ABSTRACT

The chemical diffusivity of oxygen has been measured in strontium-substituted cobaltite La$_x$Sr$_{2-x}$CoO$_{3.8}$ by means of a thermogravimetric reequilibration method at temperatures between 650 and 1050°C and at oxygen partial pressures between approximately 0.002 and 1 atm. Although it appears that oxygen diffusivity is fairly high in this compound, the chemical diffusion coefficient extending from about $2 \times 10^{-6}$ to $10^{-4}$ cm$^2$/s, the reequilibration process is partly hindered by a slow surface reaction in a large portion of the experiments and more specifically at the lower temperatures. This effect is further described within this paper and so is the relationship between oxygen diffusivity and oxygen ionic conductivity.

INTRODUCTION

It is now a well-reckognized fact that the high electrocatalytic activity of lanthanum-based perovskite materials for the air electrode in solid oxide fuel cells (SOFCs) depends a great deal upon the combination of high oxygen ionic mobility and high electronic conductivity [1-2]. As the operating temperature would be lowered in the 800°C range for future reduced temperature SOFCs, there is correspondingly a greater concern about whether or not the air electrode would maintain sufficient activity in regard to a satisfactory operation [3]. The oxygen ionic mobility, a key parameter in such a case, can be accessed in various ways including polarization experiments, permeation studies, and chemical reequilibration experiments. Up to now, there have been but a few studies of this latter type on oxide materials for SOFCs. In regard to chemical composition, the available results are just too fragmentary to let any major tendency be drawn upon its effect on oxygen conductivity. For strontium-substituted lanthanum cobaltites, La$_{1-x}$Sr$_x$CoO$_{3.4}$, the available studies are still rather sparse [4-7] and need to be further complemented. Within the present work, an intermediate composition with $y = 0.5$ is further investigated and an attempt is made to correlate it with previous works and to oxygen ionic conductivity within the same material.

BASIC EQUATIONS FOR CHEMICAL REEQUILIBRATION

For a compound with a fixed-reference frame, the chemical diffusion coefficient $D$ is defined by Fick’s first law whereby
\[ j_i = - \bar{D} \frac{\partial c_i}{\partial x} \]  

Equation 1

\( j_i \) stands for the flux of species \( i \) and \( c_i \) is the concentration in appropriate units. The mass conservation law leads to Fick’s second law which is here expressed in its general form:

\[ \frac{\partial c_i}{\partial t} = \frac{\partial}{\partial x} \left( j_i \right) \]  

Equation 2

with \( t \) and \( x \) having their usual meaning. Most analytical solutions are based on constant values of \( \bar{D} \). Eq. 2 thus simplifies to

\[ \frac{\partial c_i}{\partial t} = -\bar{D} \frac{\partial c_i}{\partial x^2} \]  

Equation 3

In reequilibration experiments, an abrupt change is applied to the surrounding atmosphere such that the following time and boundary conditions are expected to apply:

\[ c_i(x, 0) = c_0 \]  

Equation 4a

\[ c_i(0, t) = c_f \]  

Equation 4b

Adapting Eqs. 3 to 4b for a cylindrical shape and solving leads to

\[ c_i = f(T_1) \cdot g(T_2) \]  

Equation 5a

where

\[ f(T_1) = \sum_{n=1}^{\infty} 4 u_n^2 \cdot (n + \frac{1}{2})^2 \cdot \exp \left[ u_n^2 \cdot T_1 \right] \]  

Equation 5b

\[ g(T_2) = \sum_{n=0}^{\infty} 2 \pi^2 (n + \frac{1}{2})^2 \cdot \exp \left[ -\pi^2 (n + \frac{1}{2})^2 \cdot T_2 \right] \]  

Equation 5c

\[ T_1 = \frac{\bar{D} t}{r^2} \]  

Equation 6a

\[ T_2 = \frac{\bar{D} t}{a^2} \]  

Equation 6b

\[ c_i = (\bar{c} - c_f) / (c_0 - c_f) \]  

Equation 6c

\( \bar{c} \) represents the average concentration through the sample at time \( t \). \( r \) stands for the cylinder radius and \( a \) for its half-length. \( u_n \) is the \( n \)th root of the zero-order Bessel function. In practical experiments, \( c_i \) can be accessed directly by means of the relative weight variation whereby \( W_r = c_i \) and is defined as

\[ W_r = (W - W_f) / (W_o - W_f) \]  

Equation 7

Although further relations may be developed in regard to \( \bar{D} \), Eqs. 1-7 are self-sufficient for the determination of chemical diffusivity in cylindrical samples. In brief, the main conditions for the following experiments are a constant \( \bar{D} \) and the boundary conditions expressed by Eqs. 4a-b. In order to keep a tighter follow-up on these conditions, the full analytical solution has been applied throughout data reduction within the present work. Fitting procedures based on approximations of Eqs. 5a-c, although very convenient, have been avoided since they may often conceal the actual diffusional behavior of the samples and, consequently, lead to misinterpretation of diffusion data.
PROCEDURE

La$_{5}$Sr$_{5}$CoO$_{3.8}$ powders were prepared by the glycine nitrate process [8-9]. Considerable care was taken to avoid any second phase formation as it has been shown that these are easily formed in strontium-substituted lanthanum cobaltite for any departure of the stoichiometric A/B ratio from unity between A and B sites (A=La, Sr; B=Co) [9]. These powders were isostatically pressed into cylinders and sintered between 1250 and 1300°C. The resulting cylinders were about 2.5mm in diameter and 10mm in length. Their relative density was above 99% as observed by scanning electron microscopy on metallographically polished cross-sections. Room temperature density by an immersion method calibrated with an annealed aluminum 5N sample led to an absolute value of 6.48 g/cm$^3$. For oxygen nonstoichiometry measurements, additional samples were sintered at 1400°C and reground in an agate mortar before thermogravimetric runs.

The Setaram B92 thermobalance used for chemical reequilibration experiments had a useful sensitivity of ± 1 µg and a temperature stability within a few tenths of a degree Celsius. The gas-handling equipment allowed abrupt pressure changes in pure oxygen within the high temperature chamber: overall pressure changes occured within one second. Although, this led to a negligible uncertainty on time $t = 0$ for reequilibration runs, the actual time required for the weighing system to fully recover from the initial weight swing extended to about 10-12 seconds after the initial change. The accuracy on time for the reequilibration process remained unaffected, but an equivalent dead zone was created for recording. The above procedure was nonetheless preferred to a simple switching procedure between two flowing gas mixtures due mainly to the accuracy on the initial time of the experiments.

RESULTS

Depending upon temperature, La$_{5}$Sr$_{5}$CoO$_{3.8}$ may reequilibrate extremely rapidly. In Fig. 1, only the final portion of the reequilibration process is observable at 1036°C while, at 834°C and below, the whole reequilibration curves are made available. Nonetheless, reequilibration curves at all temperatures end up into a well-defined plateau thereby indicating a rather simple process. This in contradistinction to a slow continuous weight shift already observed for lanthanum manganite at long reequilibration times [10].

In Fig. 2, $E$ has been calculated continuously as a function of the degree of reequilibration, following the full analytical solution from Eqs. 5a-c. Uncertainties are expected to be higher at both ends of the reequilibration process. Nonetheless, this kind of representation should approach a perfectly horizontal line if all conditions leading to Eqs. 5a-c are fulfilled. Such is not the case, especially at the lower temperatures where $D_{app}$ is found to increase almost steadily as $W_r$ decreases. This is most significant of a slow surface reaction between oxygen from the surrounding atmosphere and the oxide sample. In addition, the same experiments were repeated at a higher oxygen pressure. The corresponding results are reported in Fig. 3. The reequilibration curve at 834°C now reasonably fits a horizontal line while the curve at 632°C still shows some tendency to
increase. At both temperatures, values of $D_{app}$ are definitely higher than the preceding ones. The existence of a slow surface reaction is thus definitely confirmed with the effect of such a reaction becoming more or less negligible at higher temperatures and higher oxygen pressures. In the latter case, $D_{app}$ becomes indicative of true chemical diffusivity.

For every single run, $D_{app}$ is averaged out between $0.55 \leq W < 0.1$ thereby leading to $D_{avw}$ which gives equal weights to all portions of this reequilibration range. $D_{avw}$ has been reported in Fig. 4 vs the reciprocal of temperature for reequilibration runs at several final oxygen pressures. The effect of a slow surface reaction is again confirmed, but the higher values are believed to be quite close to true chemical diffusivity and a tentative line has been drawn across them. This line shall be considered as a lower boundary for true chemical diffusivity. The apparent activation energy calculated from this straight line is 104 kJ/mole-°K, but the true activation energy should be somewhat lower since reequilibration runs are more affected at low temperatures.

In view of its requirement for the calculation of oxygen ionic conductivity, the oxygen nonstoichiometry in La$_{0.5}$Sr$_{0.5}$CoO$_{3-d}$ has been further estimated within the range used for present reequilibration experiments. In Fig. 5, our own experimental data are reported together with data from the literature on La$_{0.5}$Sr$_{0.5}$CoO$_{3-d}$ at $p_{O_2} = 1$ atm and within the same temperature range [11]. We have taken the reference state $\delta = 0$ as the oxygen saturation value at low temperature and $p_{O_2} = 1$ atm as per ref. 11. The asymptotic behavior actually observed gives strong confidence in that procedure although, strictly speaking, it is not an inflexion point in the way suggested by Wagner [12]. The agreement between our data and the previous ones is poor except for the high end of the temperature range where it becomes acceptable. This can be explained by the fact that very stable equilibria and total reversibility were reached at lower temperatures and confirmed by long duration anneals within the present study. This is in contradistinction to previous observations were oxygen nonstoichiometry was found to continuously evolve in La$_{0.5}$Sr$_{0.5}$CoO$_{3-d}$, even very close to room temperature. Thus, previous data from ref. 11 are believed to be overestimated, in part due to a different estimation on $\delta = 0$.

**GENERAL DISCUSSION**

*Slow surface reaction*

Although the present study was primarily aimed at oxygen diffusivity, it becomes obvious that a large portion of the reequilibration runs are plagued with a slow surface reaction. A slow surface reaction has already been reported for La$_{0.5}$Sr$_{0.5}$CoO$_{3-d}$ [7]. In the latter case, it occurred with argon-oxygen mixtures while here it also does in pure oxygen atmospheres. There would be two ways of further working out this phenomenon. One would be to modify some of the experimental conditions as to make the slow surface reaction negligible for all temperatures and $p_{O_2}$s under consideration. This has already been done successfully at least for cobaltous oxide by increasing sample size and the absolute oxygen pressure change [13]. The other approach would imply modelling the surface reaction kinetics for the entire reequilibration range and may require further knowledge about the basic mechanisms underlying this reaction. On the other hand, the slow surface reaction is not unique to the initial portion of the transitory regime involved.
by the reequilibration method. It has also been observed for various strontium-substituted lanthanum cobaltites [14] in permeation studies, normally assimilated with a steady state process. In all cases, the oxygen exchange reaction plays an important role at the air electrode and becomes increasingly limiting at lower temperatures.

**Oxygen diffusivity**

In $\text{La}_{1-y}\text{Sr}_y\text{CoO}_3$ within the present temperature range, there is no indication of any significant cationic mobility in comparison to oxygen. Therefore, the chemical diffusivity is entirely attributed here to oxygen diffusion. One interesting point regarding diffusivity is the effect of strontium doping upon its evolution. In Fig. 6, diffusivity data from various sources have been gathered for $0 < y < 0.7$ [4-7]. These come exclusively from reequilibration experiments to eventually avoid additional discrepancies from different methods. The regression line for ref. 7 requires further explanations. We have been using their coefficient identified as $D_1$ which is in fact representative of the major portion of the reequilibration process in their samples. We do not believe that their coefficient $D_2$ is significant at all since the corresponding data have been derived in a totally empirical manner and are concerned only with the tail portion of their reequilibration runs. Furthermore, a significant variation of $D_1$ with $p_{O_2}$ was reported. If there is such an effect upon diffusivity, it would most probably overlap with the slow surface reaction also reported by these authors. Consequently, the regression was performed for the higher $p_{O_2}$ range of their data on $D_1$, more specifically at $p_{O_2} = 0.73$ atm which also corresponds to the oxygen pressure for our main results on diffusivity.

Taken into consideration some slight discrepancies coming out from using different data sets, there is nonetheless a strong tendency for chemical diffusivity to increase with $y$, the degree of strontium substitution. This effect varies by a factor of 3-4 within the range under consideration. To further refine this comparison would require additional precision from diffusivity measurements. To a lesser degree, the crystal structure of $\text{La}_{1-y}\text{Sr}_y\text{CoO}_3$ would also require further attention since it is known to evolve mainly as a function of $y$ and temperature with a tendency to become cubic at high temperature. Defect ordering has also been mentioned by Kruidhof et al. [14] for lower temperatures in their permeation study although no such evidence was found here in reequilibration experiments.

Following the Nernst-Einstein relation, $\sigma_0$, the oxygen ionic conductivity in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$, can be expressed as

$$\sigma_0 = \left( \frac{D_v}{RT} \right) \cdot \left( \frac{\delta \cdot \rho}{M_{ox}} \right) \cdot 4 F^2 \quad [8]$$

$D_v$ is the oxygen vacancy diffusion coefficient, $\rho$ the oxide density, $M_{ox}$ its molecular weight. $R$ and $F$ stand for the ideal gas constant and the Faraday number, respectively. For oxygen vacancies, $D_v$ is simply related to the chemical diffusion by

$$D_v = \frac{\tilde{D}}{3} \quad [9]$$

The equations above should suffice in describing the oxygen ionic conductivity although more complex thermodynamical developments are also available. The oxygen

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Ionic conductivity in $La_{0.5}Sr_{0.5}CoO_3$ at $p_{O_2} = 1$ atm is about $0.64 \Omega^{-1}\text{cm}^{-1}$ at 1000°C and 0.084 at 800°C. Based on a total conductivity of about 1000 $\Omega^{-1}\text{cm}^{-1}$, that leads to an oxygen transference number close to $1 \times 10^{-3}$ at 1000°C and $1 \times 10^{-4}$ at 800°C and one atm oxygen pressure. Although, the expression mixed-ionic conductor is often used for $La_{0.5}Sr_{0.5}CoO_3$, the electronic conduction remains largely prevalent within that material. As also expected, the effect of $p_{O_2}$ on the above properties is relatively small, but becomes increasingly important as the temperature is decreased.

CONCLUSION

The oxygen diffusivity has been measured in $La_{0.5}Sr_{0.5}CoO_3$ by the chemical reequilibration method and nonstoichiometry measurements were additionally performed on the same material. The oxygen diffusivity varies from a value equal or greater than $2.4 \times 10^{-6}$ cm$^2$/s at 650°C to $9.9 \times 10^{-6}$ cm$^2$/s at 1000°C. This high diffusivity coupled with a large departure from stoichiometry leads to a calculated value of oxygen conductivity as high as $0.6 \Omega^{-1}\text{cm}^{-1}$ at 1000°C and one oxygen atmosphere, that parameter decreasing to $0.08 \Omega^{-1}\text{cm}^{-1}$ at 800°C. The measured chemical diffusivity apparently decreases more rapidly than expected with temperature, but this effect is unambiguously attributed to a slow surface reaction with the oxygen surrounding atmosphere. This latter phenomenon, also present in polarization effects at the cathode of solid oxide fuel cells, should deserve further attention in reequilibration experiments at lower temperatures.

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Fig. 1. Reequilibration curves at various temperatures.

Fig. 2. Evolution of the calculated diffusivity vs the degree of reequilibration at an oxygen final pressure of 0.13 atm.
Fig. 3. Evolution of the calculated diffusivity vs the degree of reequilibration at an oxygen final pressure of 0.72 atm.

Fig. 4. Averaged diffusivity as a function of temperature for reequilibration runs at various final pressures.
Fig. 5. Departure from stoichiometry in \( \text{La}_{0.5}\text{Sr}_5\text{CoO}_{3.8} \) as a function of oxygen partial pressure and temperature.

Fig. 6. Oxygen diffusivity in \( \text{La}_{1-y}\text{Sr}_y\text{CoO}_{3.8} \) at various degrees of strontium substitution.