SPACE EXPANSIONS OF THE REGULAR OXYGEN ELECTRODE
REACTION ON YSZ - II. SILVER ELECTRODES

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ABSTRACT

Measurements have been carried out on micro-electrodes made of in situ solidified silver droplets on YSZ and on silver painted on YSZ / Al₂O₃ composites. The results show evidence for two electrode reaction mechanisms in parallel. The variations of the corresponding reaction rates as functions of the electrode interface geometry are more complex than the expected simple proportionality to the triple phase line length or to the electrode interface area. Electronic thermoemission may also contribute to the electrode reaction zone expansion over the free electrolyte surface.

INTRODUCTION

In order to optimize the microstructure of the fuel cell electrodes and to gain insight into the electrode reaction mechanisms, various attempts (1-5) have been made to correlate the electrode reaction rate with the length of the Triple Phase Boundary (TPB) and also to evaluate the possible expansions of the electrode reaction zone over the electrolyte surface (5,6). Figure 1 shows a grain of the electrode material in contact with the electrolyte. For simplicity, it is supposed to be a small cylinder of radius r.

The basic statement of this work is: the electrode reaction expands to some extent over the electrolyte surface, from the TPB. If this were not the case, the local ionic current entering the electrolyte under the TPB line would be beyond reasonable limits to account for the observed overall cathodic currents in the SOFC's. The expansion can mainly occur toward the Outside, over the free electrolyte surface, with an average width called Oe, or/and toward the Inside, between the electrode material and the electrolyte, with an average expansion width Ie. These parameters may vary with the experimental conditions, especially the oxygen pressure P(O₂) and temperature T (6). Our strategy has been to work with micro-electrodes of average radius r, hopefully, of the same order of magnitude as Oe or/and Ie. Then, the variations as functions of r, of the electrode reaction parameters should reveal the prevalent expansion Oe or Ie.

If r has not been properly selected and is much larger than both Oe and Ie, then the electrode reaction rate will simply be proportional to the TPB length (2πr for the grain electrode of Fig.1), as it has been observed with differently designed electrodes (1-5). Conversely, if the outward expansion is much larger than the electrode interface radius r,

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whatever the inward expansion, then the variations of $r$ will not have any influence on this rate. If the inward expansion is prevalent and of the same order of magnitude as $r$, then the electrode reaction rate will approximately vary as the interface area ($\pi r^2$).

This simplified presentation supposes a uniform electrode current density over the electrode expansions (or an appropriate definition of their average widths). When the electrode reaction can be decomposed into several "elementary" mechanisms, the above derivation can be applied to each of them, as we will see below.

By providing us with pieces of evidence for the specific space distributions of the elementary mechanisms, the influence of $r$ can help us to identify them and to verify assumptions made on them. For instance, let us imagine that a semicircle is viewed as the characteristic of the true charge transfer process, with the measured resistance being the transfer resistance $R_{ct}$ and the measured capacitance, the double layer capacitance $C_{dl}$. This assumption implies that both components $R_{ct}$ and $C_{dl}$ are distributed over the same electrode reaction zone. Accordingly, they should vary in related ways as functions of $r$. If they are distributed over a narrow ring along the TPB for example, $R_{ct}$ will vary as $r^{-1}$ and $C_{dl}$ as $r$. The relaxation frequency of the corresponding semicircle which is proportional to $R_{ct} \times C_{dl}$ should accordingly not vary with $r$. If it is not the case, we will have to conclude that the measured resistance and capacitance are not distributed over the same zones and therefore that the assumption of a true transfer response is not correct. This type of derivation assumes that the examined properties are at least proportionally distributed over the reaction zones. Departures from this realistic assumption may account for small variations of the relaxation frequency.

In a recent report (7), a systematic investigation of metallic micro-electrodes of small radius (0.05 - 0.35 mm) concluded that:

- Newman equation

$$R = \frac{1}{4\pi \sigma}$$

which correlates the measured electrolyte resistance $R$ in series with the electrode, the electrolyte conductivity $\sigma$ and the average radius of the interface area $r$, is well obeyed. The experimental scatter is 25%. It allows us to conveniently determine the micro-electrode average interface radius by simply measuring the corresponding electrolyte impedance at high frequencies.

- Arrow-headed electrodes gently pressed on the electrolyte surface are unfortunately not reliable enough for the determination of any relationship between the interface area and the reaction rate parameters, because of microstructural defects over the electrode material surface. On the other hand, they have been proved to be quite convenient for the investigation of the parameter variations with oxygen pressure or temperature (6).

- Silver droplets in situ solidified on the electrolyte surface under appropriate conditions exhibit fairly reproducible electrode characteristics and can be used for our purpose. Varying their sizes has clearly shown that the two main components of the oxygen reaction vary differently as functions of the interface radius. Figure 2 shows three diagrams corresponding to different interface radii. They indicate that the larger the interface radius, the less important the relative contribution of the low frequency mechanism.
As shown in Figure 2, the impedance diagrams of these solidified droplets are easily resolved into two components without ambiguity. The data we have fitted have indicated that these components can be dealt with, as a first approximation, as semicircles. The variations of their parameters as functions of the experimental conditions and especially as functions of the droplet average interface radius will be reported below. Other reported results have been obtained with conventionally painted electrodes coated on composite electrolytes made of Yttria Stabilized Zirconia (YSZ) and Alumina. This second component can be regarded as an insulator in our experimental conditions. Finally, we will briefly recall ancient results showing that the electronic emission from the materials may induce a specific electrode reaction which involves the free electrolyte surface.

EXPERIMENTAL

The cells used for the first series of measurements were essentially based on an YSZ single crystal (CRISMATEC) containing 10 mol% Y₂O₃. A porous platinum coating (DEMETRON 308 A) formed the counter electrode. The silver droplets were melted under reducing conditions (7) and slowly cooled to the measurement temperature (10 °C/h). Below about 600 °C, erratic results indicated that some detachment of the droplets may occur because of a too large thermal expansion with respect to YSZ. Using this technique, we could vary the average interface radius from approximately 0.2 to 2 mm. The electrical connection to the measuring unit was made using an alumina capillary containing a silver plug and a platinum wire (Fig. 3).

The composite electrolytes used in the second series of measurements were prepared from an YSZ containing 8 mol% Y₂O₃ (TOSOH TZ8Y) and nominally pure alumina (SUMITOMO AES12) co-grinded in ethanol, pre-pressed under 20 MPa, isostatically cold pressed under 400 MPa and sintered at 1500 °C for 2 hours. The densities were close to 99 % of the theoretical values. Figure 4 shows a typical micrograph of these materials. The electrolyte surfaces were polished on a SiC polishing paper grade 1000 and ultrasonically cleaned. The silver electrodes used on them (DEMETRON 204) were baked at 650 °C (2 h).

The oxygen partial pressure over the investigated electrodes could be continuously varied with a conventional gas circuit equipped with an oxygen pump and sensors. The measurements were performed by impedance spectroscopy under zero d.c. polarization using an HEWLETT-PACKARD impedancemeter (HP 4192 A) in the 5-13x10⁶ Hz range for the electrolyte response and an Autolab from ECO CHEMIE in the 10⁻⁴-5x10⁴ Hz range for the electrode reaction proper. The HP impedancemeter signal amplitude was 100 mV. That of the Autolab was 15 mV.

RESULTS AND DISCUSSION

Solidified Droplets

Let us first examine the influence of the interface radius on the relaxation frequencies, following the examination procedure outlined in the introduction. Figure 5
shows the variations determined at 800 °C, under 1 atm of oxygen. They clearly indicate that, at least under these experimental conditions, the high relaxation frequency is constant as it should be for a "regular" elementary mechanism. To the contrary and quite unexpectedly, the low relaxation frequency is markedly variable. Therefore, the resistance $R_{LF}$ and capacitance $C_{LF}$ associated with this semicircle are likely to describe responses of different parts of the materials forming the electrode.

**LF semicircle**

Figure 6 shows that $R_{LF}$ varies as $r^{-1.35}$. This seems to indicate a prevalent inward expansion of the corresponding reaction zone, probably with a non uniform distribution of the value of the local resistance $\delta R_{LF}/\delta r$ along the interface radius. This could correspond to oxygen diffusing through the silver droplet in the TPB vicinity (Fig. 8).

The corresponding capacitance $C_{LF}$ varies as $r^3$ (Fig. 7). It is proportional to a certain volume of the electrode material. Furthermore, it is likely to be an electrochemical pseudocapacitance. Expressed in Farad per interface unit area, the measured values are in the 1-10 $\text{Fcm}^{-2}$ range. $C_{LF}$ would be associated with concentration variations of oxygen dissolved in a certain volume of the silver droplet above the whole interface (Fig. 8). A similar model has been found to quantitatively fit the responses of reduced lanthanum manganite electrodes (8). Another argument in favor of this interpretation can be found in the shape of the low frequency part of the impedance diagrams which indicates that a limited Warburg characteristic might better fit the experimental results.

$R_{LF}$ and $C_{LF}$ are proportional to the square root of the oxygen pressure (Figs. 9 and 10), as frequently observed (6). This confirms that oxygen atoms are the main oxidized electroactive species for these two parameters, which is consistent with the picture of Figure 8.

The variations with temperature are reported in Figures 11 and 12. 
- The $R_{LF}$ activation energy (1.05 eV) is quite similar to that of the electrolyte resistivity as already reported with other electrode microstructures (6). 
- $C_{LF}$ slightly increases with temperature. It would be fairly consistent with the interpretation sketched in Figure 8. At higher temperature, oxygen diffuses faster in the electrode material. Accordingly, the part of the droplet volume involved in the pseudocapacitive effect would be bigger, and so would be the quantity of electroactive oxygen.

**HF semicircle**

The variations of the high frequency parameters as functions of $r$ are reported in Figures 6 and 7. In agreement with the relaxation frequency independence of $r$ (Fig. 5), $R_{HF}$ and $C_{HF}$ vary in correlated ways as functions of $r$ ($R_{HF} \approx r^{-0.6}$ and $C_{HF} \approx r^{0.6}$). This type of variation seems to point to a significant outward expansion of the corresponding mechanism according to the derivation sketched in the introduction. The corresponding reaction zone may simultaneously expand over the electrode interface between the droplet and the electrolyte.

The variations of $R_{HF}$ with the oxygen pressure and temperature ($R_{HF} \approx P(O_2)^{1/4}$ and $E(R_{HF}) = 2.1$ eV) (Figs. 13 and 14) are fairly convincing evidences for a close correlation between $R_{HF}$ and the electronic conductivity of the electrolyte, which varies
in the same ways (9) (There is a disagreement with a previous measurement of $E(R_{HF})$ quoted in (6)).

The variations of $C_{HF}$ with $P(O_2)$ and especially with $T$ are much smaller than that of the other parameters. They could be regarded as typical behavior of a double layer capacitance on YSZ. This capacitance being mainly fixed by the mobile ionic carriers should not vary much with $P(O_2)$, for instance. A remark has to be made about its magnitude: expressed in Farad per electrode interface area unit, it is of the order of 3 mFcm$^{-2}$. It is significantly higher than the values reported in the literature for large surface porous electrodes. That could also be regarded as an indication of a rather broad outward expansion which would give a greater area to the effective reaction zone than calculated from the electrode interface.

A puzzling result is the transient variation of the HF parameters after a change in the oxygen pressure. Typical results are shown in Figure 15. They correspond to the effect of a rapid increase in $P(O_2)$ from $10^{-2}$ to 1 atm at 650 °C. As can be checked from the electrolyte resistance constancy, the electrode interface area is not altered during the evolution which follows. The LF process stabilizes in less than 1 hour (except for a small drift of $R_{LF}$). To the contrary, it takes an extremely long time, longer than 10 hours, for the HF mechanism to reach its steady state. A quite similar observation has been made on large surface porous LSM electrodes (10), not after a change in $P(O_2)$, but after a polarization of the electrode. It is difficult to imagine for a mechanism which significantly expands over the free electrolyte surface that it takes so long to equilibrate with the surrounding atmosphere. Let us note that a "third semicircle" relaxing at very low frequency has been reported (11). It could correspond to this slow process. If it is the case, we could conclude that the HF and the third semicircle are related.

**Composite electrolytes**

Results obtained with composite electrolytes are illustrated in Figure 16. They show that the silver electrode overpotential resistance and capacitance are quasi independent of the presence of a very large concentration of insulating grains covering up to about 80% the electrolyte surface. Results previously published (12) have shown that the alumina concentrations investigated here induce variations by factors of 16 and 250 respectively for the bulk and d.c. resistivities, with respect to pure YSZ. The same independence was observed under higher and lower oxygen pressures (1 to $10^{-4}$ atm). These are strong evidences for the metal electrode playing the determining role in controlling the electrode overpotential. This supports the interpretations given above of $R_{LF}$ and $C_{LF}$ being controlled by oxygen dissolved in silver.

**Electronic thermoemission**

Regarding the outward expansion, it should also be stressed that the electronic thermoemission of the materials forming the electrode can also contribute a specific reaction process. In an SOFC this electronic exchange process can easily occur in the pores immediately over the electrolyte surface, especially when the cell is operated at high temperature. Such electrode reactions were examined in some details, a few decades ago (13) and has not been recently re-investigated. Just as an example, Figure 17 shows a steady state $U(I)$ characteristics previously reported (13), of a platinum tip electrode maintained slightly above the electrolyte surface, without contact. It clearly demonstrates that a non negligible current can be exchanged between the electronic conductor and the
electrolyte surface because of the electronic emission of the materials, even in the direction corresponding to electrons being emitted from the electrolyte surface.

CONCLUSIONS

* The use of solidified silver droplets as electrodes has allowed us to quantitatively determine the influence of the area of intimate electrode contact on the parameters of the commonly observed semicircles of the oxygen electrode impedance diagrams.
* The following experimental conditions are favorable to the observation of a relatively large high frequency semicircle: low temperature, high oxygen pressure, high intimate contact coverage. Conversely, high T, low P(O\(_2\)) and electrodes made of small grains, which has been so far the most common situation, are more favorable to highly dominant LF semicircles.
* The reaction mechanisms responsible for the low and high frequency semicircles are not "successive" steps of a single electrode reaction. Their space distributions are different. It would probably be closer to reality to assume that they are processes acting in parallel.
* The low frequency resistance characterizes the oxygen flux whichdiffuses through the metal electrode in the vicinity of the triple phase boundary, under dc conditions. The corresponding capacitive effect is a pseudocapacitance associated with variations in the oxygen concentration occurring under ac conditions in a certain volume of the metal over the whole electrode interface.
* Relative to the other parameters, the high frequency capacitive effect varies only a little as a function of r, P(O\(_2\)) and T. The high frequency resistance also varies a little as function of r and P(O\(_2\)) (but it varies a lot with T). Similar observations have been made with LSM electrodes (10) which exhibit enormous variations of the LF semicircle under chemical reduction of the electrode material, while the HF semicircle does not seem to be markedly altered by the chemical change.

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Figure 1. Diagram of an electrode grain contacting the electrolyte. Oe and Ie : average widths of the Outside and Inside electrode reaction zone expansions.

Figure 2. Typical electrode impedance diagrams obtained with different interface areas.
Figure 3. Silver droplet electrode.

Figure 4. Micrograph of a YSZ / Al₂O₃ composite electrode containing 50 vol % Al₂O₃.

Figure 5. Influence of the electrode interface radius on the relaxation frequencies of the semicircles.

Figure 6. Influence of the electrode interface radius on the semicircle diameters.

Figure 7. Influence of the electrode interface radius on the capacitive effects.

Figure 8. Space distributions of the oxygen atomic species involved in the low frequency mechanism.
Figure 9. Influence of the oxygen pressure on the semicircle diameters.

Figure 10. Influence of the oxygen pressure on the LF capacitive effect.

Figure 11. Arrhenius diagram of the low frequency semicircle diameter.

Figure 12. Arrhenius diagram of the low frequency capacitive effect.

Figure 13. Variation with $P(O_2)$ of the high frequency semicircle diameter.

Figure 14. Arrhenius diagram of the high frequency semicircle diameter.
Figure 15. Variation with time of the resistances deduced from the impedance diagrams after an increase in oxygen pressure from 10^{-2} to 1 atm.

Figure 16. Electrode impedances of porous silver electrodes coated on YSZ/Al_{2}O_{3} composites.

Figure 17. Steady state U(I) characteristics of the current emitted by YSZ and collected by a platinum tip.