TRANSITION METAL ION IMPLANTATION FOR MODIFICATION OF CATHODIC INTERFACES

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ABSTRACT

The ion implantation technique has been used in order to modify the YSZ electrolyte surface with transition metal elements. The electrochemical behaviour of the cathodic interface is shown to be substantially different according to the element implanted. Investigations with cerium show its catalytic role in oxygen reduction. Quantity effects are clearly present when manganese is used and the reaction mechanism is affected. Results are presented and discussed taking into account the redox and catalytic properties.

INTRODUCTION

The choice of adequate electrode and electrolyte materials is crucial in obtaining a high performance Solid Oxide Fuel Cell (SOFC). At the same time, the requirement of an improved electrolyte/electrode interface is also necessary for that purpose. For example, in the electrolyte plane, an improvement can be made by maximizing the contact area between the electrode and the electrolyte relative to the projected electrode surface. Normal to that plane, an improvement can be obtained by making an interface with structured physical properties (1,2,3). With that last perspective in mind, similar experiments were also carried out in our laboratory (4,5).

In order to get a better insight of the phenomena, the ion implantation technique has been used to modify the electrolyte near-surface zone in a controlled way. In this study, the effect of the doping ion and its quantity in...
the electrolyte is successively examined, with attention focused on the
cathodic oxygen reduction reaction.

EXPERIMENTAL

Preparation of the electrochemical cell

Hot pressed 6 mol% Yttria Stabilised Zirconia (6YSZ, 2 mm thick), supplied by Metoxit (Switzerland) was used as electrolyte. Prior to implantation it was polished with 220, 320, 500 grit SiC papers.

Ion implantation in the electrolyte was performed with a Whickham 200 keV high current machine at 600 °C and 4x10⁻⁷ mbar pressure (approximately 50% H₂O, 50% N₂). A low (10¹⁵ atoms/cm²) and a high dose (2x10¹⁶ atoms/cm²) of each element (Mn, Ce) were injected in YSZ with a 200 keV energy.

In order to evaluate the influence of implantation on the cathodic behaviour of the cell, platinum paint (Degussa) was chosen as contacting electrode because its electrochemical response under equilibrium and dynamic conditions is known and reproducible (6). A 1 cm² cathode was applied by brush on the implanted side. The anode was painted symmetrically on the opposite side, with the reference electrode, in order to avoid possible short circuits with the cathode. Platinum grids and wires ensure the electrical connections to the electrochemical device. The temperature was measured by a thermocouple placed near the electrode.

The cell was then conditioned at 750 °C for 24 hours, after which time the platinum impedance response is stable. The sample never reached a higher temperature than 750 °C to avoid diffusion of the implanted ions. No difference in the electrochemical behaviour was observed whether the sample was previously heated for preoxidation or not.

Data acquisition

Impedance spectroscopy measurements were taken with a Solartron 1253 frequency response analyzer, connected via the Solartron 1286 electrochemical interface (potentiostat) with an HP computer system that acquired, stored and analyzed the data.

RESULTS

It should be noted that the interface Air, Pt/cerium (high dose) implanted region-YSZ will be abbreviated as CeHD. Similarly, the low dose

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The concentration depth profiles were not measured. But according to the results of Scholten et al. (9) on iron implanted YSZ, the theoretical coordinates values for doses up to 4x10^{16} at/cm^2 match well the measured ones and the concentration values are in the correct order of magnitude. So the figures in table 1 are considered as a good estimation of reality.

Equilibrium conditions

1. Cerium

Figure 2 shows the impedance spectra of the cerium implanted samples under open-circuit conditions, prior to operation of the cell under load. Half of the impedance spectrum of the untreated platinum cathode is also shown. Under these experimental conditions, its IS response is a depressed
semi-circle. From figure 2, we can see that cerium implantation has the positive effect of lowering the electrode resistance, as listed in table 2: from 49 ohms for platinum on unimplanted YSZ, it decreases to 7.3 ohms, and to 2.2 ohms, for the low dose and high dose sample respectively.

Table 2:
Comparisons of platinum electrode resistance on several, modified or not, electrolytes.

| Electrode resistance (ohms) | Pt  | CeLD | CeHD |
|-----------------------------|-----|------|------|
| YSZ                         | 49  | 7.3  | 2.2  |
| Improvement                 | -   | 6.7 x| 22.3 x|
| GDC                         | 6   | -    | -    |

It is clear that cerium implantation in YSZ improves the electrochemical properties of the cathodic interface, already under open circuit conditions.

2. Manganese

The impedance spectra of the manganese implanted samples under equilibrium is shown in figure 3. The addition of a small quantity of manganese does not induce any changes on the cathodic behaviour compared to a YSZ interface without implantation. But with a high dose, two striking features appear: firstly, the lowering of the electrode resistance and secondly, the appearance of an additional semi-circle.

DISCUSSION

Cerium

For the two concentrations tested, it is clear that the higher the dose, the better the effect. However, the improvements measured from CeLD to CeHD cannot be related proportionally to any of the figures in Table 1. In addition, despite cerium implantation, the spectrum shape remains always the same, indicating that the rate determining step does not change. It is
still the diffusion of O-adatoms on the surface of platinum that governs the reaction mechanism (6,10,11).

Implantation causes a substantial amount of crystalline damage (7), which must be repaired for the dopants to be included in the lattice. While the sintering temperature of YSZ is around 1400 °C, implantation at a temperature above the recrystallisation temperature (530 °C for ZrO₂ (9,12)) should result in some degree of dynamic crystal regrowth.

From the literature, it is known that cerium is highly soluble in yttria stabilised zirconia (more than 40 mol%) and does not modify the lattice structure (13). As a matter of fact, cerium in pure zirconia enters the lattice on zirconium sites and stabilises partially its cubic structure. As cerium is also tetravalent, this phenomenon cannot be explained by the traditional stabilisation reaction which generates oxygen vacancies. A size effect is generally invoked (14). However, this should play a very minor and marginal role in our case, where the cerium concentrations are small (<2 at%) and the zirconia already stabilised. So, a structural change cannot explain the above observations.

Schouler et al. (2) studied the effect of cerium insertion in YSZ for water reduction. Experiments were done under low oxygen partial pressure so that the cerium oxidation state was lowered. It was observed that small quantities only diminished the magnitude of the impedance response of the electrode (15), whereas a higher quantity (30 weight%) modified the shape of the spectrum. These phenomena were explained in terms of mixed conductivity of the surface, resulting from the cerium (III) presence. In our case, the results cannot be explained with that model. Indeed, in our experimental conditions the presence of Ce(III) can be surely excluded because it should give a red color to our sample (16). The sample just after implantation had such a color, because it was done under low oxygen partial pressure, but it became fully beige after oxidation in warm air. This color is characteristic of the Ce(IV) state (16). Moreover the reducibility of Ce(IV) in the ternary solution CeO₂-Y₂O₃-ZrO₂ is highly diminished and significant electronic conductivity due to cerium reduction for use as a mixed conductor is found only at 1200 °C under low oxygen partial pressure (13,17). As we work in air and 750 °C, it is evident that cerium is in its highest oxidation state. So, in the absence of ionic current and in air, a redox effect cannot explain the improvements observed at such a cathode, compared to the unimplanted case.

For oxygen pressures higher than 10⁻⁷ atm, the electronic transport number has been evaluated to be few percent (18,19) in (ZrO₂)₀.₈₇(Y₂O₃)₀.₁₂(CeO₂)₀.₀₁ at 1000 °C. Despite our lower working temperature, this percentage should not fluctuate too much because of the low cerium content. If so, it is very likely that a small electronic conductivity exists at the surface of the implanted electrolyte and offers a new reaction path for oxygen reduction. So, the delocalisation of the reaction onto the electrolyte surface enhances the total oxygen reduction rate. This is the reason why a lowering of the electrode resistance is observed. This explanation makes our results comparable with those of...
Olmer et al. (15). Nevertheless, it is interesting to note that even small quantities of dopant (for example CeLD) can affect the resistance of the electrode. In that case the superficial electronic conductivity of the electrolyte should be extremely low. In that regard, it would be abusive to explain the improvements in terms of a "mixed ionic electronic" conductivity because the criterion of equivalence of the ionic and electronic transport numbers, \( t_i/t_e = 1 \) (20) is not fulfilled. In Table 2, the electrode resistance of the same platinum electrode on a ceria gadolinia-doped electrolyte is added for comparison. At the same temperature, it gives an electrode resistance of 6 ohms. As no additional feature appears on the IS (which would mean that another rate determining step exists) and that the resistance of the same electrode on a cerium electrolyte is higher, we can interpret these observations as being a catalytic effect of cerium on the oxygen reduction reaction.

**Manganese**

For the manganese samples, an effect is visible only for the MnHD. In this set of experiments, as for cerium, the improvement is not proportional to the peak or surface concentrations. Another explanation has to be found.

In order to understand the results it is necessary to give a definition of the doped interface: manganese is a transition metal element that possesses multiple valences and its solubility in YSZ is limited. Yokokawa et al. (21) calculated values of less than 10 mol% at 1000 °C. These figures were than confirmed experimentally by Kawada et al. (22). At 1000 °C, they obtained a solubility of 5.6 mol%. A unique feature of manganese among other transition metal elements is that it dissolves under two forms in YSZ, that is \( \text{Mn}^{\text{III}}_\text{Zr} \) and \( \text{Mn}^{\text{IV}}_\text{Zr} \) (21,23). Subsequently, an enhancement of hole conductivity of one order of magnitude was noticed in YSZ, without removing the predominantly ionic character of that material. This suggests the following reactions:

\[
\begin{align*}
\text{Mn}^{\text{III}}_\text{Zr} & \rightarrow \text{Mn}^{\text{IV}}_\text{Zr} + \cdot h^+ \\
2\text{Mn}^{\text{III}}_\text{Zr} + \text{O}_2^x & \rightarrow 2\text{Mn}^{\text{IV}}_\text{Zr} + \text{V}_0^{**} + \frac{1}{2}\text{O}_2
\end{align*}
\]

Kawada et al. (22) tested also manganese surface-doped samples, which were done in the solubility limit of the element. Platinum was the contacting electrode. They could notice a diminution of the magnitude of the impedance spectra without change in the shape. They attributed this
phenomenon much more to surface morphology effects rather than to a doping effect. The more typical effect of manganese was observed at lower oxygen partial pressure with the increasing surface capacity of the Pt/Mn-YSZ interface.

The above review in the literature permits us to affirm that Mn(III) and Mn(II) are simultaneously present in our samples. Nevertheless, extrapolation of Kawada’s results (22) to 750 °C gives a solubility limit of 3.4 mol% Mn in YSZ. From table 1, it appears that the MnHD sample contains a slight excess of manganese. This latter precipitates as Mn$_2$O$_3$. At higher temperature, it would be Mn$_3$O$_4$ (24,25,26). In our experiments, a small concentration of manganese at the interface does not affect the electrode spectrum at all and this is consistent with (22). With no net charge transport, it seems that dissolved manganese does not affect the reaction mechanism. The electronic conductivity induced by doping is probably not high enough to produce the same effect as for cerium. The induced oxygen vacancies do not play a visible role too. On the contrary, a quantity above the solubility limit does.

Using the same implantation technique, similar experiments were earlier reported with implanted iron in YSZ, with gold electrodes (1). The implantation was made there in order to obtain a graded interface. A few nanometers of iron oxide were measured on the electrolyte surface. Although the quantity was high above the solubility limit of iron in that material, only a change in the magnitude of the spectrum was noticed. A small additional semi-circle was attributed to a contact resistance between the oxide layer and the zirconia. For the MnHD sample, a second arc appears too. But from preceeding experiments (5), we noticed that it did not come from a contact resistance because it is a function of current. In fact, it was strongly related to the quantity of manganese added. So concerning the above results, it is indicated that the precipitated manganese oxide participates in the oxygen reduction reaction. Mn$_2$O$_3$ is an electronic conductor (25). Its conductivity reaches 3.54 Scm$^{-1}$ at 750 °C whereas that of LaMnO$_3$ is 0.1 Scm$^{-1}$ at 700 °C (27). It confers an electronic conductivity on/in the electrolyte. As such, it offers a parallel way for oxygen reduction whose rate determining step generates a second semi-circle. As the total available current is increased, the total electrode resistance appears to decrease.

At this stage, it should be pointed out that with excessive quantities of manganese, cell performance can be diminished. As the resistance is low in the MnHD case, it suggests that the calculated concentration profile approaches reality. But a high dispersion of the oxide could also produce the same effect.
CONCLUSION

Ion implantation has been used successfully for modifying the YSZ surface in a controlled way. It allowed us to show that the existence of a superficial electronic conductivity, even small, can positively affect the oxygen reduction rate under equilibrium. The effect is strongly dependant on the type of ion. In relation to impedance spectroscopy, dissolved cerium can be considered to act like a catalyst, whereas the major improvements with manganese are attributed to its precipitated form, taking part in the electrochemical reaction.

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Figure 1: Simulated (8) concentration profiles of the manganese and cerium ions.
Figure 2: Impedance spectra of CeLD and CeHD interfaces under zero current. Half of an uncatalysed Pt cathode is represented for clarity reasons.

Figure 3: Nyquist plot of the MnHD interface under zero current. Uncatalysed platinum and MnLD have the same spectrum.