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Electrodeposition of iron in sulphate solutions

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Abstract

The kinetics of iron electrodeposition from acid sulphate solutions onto a platinum electrode was investigated by means of stationary polarisation curves and electrochemical impedance spectroscopy. Together with interfacial pH data previously obtained, the effect of pH was analysed. The formation of at least three adsorbed intermediates at the cathode surface was evidenced in all pH values. The relative rate of their formation and its surface concentration depend on the solution pH as well as on the electrode potential. It is suggested that two of these species catalyses the H⁺ reduction whereas the other one may have a blocking effect on this reaction.

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1. Introduction

Investigations on iron electrodeposition have been basically restricted to the effects of deposition parameters on the morphological, structural and magnetic properties of the deposits [1-3]. Moreover, the fundamentals of the mechanism that governs iron electrodeposition have received less attention if compared to the highly investigated Fe alloy systems. Indeed, the nature of the anomalous electrodeposition of Fe alloys, such as Zn-Fe, Co-Fe and Ni-Fe, has been the subject of many researches [4-6] but the mechanisms still require improvements. In this particular case, to better understand the codeposition processes, the knowledge on the individual deposition mechanisms must be established. In addition, the increasing interest on the development of Fe thin deposits for magnetic applications [3,7] also calls for the comprehension of the elementary steps that take place during the electrodeposition.

Kabanov et al. [8], Bonhöeffer and Jena [9] and later Bockris et al. [10] were the earliest to mention the formation and participation of Fe hydroxide species during iron electrodissolution/electrodeposition. Some other more recent works [11,12] have also considered the contribution of this species that result from the increase on the pH of the solution adjacent to the cathode. The presence of this species at the electrode/solution interface might generate adsorption/desorption processes. By investigating Fe nucleation kinetics on a vitreous carbon electrode through electrochemical techniques and AFM microscopy, Grujicic and Pesic [13] proposed a theoretical model for Fe electrodeposition based on a progressive nucleation mechanism that was associated with the degree of inhibition of the nucleation sites.

Evidences of surface alkalination during Fe-group metal and their alloy electrodeposition have been found by means of pH measurements at the vicinity of the electrode using different techniques [14,15]. In a previous work [16], interfacial pH measurements were performed during Zn–Fe electrodeposition using an in-situ non-intrusive setup. It was verified that the interfacial pH increases during individual Fe electrodeposition, meaning that it occurs with simultaneous H⁺ consumption.

Electrochemical impedance technique provides information on electrodeposition processes by means of time constants associated with the elementary steps of these systems. Epelboin et al. [17] indicated that the charge transfer in multiple steps might take place at the electrode surface through adsorbed

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intermediates, which can interact with other inhibiting species. The coupling between these charge transfer reactions and the adsorbates generates relaxation processes that strongly depend on the electrolyte composition, pH, nature of the anion, polarisation and hydrodynamic conditions [18]. Nickel electrodeposition is an example of a process where strong surface interactions between Ni²⁺ and H⁺ take place. These interactions, together with the anion influence, were considered to account for the electrochemical impedance results [19,20]. The interpretation of the experimental results was done in terms of adsorbed intermediates as well as of the potential dependence of growth sites.

The objective of the present work was to study the kinetics of Fe electrodeposition as a function of solution pH by means of potentiostatic polarisation curves and electrochemical impedance spectroscopy in sulphate medium. Taken into account the results on interfacial pH presented elsewhere [16], it is suggested the formation of three adsorbed intermediates at the cathode surface. The presence of these intermediates validates the participation of H⁺ and/or OH⁻ on iron electrodeposition process. The rate of their formation and their relative predominance depends on both potential and solution pH. The features discussed in the present work are essential to the establishment of a model for ZnFe alloy electrodeposition [16].

2. Experimental

The electrolyte used in this work consisted of 0.9 MFeSO₄·7H₂O solution at different pH values. A sodium sulphate solution in the same concentration was also employed as a blank solution. The solutions were prepared from analytic grade chemicals and double distilled water, without addition of any other substance such as additives, complex agents or supporting electrolyte. The adjustment of the pH of solutions was done by 0.9 M sulphuric acid additions.

Cathodic potentiostatic (steady state) polarisation curves and electrochemical impedance measurements, in both potentiostatic or galvanostatic modes, were performed in a conventional three-electrode cell, using a Pt rotating disc electrode (RDE) with 0.2 cm^2 as working electrode. All experiments were carried out at 500 rpm of electrode rotation speed. The counter electrode was a circular Pt grid (300 cm²) that was separated from the working electrode by a sintered glass filter. A saturated Hg/Hg₂SO₄ electrode (SSE) was used as reference. The potential values given in this work were always versus SSE. All experiments were performed at room temperature and in the absence of O₂ with iron powder at the bottom of the cell to prevent Fe(II) oxidation.

An OMNIMETRA mod. PG19 potentiostat and a frequency response analyser SOLARTRON SI1254, coupled with a PC were used in the impedance measurements. The signals were filtered by means of a KEMO mod. VBF-8 Filter in low-pass mode. The rotating electrode was an Asservissement Eletron-ique device. In most of the experiments the impedance diagrams, in potentiostatic or galvanostatic modes, were obtained in the frequency range of 40 kHz–1.3 mHz with a signal amplitude of 7–15 mV. The polarisation curves were corrected from



Fig. 1. Cathodic polarisation curves obtained in the 0.9 M FeSO₄ \cdot 7H₂O solution as a function of pH.

ohmic drop through the high frequency limit of electrochemical impedance plots.

3. Results

Fig. 1 presents the cathodic potentiostatic polarisation curves obtained in the 0.9 M Fe sulphate solution in different pH values. These curves can be divided into two distinct regions independently of the pH. In the first one, at low polarisations, the current varies slowly with cathodic polarisation. In this region, as previously discussed [16], the efficiency for metallic deposition is extremely low and the H⁺ reduction reaction prevails. With further polarisation increase, the current densities show a sudden increase that confers an abrupt change in the slope of the curves, which start to vary in a quite linear way with cathodic potential. High efficiency in metallic deposition was only detected at this part of the curves, for all the solution pH investigated. Only for reference, and following a general tendency in the literature, hereafter in this text, the two parts of the curves will be called as "non-linear", wherein H⁺ reduction prevails, and a "linear" one, mainly related to Fe electrodeposition. This was done to make easier the discussion and to differentiate the two regions of the curves where distinct cathodic process predominates.

With increasing pH, a decrease in current densities in the non-linear region is observed in Fig. 1. For each pH value, a current maximum is also detected in this potential range, which depends on solution pH. After this maximum, all curves present a slow decrease in current values and, subsequently, increase abruptly with polarisation. As can be seen from Table 1, the current maximum and the beginning of the linear part of the curves are shifted to less cathodic potentials with increasing pH.

Fig. 2 shows the cathodic polarisation curves obtained in both $0.9 \text{ M} \text{ Na}_2 \text{SO}_4$ and 0.9 M Fe sulphate solutions at pH 3.0. As can be seen in this figure, before -1200 mV, where the curve for Fe(II) solution presents a maximum, the current densities associated with this solution are higher than those for the

Table 1 Potential values at the current maximum and at the beginning of the linear part of the polarisation curves in Fig. 1

Solution pH	Potential at current maximum (mV _{SSE})	Potential at the current minimum (mV _{SSE})
2.5	-1223	-1322
3.0	-1201	-1309
3.5	-1174	-1295
4.0	-1165	-1255
5.0	-1160	-1230

Na₂SO₄ solution. After this potential, the current values for the Na₂SO₄ solution become higher than those for the Fe(II) solution. Although not shown in this paper, a similar behaviour was observed for all the pH values investigated. As already described [16], at the potential range corresponding to the non-linear part of the curves in Fig. 1, the main electrochemical process is the H⁺ reduction, even though Fe electrodeposition can occur with very low efficiency. Accordingly, the higher current values observed until -1200 mV in the presence of Fe(II) can be considered as a result of a catalytic effect on the H⁺ reduction.

Fig. 3 displays the impedance diagrams obtained in the Na_2SO_4 solution at pH 3.0 and in Fe(II) sulphate solution at pH 2.5, 3.0, 3.5, 4.0 and 5.0, all at potential values corresponding to the region before the current maxima at the non-linear part of the polarisation curves in Fig. 1. For each diagram, the capacitive loop at high frequencies is related to the charge transfer resistance in parallel with the double layer capacitance, whose values



Fig. 2. Typical cathodic polarisation curves obtained in $0.9\,M\,Na_2SO_4$ and $0.9\,M$ FeSO4, at pH 3.0.

lie between 3 and 80 μ F cm⁻². From now on, only the features in the low frequency domain related to the faradaic response will be discussed. The diagram obtained in the Na₂SO₄ solution shows two capacitive loops in the low frequency range that are associated with the H⁺ reduction as the single cathodic reaction. The characteristic frequencies (the frequency at the maximum) of these loops are 0.7 and 0.03 Hz. Analogous results were obtained for Fe(II) solution in all pH values: two capacitive loops were also detected in the low frequency domain, independently of the



Fig. 3. Impedance diagrams obtained in 0.9 M Na₂SO₄ (pH 3.0) and in 0.9 M Fe(II) solution at different pH and at the potential region before the current maximum of polarisation curves in Fig. 1 (frequencies in Hz).



Fig. 4. Impedance diagrams obtained in 0.9 M Na₂SO₄ (pH 3.0) and in 0.9 M Fe(II) solution at different pH and at the potential region just after the corresponding current maxima in the polarisation curves in Fig. 1 (frequencies in Hz).

pH. The similarity between the diagram obtained in the Fe(II)free solution and those for the Fe(II) solutions confirms that the H⁺ reduction is the major cathodic reaction at this potential region. This fact is in agreement with previous data related to the interfacial pH [16] and confirms that the results in Fig. 2 correspond mainly to a catalytic effect due to the presence of Fe(II) ions in the solution.

In Fig. 4, the diagrams show the typical behaviour at the potential region just after the current maximum at the non-linear part of the polarisation curves (Fig. 1) obtained in Fe(II)containing solution. A diagram obtained in the Na₂SO₄ solution, at a potential value corresponding to this region, is also displayed. As can be seen, this diagram is basically the same as the one presented in Fig. 3 for the same solution, which is related to the H⁺ reduction process. Conversely, for the Fe(II)-containing solution at different pH values, the diagrams changed, if compared to those in Fig. 3. At low pH values (2.5 and 3.0) the diagrams show a negative polarisation resistance (R_p) . In contrast, at higher pH values (3.5, 4.0 and 5.0), the negative $R_{\rm p}$ is no longer verified but the capacitive loop at very low frequencies increases significantly. These results are in conformity with the decrease in current values observed in non-linear part of the curves in Fig. 1. Since in this region the metallic electrodeposition efficiency is still extremely low, a blocking effect on the H⁺ reduction reaction might be assumed in the Fe(II)-containing solutions [16].

Figs. 5–9 present the impedance diagrams obtained in the potential range corresponding to the linear region of the polari-

sation curves (Fig. 1) in the Fe(II)-containing solution at pH 2.5, 3.0, 3.5, 4.0 and 5.0, respectively. Independently of the pH value, the diagrams show the same qualitative behaviour. At the very beginning of the linear part of the polarisation curves (diagrams (a) in Figs. 5–9) two inductive loops can be observed at the low frequency domain. With further polarisation increase a new loop appears between those two inductive loops in the diagrams for all the pH values studied. This new loop is a capacitive feature that increases in size with increasing polarisation and solution pH.

In fact, from Figs. 5–9, it is noteworthy that this general behaviour becomes more evident as the solution pH increases: the polarisation level in which the capacitive loop at medium frequencies appears decreases with increasing pH. For instance, at pH 2.5 the capacitive loop emerges at a current density around 25 mA cm^{-2} (Fig. 5(e)), while at pH 5.0 this loop is already present in the diagram obtained in 5.6 mA cm⁻² (Fig. 9(c)). Additionally, at pH 2.5, the dimension of this loop remains very small even at high polarisation (Fig. 5(f)) if compared to the one seen at pH 5.0 at lower current density (Fig. 9(c)).

Figs. 5–9 also show that the inductive loop at higher frequencies (≥ 0.6 Hz) decreases in size and presents a great shift of the characteristic frequency value with increasing polarisation, especially at low pH. The lower the solution pH, the more remarkable is this trend. Correspondingly, for a given pH, the inductive loop at lower frequencies (≤ 0.06 Hz) increases with the polarisation and its characteristic frequency does not show a considerable change. With pH increase, however, a decreas-



Fig. 5. Impedance diagrams obtained in the Fe(II) solution, pH 2.5, at the linear part of the polarisation curves in Fig. 1 (frequencies in Hz).

ing on the characteristic frequency of this inductive feature is observed (from 0.06 Hz, at pH 2.5 to <0.01 Hz, at pH 5.0). Consequently, it becomes hard to observe this inductive loop at high polarisations. For this reason, and to help the visualization, some of the diagrams have this loop extrapolated until the R_p value associated with the slope of the corresponding polarisation curves in Fig. 1.

4. Discussion

From the results above presented, it is clear that the mechanism of iron electrodeposition from acid sulphate solutions must include at least three adsorbed species. Thus, to account for these experimental data, the following general kinetic model can be considered:

$$Fe(II) + e^{-} \xrightarrow{K_{1}} Fe(I)_{ads} \xrightarrow{K_{2}} Fe$$

$$Fe(II) + e^{-} \xrightarrow{K_{1}} Fe(I)_{ads} \xrightarrow{K_{2}} Fe$$

$$Fe(I)^{**}_{ads} \xrightarrow{K_{2}} Fe(I)^{**}_{ads} \xrightarrow{K_{2}} Fe(I)^{*}_{ads} Fe(I)^{*}_{ads} \xrightarrow{K_{2}} Fe(I)^{*}_{ads} \xrightarrow{K$$

Taking into account that the corresponding rate constants, K_i , of the reactions vary with the cathodic potential, E, in the form:

 $K_i = K_{0i} \exp b_i E$

with $b_i < 0$ for the cathodic reactions (I < 0) and $b_i > 0$ for anodic reactions (I > 0), then the main global reactions for Fe electrode-position mechanism can be written as:

$$Fe(II) + e^{-\frac{K_1}{\longrightarrow}}Fe(I)_{ads}$$
 $(\theta_1 \equiv Fe(I)_{ads})$ (I)

$$Fe(I)_{ads} + e^{-\frac{K_2}{\longrightarrow}}Fe$$
(II)

$$\operatorname{Fe}(\mathrm{I})_{\mathrm{ads}} + \operatorname{H}_{2}\mathrm{O} \underset{K_{-3}}{\overset{K_{3}}{\leftarrow}} \operatorname{Fe}(\mathrm{I})_{\mathrm{ads}}^{*} + \mathrm{H}^{+} \qquad (\theta_{2} \equiv \operatorname{Fe}(\mathrm{I})_{\mathrm{ads}}^{*}) \qquad (\mathrm{III})$$

$$\operatorname{Fe}(\mathrm{I})_{\mathrm{ads}} + \operatorname{H}_{2}\operatorname{O} \underset{K_{-4}}{\overset{K_{4}}{\leftarrow}} \operatorname{Fe}(\mathrm{I})_{\mathrm{ads}}^{**} + \operatorname{H}^{+} \qquad (\theta_{3} \equiv \operatorname{Fe}(\mathrm{I})_{\mathrm{ads}}^{**}) \qquad (\mathrm{IV})$$

$$\operatorname{Fe}(I)_{\operatorname{ads}}^{*} + \operatorname{Fe}(II) + 2e^{- \underset{\operatorname{Mas}}{\overset{K_{5}}{\longrightarrow}}} \operatorname{Fe}(I)_{\operatorname{ads}}^{*} + \operatorname{Fe}$$
(V)

$$Fe(I)_{ads}^{*} + H_{ads} + e^{-\frac{K_{5}^{*}}{\longrightarrow}}Fe + H_{included}$$
 (V')

$$Fe(I)_{ads}^{**} + Fe(II) + 2e^{-\frac{K_6}{\longrightarrow}}Fe(I)_{ads}^{**} + Fe$$
(VI)

where θ_i corresponds to the electrode coverage for the corresponding adsorbates quoted in the above reactions.

To account for the stoichiometry of K_3 , K_{-3} and K_4 , K_{-4} reversible reactions, the structure of both the intermediates, Fe(I)^{*}_{ads} and Fe(I)^{**}_{ads}, must contain the (OH)⁻ anion in their structures. As already proposed for Fe electrodissolution [21,22], the adsorbed species associated with θ_1 – θ_3 can be differentiated by the presence of anions in their respective structure. Moreover,



Fig. 6. Impedance diagrams obtained in the Fe(II) solution, pH 3.0, at the linear part of the polarisation curves in Fig. 1. R_p represents the slope of the corresponding polarisation curves at the polarisation conditions where each diagram was obtained (frequencies in Hz).

the rate of reaction (V') is considered to be very small. Similar to what was proposed for nickel electrodeposition [19], this postulation accounts for the hydrogen inclusion into the deposits.

The simultaneous hydrogen reduction may occur by means of the following reactions:

$$\operatorname{Fe}(I)_{ads} + H^+ + e^- \xrightarrow{K_7} \operatorname{Fe}(I)_{ads} + H_{ads} \qquad (\theta_4 \equiv H_{ads}) \quad (VII)$$

$$Fe(I)_{ads}^{**} + H^+ + e^- \xrightarrow{\kappa_8} Fe(I)_{ads}^{**} + H_{ads}$$
(VIII)

$$\mathrm{H}^{+} + \mathrm{e}^{-} \xrightarrow{K_{9}} \mathrm{H}_{\mathrm{ads}}$$
(IX)

$$H_{ads} + H_{ads} \xrightarrow{\kappa_{10}} H_2 \tag{X}$$

Considering that the Langmuir isotherm law is valid, the current associated with the above set of reactions can be described by the following equation:

$$-\frac{I}{F} = K_1(1 - \theta_1 - \theta_2 - \theta_3 - \theta_4) + K_2\theta_1 + 2K_5\theta_2 + 2K_6\theta_3$$
$$+K_7[\mathrm{H}^+]\theta_1 + K_8[\mathrm{H}^+]\theta_3$$
$$+K_9[\mathrm{H}^+](1 - \theta_1 - \theta_2 - \theta_3 - \theta_4) + K_5^*\theta_2\theta_4 \tag{1}$$

where $-\frac{I_{\rm H}}{F} = K_7[{\rm H}^+]\theta_1 + K_8[{\rm H}^+]\theta_3 + K_9[{\rm H}^+](1 - \theta_1 - \theta_2 - \theta_3 - \theta_4) + K_5^*\theta_2\theta_4$ is the current related to the hydrogen

reduction. Therefore, Eq. (1) can be re-written as:

$$-\frac{I}{F} = K_1(1-\theta_1-\theta_2-\theta_3-\theta_4) + K_2\theta_1$$
$$+2K_5\theta_2 + 2K_6\theta_3 - \frac{I_{\rm H}}{F}$$

From Eq. (1), the admittance can be written as:

$$\frac{\tilde{I}}{\tilde{E}} = \frac{1}{R_{t}} + F[K_{1} - K_{2} - K_{7}[H^{+}] + K_{9}[H^{+}]]\frac{\tilde{\theta}_{1}}{\tilde{E}}
+ F[K_{1} - 2K_{5} + K_{9}[H^{+}] - K_{5}^{*}\theta_{4}]\frac{\tilde{\theta}_{2}}{\tilde{E}}
+ F[K_{1} - 2K_{6} - K_{8}[H^{+}] + K_{9}[H^{+}]]\frac{\tilde{\theta}_{3}}{\tilde{E}}
+ F[K_{1} + K_{9}[H^{+}] - K_{5}^{*}\theta_{2}]\frac{\tilde{\theta}_{4}}{\tilde{E}} -
F[K_{9}(1 - \theta_{1} - \theta_{2} - \theta_{3} - \theta_{4}) + K_{7}\theta_{1} + K_{8}\theta_{3}]\frac{[\tilde{H}^{+}]}{\tilde{E}}$$
(2)

where R_t is the charge transfer resistance and F is the Faraday's constant.

The mass balance leads to the following equations:



Fig. 7. Impedance diagrams obtained in the Fe(II) solution, pH 3.5, at the linear part of the polarisation curves in Fig. 1. R_p represents the slope of the corresponding polarisation curves at the polarisation conditions where each diagram was obtained (frequencies in Hz).

$$\beta \frac{d\theta_1}{dt} = K_1 (1 - \theta_1 - \theta_2 - \theta_3 - \theta_4) - K_2 \theta_1 - K_3 [H_2 O] \theta_1 + K_{-3} [H^+] \theta_2 - K_4 [H_2 O] \theta_1 + K_{-4} [H^+] \theta_3$$
(3)

$$\beta \frac{d\theta_2}{dt} = K_3 [H_2 O] \theta_1 - K_{-3} [H^+] \theta_2 - K_5^* \theta_2 \theta_4 \tag{4}$$

$$\beta \frac{d\theta_3}{dt} = K_4 [H_2 O] \theta_1 - K_{-4} [H^+] \theta_3$$
(5)

$$\beta \frac{d\theta_4}{dt} = K_7[H^+]\theta_1 + K_8[H^+]\theta_3 + K_9[H^+] \times (1 - \theta_1 - \theta_2 - \theta_3 - \theta_4) - K_{10}\theta_4^2 - K_5^*\theta_2\theta_4 \qquad (6)$$

At the beginning of the non-linear part of the polarisation curves in Fig. 1, before the current maxima, the major contribution to the current is considered to be given by $2K_2\theta_1 + I_H$, since only reactions (I), (II), (VII) and (IX) have a significant input on the charge transfer in this potential range. In this condition, I_H consists essentially of $K_7[H^+]\theta_1 + K_9[H^+](1 - \theta_1 - \theta_2 - \theta_3 - \theta_4)$. In contrast, Fe electrodeposition would be likely to occur through θ_1 , via reaction (II). However, since the efficiency for metallic deposition is, in this potential range, insignificant, then $K_2\theta_1$ becomes negligible if compared to $I_{\rm H}$. Therefore, the principal reaction at this potential range should be the H⁺ reduction. This is in agreement with the previous results [16] and coherent with what is shown in Fig. 3.

In this region, before the current maximum in the curves for Fe(II)-containing solution, if the hydrogen reduction reaction is considered to occur mostly through $K_9[H^+](1 - \theta_1 - \theta_2 - \theta_3 - \theta_4)$, then the current values in the polarisation curves for both, Fe(II)-free and Fe(II)-containing solutions, Fig. 2, would be the same. However, as seen in this figure, the current densities associated with the curve for the Fe(II) solution are higher than those for the Na₂SO₄ solution. Consequently, one realize that the θ_1 might play a catalytic role on the H⁺ reduction as a supplementary source for H_{ads} production (reaction (VII)), through the $K_7[H^+]\theta_1$ contribution in $I_{\rm H}$.

With increasing polarisation, after the potential corresponding to the current maximum in the curve for Fe(II)-containing solution, the current values for the Na₂SO₄ solution become higher than those for the Fe(II) solution (Fig. 2). Moreover, in the same potential range, a decrease in the current densities for the Fe(II) solution and a negative polarisation resistance in the corresponding impedance diagrams (Fig. 4) are observed. This drop in the current density can be explained by means of the launching of θ_2 participation. From the above reaction model, θ_2 is produced by the consumption of θ_1 , previously formed (reac-



Fig. 8. Impedance diagrams obtained in the Fe(II) solution, pH 4.0, at the linear part of the polarisation curves in Fig. 1. R_p represents the slope of the corresponding polarisation curves at the polarisation conditions where each diagram was obtained (frequencies in Hz).



Fig. 9. Impedance diagrams obtained in the Fe(II) solution, pH 5.0, at the linear part of the polarisation curves in Fig. 1. R_p represents the slope of the corresponding polarisation curves at the polarisation conditions where each diagram was obtained (frequencies in Hz).

tion (III) and Eq. (4)). Therefore, as the polarisation increases, θ_2 increases, replacing θ_1 at the electrode surface and, as a consequence, $K_7[H^+]\theta_1$ contribution decreases. Assuming that θ_2 does not catalyse the H⁺ reduction, this process becomes to occur simply via $K_9[H^+](1 - \theta_1 - \theta_2 - \theta_3 - \theta_4)$, whose rate should be lower than that of $K_7[H^+]\theta_1$. In addition, the available surface area for the reduction of H⁺ through $K_7[H^+]\theta_1$ also starts to decrease with the increase of θ_2 . Consequently, one can expect that, at a given potential value, θ_2 may be so high that the global current for H⁺ reduction starts to decrease. Since in this potential range, which corresponds to the non-linear part of the curves in Fig. 1, the efficiency of the metallic deposition is still extremely low, a decrease in current density values is observed in Fig. 1. Accordingly, this current diminution is accompanied by a drop in the interfacial pH, previously reported [16].

Taking into account the effect of the solution pH on the Fe electrodeposition kinetics, the formation of θ_2 from θ_1 is considered to be pH dependent (reaction (III)). This means that $K_3[H_2O]\theta_1$ corresponds to the conversion of θ_1 into θ_2 whereas $K_{-3}[H^+]\theta_2$ corresponds to the conversion θ_2 into θ_1 . According to this reaction, the lower the solution pH the slower will be the formation of θ_2 . Consequently, the production of θ_2 will be speeded up by the pH increase. As above discussed, the maximum of the current in this potential range is a result of the transition on H⁺ reduction rate: from $K_7[\mathrm{H}^+]\theta_1 + K_9[\mathrm{H}^+](1-\theta_1-\theta_2-\theta_3-\theta_4)$ to only $K_9[H^+](1-\theta_1-\theta_2-\theta_3-\theta_4)$, when θ_2 begins to replace θ_1 at the electrode surface. Actually, the position of current maxima in the non-linear part of the polarisation curves (Fig. 1) depends on the ratio between θ_1 and θ_2 (Eq. (4)) and will occur at lower potentials with increasing solution pH, as observed in Fig. 1 and detailed in Table 1.

In addition to the diminution of the value of the cathodic potential where the current maxima take place, the increase in solution pH causes the decrease of current densities in the nonlinear part of the curves in Fig. 1. This is due to a decrease of the H⁺ concentration available for $I_{\rm H}$. Therefore, the negative $R_{\rm p}$ observed in the impedance diagrams in Fig. 4 (pH 2.5 and 3.0) can be attributed to a blocking effect on the H⁺ reduction at the electrode surface brought about by the effect of a high θ_2 . At higher pH values (3.5, 4.0 and 5.0), the blocking effect on the H⁺ reduction still exists, as confirmed from the decrease in the interfacial pH, already reported [16]. However, the negative $R_{\rm p}$ in the corresponding diagrams in Fig. 4 is no longer observed owing to the lower H⁺ concentration in these solutions.

Going further on cathodic polarisation, θ_2 is enhanced and the corresponding current densities continue going down until reaching a minimum. As can be seen in Fig. 1, after the current minima, for all polarisation curves, the current starts to rise sharply and vary in a quite linear way with cathodic potential increase. As already mentioned, high efficient metallic deposition was only observed in this region. Accordingly, the beginning of the linear part of the curves can thus be associated with the rate of θ_2 formation. If the production of this intermediate is favoured, the potential value where the linear region starts becomes lower. Therefore, the minimum of current densities in the non-linear part of all the polarisation curves in Fig. 1 will take place at lower potentials with increasing solution pH, as shown in Table 1.

The impedance diagrams obtained at the very beginning of the linear part of the polarisation curves for the Fe(II) solutions (diagrams (a) in Figs. 5–9) are characterized by two inductive loops at the low frequency domain. At this potential range, $\frac{\tilde{\theta}_3}{\tilde{E}}$, $\frac{\tilde{\theta}_4}{\tilde{E}}$ and $\frac{[\tilde{H}^+]}{\tilde{E}}$ are considered negligible and the main relaxation occurs via $\frac{\tilde{\theta}_1}{\tilde{E}}$ and $\frac{\tilde{\theta}_2}{\tilde{E}}$, both considered as positive. Moreover, the assumptions of $K_1 + K_9[H^+] > K_2 + K_7[H^+]$ and $K_1 + K_9[H^+] > 2K_5 + K_5^*\theta_4$ are necessary to assure that the relaxation of both θ_1 and θ_2 can generate inductive behaviours. However, with additional polarisation increase, a θ_3 enrichment occurs, giving rise to the emergence of a capacitive loop between the two inductive ones previously formed. From Eqs. (3)–(5) the main relaxation frequencies associated with $\frac{\tilde{\theta}_1}{\tilde{E}}$, $\frac{\tilde{\theta}_2}{\tilde{E}}$ and $\frac{\tilde{\theta}_3}{\tilde{E}}$ ($f\theta_1$, $f\theta_2$ and $f\theta_3$, respectively) can be calculated by [21,22]:

$$\beta f \theta_1 = K_1 + K_2 + K_3 [H_2 O] + K_4 [H_2 O]$$
(7)

$$\beta f \theta_2 = K_{-3} [\mathrm{H}^+] + K_5^* \theta_4 \tag{8}$$

$$\beta f \theta_3 = K_{-4} [\mathrm{H}^+] \tag{9}$$

Furthermore, the following kinetic conditions are required: $K_1 + K_9[\mathrm{H}^+] < 2K_6 + K_8[\mathrm{H}^+]$, to guarantee the capacitive relaxation of $\frac{\tilde{\theta}_3}{\tilde{E}}$; and $K_{-3} + K_5^*\theta_4 < K_{-4}$, to oblige the value of the characteristic frequency of $\frac{\tilde{\theta}_3}{\tilde{E}}$ to lie between those of $\frac{\tilde{\theta}_2}{\tilde{E}}$ and $\frac{\tilde{\theta}_1}{\tilde{E}}$.

From the results in Figs. 5–9, the potential value in which the capacitive loop associated with the relaxation of θ_3 appears depends on the pH of the solution. To take into account this result, the formation of θ_3 from θ_1 via reaction (IV) is proposed. According to this reaction, the lower the solution pH, the more difficult becomes the formation of θ_3 . Therefore, the lower the pH, the higher will be the potential in which the capacitive loop might appear. Indeed, in the solution at pH 2.5, only at 25 mA cm² (Fig. 5(e)) a very small capacitive loop appears, while at pH 5.0 the diagram obtained at 5.6 mA cm² (Fig. 9(c)) already presents a big capacitive loop.

For even higher polarisations, the capacitive loop becomes bigger, indicating a continuous increase on θ_3 , as seen in Figs. 5–9. Simultaneously, the inductive loop at higher frequency considerably decreases in size. From the reaction model, since θ_3 is produced at the expense of θ_1 , the mentioned inductive feature is then associated with the relaxation of θ_1 , which is progressively consumed.

Correspondingly, the inductive loop in very low frequencies can be attributed to the relaxation of θ_2 . Another hypothesis is that this inductive loop at very low frequencies could be related to the coupling of the θ_2 with θ_4 relaxations via reaction (V'), as an analogy with what was proposed by Epelboin et al. [19] for nickel electrodeposition from acid sulphate solution. In this case, to describe this loop at very low frequencies, $\frac{\tilde{\theta}_4}{\tilde{E}}$ should be considered as negative, which is most probably to occur in this potential range. The decision between the correlation of this inductive loop simply with $\frac{\tilde{\theta}_2}{\tilde{E}}$ or coupled with $\frac{\tilde{\theta}_4}{\tilde{E}}$ will only be possible during the simulation, already underway.

To summarize the above considerations, taking into account the data in Figs. 5–9, one should conclude that the Fe deposition with high efficiency begins to occur essentially through θ_1 and θ_2 , via reactions (II) and (V), respectively. However, with further polarisation increase, a θ_2 and θ_3 enrichment takes place at the expense of θ_1 , whose concentration progressively decreases. Despite the vanishing of θ_1 , which is a catalyser for H⁺ reduction, an increase in the interfacial pH was observed in the potential range related to the linear branch of the polarisation curve for the Fe(II) solution [16]. This behaviour can be attributed to the presence of high θ_3 concentrations that also catalyses H⁺ reduction through reaction (VIII). As a consequence, at very high polarisations, Fe electrodeposition takes place mainly by means of reactions (V), (V') and (VI). This means that, at this polarisation condition, the electrodeposition becomes to occur through the relaxation of both, θ_3 and θ_2 that give rise to big loops at the low frequency domain, a capacitive and an inductive one, respectively, due to their corresponding enrichment at the electrode surface.

5. Conclusions

The experimental results presented in this paper show that iron electrodeposition in acid sulphate medium occurs by means of at least three adsorbed intermediates. At the non-linear part of the polarisation curves, iron electrodeposition takes place at very low efficiency. In this region, the main cathodic reaction is the hydrogen reduction and the low efficient iron electrodeposition proceeds by means of two intermediates. One of this two adsorbed species catalyses the hydrogen reduction, whereas the other blocks this process. The third intermediate species appears only at the potential range corresponding to the linear part of the polarisation curves. The surface concentration of this species shows a strong dependence on the electrode potential.

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Appendix A. Nomenclature

- b_i activation coefficient for electrochemical reactions (V^{-1})
- *E* potential (V)
- \tilde{E} fluctuation of the potential (V)

- *F* Faraday's constant, 96,500 C/eq
- $f\theta_i$ relaxation frequency associated with electrode coverage by the adsorbed species i (s⁻¹)
- $[\tilde{H}^+]$ fluctuation of H^+ concentration (mol)
- *I* current density $(A \text{ cm}^{-2})$
- \tilde{I} fluctuation of current density (A cm⁻²)
- $I_{\rm H}$ current density for hydrogen evolution (A cm⁻²)
- Im imaginary part of the electrode impedance in the Nyquist diagram ($\Omega \text{ cm}^2$)
- K_i rate constants of the reaction (I) (mol s⁻¹)
- Re real part of the electrode impedance in the Nyquist diagram $(\Omega \text{ cm}^2)$
- $R_{\rm p}$ polarisation resistance ($\Omega \, {\rm cm}^2$)
- $R_{\rm t}$ charge transfer resistance ($\Omega \, {\rm cm}^2$)

Greek symbols

- β surface concentration of atoms (mol cm⁻²)
- θ_i electrode coverage by the adsorbed species *i*
- $\tilde{\theta}_i$ fluctuation of the electrode coverage by the adsorbed species *i*

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