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Journal of the European Ceramic Society 24 (2004) 1319–1323

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Oxygen transport through dense $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ perovskite-type permeation membranes

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Abstract

In this study, we examine the parameters that govern the overall oxygen flux through a permeation membrane. The chemical diffusion (D^δ) and the surface exchange (k^δ) coefficients for oxygen in $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ were determined as a function of temperature using a specially designed electrochemical cell combined with impedance spectroscopy. Typically, $D^\delta = 1.7\ 10^{-5}$ cm^2/s and $k^\delta = 3.6\ 10^{-4}$ cm/s in air at 900 °C. These values were compared with literature $^{18}O/^{16}O$ isotope exchange data. Oxygen permeation measurements were also performed on the same material in an air/Ar gradient, in the temperature range 800–1000 °C. At 900 °C, the oxygen flux across a 1.53 mm thick membrane was 8.0 10^{-8} mol/(cm^{2}s). The measured fluxes were compared with fluxes calculated on the basis of the D^δ and k^δ values using expressions derived from Fick's law. Comparison showed that the flux is controlled by both bulk diffusion and surface exchange, even for such thick membranes, and that the apparent k^δ varies significantly from one experiment to another.

Keywords: Diffusion; Perovskites; Membranes; Oxygen permeation

1. Introduction

Mixed conducting perovskite-type oxides have aroused considerable research over the last decades for their utilisation in numerous high temperature solid state electrochemical devices. They have in particular been studied as candidate materials for SOFC electrodes, oxygen permeation membranes for air separation and for the catalytic upgrading of natural gas to value added products. Among others, the $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ compound has received much attention.[1–5]

In all applications, oxygen transport plays a crucial role and, thus, an understanding of the parameters that govern the transport in the bulk and through the surfaces of mixed conducting perovskites is of prime importance. For a mixed conducting oxide subject to an oxygen chemical gradient, the bulk transport is usually described by the chemical diffusion coefficient (D^δ), while the reactions taking place at the gas–solid interfaces are usually assigned first order rate constants (k^δ) called surface exchange coefficients. Whereas D^δ relates to a property of the material, k^δ can represent a large variety of surface reactions[6] (adsorption, charge transfer,...) and is strongly influenced by the state of the surface (morphology,[7] presence of impurities or adsorbed species[8]...). It can thus vary significantly from one sample to another depending on the conditions of preparation and measurement. This often reduces the predictive value of measured k^δ data for modelling electrochemical devices.

In this work, we examine the correspondence between transport coefficients obtained by two different techniques and the effective flux across an oxygen separation membrane. For this purpose, D^δ and k^δ data for $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ were measured using a specially designed electrochemical cell combined with impedance spectroscopy (EIS) and compared with the corresponding $^{18}O/^{16}O$ isotope exchange coefficients (D^* and k^*) from literature. These values were then used to model the oxygen flux across a membrane. Permeation measurements were finally carried out for direct comparison.

2. Experimental

All samples were produced from commercial $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ powder (Praxair Speciality

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0955-2219/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00503-X

Chemicals, Seattle), uni-axially pressed at 200 MPa and sintered in air at 1300 °C for 3 h. The density of the sintered samples was confirmed as in excess of 97% theoretical density by the Archemedes method.

The electrochemical measurements were performed on disc-shaped pellets (8 mm diameter) in the temperature range 800–900 °C, using the electrochemical cell design shown in Fig. 1. It consisted of a dense specimen pellet blocked ionically on one surface by a platinum foil. The opposite surface was left bare. An annular gold spacer separated the surface from a YSZ slab coated on both sides with porous platinum. The latter was used as an oxygen pump enabling control of the oxygen partial pressure within the gas space between the specimen and the YSZ slab. $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ being a good electronic conductor,[1] the upper porous Pt layer was connected to the current feeder across the specimen pellet. The cylindrical surface of the specimen was sealed with glass. The cell was clamped between two alumina tubes at the centre of a cylindrical furnace.

A complete description of the EIS technique applied to oxygen transport and the analysis methodology is given elsewhere.[9] Basically, it consists of applying a modulated voltage across the cell, which results in the modulation of the oxygen activity within the gas space. For high frequencies of modulation, the response of the cell will be governed by the kinetics of the oxygen pump, but, as the frequency is lowered, it will start showing how the sample accommodates the change in the surrounding oxygen activity through diffusion. The EIS response is then fitted with the equivalent circuit of the cell (derived from basic electrochemical equations) to obtain the oxygen transport parameters D^δ and k^δ.[9]

The EIS measurements were performed using an *EG&G* (PAR 273) potentiostat combined with an *EG&G* (1025) frequency response analyser, run by M398 software.

The permeation measurements were performed on $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$ 24 mm diameter disks (relative density = 96%). The experimental set-up is sketched in Fig. 2. The ~1.5 mm thick discs are tightened between two open-ended alumina tubes by means of gold rings fabricated from a gold wire. This arrangement is slid into a single mullite ceramic tube that fulfils multiple functions: (i) It provides a guiding tube for positioning and securing the gold ring seals. (ii) It allows to flush the disk periphery with inert gas in order to control its contribution or loss to the permeation flux of oxygen. In addition, the disk periphery is coated with gold paste so as to minimise this contribution. (iii) It allows for the detection of leaks around the gold seals by analysing the inlet and outlet compositions of the gas flushing through this mullite tube.

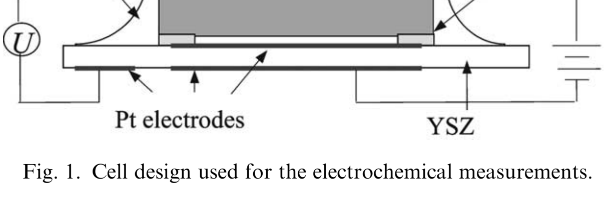

Fig. 1. Cell design used for the electrochemical measurements.

The whole set-up is swagelocked with Teflon ferrules at its extremes (in the cold) and spring-loaded so as to control the pressure on the gold seals, and mounted into a tiltable tubular furnace. Temperature is brought close to the melting temperature of gold (~1050 °C) in order to seal, via the pressurised gold rings, the two alumina tube chambers on either side of the membrane pellet. Then temperature can be varied maintaining controlled tightness. Air is passed in one alumina tube, and argon in the other tube, in order to provide an oxygen partial pressure gradient. Oxygen permeates through the dense pellet from the air chamber to the other tube, and is detected at the outlet by an in house built oxygen sensor. Detailed composition analysis of the outlet gas is monitored by on-line mass spectrometer and measured by off-line gas chromatography (*Gowmac*). The latter consists of a Molecular Sieve 5 Å with argon gas carrier, capable of detecting O_2 and N_2. Any contribution due to leakage could be corrected on the basis of the content of N_2.

3. Theory

The oxygen flux through a mixed conducting membrane of thickness L can be expressed as a function of the bulk chemical diffusion coefficient (D^δ), and the exchange coefficients assigned to both surfaces, k_0^δ and k_L^δ respectively:[10]

$$j_{O_2} = \frac{C_L - C_0}{2\left[(k_0^\delta)^{-1} + (k_L^\delta)^{-1} + L/\bar{D}^\delta\right]} \tag{1}$$

where C_0 and C_L are the lattice oxygen concentration at both surfaces of the membrane and

$$\bar{D}^\delta = \int_{C_0}^{C_L} D^\delta(C)dC/(C_L - C_0)$$

is an average diffusion coefficient.

In order to compare our results with $^{18}O/^{16}O$ exchange literature data, the following relation between the chemical and the tracer diffusion coefficients was used:[4,6]

$$D^\delta = \frac{D^*}{HR}\frac{\partial \ln a_O}{\partial \ln C_O} = \frac{D^*}{HR} w_O \tag{2}$$

where HR is the Haven ratio, a_O is the activity of lattice oxygen, C_O its concentration and w_O the thermodynamic factor. The latter can be obtained from TGA measurements of oxygen nonstoichiometry (δ) as a function of oxygen partial pressure.[4] In the limit of the dilute approximation and for an electron rich material, w_O can be expressed as:[6]

$$w_O = -\frac{(3-\delta)}{2}\frac{\partial \ln p_{O_2}}{\partial \delta} \cong 3/\delta \tag{3}$$

In the case of the surface exchange coefficients, the relation is not as straightforward since the rate limiting step can vary from one sample to another depending on the surface conditions, as discussed above. This thoroughly complicates the comparison. In the case of identical mechanisms (rate limiting steps), we have[6]

$$k^{\delta} = k^{*} w_O \tag{4}$$

4. Results and discussion

Fig. 3 shows the EIS response of the electrochemical cell subject to a 5 mV perturbation along with the best fit to the equivalent circuit of the cell (also displayed in the same figure). The latter corresponds to the complex impedance ($\bar{Z}$) of the cell derived elsewhere from basic electrochemical equations:[9]

$$\bar{Z}(j\omega) = R_e + \left(\frac{1}{R_p} + j\omega C_p\right)^{-1} + \left(\frac{1}{R_S + \frac{k^{\delta} R_S}{\sqrt{j\omega D^{\delta}}}\coth\sqrt{\frac{j\omega L^2}{D^{\delta}}}} + j\omega C_g\right)^{-1} \tag{5}$$

where $j = \sqrt{-1}$, R_e is the ohmic resistance of the electrolyte, R_p the polarisation resistance of the Pt electrodes, C_p the double layer capacitance, R_S the resistance of the surface exchange reaction, which is proportional to $(k^{\delta})^{-1}$, and C_g the gas space capacitance.

Starting from the high frequencies (left in Fig. 3), two partially overlapping depressed circles can be observed. The first loop can be attributed to the response of the oxygen pump, whereas the second corresponds to the gas space capacitance (C_g) in parallel with the resistance of the surface exchange reaction (R_s). At low frequencies, the EIS data displays a 45 ° slope in the complex plane, which is the signature of a diffusion process, followed by a vertical line (pure capacitance) resulting from the ionically blocked upper surface of the sample. The chemical diffusion and surface exchange coefficients obtained from fitting the above equivalent circuit to the EIS data are displayed versus the inverse temperature in Fig. 4. For comparison with isotope exchange data for the same material, chemical diffusion and surface exchange coefficients were calculated from the corresponding tracer coefficients, D^* and k^*, and the oxygen nonstoichiometry data reported by Benson et al.[3] using Eqs. (2) and (4), respectively, with $HR = 0.69$.[3] These are also shown in Fig. 4. The measured and calculated chemical diffusion coefficients show a good agreement within the limits of experimental uncertainty. On the

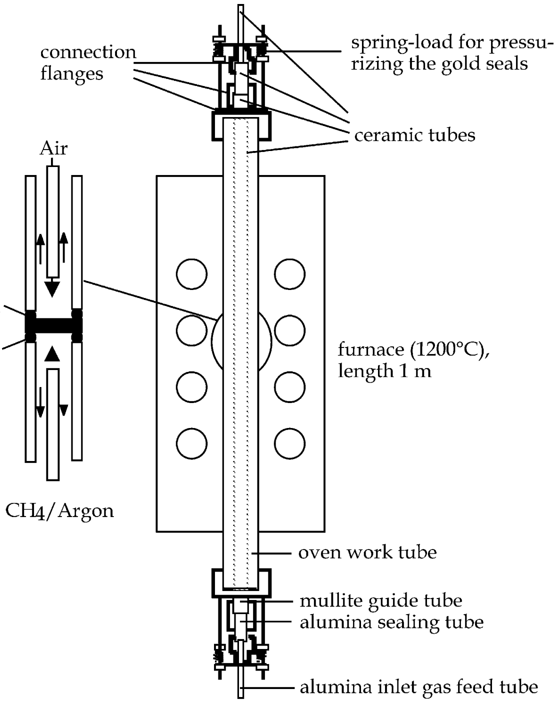

Fig. 2. Experimental set-up for the permeation measurements.

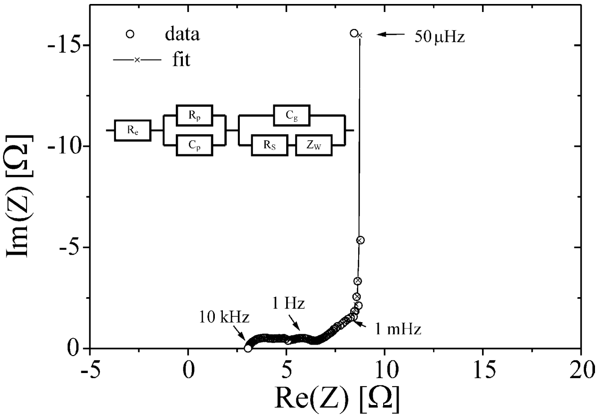

Fig. 3. EIS response of a $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ sample to a 5 mV modulation, with a −20 mV vs. air dc-bias, in the frequency range of 100 kHz to 50 μHz at 900 °C. A clear Warburg behaviour corresponding to diffusion is observed between 25 and 0.4 mHz. The line (—×—) corresponds to the best fit to the data with the equivalent circuit displayed in the same figure. Refer to text for an explanation of the equivalent circuit elements.

other hand, the calculated values for k^{δ} are systematically larger. This discrepancy is, however, not surprising according to the very nature of the surface exchange coefficient, as discussed above. Lane et al. observed the same trend when comparing the data obtained from isotope exchange and conductivity relaxation.[4] This discrepancy simply means that the rate limiting steps in both experiments are not the same or that the state of the surfaces are not similar. Nevertheless, it is now interesting to see how these different oxygen transport data relate to measured oxygen permeation fluxes.

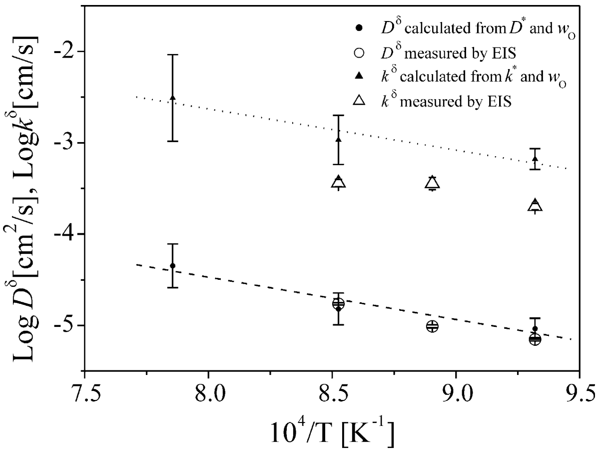

Fig. 4. Arrhenius plot of the chemical diffusion (D^{δ}) and the surface exchange (k^{δ}) coefficients obtained from fitting the electrochemical cell equivalent circuit to the EIS data in the temperature range 800–900 °C. Calculated D^{δ} and k^{δ} values from $^{18}O/^{16}O$ isotope exchange data using Eqs. (2)–(4) are also shown for 800–1000 °C. The error bars correspond to the experimental uncertainty with a 95% confidence level.

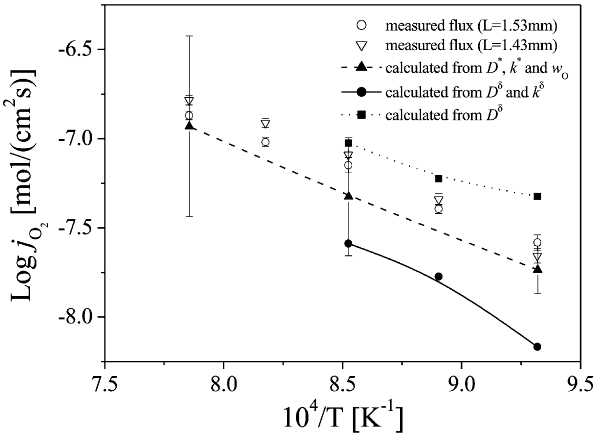

Fig. 5. Arrhenius plot of the oxygen permeation fluxes measured through two $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ membranes of different thickness, in the temperature range of 800–1000 °C. Calculated fluxes from the D^{δ} and k^{δ} values using Eq. (1) are also shown for comparison. The error bars correspond to the experimental uncertainty with a 95% confidence level.

The oxygen fluxes through two disk-shaped membranes of similar thickness (1.56 and 1.43 mm) measured between air and argon are displayed in Fig. 5 versus the inverse temperature, in the range 800–1000 °C. The two samples give similar results accounted for the uncertainty of the measurements and the small thickness difference. In order to check the consistency between the above oxygen transport data (D^{δ}, k^{δ}, D^* and k^*) and the permeation measurements, oxygen fluxes were calculated from the chemical and the tracer coefficients on the basis of Eq. (1). As previously, the isotopic exchange and oxygen nonstoichiometry data were taken from Benson et al.[3] The fluxes calculated from the tracer data have a large uncertainty since these values have been extrapolated from data measured in the 400–800 °C temperature range.[2] Despite this fact, they are consistent with the measured fluxes regarding both magnitude and temperature dependence. On the other hand, the fluxes calculated from the EIS data are systematically smaller. According to the above results displayed in Fig. 4, this can be attributed to the smaller values of the surface exchange coefficients measured by EIS. Fig. 5 also shows the values of the flux in the absence of surface limitation ($k^{\delta}\rightarrow\infty$), i.e. the oxygen transport is governed by bulk diffusion only. As these values are systematically too large, we can conclude that the permeation rate is controlled by both bulk and surface, and that the surface exchange coefficients obtained from k^* are in this case more representative of the limitations at the permeation membrane surfaces.

5. Conclusions

Chemical diffusion (D^{δ}) and surface exchange (k^{δ}) coefficients for $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-\delta}$ were obtained from EIS data in the temperature range 800–900 °C. Comparison with literature data showed good agreement for D^{δ} but not for k^{δ}. This was explained by the fact that k^{δ} is not univocally determined by the material but depends on the state of the surface.

Permeation fluxes were measured through dense membranes of the same material in the temperature range of 800–1000 °C. These were compared with calculated fluxes based on the D^{δ} and k^{δ} data. It was shown that the flux across the permeation membrane was governed by both bulk diffusion and surface exchange.

Acknowledgements

This work was supported by the Swiss Natural Gas Union Funding (FOGA). The authors wish to thank the COST action 525 for meeting the costs of the conference.

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