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Electrode polarization and electrical properties of the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, O_2 /yttria stabilized zirconia interface: Effect of gas phase composition and temperature

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Abstract

The steady-state current-overpotential characteristics of the $\text{O}_2/\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}/\text{YSZ}$ interface have been studied as a function of oxygen partial pressure and temperature. Ideal Nernst behaviour is observed in the temperature range between 400–900°C and oxygen pressure range between 0.5–100 kPa. The results of $I-\eta$ measurements indicate that in the potential range 0.05–0.25 V, the apparent anodic and cathodic charge transfer coefficients are close to unity: $\alpha_a = \alpha_c = 1$. The logarithm of the equilibrium exchange current density (I_0) shows a positive dependence on the logarithm of the oxygen partial pressure with a slope $m = 0.25 \pm 0.05$. These observations are in agreement with a proposed reaction model in which the diffusion of singly ionized oxygen adatoms (O_{ads}^-) on the oxide surface is assumed to be the rate determining step of the electrode reaction.

Keywords: Polarization; Perovskite–zirconia interface; Overpotential

1. Introduction

In recent years, considerable attention has been paid to mixed conducting perovskite oxides $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) as electrode material in order to reduce the operating temperatures of solid electrolyte cells [1]. The increased interest in these materials is because of their high values for the ionic and electronic conductivity. For mixed conducting electrodes, it is envisaged that oxygen

species will be supplied to the electrolyte/electrode interface through the bulk electrode material as well as along the electrode surface to the three phase boundary (TPB) between the gas, electrode and electrolyte. In this way, large oxygen fluxes can be sustained and the losses associated with electrode polarization will be less compared with electrode materials where the cathodic reduction of oxygen is restricted to the TPB.

The extent of oxygen deficiency appears to be a crucial factor in determining the structural and electrical properties of LSCF Perovskites. The partial substitution of, for instance, Sr^{3+} for La^{3+} , increases

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the concentration of oxygen vacancies in the lattice in order to maintain charge neutrality [2,3]. The increased concentration of oxygen vacancies tends to increase the oxygen anion conductivity and thus will reduce electrode polarization losses. Oxygen permeation measurements and four-probe dc-measurements using electron blocking electrodes [4–6], indicate a significant amount of ionic conductivity in LSCF. In usual ranges of temperature and oxygen partial pressure electronic conductivity remains predominant. The latter is assumed to occur via small polaron hopping of p-type charge carriers [7].

The main aim of the present work is to study the effect of oxygen partial pressure and temperature on the electrode polarization of porous perovskite LSCF on YSZ in order to find the rate determining step of the electrode reaction.

2. Experimental

The equipment used in the present study is depicted in Fig. 1 and it has been described in detail in previous works [8]. A Hewlett Packard 5890 Gas Chromatograph was used for analysis of reactants and products. Two Bargraph D.M.M. units, a differential Voltmeter and a Galvanostat-Potentiostat, were used to measure potentials and impose currents through the electrochemical cell, respectively.

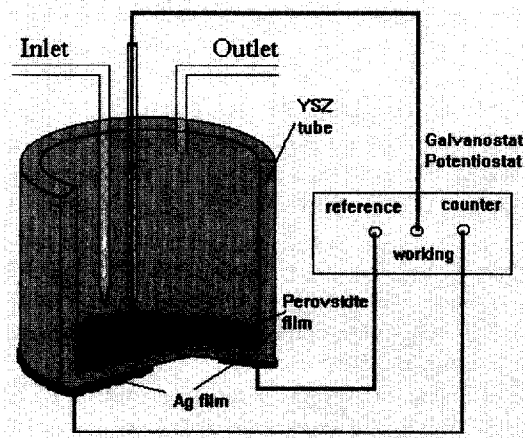


Fig. 1. Three electrode system.

The reactor consisted of a 15 cm long YSZ tube, with a 1.9 cm OD. The tube was closed on one end. Reactants were certified standards of $\text{CH}_4\text{-N}_2$ and $\text{O}_2\text{-N}_2$ mixtures. They could be further diluted in pure N_2 (99.99%). The results reported here are typically obtained with total flow-rates of $0.6\text{--}3\text{ cm}^3\text{ STP/sec}$.

The perovskite powder was prepared by the EDTA (ethylene diamine tetra acetic acid) method [9,10]. After the powder preparation, the perovskite was mixed with ethyl glycol and the mixture was heated until half of the volume was evaporated. The resulting viscous suspension was deposited on the inside bottom of the zirconia tube by painting. The tube was then heated to 1200°C . The heating rate was kept at about 200°C/h . The perovskite electrode thus formed had a superficial surface area of 2 cm^2 and a thickness of $5\text{--}20\text{ nm}$. Fig. 2 represents a Scanning Electron Micrograph (S.E.M) of the perovskite/YSZ interface.

Two silver films were deposited on the outside wall of the YSZ tube (Fig. 1) exposed to ambient air. They served as counter and reference electrodes, respectively. Their superficial surface areas were about 1 cm^2 (counter) and 0.2 cm^2 (reference). To examine the overpotential characteristics the current interruption method was used [11].

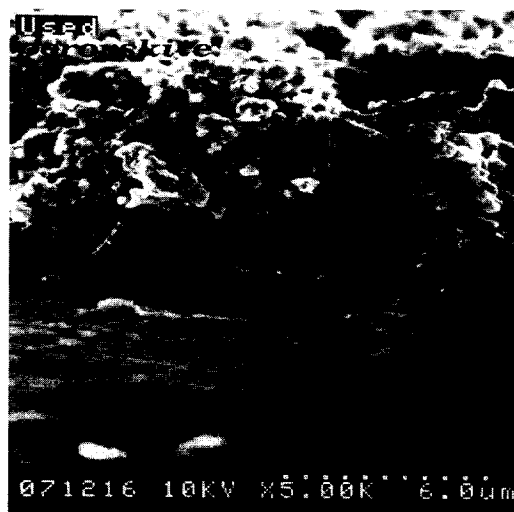


Fig. 2. S.E.M. micrograph of the perovskite/YSZ interface.

3. Theory

The fundamental electrochemical reaction, taking place at the LSCF/YSZ interface is the exchange of oxygen between the gas phase and the electrolyte,



which overall reaction can be broken down into a number of sequential reaction steps [12]. Each of these reaction steps contributes to the overall electrode polarization behaviour.

For multi step reaction, the electrode kinetics can be modelled into a form of the Butler–Volmer equation [13]

$$I = I_0 [\exp(\alpha_a F \eta / RT) - \exp(-\alpha_c F \eta / RT)] \quad (2)$$

where α_a and α_c are the anodic and cathodic charge transfer coefficients respectively, F is Faraday's constant, R is the ideal gas constant and I_0 is the exchange current. The apparent anodic and cathodic coefficients are given by

$$\alpha_a = \gamma_a / \nu + r(1 - \beta), \quad (3)$$

$$\alpha_c = \gamma_b / \nu + r\beta, \quad (4)$$

respectively. The stoichiometric number ν is the number of times the rate determining step (rds) occurs for one act of the overall reaction, r is the number of electrons transferred in the rds, and γ_a and γ_b are the numbers of electrons transferred after and before the rds, respectively. The symmetry coefficient β is usually set to 0.5. The basic assumption made is that of pseudo-equilibrium for all sequential reaction steps except for the rds. The fractional coverage of absorbed intermediates, if any, is assumed to be very small. It may be shown that [13]

$$\alpha_a + \alpha_c = n / \nu \quad (5)$$

where n is the total number of electrons involved in the overall reaction. For the cathodic reduction of molecular oxygen, n is equal to 4. An empirical relationship often found for the exchange current density is

$$I_0 \propto (P_{\text{O}_2})^m. \quad (6)$$

Depending on whether atomic or molecular oxygen is involved in the rds, the power m is given by [14]:

$$m = \alpha_a / [2(\alpha_a + \alpha_c)] \quad \text{for atomic oxygen,} \quad (7)$$

$$m = \alpha_a / (\alpha_a + \alpha_c) \quad \text{for molecular oxygen.} \quad (8)$$

4. Results and discussion

The results reported here were obtained in a temperature range between 400 and 900°C. Although at these temperatures, the LSCF is not expected to react with the YSZ, it is possible however, that such an interaction occurred during the electrode preparation procedure in which temperatures as high as 1200°C were used. It has been shown by XRD analysis that reaction and interdiffusion occurred at temperatures as low as 800°C between LSCF and YSZ [15]. Therefore, it is possible that the results reported here were obtained over the products of the interaction between YSZ and LSCF.

4.1. The emf dependence on temperature and oxygen partial pressure

Experimental and thermodynamically expected values of the emf (open circuit potential) for six P_{O_2} at different temperatures between 400 and 900°C are shown in Fig. 3. The oxygen partial pressure at the side of the reference electrode was kept constant at 21 kPa (ambient air). Oxygen partial pressures at the side of the working electrode were fixed to 0.1, 1, 4.4, 10, 22 and 100 kPa respectively. In the above temperature range, a very good agreement between the experimental results and the theoretical values predicted by the Nernst equation:

$$E = (RT/nF) [\ln(P_{\text{O}_2,\text{W}}/P_{\text{O}_2,\text{R}})] \quad (9)$$

was observed, where W and R stand for working and reference electrodes respectively. In Eq. (9), E is the open circuit potential (emf), n is the number of electrons transferred in the charge transfer process, $P_{\text{O}_2,\text{in}}$ is the oxygen partial pressure at the surface of the working electrode and $P_{\text{O}_2,\text{out}}$ is the oxygen partial pressure at the reference electrode (exposed to ambient air).

For $P_{\text{O}_2} > 21$ kPa, the open circuit potential is positive and increases with increasing temperature. In contrast, for $P_{\text{O}_2} < 21$ kPa, the open circuit po-

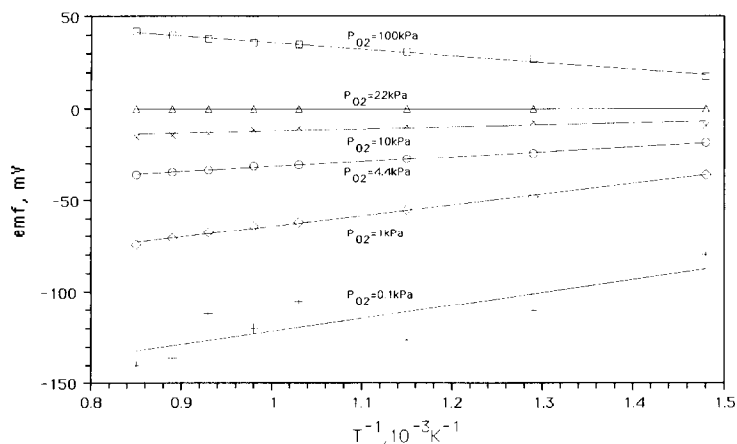


Fig. 3. Effect of temperature, T , on the open circuit potential (e.m.f.).

tential decreases with increasing temperature. For constant temperature, the open circuit potential decreases with decreasing P_{O_2} . The scattering at $P_{O_2} = 0.1$ kPa is probably due to the non-appropriate control of the gaseous composition.

4.2. Electrokinetic measurements

Fig. 4 shows a typical relation between the overpotential, η , and the current density, I , for the Perovskite/YSZ interface. The overpotential η is defined as:

$$\eta = V_{WR} - V_{WR}^o \quad (10)$$

where V_{WR}^o is the open circuit catalyst potential relative to the reference electrode. Fig. 4 shows the effect of the activation overpotential on the electrical current for different oxygen partial pressures (0.5, 1.1, 2.2, 4.4 kPa) at constant temperature ($T = 800^\circ\text{C}$). It can be seen that the perovskite electrode exhibits symmetrical behavior, i.e. no difference whether the electrode is used as an anode or as a cathode. The values of the apparent charge transfer coefficients were calculated from the slope of the

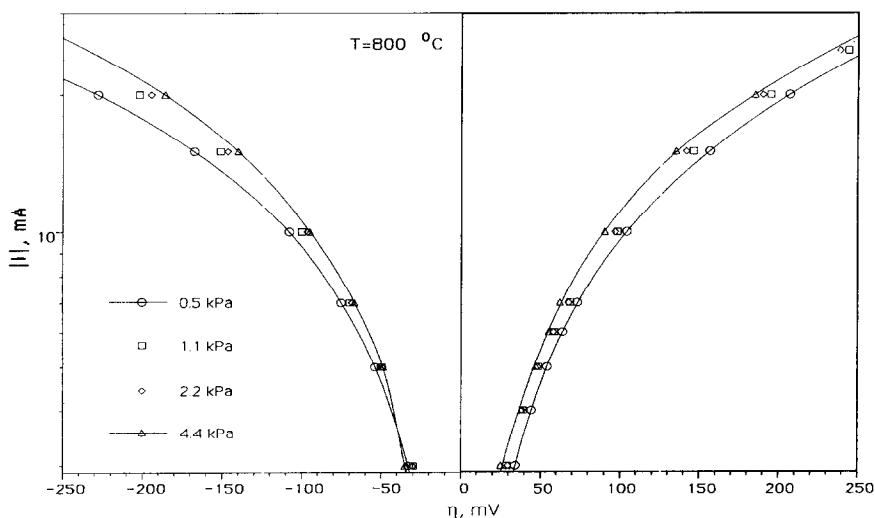


Fig. 4. Tafel plots of anodic and cathodic overpotential, η , vs current, I .

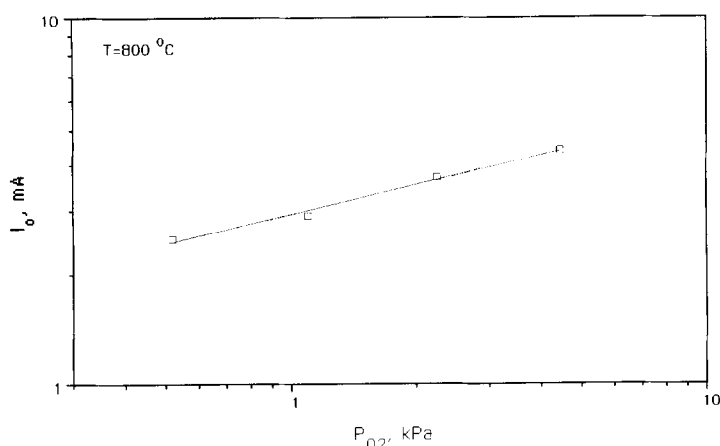


Fig. 5. Effect of P_{O_2} on the exchange current density, I_0 .

curves and were found to be equal to unity ($\alpha_a = \alpha_c = 1$).

Fig. 5 shows the dependence of I_0 on the oxygen partial pressure. The slope m of the curve (Eq. (6)) was found to be equal to 0.25. If both the apparent charge transfer coefficients α_a and α_c are unity and the exchange current density (I_0) varies with oxygen partial pressure in accordance with Eq. (6) with $m=0.25$, it is not the charge transfer process itself that determines the rate. With the aid of the theory presented in Section 3 and by considering that only one electron transfer can take place at a time, one can easily find the following step mechanism for the oxygen exchange reaction which accounts for the observed facts,



In this scheme, S indicates a surface site at which O^- species becomes further reduced to O^{--} and subsequently incorporates in the oxide lattice, as indicated in step (14). The symbols O_S^- , $V_O^{\bullet\bullet}$ and O_O^{\times} refer to further reduced oxygen on S sites, vacancies and oxygen anions in the electrolyte, respectively. Step (13) is assumed to be rate determining. This step

represents either the surface diffusion of oxygen species to the TPB or than from one surface site to another, where step (14) can take place. Within the above assumptions, no other step mechanism fits the observed data. It should be noted, however, that in addition to the above assumptions, low coverage of oxygen intermediate species and the same rds for the cathodic and the anodic processes are also considered.

5. Summary

The present electrokinetic analysis shows that in the presence of oxygen–nitrogen mixtures over perovskite–YSZ interface, the apparent anodic and cathodic transfer coefficients are very close to unity. Preliminary experiments [10] indicate that in the presence of methane, the values of these coefficients are considerably lower. It is possible that charge transfer and oxygen diffusion are both dominating the process. Experimental work that could provide further information on the mechanism of conduction through these materials is currently underway.

Acknowledgments

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