Polarisation Behaviour of Mixed Conducting Perovskite Cathode Materials.

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ABSTRACT

Electrode materials with improved polarisation characteristics are required for a reduction in the operating temperature of solid oxide fuel cells (SOFC) to be technologically feasible. Oxide cathode materials that possess a high degree of oxide ion conductivity as well as electronic conductivity are expected to exhibit lower values of electrode polarisation than current cathode materials with negligible ionic conductivity. Some perovskite oxides based on the system La$_{1-x}$Sr$_x$Fe$_{1-y}$Co$_y$O$_3$ have been shown to possess a significant amount of ionic conductivity by $^{18}$O/$^{16}$O isotopic exchange and dynamic secondary ion mass spectrometry (SIMS) investigations. AC impedance spectroscopy has been used to examine the electrode polarisation behaviour of these oxides as a function of temperature and oxygen partial pressure. This behaviour has been modelled and attributed to definite ionic charge and mass transfer mechanisms.

INTRODUCTION

The cost of ceramic fuel cells can be significantly reduced if their operating temperature is decreased to intermediate temperatures, 750-850°C, so that conventional stainless steels can be used to fabricate the stack’s ‘balance-of-plant’ equipment rather than expensive corrosion resistant special alloys. A reduction in operating temperature, however, reduces the overall performance and efficiency of the SOFC due to increased polarisation losses associated with the cell components. The practicable reduction of the SOFC operating temperature requires the use of alternative electrode and electrolyte materials with improved performance. Doped ceria electrolyte materials are available that exhibit higher oxide ion conductivity than more conventional yttria-stabilised zirconia (YSZ) electrolytes and developments in processing techniques allow for the production of thin ceramic sheets with lower ohmic losses. Therefore, further development activities are principally focused on the fabrication and evaluation of alternative electrode materials.
There is plenty of evidence to suggest that perovskite oxide cathode materials that possess a significant amount of oxide ion conductivity as well as high electronic conductivity exhibit lower values of electrode polarisation losses than currently used cathode materials such as La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} which, under cathodic conditions, have negligible ionic conductivity (1). For a mixed ionic and electronic conducting cathode it can be envisaged that oxygen species will be supplied to the electrode/electrolyte interface through the bulk electrode material as well as along the electrode surface to the three-phase boundary between the oxidant gas, electrode and electrolyte. In this way the cathode is able to sustain large fluxes of oxygen through the cell and the losses associated with the polarisation of the electrode are less than those for a cathode where the cathodic reduction of oxygen occurs only by the three-phase boundary mechanism (2).

Cobalt containing perovskite oxides tend to exhibit higher ionic conductivity due to a greater concentration of oxide vacancies than other perovskite cathode materials. However, cobaltate perovskites are chemically unstable at high temperature in intimate contact with YSZ and deleterious reaction products are formed that increase the overall resistance of the cell and reduce its efficiency (3). There is also a large difference in thermal expansion behaviour between YSZ and most cobaltates which may lead to degradation of the performance of an SOFC stack during thermal cycling. The use of a ceria electrolyte reduces these problems to some extent as it is chemically stable with cobaltate perovskites at SOFC operating temperatures and possesses a higher thermal expansion coefficient than yttria-stabilised zirconia. Perovskite materials based on the system La\textsubscript{1-x}Sr\textsubscript{x}Fe\textsubscript{1-y}Co\textsubscript{y}O\textsubscript{3} possess suitably high values of oxide ion conductivity and for cobalt contents y \leq 0.2 the thermal expansion behaviour is similar enough to that of a ceria electrolyte for the mechanical integrity of a fuel cell stack to be maintained with long-term use. The optimisation of these perovskite mixed conducting materials as SOFC cathodes requires a detailed understanding of the reaction steps in the cathodic reduction of oxygen.

The aim of this study was to examine the electrode polarisation behaviour of the perovskite oxide La\textsubscript{0.6}Sr\textsubscript{0.4}Fe\textsubscript{0.8}Co\textsubscript{0.2}O\textsubscript{3-δ} as a function of temperature and oxygen partial pressure using AC impedance spectroscopy in order to ascertain the rate limiting step in the cathodic reduction of oxygen by a mixed conducting perovskite oxide. The current-overpotential characteristics of a similar electrode set-up have also been measured and this behaviour has been compared to a model suggested for the electrode reaction of a cathode material that exhibits considerable oxide ion conductivity.

**EXPERIMENTAL**

The preparation of samples for analysis by AC impedance spectroscopy has been described in detail in a previous paper (4). Symmetrical electrodes were applied to both sides of a thin, dense pellet of an electrolyte substrate, Ce\textsubscript{0.9}Gd\textsubscript{0.1}O\textsubscript{1.95} (Rhone-Poulenc), Figure 1. The pellet was sintered at 1150°C for 5 hours with heating and cooling rates of 2°C/min. Platinum gauze contacts were attached to either side of the pellet and connected by platinum wire to a frequency response analyser (FRA Schumberger 1260). AC impedance spectra at frequencies 10\textsuperscript{2} to 10\textsuperscript{7} Hz with an excitation voltage of 10 mV to
ensure a linear response were taken at temperatures between 100 and 930°C. From these spectra values for the polarisation associated with the cathodic electrode reaction are obtained in addition to the grain interior and grain boundary conductivity of the ceria electrolyte. An activation energy for the electrode polarisation resistance, \( R_{ad} \), is obtained from an Arrhenius plot of log \( R_{ad} \) versus 1/T.

AC impedance analysis was also carried out as a function of oxygen partial pressure using \( \text{O}_2/\text{Ar} \) and \( \text{O}_2/\text{He} \) mixtures at 1 atm pressure in the furnace containing the impedance sample. The oxygen partial pressure was recorded using a zirconia oxygen probe adjacent to the impedance sample and another downstream from the furnace. The impedance spectra were analysed using a non-linear least squares (NLLS) fitting routine to an equivalent circuit shown in Figure 2.

The cathodic current-overpotential behaviour of a similar electrode configuration were also examined. \( \text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3 \) electrodes were applied to one half of each side of a thin ceria electrolyte substrate as the working and counter electrodes, Figure 1. On one side of the substrate was also attached a small platinum reference electrode and these three electrodes were attached by platinum wires to an electrochemical interface (Schumumberger 1286). A cathodic overpotential was applied across the working and reference electrodes and the corresponding cathodic current through the counter and reference electrodes was measured. The potential drop across the electrolyte was measured by AC impedance spectroscopy and by a current interruption technique and the final results have been compensated for this parasitic impedance.

**MODEL**

The cathodic reduction of oxygen at an SOFC electrode can occur along several different paths. Each of these pathways consists of specific reaction steps which contribute to the electrode polarisation. For a cathode material that possesses significant mixed ionic and electronic conductivity the following reaction steps have been proposed.

The first reaction step is the dissociative adsorption of oxygen from the surrounding gas phase on the electrode surface given by equation [1].

\[
\text{O}_2 \ (g) \quad \leftrightarrow \quad 2\text{O}_\text{ad}
\]  

This is then followed by the oxygen exchange redox reaction on the electrode surface between the adsorbed oxygen and the bulk electrode material shown by equation [2].

\[
\text{O}_\text{ad} + \text{O}_\text{electrode}^\text{O} \quad \leftrightarrow \quad 2e^\text{e} \quad \text{O}_\text{electrode}^\text{O}
\]  

Step 3 involves the transport of oxygen species from the electrode/gas surface to the electrode/electrolyte interface through the bulk electrode material which occurs by a
chemical diffusion process involving oxide vacancies. The final step of the cathodic electrode reaction is the transfer of oxide species from the electrode to the electrolyte across the two phase boundary and is illustrated by equation [3].

\[
O_{\text{electrode}}^\kappa + V_{\text{electrolyte}} \rightleftharpoons O_{\text{electrode}}^\kappa + V_{\text{electrolyte}} \tag{3}
\]

Each of these individual reaction steps contributes to the overall electrode polarisation however, their is usually one step that occurs more slowly than the others, termed the rate limiting step. Siebert et al. (5) have proposed a model where, for a mixed conducting perovskite cathode material, the diffusion of oxygen through the bulk electrode, step 3, is assumed to be rate limiting and dominates the electrode polarisation. The electronic conductivity of this perovskite material is high and so the diffusion process is purely chemical and the driving force is assumed to be a chemical potential gradient of oxygen vacancies in the electrode material between the interface with the gas phase and that with the electrolyte. It is further assumed that the chemical potential of the oxygen vacancies is directly related to their concentration and that the diffusion of oxygen species through the electrode is a one dimensional process with a characteristic diffusion length \( l \).

Siebert et al. (5) derive the electrode impedance of the diffusive step for an AC modulation of the electrode potential at an angular frequency \( \omega \) as

\[
Z = \frac{R T}{4 F^2 S} \frac{l}{D} \left( \frac{1}{[V_0]^x=0} \right) \tanh \sqrt{j \omega l^2/D} \tag{4}
\]

where \( D \) is the oxide vacancy concentration, \( S \) is the area of the electrode, \([V_0]^x=0\) is the concentration of oxide vacancies at the electrode/electrolyte interface and the other symbols have their usual meanings. This is typical of a finite length Warburg diffusion impedance which at high frequency gives a straight line at 45° to the real axis of the impedance plot and at low frequencies resembles a semi-circle that intercepts the real axis to give the electrode diffusion resistance.

The steady state current-overpotential behaviour for a diffusion limited step is given by equation [5] (5).

\[
I = -\frac{2 F D S}{l} \exp \left( -\frac{2 F (E - E^*)}{R T} \right) \tag{5}
\]
RESULTS AND DISCUSSION

The AC impedance spectra obtained for a La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-δ} electrode on a ceria electrolyte are shown in Figure 3 for several temperatures in 1 atm oxygen. The shape of these spectra are dominated by a finite length diffusion impedance, however, at high frequencies there is a second arc which is clearly visible at low temperatures and separate from the diffusion impedance and the response due to the electrolyte grain boundary impedance. This high frequency arc has been attributed to the transfer of oxide species across the electrode/electrolyte interface, equation [3] above. There is also a characteristic inductance associated with the measuring apparatus and contact leads that dominates at high frequencies which is denoted by the element L in Figure 2. At high oxygen partial pressure the equivalent circuit of Figure 2 without the low frequency parallel resistance-capacitance elements was used to fit the spectra. When the partial pressure of the surrounding gaseous atmosphere was lowered a third arc at low frequencies appeared and the complete equivalent circuit of Figure 2 was required to fit the spectra. This low frequency arc increases in size with lower oxygen partial pressure and, from Figure 4(d), at the lowest oxygen partial pressures it completely dominates the electrode impedance response. This low frequency arc is attributed to a gas phase diffusion limitation which restricts the supply of gaseous oxygen to the electrode surface.

Figure 5 shows some Arrhenius plots of the total electrode resistance, $R_{\text{el}}$, and those resistances assigned to the diffusion of oxygen through the bulk electrode material, $R_D$, and the oxide ion transfer resistance, $R_{\text{oi}}$. At high oxygen partial pressure the diffusion resistance clearly dominates the total electrode response with an activation energy of $\sim 1.6$ eV. At lower pO$_2$ the total electrode resistance is greater due to a large contribution from the gas phase diffusion resistance, $R_{\text{GD}}$.

The change in the resistances attributed to each of the individual steps of the cathodic reaction at the electrode are displayed as a function of the oxygen partial pressure of the surrounding gaseous atmosphere at several temperatures in Figure 6. From equation [4] the bulk electrode diffusion resistance is expected to vary inversely with the concentration of oxygen vacancies. For an acceptor doped perovskite material it has been shown that when the vacancy concentration is small then the following relationship holds between oxygen partial pressure and the oxide vacancy concentration (6).

\[
\left[ V_0 \right] \propto \frac{1}{\sqrt{\text{pO}_2}} \tag{6}
\]

Under such conditions of low vacancy concentration the diffusion resistance would therefore be expected to vary in the manner given by equation [7].

\[
R_D \propto \sqrt{\text{pO}_2} \tag{7}
\]
This is clearly demonstrated in Figure 6(b) at low temperature where the assumption of low vacancy concentration is valid. At higher temperatures the vacancy concentration becomes greater and approaches a limiting value governed by the level of acceptor dopant in the perovskite and so the vacancy concentration shows less dependence on oxygen partial pressure. Consequently, at higher temperature the diffusion resistance exhibits less dependence on $pO_2$ and at 900°C is approximately constant.

The transfer of oxide species from the electrode to the electrolyte would be expected to behave in a similar manner and from equation [3] the resistance associated with this reaction step should vary with the concentration of oxide vacancies as described by equation [8]

$$R_{ct} \propto \frac{1}{\sqrt[V_0]}$$

assuming that the vacancy concentration in the electrode is small and that the vacancy concentration in the electrolyte material is independent of oxygen partial pressure. The resistance, $R_{ct}$, is therefore expected to vary as the fourth root of the oxygen partial pressure. Figure 6(a) again illustrates this behaviour at low temperature where the assumption of low vacancy concentration in the electrode material, $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$, is valid and that at higher temperatures where the vacancy concentration becomes large then the dependence is reduced and $R_{ct}$ remains constant with changing oxygen partial pressure.

The gas phase diffusion resistance, $R_{GD}$, in Figure 6(c) shows the characteristic dependence on $pO_2$ given by equation [9].

$$R_{GD} \propto \frac{1}{pO_2}$$

There is a marked change in this resistance on changing the dilutant gas from argon to helium which is also characteristic of a gas phase diffusion limited reaction step.

The cathodic current-overpotential characteristics for a $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$, electrode on a ceria electrolyte are illustrated in Figure 7 on two Tafel plots, log current, $I$ versus overpotential, $\eta$. At low temperature and high oxygen partial pressure which are the conditions for the plot of Figure 7(a) the behaviour is similar to that predicted by equation [5] for a rate limiting diffusion process through the bulk electrode material and consists of a straight line in the cathodic region. At the highest values of overpotential there is a departure from this behaviour which may be caused by a limiting concentration of oxygen vacancies at the electrode/electrolyte interface. At lower oxygen partial pressure, Figure 7(b) where the electrode resistance is dominated by the gas phase diffusion resistance the Tafel plot exhibits a characteristic limiting current for a mass transport restricted reaction step.
CONCLUSIONS

The polarisation behaviour of the electrode material La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_{3-δ} has been shown to closely resemble that of a model derived for mixed ionic and electronic conducting materials where the rate limiting cathodic reaction step is the diffusion of oxide species through the bulk electrode material. The similarity is closest where the assumption of low oxide ion vacancy concentration in the electrode material is most valid. However, for the cobaltate material under consideration this only occurs at low temperature and at higher temperatures the model may be invalid. The large gas phase diffusion resistance contribution to the overall electrode resistance is thought to be due to the particular experimental set-up employed and is not thought to be typical of all mixed conducting electrodes.

It must also be noted that this model assumes a one dimensional geometry whereas the experimental electrode structure was porous and far from one dimensional. More complex modelling has been carried out at our laboratory and will be presented in another paper at this symposium (7).

REFERENCES

1. C.C. Chen, M.M. Nasrallah and H.U. Anderson, in Third international Symposium on Solid Oxide Fuel Cells/1993, S.C. Singhal and H. Iwahara, Editors, PV 93-4, p.252, The Electrochemical Society Proceedings Series, Pennington, NJ (1993).
2. M. Kleitz, T. Kloidt and L. Dessemond, in Proceedings of the 14th Riso International Symposium on Materials Science/1993, F.W. Poulsen, T. Jacobsen, E. Skou and M.J.L. Østergård, Editors, p.89, Riso National Laboratory, Roskilde, Denmark (1993).
3. C.C. Chen, M.M. Nasrallah and H.U. Anderson, in Third international Symposium on Solid Oxide Fuel Cells/1993, S.C. Singhal and H. Iwahara, Editors, PV 93-4, p.598, The Electrochemical Society Proceedings Series, Pennington, NJ (1993).
4. J.A. Lane, P.H. Middleton, H. Fox, B.C.H. Steele and J.A. Kilner, in Second International Symposium on Ionic and Mixed Conducting Ceramics/1994, T.A. Ramanarayanan, W.L. Worrell and H.L. Tuller, Editors, PV 94-12, p.489, The Electrochemical Society Proceedings Series, Pennington, NJ (1994).
5. E. Siebert, A. Hammouche and M. Kleitz, to be published in Electrochimica Acta.
6. H.U. Anderson, in Proceedings of the 14th Riso International Symposium on Materials Science/1993, F.W. Poulsen, T. Jacobsen, E. Skou and M.J.L. Østergård, Editors, p.1, Riso National Laboratory, Roskilde, Denmark (1993).
7. S. Adler, P.H. Middleton, J. A. Lane and B.C.H. Steele, this symposium.
Figure 1. (a) Symmetrical electrode configuration for AC impedance measurements, (b) three electrode configuration for measuring current-overpotential characteristics.

Figure 2. Equivalent circuit used to model AC impedance spectroscopy behaviour. $R_b$ is the resistance of the electrolyte and $L$ is the characteristic inductance of the measuring leads. The parallel resistance and constant phase elements $R_{GD}$-$Q_{GD}$ are only included for the lower oxygen partial pressures.
Figure 3. AC impedance spectra for a La$_{6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-x}$ electrode on a ceria electrolyte, P$_{O_2}$ = 1 atm,
(a) 850°C, (b) 750°C, (c) 575°C, (d) 425°C.
Figure 4. AC impedance spectra for a symmetrical La$_{0.6}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_{3-\delta}$ electrode on a ceria electrolyte at 700°C as a function of $p\text{O}_2$. Solid line indicates fit to the equivalent circuit of Figure 2. Labels show log frequency (Hz).
Figure 6. $pO_2$ dependence of
(a) oxide ion transfer resistance $R_{o^+}$
(b) diffusional resistance $R_{dp}$
(c) gas phase diffusion resistance $R_{dp}$

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Figure 7. Current-overpotential characteristics for a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ electrode on a ceria electrolyte at 600°C,
(a) $\text{pO}_2 = 0.1 \text{ atm}$, (b) $\text{pO}_2 = 0.0015 \text{ atm}$. 