ABSTRACT

Oxide perovskites of the general formula \((\text{La}_{1-x}\text{Sr}_x)\text{MnO}_3\) are being used as air electrodes in high temperature solid oxide fuel cells. The chemical diffusion coefficient of oxygen in \((\text{La}_{0.79}\text{Sr}_{0.20})\text{MnO}_3\) was measured using the potentiostatic step method. This solid state ionic technique involved the use of a stabilized zirconia oxide electrolyte. The diffusion coefficient of oxygen in this mixed-conducting perovskite was found to be of the order of \(10^{-7}\) cm\(^2\)/sec at temperatures between 700°C and 860°C and at oxygen partial pressures between 0.21 atm and \(10^{-8}\) atm.

INTRODUCTION

Perovskite type oxides of transition metals are interesting materials for oxygen electrodes and oxidation catalysts [1]. The general formula is \((\text{Re}_{1-x}\text{M}_x)\text{MnO}_3\), where \(\text{Re}\) is a rare earth metal, typically lanthanum, \(\text{M}\) is an alkali earth metal (Ca or Sr), and \(\text{Mn}\) denotes a first row transition metal (Cr, Mn, Fe, Co, Ni). Members of the series \((\text{La}_{1-x}\text{Sr}_x)\text{MnO}_3\) are, in particular, being used as air electrodes in high temperature solid oxide fuel cells. All these oxides are mixed conductors in which the transport of oxide ions plays a major role in the oxygen electrode reaction. The knowledge of the transport parameters for oxygen will help in the characterization and selection of materials for special purposes as well as in understanding the reaction mechanisms involved. In this work a solid state electrochemical method was used to measure the chemical diffusion coefficient of oxygen in the mixed-conducting oxide \((\text{La}_{0.79}\text{Sr}_{0.20})\text{MnO}_3\).

THEORETICAL CONSIDERATIONS

The experimental arrangement is shown in Figure 1. It can be represented as:

\[ (+) \text{ oxygen reference electrode / solid oxide electrolyte / mixed conducting sample (-)} \]

The activity of oxygen in the sample at the sample/electrolyte interface can be calculated from the open circuit voltage, "OCV", of the cell using the Nernst equation. Conversely, the oxygen activity at the sample/electrolyte interface can be controlled by imposing a voltage across the cell.

It is assumed that initially the activity \(a^0\) of the electroactive species is uniform throughout the sample. In a potentiostatic step experiment the activity \(a_{t=0}\) at the interface is set to a different value \(a'\) at time \(t=0\) by imposing a voltage step on top of the OCV. The volume of the sample is allowed to reequilibrate with the interface by a diffusional process. The rate of transport of the oxygen addition or deletion from the sample by solid state diffusion is
monitored by measuring the cell current as a function of time. It has been shown elsewhere, that the solution to the current-time behaviour under these conditions has two approximations relating to short or long times [2,3].

According to the short time approximation the cell current is a linear function of $t^{-1/2}$. The chemical diffusion coefficient $D$ of the electroactive species in the sample material is obtained from the slope $S$ of the cell current, plotted as a function of $t^{-1/2}$, as follows:

$$D = [S \cdot (V_m \pi^{1/2}) \cdot 1/(AzF) \cdot (\frac{\delta E}{\delta y}/\Delta E)]^2$$ (1)

Here, $V_m$ is the molar volume of the sample substance, $A$ is the geometrical contact area between the sample and the electrolyte, $z$ is the charge number of the electroactive species, and $F$ is the Faraday constant. $\Delta E$ is the applied potential step. $\delta E/\delta y$ is the slope of the open circuit voltage as a function of the stoichiometric number $y$ of the electroactive species, i.e. the local slope of the coulometric titration curve. (In this case : $y = 3-\delta$)

Assuming that the slope is constant within the composition range of an experiment, $1/\Delta y$ can be substituted for $(\frac{\delta E}{\delta y}/\Delta E)$. $\Delta y$ is calculated from the total charge flux per experiment.

The long time approximation is given by:

$$\ln(I) = \ln\left\{ \frac{2aAz}{F(V_m) \cdot (\Delta E/(\delta E/\delta y)) \cdot D} \right\} - \left( \frac{1.071}{L^2} \right) \cdot D \cdot t$$ (2)

The chemical diffusion coefficient may be determined from either the intercept or the slope of $\ln(I)$ plotted as a function of time. In the latter case only the sample thickness $L$ is needed as an additional parameter to obtain $D$.

By carrying out the potentiostatic step experiment until equilibrium is attained, and repeating it at stepwise increasing or decreasing voltages, the diffusion coefficient can be obtained as a function of the oxygen activity in the sample. At the same time a point of the equilibrium coulometric titration curve is obtained during each experiment. The slope of the coulometric titration curve can be used to calculate the "thermodynamic enhancement factor" $\delta \ln(a)/\delta \ln(c)$ [2] :

$$\delta \ln(a)/\delta \ln(c) = (zqy/kT) \cdot (\frac{\delta E}{\delta y})$$ (3)

By this factor the diffusion is enhanced if a composition gradient is present in the sample.

**EXPERIMENTAL**

A single crystal slab of 10 m% Y$_2$O$_3$ stabilized zirconia of about 12 mm in diameter and 0.6 mm in thickness was used as solid oxide electrolyte. Both faces of the zirconia slab were polished to mirror shine using 1 micron diamond paste. A porous platinum electrode layer was deposited on one face using Hanovia platinum paste.
The sample was a sintered pellet of \((\text{La}_{0.79}\text{Sr}_{0.20})\text{MnO}_3.5\). The mass of the pellet was 0.2 g, the thickness \(L\) was 1.7 mm and the cross sectional area, which equals the geometrical contact area between the pellet and the zirconia slab, was 0.2 cm\(^2\). One face of the pellet was polished by using 6 micron diamond paste.

All the other external surfaces of the pellet were covered by a layer of gold using Hanovia paste which was subsequently fired at 850°C in air. The uncoated surface of the pellet was then pressed by a spring mechanism on to the bare face of the zirconia slab. A platinum foil electrode 12 mm in diameter was pressed against the gold coated back side of the pellet.

The gold layer was intended to act as a diffusion barrier for oxygen. In order to provide further sealing of the sample volume and to prevent air from leaking into the zirconia/sample interface, the volume remaining around the sample between the Pt foil and the zirconia slab was filled with Pyrex powder. The setup was then fired in air at 850°C in order to consolidate the Pyrex and kept at temperatures of 700°C and above during the subsequent diffusion measurements.

Diffusion measurements were carried out at temperatures between 700°C and 860°C. Voltage steps of typically 100mV were applied to the cell. The sample was kept at negative potentials versus the Pt/air electrode - i.e. at oxygen activities below 0.21 atm. The maximum voltage applied was 400mV, corresponding to oxygen partial pressures of \(3 \times 10^{-9}\) atm and \(1.5 \times 10^{-8}\) atm at 760°C and 860°C, respectively. Usually oxygen was depleted from the sample. For some experiments the cell was shortcircuited and the sample thus replenished with oxygen to reach equilibrium with the atmospheric oxygen pressure again. A summary of the experimental conditions and results is given in Table 1.

RESULTS AND DISCUSSION

The validity range of the short time approximation given by equation (1) was determined from log/log plots of the current/time behaviour. A dependence of the form \(I = k \times t^{1/2}\) was found for time intervals of roughly 2000 to 20,000 sec at 700°C, varying to about 300 to 3000 sec at 860°C. An exponential current decay according to equation (2) was found at times \(\geq 30,000\) sec (8h) at 700°C and \(\geq 10,000\) sec (3h) at 860°C. The diffusion coefficients for "long times" given in Table 1 were calculated from the slope of the \(\ln(I)/t\) plot.

The diffusion coefficient for oxygen in \((\text{La}_{0.79}\text{Sr}_{0.20})\text{MnO}_3.5\) is of the order of \(10^{-7}\) cm\(^2\)/sec at 700°C and reaches values of \(10^{-6}\) cm\(^2\)/sec at 860°C. It increases by a factor of 5 (short-time results) to 9 (long time results) in that temperature range. This corresponds to an activation energy of 1.0 to 1.3 eV (22 to 30 kcal/mole) for the diffusion of oxygen in this material. It should be noted that the diffusion coefficient also depends strongly on the oxygen partial pressure, generally decreasing as the oxygen partial pressure decreases. It was observed that its value varies considerably within a voltage step of 100 mV. This may account partially for the observed scatter in the diffusion data in an Arrhenius plot. Measurements using voltage steps smaller than 100mV should yield the activation energy with less scatter.
The diffusion coefficients obtained from the short time behaviour are systematically smaller than those obtained from the long time behaviour. This may be due to the contact resistance between the sample and the electrolyte. A high contact resistance will cause an ohmic voltage drop at the interface and thus lower the effective activity step. This, however, affects only the short time behaviour. In any case, the results from the short and the long time behaviour are of the same order of magnitude and show the same trends as functions of temperature and oxygen partial pressure.

The thermodynamic enhancement factor for the chemical diffusion of oxygen is of the order of $10^4$. This is a comparatively high number. Enhancement factors of this order of magnitude were observed earlier for the diffusion of Li in Li$_3$Sb and for the diffusion of Cu in Cu$_2$S and Ag in Ag$_2$S [4].

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Table 1: Diffusion coefficients and enhancement factors for oxygen in \((\text{La}_{0.79}\text{Sr}_{0.20})\text{MnO}_{3.8}\)

| T [°C] | ΔE [V] | D_{\text{short times}} [cm^2/sec, \times 10^7] | D_{\text{long times}} | dE/dy [V] | d\ln(a)/d\ln(c) |
|------|-------|---------------------------------|----------------|--------|----------------|
| 700  | 42.5  | 1.0                             | 3.5             | 444    | 32,000         |
|      | -> 140|                                 |                 |        |                |
| 140  | -> 240| 3.8                             | 7.4             | 1140   | 81,000         |
| 760  | 0     | 2.5                             | 8.8             | 249    | 17,000         |
|      | -> 100|                                 |                 |        |                |
| 100  | -> 200| 5.5                             | 15              | 339    | 23,000         |
| 200  | -> 300| 3.3                             | 9.8             | 307    | 21,000         |
| 300  | -> 400| 2.2                             | 5.3             | 280    | 19,000         |
| 780  | 21.3  | 6.8                             | 10              | 257    | 17,000         |
|      | -> 0  |                                 |                 |        |                |
| 815  | 24    | 7.5                             | 8.1             | 202    | 13,000         |
|      | -> 0  |                                 |                 |        |                |
| 100  | -> 200| 3.8                             | 0.96            | 142    | 9,100          |
| 860  | 0     | 12                              | 17              | 139    | 8,600          |
|      | -> 100|                                 |                 |        |                |
| 100  | -> 200| 4.3                             | 13              | 94     | 5,800          |
| 200  | -> 300| 1.8                             | 8.8             | 84     | 5,200          |
| 300  | -> 400| 0.28                            | 4.5             | 47     | 2,900          |

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Fig. 1 Assembly of the solid state electrochemical cell