ELECTROCHEMICAL CORROSION OF IRON IN MOLTEN
Ca(NO₃)₂ • 4 H₂O AT 80°C

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ABSTRACT

The polarization curve of iron (v = 1 mV s⁻¹) in
molten Ca(NO₃)₂ • 4 H₂O at 80°C showed two peaks of
activation on a motionless electrode and only one
peak on a rotating electrode; in the two cases,
this behaviour is characteristic of multiple steady
states. If on a rotating electrode that is due to
ohmic drop, in the case of a motionless electrode,
it is the simultaneous effect of ohmic drop and of
an electrochemical reduction reaction which is
responsible for this multivocal behavior.

From electrochemical impedance measurements
associated to electrochemical tests, it is possible
to propose a mechanism for iron passivation in
molten tetrahydrate calcium nitrate at 80°C.

I INTRODUCTION

Multiple steady states behavior was observed for example
with iron in nitric acid (1,2,3) and in sulphuric acid
(2,4,5,6), with tin and zinc in basic solutions (7,8,9,10),
with gold in KCl 1M, H₂SO₄ 0,25 M (12), with cobalt in
sulphuric acid (13) and with titanium in fluorhydric
solutions (14).

In molten salt, this kind of behavior was observed in molten
cryolite with graphite polarized anodically (15,16,17).

II EXPERIMENTAL APPARATUS AND TECHNIQUES

The glass electrochemical cell had a water-jacket for
circulation of hot water to maintain the temperature at
80°C. The counter electrode was a gold plate (5 cm²). Two types of iron working electrode (J.M.C. quality) were used: a rotating electrode (0.2 cm²) and a motionless electrode (1 cm²). All potentials are reported to Ag/Ag⁺ reference electrode (18). The impedance measurements were carried out from $10^4$ Hz to $10^{-2}$ Hz by a Solartron Schlumberger apparatus interface 1186 and analyzer 1250. The polarization curves were obtained by the interface 1186 and a signal generator (G.S.T.P. Tacussel).

III THE IRON BEHAVIOUR UNDER POLARIZATION

III.1 Motionless electrode

The polarization curve (fig. 1a) was plotted in quasi-stationary conditions ($v = 1$ mV s⁻¹); it showed two activation peaks. The transition between the first and the second peak occurred suddenly at a potential $E = -0.40$ V. It was shown that a gas evolved at the electrode. During the backward scanning, the polarization curve did not exhibit any reactivation phenomenon.

When the polarization curve (fig. 1b) of the same electrode in the same conditions was obtained with an internal negative resistance regulator, the transition between the two activation peaks occurred continuously exhibiting a multiple steady states behaviour.

After the polarization test, the observation of the electrode surface using a scanning electronic microscope (JEOL 540) showed the existence of oxidized grains and non-oxidized grains (fig. 2).

III.2 Rotating electrode

The polarization curve ($v = 1$ mV s⁻¹ (fig. 3a) of a rotating electrode ($\omega = 2000$ rpm) showed only one activation peak. The transition from the activation to the passivation domain yet occurred suddenly. The polarization curve (fig. 3b) plotted with an internal negative resistance regulator showed that the transition between the two states occurred continuously. Then, even in the case of a rotating electrode, the polarization curve is under a multiple steady states control. During the backward scanning potential, the polarization curve did not exhibit a reactivation phenomenon. This was probably due to a change in the structure of the oxide layer. After the polarization test, the electrode surface was black and bright.
III.3 Surface observation and analysis

The observation in the scanning electronic microscope of a passivated iron electrode did not indicate the presence of a passivation layer. So the thickness of this layer is lower than the microscope detection limit (about 1 \( \mu \text{m} \)). The surface analysis of the same electrode by XPS (fig. 4) showed the presence of iron, oxygen and calcium even after a 300 Å thick by ionic bombardment erosion. So, the passivation layer was a mixed oxide of iron and calcium, its thickness was between 300 Å and 1 \( \mu \text{m} \).

IV IMPEDANCE MEASUREMENTS

The electrochemical diagrams (fig. 5) plotted under linear conditions (alternative signal 10 mV) at different potentials on the polarization curve showed a high frequency capacitive loop, a medium frequency inductive loop and a low frequency capacitive loop. The size of the inductive loop decreased when the potential increased. In A and B domain of the polarization curve, the impedance diagrams were not reproducible because of the instability of experimental conditions.

V. DISCUSSION

The multiple steady state can be caused by (9,19):
- the ohmic drop
- the diffusion in solution phenomenon
- an autocatalytic or a supplementary electrochemical reaction

The "Z" form of polarization curve was obtained both on a motionless or a rotating electrode. In the case of rotating electrode, the rotation speed did not involve a significant modification on the polarisation curve shape; so the diffusion phenomenon is not responsible for the observed behavior.

V.1. Electrolyte resistance measurement

The iron current dissolution in molten calcium nitrate tetrahydrate was more important with a rotating than with a motionless electrode; so the ohmic drop could be more important and it was necessary to measure this term to correct the polarization curve.

The resistance of the electrolyte between the reference electrode and the working electrode was determined by
impedance measurements. The extrapolation to high frequencies of the impedance diagrams gave the value $Re = 4 \ \Omega \cdot \text{cm}^2$ at 80°C.

V.2. Phenomenon responsible for the multiple steady states behavior

In the case of a rotating electrode, after ohmic drop correction ($E_{corr} = E_{exp} - Re \times I$), the polarization curve did not show the multiple steady states behavior (fig. 6). The "Z" form was then assigned to ohmic drop.

In the case of a motionless electrode for which the ohmic drop is less important (lower current density), the corrected polarization curve remained multivocal (fig. 7). The gas evolution at the electrode indicated that multiple steady states must be attributed to the simultaneous effect of the ohmic drop and of an electrochemical reduction reaction which led to the gas evolution.

V.3. Identification of the gas formed

On a rotating platinum electrode, the addition of $H^+$ ions (as HCl or HNO$_3$) in the melt gave a reduction wave at $-0.35 \ \text{V}$ (fig. 8b) which did not exist in the pure melt (fig. 8a). The reduction limiting current was proportional to $H^+$ concentration. This reduction wave could not be attributed to $H_2$ evolution which appeared at a potential more cathodic (20). So the electrochemical reaction involves the intervention of NO$_3^-$ species. The study by cyclic voltamperometry with convolutional analysis and by impedance measurement showed that the reduction wave corresponded to an electrochemical reaction with one exchanged electron according to:

$$\text{NO}_3^- + 2 \text{H}^+ + \text{e}^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}$$

For this reaction to occur on iron in the pure melt, $H^+$ ions had to be in a sufficient quantity near the electrode; they are produced by iron oxidation according to

$$\text{Fe} + x\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_x + x\text{H}^+ + xe^-$$

As the molten salt at 80°C is viscous (16 cp), the $H^+$ ions formed remain near the electrode to react according to reaction -1-.

For impedance measurements, if the high frequencies capacitive loop is assimilated to a parallel R-C circuit,
the deduced $C_{HF}$ value was higher than the normal value of double layer capacitance in molten salts; $C_{HF}$ varied linearly and $R_{HF}$ varied exponentially with electrode potential (fig. 9). The product $R_{HF} \times i = 50 \text{ mV}$ was independent from the set-on potential if $E < -0.25 \text{ V}$; so $R_{HF}$ can be simulated to a charge transfer resistance and the constant product $R_{HF} \times i = R \times T/(\alpha \times n \times F)$ at $80^\circ \text{C}$ gave an $\alpha \times n$ value equal to 0.66.

In the case of a rotating electrode, the Tafel representation $E = f(\log i)$ of the polarization curve corrected for ohmic drop showed a linear portion in the activation domain with a slope equal to 47 mV (fig. 10).

The low frequencies capacitive phenomenon corresponds to the limiting step in the passivation process. The $R_{BF}$ resistance associated to this loop and the product $R_{BF} \times i$ increased linearly with the potential. The slope of the straight line $R_{BF} \times i = f(E)$ was equal to 0.7, value near the unity. This phenomenon should be attributed to the conduction and the growth of semi-conducting passive layer (21).

The medium frequencies inductive loop and the lower frequencies capacitive loop was associated in literature to different phenomena; in particular they were attributed to the oxide layer properties of valve metals (22). It was also showed that it is necessary to have at least two different adsorbed species in a reaction mechanism for having an inductive loop with double point (23). We have then introduced the adsorbed species Fe(OH) and Fe(OH)$_2$ in the following mechanism:

\[
\begin{align*}
\text{Fe} + \text{H}_2\text{O} & \quad \Rightarrow \quad \text{Fe(OH)}_{\text{ads}} + \text{H}^+ + \text{e}^- \\
\text{Fe(OH)}_{\text{ads}} + \text{H}_2\text{O} & \quad \Leftrightarrow \quad (\text{Fe(OH)}_2)_{\text{ads}} + \text{H}^+ + \text{e}^- \\
\text{Fe(OH)}_{\text{ads}} & \quad \Rightarrow \quad \text{Fe(OH)}^+ + \text{e}^-
\end{align*}
\]

The numerical simulation of this mechanism behavior allowed us to determine the characteristic kinetic constants which gave us a general description of experimental results (24).

**SUMMARY**

The polarization curve of iron showed a multiple steady
states behavior in molten Ca(NO₃)₂ · 4 H₂O at 80°C. In the case of rotating electrode, ohmic drop is essentially responsible for this kind of behavior. On the other hand for a motionless electrode, the multivocal behavior was attributed to a simultaneous effect of ohmic drop and a supplementary reduction reaction which lead to NO₂ gas evolution.

The reduction reaction was:

\[ H^+ + NO_3^- + 1e^- \rightarrow NO_2 + H_2O \]

H⁺ ions were produced during iron oxidation as follows:

\[ Fe + xH_2O \rightarrow Fe(OH)_x + xe^- + xH^+ \]

The impedance measurements allowed us to propose the following dissolution passivation mechanism:

\[ Fe + H_2O \rightarrow Fe(OH)_{ads} + H^+ + 1e^- \]
\[ Fe(OH)_{ads} + H_2O \leftrightarrow (Fe(OH)_2)_{ads} + H^+ + 1e^- \]
\[ Fe(OH)_{ads} + H_2O \rightarrow Fe(OH)^+ + 1e^- \]

The numerical simulation of the mechanism behavior allowed us to determine the characteristic kinetic constants which gave a general description of experimental results.

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Figure 1. Polarization curve of motionless iron electrode in the melt ($v = 1 \text{ mV s}^{-1}$). a: without internal negative resistance regulation. b: with internal negative resistance regulation.

Figure 2. Surface of motionless iron electrode observed by SEM after polarization test.

Figure 3. Polarization curve of rotating iron electrode ($v = 1 \text{ mV s}^{-1}$, $w = 2000 \text{ rpm}$). a: without internal negative resistance regulation. b: with internal negative resistance regulation.

Figure 4. XPS analysis of oxide layer. a: not oxidized iron. b: oxidized iron in the melt.
Figure 5. Impedance measurements at different potentials of iron rotating electrode ($\omega = 2000$ rpm). a: $E = -0.55$ V. b: $E = -0.5$ V. c: $E = -0.4$ V. d: $E = -0.35$ V. e: $E = -0.25$ V. f: $E = -0.15$ V. g: $E = 0.1$ V. logarithmic parameter frequencies.
Figure 6. Polarization curve of iron in the melt. a: motionless electrode, b: rotating electrode. (-----) as recorded. (---) with ohmic drop correction.

Figure 7. Polarization curve of platinum rotating electrode (v = 100 mV.s⁻¹, w = 2000 rpm).

- a: in pur2 melt.
- b: in melt with HNO₃,
  \[ [\text{HNO}_3] = 1.06 \times 10^{-2} \text{ M}\]

Figure 8. Evolution of \( R_{HF} \) and \( C_{HF} \) with potential.

Figure 9. Tafel plot of iron electrode polarization curve (w = 2000 rpm).

Figure 10. Evolution of \( R_{BF} \) and \( R_{BF} \times i \) with potential.