Oxygen permeation flux through $\text{La}_{1-y}\text{Sr}_y\text{FeO}_3$ limited by carbon monoxide oxidation rate

B.A. van Hassel, J.E. ten Elshof, H.J.M. Bouwmeester *

*Laboratory of Inorganic Materials Science, Department of Chemical Technology, University of Twente,
P.O. Box 217, NL-7500 AE Enschede, Netherlands*

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Abstract

The oxygen permeation flux through $\text{La}_{1-y}\text{Sr}_y\text{FeO}_{3-\delta}$ ($y=0.1, 0.2$) in a large oxygen partial pressure gradient (air/ CO , CO_2 mixture) was found to be limited by the carbon monoxide oxidation rate at the low oxygen partial pressure side of the membrane. The oxygen permeation flux through the membrane was almost independent of its thickness (1 versus 2 mm) and strontium dopant concentration. The deposition of a 50 nm thin porous platinum layer at the low oxygen pressure side of the membrane increased the carbon monoxide oxidation rate and in this way the oxygen permeation flux by a factor 1.8 ± 0.2 .

Keywords: Ambipolar diffusion; Carbon monoxide; $\text{La}_{1-y}\text{Sr}_y\text{FeO}_3$; Oxygen permeation; Perovskite; Platinum; Surface modification

1. Introduction

Solid oxide membranes showing both electronic and ionic conductivity can separate oxygen from air [1]. Oxygen permeation fluxes through perovskite materials (e.g. $\text{La}_{1-y}\text{Sr}_y\text{Co}_{1-x}\text{Fe}_x\text{O}_3$ [2]) have been reported that are sufficiently high for industrial applications. The ionic conductivity of perovskites has a high activation energy, so high temperatures are needed for this oxygen separation process.

The oxygen separation process takes place at temperatures where also selective oxidation reactions take place, e.g. syn-gas production or oxidative coupling of methane [3]. It would be advantageous to combine the oxygen separation process with selective oxidation, making cooling, storage and reheating of the separated oxygen no longer necessary. Moreover, by selective feeding of oxygen through the

* Corresponding author. E-mail: h.j.m. bouwmeester@ct.utwente.nl, Fax. (+31-53) 356024.

solid oxide membrane it may be possible to influence catalytic phenomena on the membrane surface [4].

Selective oxidation reactions take place in a strongly reducing atmosphere. Therefore materials need to be developed which are stable in a reducing atmosphere but still have a high enough oxygen permeation flux.

$\text{La}_{1-y}\text{Sr}_y\text{FeO}_{3-\delta}$ shows a considerable oxygen nonstoichiometry in a reducing atmosphere and is one of the most stable perovskites [5]. This makes it a potential candidate material for a combined oxygen separation and selective oxidation membrane. The physical and chemical properties are well understood in terms of a simple point defect model. With this point defect model it was possible to derive an analytical expression for the oxygen permeation flux through this material as a function of the oxygen partial pressure gradient [6]. In this study we report the corresponding experimental results. It will be shown that the carbon monoxide oxidation rate at the low oxygen partial pressure side of the membrane limits the oxygen permeation flux when $\text{La}_{1-y}\text{Sr}_y\text{FeO}_{3-\delta}$ is placed in a large oxygen partial pressure gradient (air/ CO , CO_2 mixture).

2. Theory

2.1. Ambipolar diffusion

A mixed conducting oxide is an oxide in which oxygen ions and electrons or corresponding lattice defects are mobile. When such a material is placed in a gradient of the chemical potential of oxygen, oxygen ions will move through the oxide from the high to the low oxygen partial pressure side. The flux of the oxygen ions is charge compensated by the transport of electronic charge carriers. When the electronic conductivity of a mixed conducting oxide is much higher than the ionic conductivity (the electronic transference number can be approximated as unity), the oxygen permeation flux can be calculated using the Wagner equation [6]:

$$J_{\text{O}_2}(\text{mol cm}^{-2} \text{ s}^{-1}) = -\frac{1}{L} \int_{\mu(\text{O}_2)_x=0}^{\mu(\text{O}_2)_x=L} \sigma_{\text{O}^{2-}} \frac{1}{4F^2} d\mu(\text{O}_2) \quad (1)$$

where L is the thickness of the membrane (cm), $\sigma_{\text{O}^{2-}}$, the oxygen ion conductivity ($\Omega^{-1} \text{ cm}^{-1}$), F , the Faraday constant (C mol^{-1}) and $\mu(\text{O}_2)$ is the chemical potential of oxygen (J mol^{-1}). Assuming that all oxygen vacancies are fully ionized and contribute to the transport through $\text{La}_{1-y}\text{Sr}_y\text{FeO}_{3-\delta}$, the ionic conductivity can be calculated from

$$\sigma_{\text{O}^{2-}}(\Omega^{-1} \text{ cm}^{-1}) = \frac{f}{H_r} \frac{4F^2 [V_{\text{O}}] D_v}{RT V_m} \quad (2)$$

where f is the correlation factor, H_r , the Haven ratio [7], $[V_{\text{O}}]$, the oxygen vacancy mole fraction, D_v , the oxygen vacancy diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), R , the molar gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), T , the absolute temperature (K) and V_m is the molar volume of the perovskite ($\text{cm}^3 \text{mol}^{-1}$). The ratio f/H_r was taken as unity.

The exact solution of the integral Eq. (1) has been given previously [6]. According to Eq. (1) the oxygen permeation flux is inversely proportional to the thickness and proportional to the ionic conductivity of the membrane provided that the surface oxygen exchange process is not rate limiting.

2.2. Coupling between chemical diffusion and surface oxygen exchange process

An oxidation–reduction model is used for describing the carbon monoxide oxidation mechanism at the low oxygen partial pressure side of the membrane. In the first stage of this model carbon monoxide reacts with lattice oxygen of the membrane:

Assuming first order kinetics with respect to carbon monoxide and lattice oxygen mole fraction (O_{O}^x), the rate expression in terms of mol oxygen consumed per unit time and area can be written as

$$r(\text{mol O}_2 \text{ cm}^{-2} \text{s}^{-1}) = k_r \text{O}_{\text{O}}^x P_{\text{CO}} \quad (3)$$

The membrane surface is restored to its initial state by chemical diffusion of oxygen through the membrane. The chemical diffusion of oxygen through the membrane can be written as

$$J_{\text{O}_2}(\text{mol O}_2 \text{ cm}^{-2} \text{s}^{-1}) = -D_{\text{chem}} \frac{1}{V_m} \frac{d\text{O}_{\text{O}}^x}{dx} \quad (4)$$

where $D_{\text{chem}} = -0.5D_v(d \ln P_{\text{O}_2}/d \ln [V_{\text{O}}])$.

In the simple case of a chemical diffusion coefficient which is independent of the chemical potential of oxygen, this set of equations can be solved, yielding for the overall rate of the oxidation of carbon monoxide:

$$r = J_{\text{O}_2} = \frac{k_r \text{O}_{\text{O}}^x(x=0) P_{\text{CO}}}{\left(\frac{k_r P_{\text{CO}} L}{D_{\text{chem}}} + 1 \right)} \quad (5)$$

The ratio between the rate of the surface reaction and the chemical diffusion process ($k_r P_{\text{CO}} L / D_{\text{chem}}$) is called the Biot number [8]. For a small Biot number the oxygen permeation flux is determined by the surface reaction rate, whereas for a large Biot number it is controlled by the chemical diffusion of oxygen through the membrane.

3. Experimental

Perovskite oxides were prepared by the thermal decomposition of precursor complexes derived from nitrate solutions using ethylenediaminetetraacetic acid (EDTA) as a complexing agent. $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$ (abbreviated as 90LSF) and $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ (80LSF) were prepared. The metal nitrates $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck, p.a.) were dissolved in stoichiometric ratios in a concentrated ammonia/EDTA solution under moderate heating, while keeping the pH at 7.5–9. For each mole of metal between 1.5–2 mol EDTA was used. The solution was pyrolysed in small batches in a stove at 200–220°C. Calcination was performed at 850°C in air for 5–6 h using heating/cooling rates of 240°C/h.

Milling experiments were performed to improve the powder characteristics. Wet milling in isopropanol resulted in smaller particles (diameter (d) = 10 μm) than dry milling (d = 40 μm), as measured with the Horiba LA-500 laser diffraction particle size distribution analyzer. Good results were obtained with 6.2–14 g LSF, 1.5–3 ml isopropanol per gram powder and 7–10 large (d = 15 mm) yttria stabilized zirconia (YSZ) milling balls in a 100 ml polyethylene milling pot. After milling, the isopropanol was removed by evaporation in air. In addition, these wet milled samples were recalcined for 30 min at 850°C in air (heating/cooling rate = 240°C/h) to remove remaining traces of isopropanol, newly formed carbonates and water absorbed by the isopropanol.

The powders were uniaxially pressed at 0.5 bar and subsequently isostatically pressed at 4000 bar for 2–3 min. Typical green densities were between 50–54% of the theoretical density. In the green state, no systematic differences were found between samples made of dry or wet milled powders. The disks were sintered at 1150–1200°C for 6 h using a heating/cooling rate of 120°C/h. Typical densities of 96–97% of theoretical were obtained.

The X-ray diffraction patterns of the samples indicated an orthorhombic crystal structure which is in accordance with literature data on LSF compounds [9].

Oxygen permeation measurements were performed in the quartz reactor, schematically shown in Fig. 1. The reactor volume is 3.2 ml. For the experiments disks were used with a diameter of 12 mm. Supremax (Schott Nederland) glass rings were used to seal the membrane material into the quartz sample holder. The temperature of the reactor was monitored by a Pt/Pt–10%Rh thermocouple at the high oxygen partial pressure side of the membrane. Sealing took place at 1130°C for 15 min. In the case of a Supremax glass ring, measurements could be performed between 800°C and 1100°C. Below about 700°C, the seal cracked and the system was no longer gastight.

The experimental set-up for the oxygen permeation measurements is shown in Fig. 2. Brooks 5800 mass flow controllers were used to control the flow of He, CO and CO_2 through the reactor. These were calibrated by means of a Brooks Volumeter. The analysis of reactants and products took place with a Varian 3300 gas

Fig. 1. Reactor for oxygen permeation measurements. Feed gas 1 is air and feed gas 2 is helium or a CO/CO₂ mixture diluted with helium.

chromatograph and an LDC/Milton Roy CL-10 integrator. A Porapak-N column was used to separate carbon dioxide. A molecular sieve column (type 13X) was used to separate oxygen, nitrogen, and carbon monoxide. The separation of oxygen and nitrogen on the molecular sieve column is important for leak testing of the sample and the Supremax glass seal. In this study the leakage of nitrogen from air from the high to the low oxygen partial pressure side of the membrane was less than $2 \cdot 10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}$. Ytria stabilized zirconia based oxygen sensors (at 740°C) were used to monitor continuously the oxygen partial pressure of the gas mixtures.

The oxygen permeation of 90LSF and 80LSF was measured in a small and large oxygen partial pressure gradient. The oxygen partial pressure gradient was adjusted by varying the helium gas flow-rate from 7.40 ml/min to 55.9 ml/min (STP) in the case of the small oxygen partial pressure gradient. In the case of continuous ideally stirred tank reactor (CISTR) conditions [10], which we assume, the composition in the reactor is uniform throughout and the effluent leaving the reactor

Fig. 2. Experimental system for oxygen permeation measurements.

has the same composition as the mixture within the reactor. At a low helium flow-rate the oxygen partial pressure in the outlet of the reactor is higher than at a high helium flow-rate. So by varying the helium flow-rate we could adjust the oxygen partial pressure gradient across the membrane. The oxygen permeation flux was calculated from the measured outlet flow-rate and the oxygen concentration analyzed by the gas chromatograph with the TCD detector. In order to obtain a much larger oxygen partial pressure gradient CO/CO₂ mixtures diluted in helium were used. A total flow-rate of 12.4 ml/min (STP) was used, from which 7.4 ml/min was helium. The oxygen permeation flux was calculated from the measured flow-rate and the difference between the amount of oxygen (present as O₂, CO or CO₂) before and after the reactor. The carbon balance during the measurements was satisfactory ($102 \pm 1\%$). The equilibrium oxygen partial pressure of the CO/CO₂ mixtures in the outlet of the reactor was calculated at 1000°C from the thermodynamic data collected by Barin and Knacke [11]. In reality the mixing of gases in the reactor may not be ideal. Departures from the ideal mixing state are currently under investigation.

4. Results and discussion

4.1. Temperature dependence

The temperature dependence of the oxygen permeation flux through 90LSF and 80LSF in a small oxygen partial pressure gradient (air/He) is shown in Fig. 3. A constant helium flow-rate of 7.40 ml/min (STP) was used for those measurements.

Fig. 3. Temperature dependence of oxygen permeation flux through 90LSF ($L = 1.04$ mm, ●) and 80LSF ($L = 1.12$ mm, ■) in a small oxygen partial pressure gradient (air/He). The helium flow was 7.40 ml (STP) /min.

As the oxygen permeation flux is strongly temperature dependent the constant helium flow-rate results in a different oxygen partial pressure gradient at each temperature. The apparent activation energies for the oxygen permeation flux through 90LSF and 80LSF are (191 ± 7) and (195 ± 6) kJ/mol, respectively.

From the detailed study by Mizusaki et al. [5] of the nonstoichiometry of $\text{La}_{1-y}\text{Sr}_y\text{FeO}_3$ high values of the energy of formation of the oxygen vacancies (ΔH_f) were calculated by Ishigaki et al. [12], as shown in Table 1. Results obtained by Ishigaki et al. [12], using ^{18}O isotope exchange techniques, indicate that the oxygen vacancy diffusion coefficient in this perovskite has a high activation energy ranging from 74 ± 24 for LaFeO_3 to 114 ± 23 kJ/mol for $\text{La}_{0.75}\text{Sr}_{0.25}\text{FeO}_3$. The ionic conductivity of $\text{La}_{1-y}\text{Sr}_y\text{FeO}_3$ is proportional to the product of the oxygen vacancy concentration and the oxygen vacancy diffusion coefficient. Thus the activation energy for the ionic conductivity is the sum of the two energies mentioned above. The experimental values of the apparent activation energy for oxygen permeation in a small oxygen partial pressure gradient, as given above, agree well with this calculated sum.

4.2. Oxygen permeation in a large oxygen partial pressure gradient (air/ CO , CO_2 mixture)

Fig. 4 shows the oxygen permeation flux through 1 and 2 mm thick samples of 90LSF as a function of the oxygen partial pressure at the outlet of the reactor. It shows that the oxygen permeation flux is independent of the thickness of the

Table 1

Literature values of the activation energy of the oxygen vacancy diffusion coefficient ($E_{\text{act}}(D_v)$) and the energy of formation of the oxygen vacancies (ΔH_f) of $\text{La}_{1-y}\text{Sr}_y\text{FeO}_3$ [12]

y	$\Delta H_f/\text{kJ mol}^{-1}$	$E_{\text{act}}(D_v)/\text{kJ mol}^{-1}$	Sum/ kJ mol^{-1}
0	137 ± 25	74 ± 24	211 ± 35
0.1	85 ± 25	79 ± 25	164 ± 35
0.25	62 ± 25	114 ± 23	176 ± 35

Fig. 4. Oxygen permeation flux of 90LSF as a function of thickness in a large oxygen partial pressure gradient (air/CO,CO₂ mixture) at 1000°C. (▲) $L = 2.00$ mm, (■) $L = 1.07$ mm, (—) Model ($L = 2.00$ mm), (---) Model ($L = 1.07$ mm).

membrane and much lower than the results of the oxygen permeation modelling study [6]. The parameters used for modelling the oxygen permeation are shown in Table 2. In that model the oxygen permeation flux was assumed to be controlled by the ionic conductivity of the membrane. This resulted in an oxygen permeation flux which was inversely proportional to the thickness of the membrane (Eq. 1). This is experimentally not observed. The model calculation predicts a continuous increase of the oxygen permeation flux starting below an oxygen partial pressure of about 10^{-3} atm. Experimentally the oxygen permeation flux starts to increase below an oxygen partial pressure of 10^{-10} atm, i.e. as soon as carbon monoxide is introduced at the low oxygen partial pressure side of the membrane reactor.

Fig. 5 shows the results of oxygen permeability measurements through 90LSF and 80LSF of about the same thickness. The strontium doping level of 80LSF is twice as high as that of 90LSF. This results in a twice as high oxygen vacancy concentration in the oxygen partial pressure range of 10^{-6} to 10^{-12} atm at 1000°C [5]. Moreover, the oxygen vacancy diffusion coefficient of 80LSF is about a factor two larger than that of 90LSF, as shown in Table 2. According to Eq. (2) this would result in a four times as high ionic conductivity for 80LSF compared with 90LSF. According to Eq. (1), the oxygen permeation is proportional to the ionic conductivity. So we could expect to observe an increase of the oxygen permeation

Table 2

Model parameters for the calculation of the nonstoichiometry and oxygen permeation flux through $\text{La}_{1-y}\text{Sr}_y\text{FeO}_3$ at 1000°C; the parameters have the same meaning as in our previous publication [6]

Parameter	$\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$	$\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$
y	0.1	0.2
$V_m/\text{m}^3 \text{mol}^{-1}\text{a}$	$3.38 \cdot 10^{-5}$	$3.38 \cdot 10^{-5}$
$D_v/\text{m}^2 \text{s}^{-1}\text{b}$	$7.41 \cdot 10^{-10}$	$1.32 \cdot 10^{-9}$
$K_4/\text{atm}^{1/2}$	$7.00 \cdot 10^{-2}$	$9.79 \cdot 10^{-2}$
K_5	$1.00 \cdot 10^{-6}$	$9.70 \cdot 10^{-7}$

^a The molar volume (V_m) was calculated from the cell parameter of $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ as published in the Powder Diffraction File [13]. ^b The oxygen vacancy diffusion coefficient (D_v) of $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$ were taken from ref. [12].

Fig. 5. Comparison of the oxygen permeation flux through 90LSF ($L = 1.07$ mm) and 80LSF ($L = 1.12$ mm) in a large oxygen partial pressure gradient (air/ CO_2 mixture) at 1000°C . ($\blacktriangle$) 80LSF ($L = 1.12$ mm), ($\blacksquare$) 90LSF ($L = 1.07$ mm), (—) Model 80LSF ($L = 1.12$ mm), (---) Model 90LSF ($L = 1.07$ mm).

flux with a factor of 4 going from 90LSF to 80LSF. As shown in Fig. 5, this is experimentally not observed.

The thickness of 90LSF was changed from 2 to 1 mm and the strontium doping was changed from a mole fraction of 0.1 to 0.2, neither of them gave an expected increase of the oxygen permeation flux. These experimental results show that some process other than the chemical diffusion of oxygen controls the oxygen permeation flux.

We applied a 50 nm thin porous platinum layer on the membrane surface at the low oxygen partial pressure side in order to check whether the oxygen permeation flux was controlled by the chemical diffusion of oxygen or by a limiting carbon monoxide oxidation rate at the membrane surface. If the oxygen permeation flux is controlled by the chemical diffusion of oxygen in the membrane then it would not be affected by this surface modification. Platinum is a good total oxidation catalyst so it could increase the rate of the surface oxygen exchange process and in this way the oxygen permeation flux. Fig. 6 shows a clear increase of the oxygen permeation flux after modifying the membrane surface with the porous platinum film. This indicates that the carbon monoxide oxidation rate at the low oxygen partial pressure side of the membrane is limiting the oxygen permeation flux.

The oxygen permeation flux can also be plotted as a function of the carbon monoxide partial pressure and this is shown in Fig. 7. In this case we observe a linear increase of the oxygen permeation flux with the carbon monoxide partial

Fig. 6. The effect of a 50 nm thin porous platinum layer on the oxygen permeation flux through 80LSF ($L = 1.12$ mm) at 1000°C . ($\blacktriangle$) Only polished, ($\blacksquare$) with porous platinum layer (thickness = 50 nm).

Fig. 7. Oxygen permeation flux through 80LSF (only polished, $\blacktriangle$) and 80LSF (modified with 50 nm thick porous platinum layer, $\blacksquare$) as a function of the carbon monoxide partial pressure at 1000°C.

pressure with a slope proportional to the carbon monoxide oxidation rate constant. After modification of the membrane surface with the 50 nm thin porous platinum layer an increase of the carbon monoxide oxidation rate is observed with a factor 1.8 ± 0.2 . Such a linear relation between the oxygen permeation flux and the carbon monoxide partial pressure can be obtained when the oxygen permeation flux is controlled by the carbon monoxide oxidation rate and not by the chemical diffusion of oxygen through the membrane. In view of the theory presented in Section 2.2., this means that the LSF membranes considered here have a small Biot number.

The measurements shown in Fig. 8 were performed in order to obtain more experimental evidence that the oxygen permeation flux was controlled by the carbon monoxide oxidation rate. In the experiment the CO/CO_2 ratio was kept constant but the mixture was diluted with helium to a greater or lesser extent. The stronger the dilution with helium, the smaller the carbon monoxide partial pressure would be. The oxygen activity would remain the same since it is governed by the CO/CO_2 ratio. The oxygen permeation flux is expected to be independent of the extent of dilution when it is controlled by the chemical diffusion of oxygen (Eq. 1). When the oxygen permeation flux is determined by the carbon monoxide oxidation rate then the flux would increase with an increase of the carbon monoxide partial

Fig. 8. Effect of diluting a CO/CO_2 mixture (feed: $F_{\text{CO}} = 2.51 \text{ ml/min}$, $F_{\text{CO}_2} = 2.47 \text{ ml/min}$ resulting in $\text{CO}/\text{CO}_2 = 1.09 \pm 0.02$) in helium ($0 < F_{\text{He}} < 28.78 \text{ ml/min}$) on the oxygen permeation flux through 80LSF at 1000°C.

Fig. 9. Schematic presentation of the carbon monoxide oxidation and oxygen evolution at the low oxygen partial pressure side of a $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ membrane.

pressure (see Eq. 4). The results shown in Fig. 8 show an increase of the oxygen permeation flux with an increase of the carbon monoxide partial pressure, indicating that the oxygen permeation flux is limited by the carbon monoxide oxidation rate.

Fig. 7 shows that the linear relation between the oxygen permeation flux and the carbon monoxide partial pressure does not cross the origin. The reason for that is shown schematically in Fig. 9. In the absence of carbon monoxide, the oxygen permeation flux is not zero but reaches a finite value which is determined either by the surface rate of the oxygen evolution reaction, the chemical diffusion of oxygen, or the oxygen incorporation reaction at the high oxygen partial pressure side of the membrane. When the carbon monoxide partial pressure is low, there is a competition between the carbon monoxide oxidation reaction and the oxygen evolution reaction. The oxygen evolution reaction was experimentally observed by the presence of small amounts of oxygen in the effluent of the reactor, where according to the thermodynamic equilibrium between carbon monoxide and carbon dioxide the oxygen concentration should have been below the detection limit of the gas chromatograph. At high carbon monoxide partial pressures, oxygen could no longer be detected in the effluent.

In the present study it is meaningless to talk about the selectivity of the membrane as carbon dioxide is the only possible product. For partial oxidation reactions, however, the presence of different oxygen species at the membrane surface, as schematically shown in Fig. 7, is expected to exert considerable influence on the selectivity. For instance, peroxide (O_2^{2-}) and superoxide (O_2^-) species are thought to promote sequential oxidation of product C_2+ hydrocarbons to CO_x in the oxidative coupling of methane. One might apply a porous top layer of an alkali, alkaline earth or rare earth catalyst [14] in order to provide the basic sites necessary for this catalytic reaction.

5. Conclusion

In a small oxygen partial pressure gradient (air/He) the oxygen permeation flux through $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ has a high apparent activation

energy of 191 ± 7 and 195 ± 6 kJ/mol, respectively. This is due to the high energy of formation of the oxygen vacancies and the high activation energy of the oxygen vacancy diffusion coefficient.

The surface oxygen exchange process, in the present case the carbon monoxide oxidation rate, limits the oxygen permeation flux through $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_{3-\delta}$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-\delta}$ membranes when placed in a large oxygen partial pressure gradient (air/ CO , CO_2 mixture). For a higher oxygen permeation flux the catalytic properties of the membrane surface need to be altered. The carbon monoxide oxidation rate and hence the oxygen permeation flux increased with a factor 1.8 ± 0.2 after the deposition of a 50 nm thin porous platinum layer at the low oxygen partial pressure side of the membrane.

The modification of the catalytic properties of the membrane surface is also important when the membrane is considered to be used for selective feeding of oxygen to catalytic partial oxidation reactions, e.g. syn-gas production or oxidative coupling of methane.

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