La}_{0.9}\text{Sr}_{0.1}\text{CoO}_{3-\delta}$  are two orders of magnitude lower for  $D^*$  and about one order of magnitude for  $k$  [7]. For  $\text{LaCoO}_{3-\delta}$  the difference is more extreme,  $D^*$  differs by up to 6 orders of magnitude, whereas  $k$  is less by up to 4 orders of magnitude [6]. It should, however, be noted that the results of Ishigaki et al. were performed on single crystals at a  $p_{\text{O}_2}$  of  $4.5 \times 10^3$  Pa. So it is clear that an increase in the Sr (acceptor)-doping level results in an increase of both  $D^*$  and  $k$ , in line with the proposed surface exchange model and standard solid state diffusion theory.

An evaluation of the  $L_c$ -values given in Table 2 shows an increase of  $L_c$  with temperature, reflecting the difference in activation energy for  $D^*$  and  $k$ . The magnitude of  $L_c$  is substantial, indicating that the surface exchange is very important during oxygen permeation through  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ , especially at low  $p_{\text{O}_2}$ -values. It further follows from this table that the surface exchange process is more important, i.e. consumes a larger portion of the driving force, at the low  $p_{\text{O}_2}$  (reducing) side of the membrane than at the

high  $p_{\text{O}_2}$  (oxidising) side. Recent computer simulation results of Islam et al. [24] indicate that the oxidation of  $\text{LaCoO}_{3-\delta}$  is exothermic, indicating a thermodynamically favourable reaction, supporting the observation of the importance of the reduction on the permeation flux.

In a previous paper we reported that under oxygen permeation conditions a segregation of Sr towards the surface exposed to the oxygen lean side occurs [2]. In a subsequent paper it was concluded that this segregated Sr is not present in the form of perovskite, but most probably as SrO [15], which has a different surface exchange than  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ . Therefore, it must be ascertained that the results reported in this paper have been obtained on non segregated samples.

XPS and AES results obtained on samples annealed in flowing  $\text{N}_2$  at temperatures and time periods in excess of those employed in this study showed no segregation of Sr towards the surface [15]. This suggests that no segregation occurs during the thermal anneals employed in this study.

Besides the samples mentioned in Section 3, two samples which have been used for the demixing experiments reported in our previous paper [15] have also been used. These were exposed to an air vs. 2%  $\text{O}_2$  gradient at 900°C for 100 h. It was reported in that paper that under these conditions an enrichment of Sr occurs [15]. During the exchange experiments, these samples cracked in such a way that they could not be used for SIMS analysis and consequently no data are available for segregated samples.

## 5. Conclusions

The surface oxygen exchange properties of  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$  have been studied by  $^{18}\text{O}/^{16}\text{O}$  exchange followed by dynamic SIMS in the temperature range  $700 \leq T \leq 1000^\circ\text{C}$  and the pressure range  $4 \times 10^2 \text{ Pa} \leq p_{\text{O}_2} \leq 1 \times 10^5 \text{ Pa}$  at 800°C.

The activation energy for the tracer diffusion coefficient at a  $p_{\text{O}_2}$  of  $2.1 \times 10^4$  Pa is  $56 \pm 4 \text{ kJ mol}^{-1}$  and for the surface exchange coefficient it is  $28 \pm 5 \text{ kJ mol}^{-1}$ . At 800°C  $D^*$  is not a function of  $p_{\text{O}_2}$ , whereas for  $k$  a  $p_{\text{O}_2}^n$  with  $n = +0.41 \pm 0.02$  dependence was observed. This can be explained if it is

assumed that both oxygen vacancies and adsorbed atomic oxygen species are involved in the rate determining step. The thickness at which the surface oxygen exchange and the bulk diffusion are equally important in determining the oxygen transport ( $L_c$ ) through  $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$  is a function of temperature and  $p_{\text{O}_2}$ .  $L_c$  ranges from 0.70 mm at 700°C to 1.3 mm at 900°C at a  $p_{\text{O}_2}$  of  $2.1 \times 10^4$  Pa and from 0.5 to 6.7 mm at 800°C in the  $p_{\text{O}_2}$  range  $1 \times 10^5$  to  $4.0 \times 10^2$  Pa.

### Acknowledgments

One of us (R.H.E. van Doorn) would like to acknowledge the financial support of the Netherlands Organisation for Scientific Research (NWO) for performing the research described in this paper.

### References

- [1] R.H.E. van Doorn, H. Kruidhof, H.J.M. Bouwmeester and A.J. Burggraaf, Proc. MRS Symposium, Boston, 1994, Eds. G.-A. Nazri, J.-M. Tarascon and M. Schreiber (1994) 377.
- [2] R.H.E. van Doorn, H. Kruidhof, H.J.M. Bouwmeester and A.J. Burggraaf, J. Electrochem. Soc. (1997) to appear.
- [3] G.K. Vdovin, B.L. Kuzin and E.Kh. Kurumchin, Poverknost, Phys. Chem. Mech. 10 (1991) 30 (Russian).
- [4] B.C.H. Steele, Solid State Ionics 75 (1995) 157.
- [5] D.B. Hibbert and A.C.C. Tseung, J. Electrochem. Soc. 125 (1978) 74.
- [6] T. Ishigaki, S. Yamauchi, J. Mizusaki, K. Fueki and H. Tamura, J. Solid State Chem. 54 (1984) 100.
- [7] T. Ishigaki, S. Yamauchi, K. Kishio, J. Mizusaki and K. Fueki, J. Solid State Chem. 73 (1988) 179.
- [8] S. Carter, A. Selcuk, R.J. Chater, J. Kajda, J.A. Kilner and B.C.H. Steele, Solid State Ionics 53–56 (1992) 597.
- [9] Ch. Ftikos, S. Carter and B.C.H. Steele, J. Eur. Ceram. Soc. 12 (1993) 79.
- [10] I. Yasuda, K. Ogasawara and M. Hishinuma, Proc. 2nd Int. Symp. on Ionic and Mixed Conducting Ceramics, Eds. T.A. Ramanarayanan, W.L. Worrell and H.L. Tuller, ECS Proc. Ser. Vol. 94-12 (1994) 164.
- [11] K. Eguchi, T. Inou, M. Ueda, J. Kamimae and H. Arai, Proc. 2nd Int. Symp. on SOFC, Athens, Greece (1991) 697.
- [12] T. Inou, K. Eguchi and H. Arai, Chem. Lett. (1988) 1939.
- [13] T. Inou, N. Seki, K. Eguchi and H. Arai, J. Electrochem. Soc. 137 (1990) 2523.
- [14] Y. Takeda, R. Kanno, M. Noda, Y. Tomida and O. Yamamoto, J. Electrochem. Soc. 134 (1987) 2656.
- [15] R.H.E. van Doorn, H.J.M. Bouwmeester and A.J. Burggraaf, Submitted to Solid State Ionics (1996).
- [16] J.A. Kilner, Proc. 2nd Int. Symp. on Ionic and Mixed Conducting Ceramics, Eds. T.A. Ramanarayanan, W.L. Worrell and H.L. Tuller, ECS Proc. Ser. Vol. 94-12 (1994) 174.
- [17] I.C. Fullarton, J.A. Kilner, B.C.H. Steele and P.H. Middleton, Proc. 2nd Int. Symp. on Ionic and Mixed Conducting Ceramics, Eds. T.A. Ramanarayanan, W.L. Worrell and H.L. Tuller, ECS Proc. Ser. Vol. 94-12 (1994) 9.
- [18] J. Crank, The Mathematics of Diffusion, 2nd Ed. (Oxford University Press, Oxford, 1975) Chaps. 3 and 4.
- [19] H.J.M. Bouwmeester, H. Kruidhof and A.J. Burggraaf, Solid State Ionics 72 (1994) 185.
- [20] R.H.E. van Doorn, H. Kruidhof, A.J.A. Winnubst, H.J.M. Bouwmeester and A.J. Burggraaf, Submitted to J. Am. Ceram. Soc. (1996).
- [21] J. Mizusaki, Y. Mima, S. Yamauchi, K. Fueki and H. Tagawa, J. Solid State Chem. 80 (1989) 102.
- [22] R.H.E. van Doorn, H.J.M. Bouwmeester and A.J. Burggraaf, in: Proc. 1st Symp. on Ceramic Membranes, Eds. H.U. Anderson, A.C. Khandkar and M. Liu, ECS Proc. Ser. Vol. 95-24 (1997) 138.
- [23] M. Cherry, M.S. Islam and C.R.A. Catlow, J. Solid State Chem. 118 (1995) 125.
- [24] M.S. Islam, M. Cherry and L.J. Winch, J. Chem. Soc., Faraday Trans. 92 (1996) 479.