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Oxygen transport through $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ membranes

II. Permeation in air/ CO , CO_2 gradients

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Abstract

Oxygen permeation measurements were performed on dense $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ($x = 0.1\text{--}0.4$) membranes in large oxygen activity gradients, i.e. air/ CO , CO_2 , in the temperature range 1173–1323 K, yielding fluxes up to $25 \text{ mmol m}^{-2} \text{ s}^{-1}$ at 1273 K. The oxygen semipermeability was linearly proportional with the CO partial pressure and the strontium content. It was concluded that the fluxes are limited by the surface exchange kinetics. Two simple models are proposed for the oxygen exchange reaction in the presence of CO . In both models oxygen vacancies at the phase boundary play a definite role in the exchange process. XPS and SEM analysis of the perovskite/ CO , CO_2 interfaces indicated segregation of strontium, being present at the surface mostly in the form of SrCO_3 and/or SrO . The enhanced oxygen fluxes in air/ He gradients as they were observed after exposure of the membrane surface to CO are probably (indirectly) related to the level of strontium segregation. Based on SEM analysis and surface profile measurements, it is suggested that the segregation process is accompanied by an enlargement of the specific surface area, which may promote the speed of the overall permeation process under exchange-controlled conditions.

Keywords: Oxygen permeation; Mixed conductor; Lanthanum strontium iron oxide; Perovskite; Carbon monoxide oxidation

1. Introduction

The defect chemistry of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ($x = 0\text{--}0.6$) is well understood as a function of Sr content, oxygen partial pressure and temperature [1,2]. Properties such as the diffusion coefficient, electron and electron hole mobilities are also known [3–5]. In part I of this paper [6] it was found that the oxygen-semipermeable properties of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ membranes ($x = 0.1\text{--}0.4$) in small partial pressure gradients, i.e. air/ He , can be described by a diffusion-

controlled mechanism. In the present paper the oxygen permeation process through the same membranes is coupled to a simple chemical reaction, i.e. the oxidation of CO . The presence of CO , CO_2 mixtures results in large oxygen activity gradients across the membrane. Preliminary results showed a linear correlation between the oxygen flux and the CO partial pressure, indicating a surface exchange-controlled flux [7] under these circumstances. Voorhoeve [8] divided oxidation catalysis by perovskite-type oxides $\text{AMO}_{3\pm\delta}$ into two types, suprafacial and intrafacial, depending on the predominant mechanism. CO oxidation at high temperature

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proceeds primarily through the partial removal of oxygen from the perovskite lattice and subsequent oxidation of the oxide bulk, and is an example of intrafacial catalysis. Thermodynamics, M–O bond strengths and oxygen diffusivity are the determining factors for this mechanism. An example of suprafacial catalysis is the oxidation of CO at relatively low temperatures, i.e. 400–650 K. It takes place by the reaction between adsorbed species and is therefore determined by the electronic configuration of localized sites on the surface. Most studies of CO oxidation on perovskite-type oxides were stimulated by the search for possible inexpensive substitutes of noble metals in automotive exhaust catalysts and were therefore performed in the range of 400–800 K at low concentrations and large space velocities [9–11]. Several relationships between the solid state chemistry and the catalytic activity of perovskites have been proposed. The catalytic activities of several $\text{LaMO}_{3-\delta}$ perovskite-type oxides ($M = \text{Cr, Mn, Fe, Co, Ni}$) at 500 K could be related to the crystal-field stabilization energy [9] or Fermi-level energy [8], revealing the suprafacial nature of the catalytic process under these conditions.

Nitadori et al. [12] observed that the catalytic activities of perovskites LnMO_3 with Ln and M being a trivalent rare-earth and a first-row transition metal cation, respectively, are determined by the nature of the transition metal cation. This implies that the activity may also be affected by the oxidation state of the transition metal. For the sake of experiment, its valency can be altered by (partial) substitution of trivalent Ln by di- or tetravalent cations. The effect of partial substitution of La^{3+} by Ca^{2+} , Sr^{2+} , Ba^{2+} , Ce^{4+} and Th^{4+} has been studied. Doshi et al. [13] found a correlation between the p-type electrical conductivity and the rate of CO oxidation on $\text{La}_{1-x}\text{Sr}_x\text{M}_{1-y}\text{M}'_y\text{O}_{3-\delta}$ ($M = \text{Co, Cr, Fe, Mn}$; $M' = \text{Nb, Ti}$). However, it should be noted that even in unsubstituted LaMO_3 , and M^{4+} cations co-exist next to M^{3+} in general, their relative concentrations being dependent on the oxygen partial pressure and temperature.

Rao et al. [14] noticed a decrease in the catalytic activity of $\text{LaCoO}_{3-\delta}$ when the catalyst was annealed in pure oxygen. It was suggested that this pretreatment lowers the oxygen deficiency and that the activity is reduced as a result. Nakamura et al.

[15,16] determined the rates of reduction by CO and re-oxidation by O_2 of samples $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ($x = 0-0.6$) as a function of the oxygen non-stoichiometry δ . The steady-state catalytic activities were estimated from the intersection of the oxidation and reduction curves, and were found to agree well with the observed trend in activity, especially for large values of x . The catalytic process was explained in terms of a redox-like (intrafacial) mechanism. The redox cycle involves a combined process of surface reaction and bulk diffusion of oxygen. To account for the discrepancies at small x , a suprafacial mechanism earlier proposed by Tascon et al. [17] for LaCoO_3 was suggested. The relationship between catalytic activity on one hand and oxygen vacancy concentration and electrical conductivity on the other has been observed also on the perovskite-related spinel-type oxide $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ [18].

In this paper the oxygen permeation properties of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ membranes ($x = 0.1-0.4$) are studied when they are placed in an air/ CO , CO_2 gradient. An attempt is made to relate the catalytic properties of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ to its oxygen vacancy concentration.

2. Theory

2.1. Bulk diffusion

In small oxygen partial pressure gradients $p'_{\text{O}_2}/p''_{\text{O}_2}$ at relatively high oxygen partial pressures ($p'_{\text{O}_2}, p''_{\text{O}_2} > 10^{-4}$ bar), the permeation properties of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ membranes can be modelled by a diffusion mechanism [6]. The permeation flux can be expressed in terms of the Wagner equation:

$$J_{\text{O}_2} = \frac{RT}{16F^2L} \int_{p''_{\text{O}_2}}^{p'_{\text{O}_2}} \frac{\sigma_{\text{ion}}\sigma_{\text{el}}}{\sigma_{\text{ion}} + \sigma_{\text{el}}} d \ln p_{\text{O}_2}. \quad (1)$$

Here L is the membrane thickness (m); σ_{ion} and σ_{el} are the ionic and electronic conductivities (S m^{-1}) respectively; p'_{O_2} and p''_{O_2} are the oxygen partial pressures at opposite sides of the membrane. At temperatures of 1000–1400 K and oxygen partial pressures $p_{\text{O}_2} > 10^{-5}$ bar, p-type electronic conduc-

tivity is predominant in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ and the electronic transference number remains very close to unity. The electronic conductivity decreases with decreasing oxygen partial pressure, until a minimum is reached, where a transition from p-type to n-type conductivity occurs. The region of minimum electronic conductivity, typically 10^{-8} – 10^{13} bar O_2 , coincides with a plateau region in the oxygen non-stoichiometry, where $\delta \approx x/2$, as shown in Fig. 1. Fig. 2 illustrates the calculated oxygen permeation fluxes. The partially limiting effect of the electronic conductivity on the oxygen permeation rate can be seen, especially for $x=0.4$, as a slight flattening of the curve at about $p_{\text{O}_2}=10^{-10}$ bar. Details of the calculations have been described elsewhere [6].

Fig. 1. Calculated oxygen contents of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ for $x=0.1$ – 0.4 as a function of $\log p_{\text{O}_2}$ at 1273 K.

Fig. 2. Calculated oxygen fluxes through 1.00 mm membranes at 1273 K as a function of the permeate side oxygen partial pressure, when oxygen is supplied at the feed side. Model parameters are described elsewhere [6].

2.2. Surface reaction

Almost no details are known about the mechanism of oxygen exchange on perovskite-type oxides. In the absence of a chemical reaction occurring at one of the gas/solid interfaces, the overall process for the incorporation and release of oxygen can be written as

using Kröger–Vink notation [19]. Based on $^{18}\text{O}/^{16}\text{O}$ exchange experiments, Boukamp et al. [20] proposed a two-step mechanism for the exchange on fluorite-type $\text{Bi}_{1.5}\text{Er}_{0.5}\text{O}_3$ in O_2 -containing atmospheres, in which dissociative adsorption plus charge transfer appears to be rate-limiting at high p_{O_2} .

Based on an observed interrelationship between the diffusion coefficients D_{O} ($\text{cm}^2 \text{s}^{-1}$) and the surface exchange coefficients k (cm s^{-1}) of several oxides of the fluorite and perovskite types from $^{18}\text{O}/^{16}\text{O}$ exchange experiments, Kilner [21] suggested the possible involvement of surface oxygen vacancies in the exchange of oxygen. Since $D_{\text{O}} \approx (D_{\text{V}}/3) \cdot \delta$ for perovskites, where the vacancy diffusion coefficient D_{V} ($\text{cm}^2 \text{s}^{-1}$) is approximately constant, the correlation between D_{O} and k suggests a correlation between k and δ as well.

In the present study the effect of CO , CO_2 on the oxygen exchange reaction of perovskites $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ is investigated. There is evidence that the mechanism of the surface reaction is changed drastically by their presence, e.g. from isotopic exchange on YSZ [22]. The overall reaction for the oxidation of CO can be written as

Yasuda and Hikita [23] found a linear correlation between the surface exchange constant and the non-stoichiometry of $\text{La}_{1-x}\text{Ca}_x\text{CrO}_{3-\delta}$ ($x=0.1$ – 0.3) in CO , CO_2 atmospheres from electrical conductivity relaxation experiments. This indicates that oxygen vacancies also play an essential role under these conditions.

3. Experimental

3.1. Permeation experiments

The preparation of the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ membranes ($x=0.1-0.4$) and experimental procedure have been described in part I of this paper [6]. The density of the membranes was measured by means of an Archimedes method. Some samples of $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ were sputtered with a 50 nm thick porous layer of Pt.

The experimental set-up is schematically depicted in Fig. 3. Unless specifically stated, air was supplied to the feed side of the membrane. Composition analysis of the permeate stream was performed by a Varian 3300 gas chromatograph coupled to a LDC/Milton Roy CL-10 integrator. O_2 , N_2 and CO were separated by a molecular sieve 13X. CO_2 was separated by a Porapak-N column. Measurements were performed only on leak-free membranes, in which case no nitrogen and oxygen were detected in the permeate stream. The oxygen fluxes were calculated from the mass balance of oxygen-containing species:

$$J_{\text{O}_2} = \frac{F}{A} \cdot \left(c_{\text{CO}_2}^{\text{out}} - c_{\text{CO}_2}^{\text{in}} + \frac{1}{2}(c_{\text{CO}}^{\text{out}} - c_{\text{CO}}^{\text{in}}) \right) \quad (6)$$

where F is the flow rate at the permeate side ($\text{m}^3 \text{ s}^{-1}$ (STP)), and A the geometric surface area at the CO-side of the membrane (m^2). c_i^{in} and c_i^{out} are the inlet and outlet concentrations of species i . During the measurements, F was kept at values between 7–25 ml/min (STP). In order to avoid deposition of

carbon, the CO/CO_2 ratio was always kept above unity. Assuming ideal gas mixing behaviour, the oxygen partial pressure at the membrane/gas interface was calculated from the outlet partial pressures of CO and CO_2 :

$$p_{\text{O}_2} = K \left(\frac{p_{\text{CO}_2}}{p_{\text{CO}}} \right)^2. \quad (7)$$

The values of the equilibrium constant K were obtained from a compilation of thermodynamic data given in Ref. [24].

3.2. Bulk analysis

XRD spectra were taken on a Philips PW 1710 with Ni-filtered $\text{CuK}\alpha$ radiation. LaB_6 was added as internal standard to powders obtained from crushed sintered membranes. The samples were measured with a 2θ scan from 20° to 130° with steps of 0.02° and the intensity was collected during 5–10 s. The $\text{CuK}\alpha_1$ ($\lambda=1.5406 \text{ \AA}$) component was used in the refinement procedure. The bulk concentrations of La, Sr and Fe were determined by X-ray Fluorescence Spectroscopy (XRF) using a Philips PW 1480/10 X-ray spectrometer.

3.3. Surface analysis

The membrane surface morphology was examined by High Resolution Scanning Electron Microscopy (HR-SEM) using a Hitachi S-800 Field Emission Microscope operating at 15 kV, which was coupled to a Kevex Delta Range Energy Dispersive X-ray analysis (EDX) system for surface element analysis. The surface profiles of the samples were measured using a Sloan DEKTAK 3030. The X-ray Photoelectron Spectroscopy (XPS) experiments were carried out in a Kratos XSAM 800 system controlled by a PDP 11 microcomputer. For the excitation, an $\text{AlK}\alpha$ radiation source (225 W) was used. The spectrometer was calibrated and its linearity checked by measuring the $\text{Ag } 3d_{5/2}$, $\text{Cu } 2p_{3/2}$ and $\text{Au } 4f_{7/2}$ peaks on clean sputtered samples. The position of the C 1s peak, relative to its normal position at 284.8 eV, was used to correct the measured binding energies (BE) for electrostatic charging of the samples. The perovskite membrane surfaces were analyzed by measur-

Fig. 3. Schematic diagram of the experimental setup.

ing the La 3d, Fe 2p and Sr 3d spectra of clean sputtered samples. Analysis was performed using a DS 800 software package. 100% Gaussians were used for the synthesis of the Sr 3d peak. Internal consistency was maintained by constraining the spin-orbit coupling $\Delta BE(\text{Sr } 3d_{3/2} - \text{Sr } 3d_{5/2})$ to 1.8 eV and the relative intensities and areas of the $3d_{5/2}$ and $3d_{3/2}$ components to a ratio of 3:2.

High Resolution Transmission Electron Microscopy (HR-TEM) and Selected Area Electron Diffraction (SAED) was performed with a Philips CM30 TWIN/(S)TEM operating at 300 keV, with an aperture of 0.1–0.2 μm (point resolution 2.3 Å), fitted with a double tilt goniometer stage ($\pm 45^\circ$). Measurements were performed on single-crystalline grains at the perovskite/CO interface at room temperature. The membranes were locally thinned with a Gatan dimple grinder, followed by ion milling.

4. Results and discussion

4.1. Crystal structure and bulk composition

No second phases were detected in any sample. For $x=0.1$ –0.3, all peaks could be indexed on the basis of an orthorhombic unit cell, whereas $x=0.4$ showed a rhombohedral symmetry. The refined unit cell parameters are given in Table 1. The results are in good agreement with those obtained by others [5]. The bulk compositions as determined by XRF are found to agree well with their corresponding nominal compositions. For the calculation of the cationic stoichiometries listed in Table 2, it was assumed that the oxygen non-stoichiometries of the samples were negligible. The membrane densities were determined from an Archimedes type of method. The values, relative to theoretical, are also listed in Table 2.

Table 1
Unit cell data from XRD at room temperature for $x=0.1$ –0.4

x	Crystal system	a (Å)	b (Å)	c (Å)
0.1	Orthorhombic	5.5403(1)	5.5549(2)	7.8351(2)
0.2	Orthorhombic	5.5254(6)	5.5513(9)	7.8267(2)
0.3	Orthorhombic	5.5210(8)	5.5478(1)	7.8054(3)
0.4	Rhombohedral ^a	5.5278(8)		13.4368(1)

^aHexagonal setting.

Table 2

Membrane densities and experimentally determined bulk composition of $\text{La}_p\text{Sr}_q\text{Fe}_r\text{O}_3$

x	$\rho/\rho_{\text{theor}}(\%)$	p	q	r
0.1	96–97	0.90	0.10	0.99
0.2	95–96	0.80	0.20	0.99
0.3	94–95	0.70	0.29	1.00
0.4	91–92	0.60	0.40	1.00

4.2. Permeation experiments

Fig. 4 shows the oxygen flux through $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_{3-\delta}$ at 1273 K versus the oxygen partial pressure. In the oxygen partial pressure range in which the measurements were performed, i.e. $p_{\text{O}_2} = 10^{-11}$ – 10^{-15} bar the non-stoichiometry $\delta \approx 0.05$. The model calculation is based on diffusion-limited permeation and would thus indicate an upper limit for the oxygen flux. Though the observed fluxes exceed this limit, the trends of theoretical and experimental behaviour differ substantially. Similar measurements for $x=0.2$ and $x=0.3$ showed no fluxes exceeding the theoretically predicted bulk diffusion limit, but the observed trends were similar to those seen for $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_{3-\delta}$. This suggests that application of the bulk diffusion model, used earlier to fit experimental data of oxygen permeation at relatively high oxygen pressures [6], is not valid when CO, CO₂ gas mixtures are present at the oxygen-lean side of the membranes.

It is not clear why the diffusion limit is exceeded for $x=0.1$. Possibly, diffusion paths parallel to bulk diffusion contribute significantly to the overall diffu-

Fig. 4. Experimental and calculated oxygen flux through a 1.00 mm membrane $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_{3-\delta}$ at 1273 K.

sion process at low oxygen partial pressures, e.g. grain boundary diffusion. Furthermore, the vacancy diffusion coefficients D_v used in the model calculations have only been determined at relatively high p_{O_2} , i.e. 10^{-3} –1 bar. Although D_v is generally considered to vary little with δ , Yasuda and Hishinuma reported changes of D_v of up to an order of magnitude at large δ in $La_{0.8}Sr_{0.2}Cr_{0.95}Ni_{0.05}O_{3-\delta}$ and $La_{0.65}Sr_{0.35}CrO_{3-\delta}$ [25], indicating that extrapolation to low oxygen partial pressures may not be allowed.

The oxygen flux is found to increase linearly with the CO partial pressure, as illustrated in Fig. 5 for $x=0.2$. In view of Eq. (5), this clearly indicates the surface reaction of CO with lattice oxygen to be the rate-limiting step in the overall permeation process. Further evidence for a surface exchange-controlled flux is found from the observation that a sample sputtered with Pt shows a significantly increased flux. In comparison with the bare membrane, the slope (dJ_{O_2}/dp_{CO}) is larger by a factor of 1.8 ± 0.2 [7]. The absence of mass transfer limitations was verified by variation of the total flow rate between 7–25 ml/min (STP) at constant p_{CO} at the outlet of the reactor. No significant change of the permeation was observed.

Variation of the membrane thickness between 0.5 and 2.0 mm did not show any influence on the observed flux. An influence was neither found from changing the oxygen pressure at the higher partial pressure side. In the latter experiments, p_{CO} was kept constant at a value of 0.12 bar, while the oxygen partial pressure at the feed side was varied between

Fig. 5. Oxygen flux through 1.0 mm thick $La_{0.8}Sr_{0.2}FeO_{3-\delta}$ membranes at 1273 K as a function of CO partial pressure.

0.02 and 1 bar. Thus, the surface reaction at the lower partial pressure side is fully limiting the oxygen flux.

The effect of Sr-doping on permeation at 1273 K is given in Fig. 6. The oxygen flux clearly increases with increasing concentration of Sr. Due to instrumental limitations, the oxygen fluxes through $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ were too large to be measured quantitatively, but the observed trends were comparable to those on other compositions. The slopes k_{exp} (dJ_{O_2}/dp_{CO}) of the plots of Fig. 6 were determined by least-squares fitting. Fig. 7 shows a linear relationship between k_{exp} and x . By considering that the oxygen partial pressures in these experiments were in all cases in the range 10^{-10} – 10^{-15} bar, in which region the oxygen non-stoichiometry of $La_{1-x}Sr_xFeO_{3-\delta}$ is virtually constant, i.e. $\delta \approx x/2$, we think that oxygen vacancies play a role in the

Fig. 6. Oxygen fluxes through $La_{1-x}Sr_xFeO_{3-\delta}$ membranes at 1273 K as a function of CO partial pressure.

Fig. 7. Slopes (dJ_{O_2}/dp_{CO}) of phases $La_{1-x}Sr_xFeO_{3-\delta}$ ($x=0.1$ – 0.3) as shown in Fig. 6.

apparent exchange mechanism. It is unlikely that the proportionality is directly related to the strontium content, since catalytic studies on perovskites AMO_3 showed that the activity was not related to the nature of the A-site cation [26,27]).

To account for the observed behaviour we may consider an Elcy–Rideal mechanism [28] in which a surface oxygen anion can only be attacked by CO when it is residing next to a surface oxygen vacancy. When $\delta \ll 3 - \delta$, the concentration of such vacancy-anion pairs will be proportional to the vacancy concentration, leading to a proportionality between the flux and δ . Since the oxygen vacancy concentrations do not exceed 5% of the total oxygen contents in the experiments presented here, $[\text{V}_\text{O}^{\bullet\bullet} - \text{O}_\text{O}^x] \approx [\text{V}_\text{O}^{\bullet\bullet}]$. Thus

A second explanation is that of a Langmuir–Hinshelwood type of mechanism in which CO adsorbs on a surface oxygen vacancy, before it reacts with a neighbouring oxygen ion:

The first step is assumed to be rate-limiting. This model is in agreement with a suggestion made by Yasuda and Hikita for $\text{La}_{0.7}\text{Ca}_{0.3}\text{CrO}_{3-\delta}$ [23]. The authors speculated that gaseous species involved in the surface reaction (CO and CO_2) may form a temporary bond with vacant lattice sites present at the surface. It should be noted that due to the high temperatures, adsorption such as is assumed in this model is physically less likely.

For both mechanisms described above, the kinetic expression for the oxygen flux will be

$$J_{\text{O}_2} = \frac{1}{2} k_\text{O} [\text{V}_\text{O}^{\bullet\bullet}] p_{\text{CO}} \quad (11)$$

$[\text{V}_\text{O}^{\bullet\bullet}] = \delta$ by definition. It is assumed that the value of k_O does not vary with the strontium content. It follows that

$$k_{\text{exp}} = \frac{1}{2} k_\text{O} \delta \quad (12)$$

From Fig. 7, a value of $1.26 \pm 0.16 \text{ mol m}^{-2} \text{ s}^{-1} \text{ bar}^{-1}$ is found for k_O .

The positive intercepts in Fig. 6 are due to the occurrence of a finite flux in the absence of CO [6], so that the overall expression for J_{O_2} can be written as

$$J_{\text{O}_2} = J_0 + \frac{1}{2} k_\text{O} \delta p_{\text{CO}} \quad (13)$$

The activation energy for oxygen permeation was determined for $x=0.3$ in the temperature range 1173–1323 K from an experiment in which $p_{\text{CO}} = 0.08 \text{ bar}$ and $p_{\text{CO}_2} = 0.32 \text{ bar}$ were measured at the outlet. The Arrhenius plot is given in Fig. 8. For the sake of comparison, the Arrhenius plot for the same composition (thickness 0.92 mm) in an air/He gradient is also shown. It is clear that under the conditions covered by the experiment, the oxygen flux is strongly enhanced by the presence of CO, but the activation energy has decreased. The calculated activation energy was found to be $31 \pm 19 \text{ kJ/mol}$. Using Eq. (11), we may interpret this activation energy as consisting of two contributions, namely the activation energy for oxygen vacancy formation and the activation energy for k_O :

$$E_{\text{act}}(J_{\text{O}_2}) = E_{\text{act}}(k_\text{O}) + E_{\text{act}}(\delta) \quad (14)$$

Since the CO/ CO_2 ratio was kept constant, the oxygen partial pressure changes considerably over the temperature interval (10^{-12} – 10^{-15} bar). The oxygen non-stoichiometry remains almost constant, varying from about 0.152 to 0.156 between 1173 and

Fig. 8. Apparent activation energies for oxygen permeation through $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$ in air/He and air/CO, CO_2 , He gradients for 1.0 mm membranes.

1323 K. Thus, within experimental error, the apparent activation energy almost refers to that of k_O .

4.3. Surface morphology and strontium segregation

In the oxidation models proposed above, it is assumed that the surface composition is the same as that of the bulk. However, segregation of earth alkali cations has been observed on several cobalt-based perovskites [29–31]. Furthermore, imposing an oxygen partial pressure gradient across the membrane appears to further increase the level of segregation [31]. Since the reaction model assumes $\delta = \frac{1}{2}[\text{Sr}'_{\text{La}}]$, an increased strontium concentration in the near-surface layer may affect the local concentration of oxygen vacancies. SEM, EDX and XPS analysis were performed to investigate segregation and surface morphology.

Several samples were quickly cooled down from reaction conditions to room temperature by quenching the quartz reactor in ice water. EDX analysis of the perovskite/ CO , CO_2 interfaces did not show a significant deviation from the bulk composition. SEM analysis showed a second phase present at the surface, next to the perovskite phase. The morphology of this phase is very similar to that of SrCO_3 as found in a previous study on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and $\text{La}_{0.8}\text{Ba}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ membranes after exposure to air/methane gradients [30]. However, much higher levels of Sr and Ba segregation were observed in the latter case. The difference is most likely related to the large difference in chemical stability between cobalt- and iron-based perovskites [32].

Semi-quantitative analysis of the level of Sr segregation was performed by XPS. Previous work on related perovskites $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ($x=0.4, 0.6$) showed that the Sr 3d spectrum can be deconvoluted into a low (131.8 eV) and a high (133.8–134.2 eV) BE contribution [33]. The low BE has an anomalously low value and was attributed to strontium in the bulk of the perovskite. The high BE was considered to be due to the presence of minor second phases at the surface, such as SrCO_3 with a reported BE of 133.1–133.5 eV [34,35], and SrO with a BE of 135.1–135.6 eV [34,36]. The strontium concentration at $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ membrane surfaces is shown in Fig. 9(a). Both fresh and used samples are enriched

Fig. 9. Normalized strontium concentration determined by XPS. (a) Overall near-surface Sr concentration; (b) Sr concentration in the near-surface perovskite lattice.

with Sr. The spectrum was deconvoluted into two components with $3d_{5/2}$ maxima at 131.4–131.8 eV and 133.2–133.9 eV. These peaks were attributed to strontium present in the form of $\text{La}_x\text{Sr}_x\text{FeO}_{3-\delta}$ and minor second phases, respectively. Their relative contributions to the total Sr 3d spectrum are given in Table 3. In each case these contributions are about 50% for the used samples, with the exception of the membrane that had only been exposed to He. The relative contributions of the high BE to the spectra of fresh samples are much smaller (12–19%). By using only the low BE contribution of the Sr 3d spectrum

Table 3
Deconvolution of XPS-Sr 3d spectrum into high and low binding energy (BE) contributions for used and fresh membranes

x	Used		Fresh	
	high BE (%)	low BE (%)	high BE (%)	low BE (%)
0.1	46	54	17	83
0.2	48	52	12	88
0.3	54	46		
0.4	47	53	19	81
0.4 ^a	31	69		

^aSample exposed only to air/He gradient.

(denoted as Sr_{lat}) the Sr enrichment in the perovskite lattice near the surface can be estimated, as given in Fig. 9(b). Within experimental error, the fresh samples show little or no enrichment, whereas a slight enrichment is found for the used samples. The La/Fe ratios were also determined, and were found to be close to the bulk ratios for both the fresh and used membranes.

In part I of this paper [6] it was reported that oxygen permeation through $La_{1-x}Sr_xFeO_{3-\delta}$ membranes in air/He gradients can be enhanced by treatment of the membranes lower partial pressure side in a CO containing atmosphere. XPS analysis of $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ surfaces that had been exposed for 48 h to an air/He and an air/0.4 bar CO gradient, respectively, indicate a higher level of segregation for the latter sample. The $[Sr/(Sr+La)]$ ratios at the surface are 0.61 and 0.73, respectively. The difference in strontium enrichment in the near-surface perovskite layers between the two samples is somewhat smaller, i.e. $[Sr_{lat}/(Sr_{lat}+La)]$ equals 0.52 and 0.59, respectively. Thus it appears that strontium segregates to the surface where it forms $SrCO_3$ and/or SrO , and that this process is accelerated by the presence of CO, CO_2 mixtures. It is very possible that the level of segregation is correlated with the enhanced rate of oxygen exchange after treatment. For instance, it is conjectured that a larger specific area on which oxygen exchange can take place is directly or indirectly related to the level of segregation. The initial increase of the oxygen fluxes with time, as described in part I [6], may be indicative of the time-scale on which the segregation process occurs.

Surface morphologies of a fresh and a used membrane (quenched from an air/CO gradient) of $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ are shown in Fig. 10 and Fig. 11. The membranes have a relative density of 96% and were taken from the same batch of material. The surface areas shown are indicative for both types of surfaces. It appears that the surface roughness of the quenched membrane is larger, which indicates a larger specific surface area. Surface profile measurements also showed a small but reproducible increase of the surface roughness for the used membranes. In comparison with fresh samples, the surface profile lengths of used membranes were larger by a factor of 1.4–1.6. These results are in agreement with studies

Fig. 10. SEM picture of surface of fresh $La_{0.9}Sr_{0.1}FeO_{3-\delta}$ membrane.

of Deng et al. [37,38], who showed theoretically that an enlargement of the specific surface area may have a very pronounced effect on the permeation fluxes through mixed conductors under conditions of surface-exchange control.

Miura et al. [39] showed that the oxygen permeation rate through dense films of $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ prepared by slip casting, was increased significantly when the surface was treated with a solution containing 2 M HNO_3 . The authors conclude that the acid treatment resulted in the removal of a surface layer containing impurities like SrO . Their XPS-Sr 3d spectrum of a freshly prepared surface showed maxima at 132 eV and 134 eV, with a shoulder at 135 eV. After the acid treatment, the low energy peak, assigned by the authors to SrO or $SrCO_3$, had disappeared completely, while the intensity of the shoulder at 135 eV had increased. However, in contrast to their findings,

Fig. 11. SEM picture of surface of exposed $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_{3-\delta}$ membrane.

XPS measurements in a study on perovskite-related superconductors $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ [40] indicate that the low energy peak is due to strontium from the perovskite lattice. XPS experiments on SrCO_3 powder performed in this laboratory showed the $\text{Sr } 3d_{5/2}$ maximum at 133.2 eV. Furthermore, Table 3 shows that treatment of the membrane results in a strongly increased contribution of the high BE peak. It therefore appears that the acid treatment [39] decomposes the perovskite surface completely, forming SrO or SrCO_3 , and is accompanied by an increased oxygen exchange rate. This result would be in agreement with the observations made here and in a methane coupling study on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ membranes [31], where an enhanced oxygen flux was reported after reduction of the membrane surface by CH_4 .

4.4. Crystal structure at the perovskite/CO interface

Previous investigations on the relationship between crystal structure and oxygen content of the $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ system [5] showed phase transitions to a cubic structure for $x=0.3$ and $x=0.4$ when the non-stoichiometry increased to a value of $x/2$. When the non-stoichiometry of these phases was small ($\delta \approx 0$), rhombohedral symmetry was found in $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$, and a mixture of rhombohedral and orthorhombic in $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$ [5]. To verify the assumption of a strongly depleted oxygen concentration at the air/CO interface, SAED experiments were performed on single crystals at the interfaces of three $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ membranes, either fresh or quenched from air/CO or air/He, respectively. In contrast to the rhombohedral symmetry found by XRD, only orthorhombic symmetry was found in the fresh sample, while both cubic ($a = 4.00 \pm 0.15 \text{ \AA}$) and orthorhombic symmetries were observed in both used samples. A SAED pattern of a cubic crystal of $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ is shown in Fig. 12. Measurements on $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$ samples gave similar results, with a unit cell parameter $a = 3.96 \pm 0.11 \text{ \AA}$ for the cubic grains.

Although the occurrence of cubic symmetry may indicate a high level of non-stoichiometry, care should be taken to attach too great a value to these results, since the mutual occurrence of more than one type of crystal symmetry, even in equilibrated samples, has been reported by Dann et al. [5]. Furthermore, the presence of orthorhombic symmetry may indicate that part of the interface has been re-oxidized during the quench. Finally, cubic crystal symmetry does not necessarily prove that the oxygen content is strongly depleted, but may also be an intrinsic high temperature crystal structure, irrespective of the level of non-stoichiometry.

5. Conclusions

The oxygen semipermeability of dense mixed-conducting membranes with nominal composition $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ($x=0.1-0.3$) in air/CO, CO_2 gradients appears to be limited by the rate of CO

Fig. 12. Electron diffraction pattern along the $[111]$ zone axis of a cubic single-crystalline grain of $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$.

oxidation at the gas/solid interface. The activation energy found on $\text{La}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$ was 31 ± 19 kJ/mol, which is much lower than in air/He gradients. The oxygen fluxes are linearly proportional to the CO partial pressure and can be explained by simple models for the oxidation of CO. Essentially, these models yield the same kinetic expression for the flux and both are based on the assumption that the non-stoichiometry parameter is approximately equal to $1/2x$ at the perovskite/CO, CO_2 interface. Although segregation of strontium was found at the surface, the enrichment of Sr in the near-surface perovskite layer was found to be small. SrCO_3 and possibly SrO was found on the membrane surface, but no signs of complete decomposition of the perovskite surface were observed. SEM analysis and profile measurements of the membrane surfaces indicated an enlargement of the specific surface area after exposure to CO, which may explain the enhanced fluxes that were observed.

SAED on single-crystalline grains at the interface of $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-\delta}$ ($x=0.3, 0.4$) showed cubic sym-

metry to be present in several grains, while no cubic symmetry was observed in fresh membranes.

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