OXYGEN REDUCTION AT La0.5Sr0.5MnO3 THIN FILM/YTTRIA STABILIZED ZIRCONIA INTERFACE STUDIED BY IMPEDANCE SPECTROSCOPY

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ABSTRACT

La0.5Sr0.5MnO3 thin films were prepared by a pyrosol technique. Films were characterized by X-ray diffraction and SEM analysis. Their electrical resistance was measured and they showed a semiconductive behaviour. The η(i) curves were drawn at 800°C and 900°C and impedance spectroscopy was performed during polarization. At low polarization, the oxygen reduction takes place at the triple contact points and is progressively delocalized to the whole surface of the electrode. At high polarizations, two components of the impedance have been identified. The first one, at high frequency, is correlated with an atomic rearrangement of the electrode (either in the bulk or at the surface), which favours the electrode reaction. At low frequencies, the impedance has been attributed to a concentration impedance due to at least two adsorbed species.

INTRODUCTION

Electronically conducting oxide perovskites are widely studied for their possible applications as cathode materials in solid oxide fuel cells (1,2). Among them, strontium-doped lanthanum manganites (LSM) of general formula La1-xSr_xMnO3 seem to offer the best compromise in terms of electrochemical performances, low reactivity and thermal expansion compatibility towards the yttria stabilized zirconia (YSZ) electrolyte. However, the mechanism of oxygen reduction on these materials is not clearly understood. A previous study (3) has shown a so-called electrocatalytic effect, i.e. a large increase in current density for polarization higher than a critical one. Another study on LSM thin films deposited by RF sputtering (4) showed that, for the La0.5Sr0.5MnO3 composition, very high current densities could be reached at low polarizations even at 800°C. This was attributed to a delocalization of the reaction process from the triple points to the whole surface of the LSM electrode when the oxygen vacancies concentration becomes high in the LSM cathode. We present here our first results in polarization measurements on La0.5Sr0.5MnO3 thin film/YSZ interface associated with impedance spectroscopy measurements.
EXPERIMENTAL

Sample preparation and characterization.

The apparatus used for thin films preparation has already been described (5). A mist of the starting nitrates solution is produced by an ultrasonic transducer. This mist is carried out into a furnace and the substrate is placed at the exit of the furnace. For furnace temperatures higher than 600°C, nitrates are decomposed into the furnace and oxide grains are deposited onto the substrate, with subsequent low mechanical properties. For furnace temperatures between 300°C and 350°C, a gel-like film is deposited. After heat treatment at 800°C in air, we obtain an oxide film well adherent to the substrate. For intermediate furnace temperatures, we get a mixture of the gel and of oxide grains, probably because the smallest droplets have had enough time to react completely in the furnace.

Films were characterized by X-ray diffraction with a Siemens θ/2θ diffractometer using the Cu Kα1 X-ray. Microscopic and chemical examinations were performed on a JEOL JSM 35 scanning electron microscope equipped with a Tracor Northern EDS analysis system. The electrical resistance of the films was measured by impedance spectroscopy with a Hewlett Packard HP4192A impedancemeter. Two platinum electrodes were pasted onto 1 cm by 1 cm film, leaving an uncovered space of 5 mm between them. Platinum leads were sealed to the electrodes with the same Pt paste.

Electrochemical measurements.

Electrochemical measurements were performed on three electrode configuration cells. The ZrO2-Y2O3 electrolyte (8 mol.% Y2O3 from KERAFOL) was a disk 20 mm in diameter and 250 μm thick. The working electrode was a film (area 0.5 cm², thickness about 10 μm) surrounded by a platinum grid working as current collector. The platinum grid was pressed onto the film with the use of an alumina disk in which holes 2 mm in diameter were regularly made. Counter and reference electrodes were placed at the opposite side of the electrolyte and made with Pt paste. The whole assembly was placed into a furnace in which gas (20 % O2, 80 % N2 ) was allowed to flow at a rate of about 1 liter/min. Sample temperature was controlled by a Pt/PtRh thermocouple placed close to the working electrode.

Galvanostatic experiments were carried out with a Tacussel PRT 20-2X potentiostat. The ohmic drop was measured using the current interruption technique with a Nicolet 1090 A digital oscilloscope and the ohmic drop was assumed to be equal to the voltage difference between the last point before interruption and the point 0.5 μs later. The working electrode voltage was recorded with a Sefram X(t) recorder. Potentiostatic and impedance spectroscopy experiments were carried out using a Tacussel Z Computer potentiostat/impedancemeter in a three electrode configuration which allows for simultaneous polarization and impedance spectroscopy measurements (10^5-10^4 Hz). Frequencies were generally limited to 10^2 Hz.
RESULTS AND DISCUSSION

Thin films characterization.

XRD spectra of La$_{0.5}$Sr$_{0.5}$MnO$_3$ thin films deposited onto yttria stabilized zirconia substrates were recorded. Only the peaks of the perovskite structure appeared with a quite low intensity and large width, which is probably due to a poor crystallinity of the film. There was no evidence of a foreign peak.

Films were composed of grains of about 0.1 μm in diameter. There were also numerous cracks probably due to gel decomposition and shrinkage. EDS analysis showed a good homogeneity of the film composition. The EDS spectrum was compared to the one of a bulk La$_{0.5}$Sr$_{0.5}$MnO$_3$ standard and showed no difference in cation composition.

Electrical conductivity.

A typical impedance plot obtained at 20°C is shown in Figure 1. It can be deconvoluted into two semi-circle arcs. They were centered on the real axis, as expected for a purely electronic conductor. The two intercepts with the real axis (called $R_{HF}$ and $R_{LF}$ respectively) are thermally activated with the same activation energy which is dependent of the substrate material and of the film thickness (Table 1). These changes in activation energy could thus be due to thermal stresses caused by the difference in thermal expansion between the substrate and the film.

From previous studies on La$_{1-x}$Sr$_x$MnO$_3$ electrical conductivities, we would expect a metallic behaviour (6,7). Such a change in conduction dependence on temperature has however been observed in the case of sputtered cobaltites films (4). It is well known that the electrical conductivity of these oxide materials is very dependent on the preparation procedure, because of possible large intergrains effects. The existence of two relaxation processes having the same activation energy has already be mentioned for oxygen ion conductors (8) and is attributed to the existence of cracks in the material. This could also happen in our case, because of the large number of cracks contained in our films.

Potentiostatic mode polarization.

Polarization curves have been drawn in potentiostatic mode at 800°C and 900°C (Figure 2). Increasing potentials (in absolute value) were applied to the working electrode without waiting for a return to equilibrium between each experiment. The corresponding current was recorded. We systematically observed an increase of the current as a function of time. When current was stabilized, an impedance diagram was drawn under polarization. Typical impedance diagrams are shown in Figure 3. At high frequencies, they show an ohmic resistance due to the electrolyte and a self due to incomplete leads shielding into the furnace. The other part of the impedance diagram is attributed to electrode impedance.
At low polarizations, this impedance shows a real limit at low frequencies and seems to be dominated by a non ideal RC circuit. However, it has not been possible to correctly deconvolute the spectra with series elements (RC elements, Randles circuits or diffusion-like circuits were tested). For higher polarizations, a loop including a selfic part (Im(Z)>0) appeared at low frequencies. For the part which did not include this loop, spectra could be deconvoluted into one (at 900°C) or two (at 800°C) RC circuits. This deconvolution allowed us to estimate with a good precision the set-up self and the ohmic drop due to the electrolyte. Low polarization data were thus corrected from the setup self and the ohmic drop was estimated by extrapolation of the impedance spectra to the real axis. Figure 4 shows the evolution of the impedance spectra with polarization at 800°C. The impedance decreases markedly when polarization increases, which is characteristic of the electrocatalytic effect. The ohmic drop resistance evolution is also remarkable. It was estimated at 6.9 Ω at 800°C and 3.4 Ω at 900°C at zero polarization and decreased down to 5.3 Ω for -180 mV at 800°C and 2.9 Ω for -100 mV at 900°C. Simultaneously, the current stabilization time increased up to more than 12 h.

**Galvanostatic mode polarization.**

Similar phenomena were observed in galvanostatic mode at 900°C. The working electrode potential decreased (in absolute value) with time and the stabilization time increased for high currents, the change occurring at about the same overvoltage than in the potentiostatic case. The ohmic drop as measured with the oscilloscope decreased strongly from about 10 Ω at zero current to 3 Ω at -400 mA. These values are higher than those observed in the potentiostatic mode. This could be due to a systematic error, because the electrode potential goes to zero in a finite time, and thus an evolution is observed in times of the order of the μs. A correct estimation of the ohmic drop should include the extrapolation of the potential decay to zero time, which has not been done. For very high currents (from -500 mA to -1000 mA), we observed a slight decrease of the ohmic drop attributed to heating by Joule effect.

**Impedance evolution after high polarization.**

We already mentioned that when current was interrupted, the working electrode potential became zero very rapidly. However, impedance diagrams evolve more slowly. In order to characterize this phenomenon, we followed the impedance of the electrode as a function of time at zero polarization after having submitted it to a current of -1 A (-2 A/cm²). These spectra (Figure 5) show clearly two phenomena. The low frequency one evolved rapidly during the first hours, and then remained constant. The high frequency one evolved constantly and its equivalent resistance varied linearly with the square root of time (Figure 6).

As we never observed a capacitive loop at low frequency under polarization, we also recorded impedance spectra under polarization and just after polarization stop. A characteristic result is shown in Figure 7. The high frequency part remains...
almost constant, but the low frequency one goes from an inductive loop under polarization to a capacitive one with no polarization.

Discussion of the results.

From our results and from those previously published by Hammouche et al. (3), we can conclude that oxygen reduction occurs by two different mechanisms depending on the electrode overpotential. At zero overvoltage, strontium-doped lanthanum manganites are known to be overstoichiometric in oxygen, the major defects being cation vacancies (9). Oxygen vacancies diffusion into the electrode is not favoured and the electrode reaction takes place at the triple contact points. When polarization increases, oxygen vacancies are created into the electrode and the reaction is progressively delocalized at the whole surface of the electrode. Since both processes are concurrent, the associated equivalent circuits should be placed in parallel and this explains why we could not deconvolute the experimental impedance spectra with series elements. The evolution of the ohmic drop is also consistent with this hypothesis. When reaction occurs predominantly at the triple contact points, current lines are focused in the vicinity of these points at zero polarization, and a striction effect could explain the relatively high ohmic loss observed in this case. As the electrode reaction is delocalized, this effect vanishes and the ohmic drop decreases.

At higher polarizations, the contribution of triple contact points to the overall kinetics becomes negligible. In this case, at least two phenomena are involved in the electrode impedance. At high frequencies, we observed two RC circuits at 800°C and only one at 900°C. The disappearance of one of the circuits can be attributed to either a vanishing of the equivalent resistance if the activation energy is sufficiently high or to a variation of the characteristic frequencies, if they become equal. More work has to be carried out for a better understanding of this phenomenon. At 900°C, a process evolving slowly with time is observed. The $t^{1/2}$ dependence of the associated resistance when polarization is stopped suggests that it could be due to atomic displacements and reordering either in the manganite or at its surface. Its origin is still unclear. It seems unlikely that it can be explained only by oxygen vacancies diffusion, because the vacancies diffusion coefficient is quite high in these materials. At low frequencies, we observed a phenomenon moving from an inductive loop under polarization to a capacitive one at zero polarization. Inductive loops at high polarizations had also been observed by Hammouche and were attributed to a concentration impedance due to at least two adsorbed species on the same sites. This explanation could also apply to our results if we suppose that the major adsorbed species change rapidly when polarization is applied.
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Table 1

| Substrate | TEC (°C⁻¹) | Thickness (µm) | Ea (eV) |
|-----------|-----------|--------------|--------|
| Alumina   | 7.5 10⁻⁶  | 10           | 0.15   |
| YSZ       | 10 10⁻⁶   | 20           | 0.07   |

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580
Figure 1.
Typical impedance plot obtained at 20°C on a La$_{0.5}$Sr$_{0.5}$MnO$_3$ thin film. Labels indicate power of ten of the frequency.

Figure 2.
$\eta(i)$ curve obtained in the galvanostatic mode at 900°C. Inside curve; $\eta(i)$ curves obtained at 800°C (squares) and 900°C (crosses) in the potentiostatic mode and at 900°C in the galvanostatic mode (circles).
Figure 3. Impedance spectra obtained at 800°C (crosses) and 900°C (circles) at zero polarization (curve a) and at -220mV (curve b).
Figure 4. Evolution of the impedance spectra at 800°C as a function of polarization. Spectra were corrected from setup self and ohmic drop. The inductive loop observed at low frequencies and high polarization has not been drawn for visibility reasons.

Figure 5. Impedance spectrum obtained at 900°C on a sample submitted to -1A after 80h relaxation. Circles: experimental points. Full line: deconvolution results including set-up self. Dotted lines: semicircles as calculated by deconvolution.
Figure 6
Evolution of the equivalent resistances of the two semicircle arcs as a function of the square root of time for a sample having been submitted to a current of -1 A.
Circles: high frequency phenomenon.
Crosses: low frequency phenomenon.

Figure 7.
Impedance spectra obtained on a sample polarized at -200 mV (crosses) and just after polarization stop (circles). The high frequency semicircle remains almost constant and the low frequency part changes markedly.