OXYGEN REDUCTION AT THE $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$/ZIRCONIA ELECTRODE

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ABSTRACT

The kinetics of oxygen reduction at the $\text{ZrO}_2 \cdot \text{Y}_2\text{O}_3/\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ electrode ($0 \leq x \leq 0.5$) has been studied by steady-state polarization and transient measurements. The electrode behavior is similar to that of conventional metal electrodes for low cathodic polarization. At high polarization, a sudden increase of the electrode kinetics is observed. This can be related to the creation of oxygen vacancies in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, as demonstrated by redox potentiometric measurements. The strontium content in the electrode is a determining parameter for this property. The experimental results suggest two different reaction pathways under low and high cathodic polarization. Rapid oxygen diffusion through the electrode material is the main characteristic of the newly observed behavior.

1. INTRODUCTION

The choice of cathode material in a solid electrolyte fuel cell is of great importance since the cell efficiency is mainly governed by the cathodic process. Besides obvious conditions to be fulfilled such as phase stability, low vapor pressure at 1000°C, chemical compatibility, matching expansion coefficient and good adherence with the solid electrolyte, other important characteristics include high electronic conductivity and high electroactivity for the oxygen reduction.

Oxides having the perovskite structure have been proposed as alternatives to platinum (1-4). Among them, lanthanum manganite has been reported to be the best candidate (5,6). Pure $\text{LaMnO}_3$ is not sufficiently conducting. When a fraction of $\text{La}_2^{3+}$ is replaced by divalent cations such as $\text{Sr}^{2+}$, the charge deficit is compensated by a valence change on manganese ions from $\text{Mn}^{4+}$ to $\text{Mn}^{3+}$ and, under certain experimental conditions, the formation of oxygen vacancies. This increases the conductivity up to several hundred $\Omega^{-1}\text{cm}^{-1}$ depending on the dopant concentration. An oxide ion conduction may also be expected, due to the presence of oxygen vacancies (1).

Few kinetics studies on the oxygen reduction mechanism have been reported on these compounds at high temperature. Takeda et al. (4,7) have studied the cathodic polarization of $\text{La}_{1-x}\text{Sr}_x\text{MO}_3$, where $\text{M} = \text{Fe}, \text{Mn}, \text{Cr}$ or $\text{Co}$, sputtered on yttria stabilized zirconia, at 800°C in air in the potential range 0-400 mV. The best performances, in the case of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, were...
obtained for $x = 0.5$. A dependence of the current density on the electrode thickness showed that the optimum is obtained for 2 $\mu$m. The observed high electroactivity was attributed to its high catalytic activity and to the large effective reaction area due to the high oxide diffusion in the material. In a previous study, Hammouche et al. (8) have compared the electrocatalytic activity of pin-shaped electrodes. This kind of electrode was used to overcome difficulties in separating the effect of morphology from the effects of the electrode composition itself. The best results were also obtained for the composition $x = 0.5$ within the same potential range. In aqueous electrolyte, a similar behavior was demonstrated a few years ago (9) and correlated with the electronic structure of the compound.

Here we will report on the oxygen reduction kinetics of the system $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3/\text{ZrO}_2$-Y$_2$O$_3$ (9 mol %) over a wide electrode potential range as a function of the oxygen pressure $P$ and strontium doping $x$. A conventional platinum electrode will be used for comparison.

2. EXPERIMENTAL

Yttria stabilized zirconia (9 mol %) noted YSZ was used as the electrolyte. It was prepared from a mixture of $\text{Y}_2\text{O}_3$ and $\text{ZrO}_2$ powders calcined at 1050°C. After grinding, the product was compacted into pellets and then sintered at 1850°C for 2 hours. The final density was greater than 95%.

The perovskites were also synthesized by high temperature solid state reactions. The starting materials were $\text{La}_2\text{O}_3$, $\text{SrCO}_3$ and $\text{MnCO}_3$ with high purity. Compositions ranging from 0 to $x \approx 0.5$ were prepared by mixing the appropriate amounts of reagents. The mixed powders were calcined at 1200°C for 20 hours, ground, pressed under 2t/cm$^2$ and sintered at 1500°C in air for 2 hours. Chemical analysis, microscopic investigation and X ray diffraction patterns were made for each sample to confirm the composition. All the compounds were found to be single phased and had the selected composition and the right crystalline structure. The results of this microscopic investigation and of the study of structural, electrical and thermal properties have been reported in detail (8,10). The compounds crystallize in the hexagonal-rhombohedral structure. The thermal expansion coefficient diverges by no more than $2.6 \times 10^{-6}$ deg.$^{-1}$ with respect to that of YSZ. The electrodes behave as p type semi-conductors with conductivities of the order of 100 $\Omega^{-1}$ cm$^{-1}$ at 950°C.

The electrochemical experiments were carried out on a three electrode cell similar to that assembled by Schouler (11) and illustrated in Fig. 1. The electrolyte was a thin pellet of YSZ (20 mm in diameter and 1.5mm thick). Two platinum-pasted electrodes (Degussa 308A) were applied on its upper-side. One of the electrodes measured about 1 cm$^2$ and was used as a counter-electrode. The other one, with a smaller area, acted as a reference electrode. The single-point contact working electrode was made of a pin-shaped sample of the investigated perovskite oxide. The electrode-electrolyte contact area was small ($\approx 10^{-4}$ cm$^2$). Three working electrodes could be simultaneously tested under the same operating conditions. For comparison, a single-point electrode made of a
pure platinum ball, produced by melting the end of a wire in an acetylene/oxygen flame, was also tested. The oxygen pressure in the surrounding atmosphere was controlled by an electrochemical oxygen pump coupled to an oxygen gauge (12). Pure argon was used as the vector gas. The working temperature was maintained at 960°C.

To compare the characteristics of the investigated electrodes, we measured their contact area with the electrolyte according to Newman's formula (13), recommended by Isaacs et al. (2):

\[ r = \frac{1}{4aR} \]

where \( r \) is the surface contact radius, \( R \) the electric resistance of the electrolyte and \( a \) its conductivity under the measurement conditions. The resistance \( R \) was measured by impedance spectroscopy.

The electrochemical studies were carried out by steady-state I(E) polarization curve analysis. The ohmic drops were determined by impedance spectroscopy. The transient behavior of the electrode was also measured under different experimental conditions. A Solartron Electrochemical Interface 1186 coupled with a Solartron 1250 Frequency Response Analyser was used for this study.

3. RESULTS AND DISCUSSION

The overall oxygen reduction reaction can be written:

\[ \frac{1}{2} O_2 \text{gas} + V_{\text{O}^0\text{elelyte}} \rightarrow 2 \text{h}^+_{\text{mang}} + O_{\text{o elelyte}}^x \]  

(Kroger notation is used.)

The subscript mang (respectively elyte) means that the species is located in \( \text{La}_x\text{Sr}_{1-x}\text{MnO}_3 \) (respectively YSZ). Previous studies on single point platinum electrodes (14) have shown that under high polarization, the current reaches a limiting value which is commonly attributed to a limitation by the oxygen supply process to the electrode reaction zone. It has been demonstrated on different metal electrodes that the general shape of the steady-state I(E) curve depends neither on the texture nor on the nature of the metal.

A typical example of a steady-state current-potential curve obtained with \( \text{La}_x\text{Sr}_{1-x}\text{MnO}_3 \) under 10 atm is shown in Fig. 2. For comparison, the curve obtained with a Pt electrode of similar contact area, under the same experimental conditions, is also plotted on the figure. The essential difference between the two curves is that in the case of the manganite electrode, two regions noted I and II on the figure can easily be distinguished:

**Low cathodic potential region (I)** - Here, the I(E) curve is similar to that of a platinum electrode. The catalytic activity for oxygen reduction is of the same order of magnitude. It has already been reported that in this potential range the electrode activity increases as the degree of strontium substitution increases. Fig. 3 shows for example the current densities per length of the
electrode contact perimeter recorded under -100 mV polarization. The best performances are obtained for x = 0.5 for which the manganite appears to be better than Pt.

**High cathodic potential region (II)** - Under high cathodic polarization, a sharp transition is observed. The current markedly increases as shown in Fig. 2. After this transition, the I(E) curve also shows a limiting current plateau at higher cathodic potential. It is much greater than that measured on platinum. A detailed investigation as a function of the oxygen pressure, showed that $I^*$ obeys a square root dependence on the oxygen partial pressure in the range $10^{-1} - 10^{-2}$ atm. As a consequence, in this potential region the performance characteristics of $La_{1-x}Sr_xMnO_3$ are markedly higher than that of Pt.

We checked that this sudden increase of the electrode kinetics could not be attributed to the sole electrochemical reduction of the electrode material. A calculation shows that the complete reduction of the electrode according to reaction [2] can account for only 1% of the quantity of electricity which crosses the cell during the electrode polarization study. The current increase can neither be attributed to the electrolyte reduction which would only occur at overpotentials more cathodic than -1.3V. We must therefore conclude that after the transition, the main electrode process is still an oxygen electrode reaction. Moreover, the definite dependence of the limiting current on the oxygen pressure confirms this statement.

On the I(E) curve, a rather accurate transition electrode potential $E_T$ can be determined (cf Fig.2). It depends on x as shown in Table I. The higher the strontium content, the easier the transition occurs (the lower the overpotential magnitude $|E_T|$). In this respect, the x = 0.5 compound also appears to be the best in terms of electrode kinetics.

Our assumption is that a change in the electrode reaction mechanism occurs at $E_T$ leading to the onset of an important electrocatalytic effect.

This point is confirmed by the analysis of the voltammograms and the transient responses of the electrode to a current or a potential step. A typical voltammogram obtained for a scan rate of 1mV/s is given in Fig. 4. The starting potential is 0mV. As usually observed, a hysteresis loop is present. However, in contrast to the response of a classical redox system, the current is larger during the backwards scan and the hysteresis becomes increasingly important as the scan rate decreases. Consistently with that, the steady-state curve shows current magnitudes much larger than those observed on the voltammogram plotted under the same experimental conditions. This behavior indicates that the enhancement of the electrode kinetics is due to a slow modification of the electrode material.

A typical response of the electrode to a current or a potential step corresponding to region II is shown in Fig. 5. At the beginning the response is similar to the usual transient behavior observed when a concentration supply overpotential is the rate determining step (15). More precisely, the variation of the transient current obeys with a good accuracy the classical Cottrell-type linear relationship as a function of $t^{-1/2}$. This relationship is checked in
Fig. 6. After a certain time, noted \( T \) on the figure, the electrode process is characterized by a depolarization phenomenon. The \( E(t) \) curve shows an overshoot while the \( I(t) \) curve shows a net current enhancement. This behavior is consistent with the voltammogram analysis and confirms that a modification in the electrode material occurs at the transition leading to a new reaction mechanism which favors oxygen reduction.

After polarization in region II, the open circuit electrode potential relaxes as shown in Fig. 7. It shows a typical plateau at a redox potential noted \( E_w \). A second small inflexion point located at -330 mV/air was also noticed. As this potential does not depend either on the electrode composition or on the oxygen partial pressure in the gas, it was attributed to the reoxidation of an impurity. Because of the small amplitude of this phenomenon, it will not be taken into consideration in what follows and only the principal wave will be examined. A study as a function of the electrode composition and of the oxygen pressure was performed. The \( E_w \) values are highly dependent on the degree of strontium doping \( x \) in the electrode. The higher the \( x \) values, the lower the magnitude of \( |E_w| \) (cf. Table I). The variation is parallel to that observed for \( |E_f| \). No significant influence of the oxygen partial pressure on \( E_w \) was detected. The parameter \( E_w \) is therefore characteristic of the electrode material.

The basic principle of this kind of transient measurement has been described in detail by Fabry et al. who used this experimental technique for the measurement of thermodynamic data on oxides (16) and for the determination of the redox potential of point defects dissolved in solid electrolytes (17). According to the arguments developed in these papers, it can be concluded, in our case, that:

- When a cathodic current flows through the cell, the electrode material is partly reduced. The following reaction can be proposed:

\[
2 \text{Mn}_{\text{Mn}}^x + \text{O}_{\text{Mn}}^x + V_{\text{elyte}}^x \rightarrow 2 \text{Mn}_{\text{Mn}}^x + V_{\text{O}}^x + \text{O}_{\text{elyte}}^x + 2h^x \quad [2]
\]

Such a reduction will result in a marked increase of the oxide vacancy concentration in the electrode material.

- As soon as the current is interrupted, the electrode is reoxidized by the oxygen present in the surrounding gas. The potential plateau can be interpreted by assuming that the reoxidation proceeds according to the following equation:

\[
\text{O}_{\text{ads}} + V_{\text{O}}^{\text{mang}} + 2 \text{Mn}_{\text{Mn}}^x \rightarrow \text{O}_{\text{O}}^x + 2 \text{Mn}_{\text{Mn}}^x \quad [3]
\]

and by assuming that the oxygen flux is constant throughout the reoxidation process. The related electrode potential variation can be calculated with the assumption that the component activities are equal to their concentrations. The theoretical curve also presents a wave whose potential at the inflexion point increases as the strontium content increases.
All the observations converge to the same conclusion: under high cathodic polarization ($E < E_f$) the electrode is partly reduced and oxygen vacancies are created. The electrode is no longer mainly an electronic conductor. A mixed conductivity has been generated resulting in a new reaction mechanism. This change of mechanism is schematically depicted in the Fig. 8.

In region I, the electrode is regarded as an electronic conductor (diagram a in the figure). The behavior of the electrode is typical of a conventional metal electrode for which the reaction zone is concentrated around the triple contact line. A concentration overpotential is clearly identified as rate determining (18). The marked influence of the strontium doping on the electrode kinetics in region I can be explained in two ways, i.e. either by the effect of the variation of the electronic Fermi level in the electrode on the electrode parameters or by assuming that Mn$^{4+}$ are active adsorption sites on the electrode surface. This second assumption supposes that the electrode surface plays a determining role in the oxygen supply to the triple contact line. In order to explain the enhancement of the electrocatalytic activity as a function of $x$, Matsumoto et al. (9) proposed to establish a parallelism between the Mn-O interactions in the bulk of the material and those existing at the surface between the Mn cation and the oxygen molecule. The former determines the magnitude of the resistivity of the oxide, the latter determines its catalytic activity for oxygen reduction. The adsorbed oxygen molecules are viewed as completing the octahedral coordination polyhedra of the Mn cations on the electrode surface. The degree of the overlap integral between their orbitals seems to be reflected by that of the overlap integral between the corresponding orbitals of the cation and oxygen ion in the oxide bulk. This parameter increases as the dopant content increases leading to an improved electronic exchange in the bulk and on the surface of the electrode (20). We also observed a parallel increase in the conductivity and the catalytic activity of these electrodes.

In region II, the electrode is a mixed electronic-ionic conductor (diagram b with figure 3). The oxygen reduction pathway is modified. The drastic increase in the reaction rate can be related to the sudden increase in the oxygen vacancy concentration inside the electrode. The actual oxygen reduction therefore occurs on the manganite surface. The oxide ions produced during this reduction diffuse to the electrode-electrolyte interface where a simple ionic transfer occurs. This reaction scheme can be written as:

$$\frac{1}{2} O_2 + V_{\text{O eleyte}}^{\text{mang}} \rightarrow O_{\text{O eleyte}}^* + 2h^*_{\text{mang}} \quad [4]$$

$$O_{\text{O eleyte}}^* + V_{\text{O eleyte}}^{\text{mang}} \rightarrow O_{\text{O eleyte}}^* + V_{\text{O eleyte}}^{\text{mang}} \quad [5]$$

The catalytic effect of the reduced manganite can be attributed to the simultaneous presence of the two electroactive species $h^*$ and $V_{\text{O eleyte}}^{\text{mang}}$ in this phase. The same conclusion has already been proposed by Schouler regarding the surface of the electrolyte (11).
More recently, a detailed analysis of the impedance diagrams plotted at different overpotentials of the steady-state polarization curve (21) has confirmed the mechanism proposed for oxygen reduction on the La$_{1-x}$Sr$_x$MnO$_3$/YSZ electrode. In region II, the diagram shape indicates a limited diffusion process confirming the mechanism proposed above. The overall process would be partly limited by the oxygen vacancy diffusion in the manganite. A corresponding diffusion coefficient has been calculated to be approximately $4 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$ at 960°C for oxygen in reduced manganite.

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| x   | $E_\tau$, mV/air determined at 0.2 atm | $E_w$, mV/air determined at 10$^{-3}$ atm |
|-----|--------------------------------------|------------------------------------------|
| 0.00| -                                    | -516                                     |
| 0.10| -160                                 | -730                                     |
| 0.19| -158                                 | -591                                     |
| 0.30| -110                                 | -547                                     |
| 0.37| -                                    | -498                                     |
| 0.50| -94                                  | -405                                     |

Table I. Influence of the strontium concentration in La$_{1-x}$Sr$_x$MnO$_3$ on $E_\tau$ and $E_w$.

Fig. 1 - Polarization cell diagram
Fig. 2 - Steady-state $I(\eta)$ characteristics of a Pt and a $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ electrode. $E_T$ is the transition potential. $P = 10^{-3}\text{atm}$, $T = 960^\circ\text{C}$, $x = 0.3$.

Fig. 3 - Dependence of the current density on electrode composition for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ at $-100\text{mV}$ overpotential.

Fig. 4 - Typical voltammogram for the reduction of $\text{O}_2$. $x = 0.4$, $P = 0.2\text{atm}$.
Fig. 5 - Typical transient responses of an electrode to: a) a current step and b) a potential step, located in region II (x = 0.1).

Fig. 6 - I(t^{1/2}) plot of the data shown in Fig.5-b for t < τ.
Fig. 7 - Relaxation of the electrode under open circuit, after polarization in region II, $x = 0.4$.

Fig. 8 - Diagram of the oxygen reduction in a solid oxide electrolyte cell with:

a) a pure electronic conductor  

b) a mixed (electronic and ionic) conductor.