The Electrochemical Behavior of Iron in Acetate Solutions Containing Perchlorate

D.S. Azambuja*, L.A. Feris, F. Ladeira and M.P. Santos

Instituto de Química-Universidade Federal do Rio Grande do Sul, Av. Bento

Gonçalves 9500, CEP 91501-970 Porto Alegre - RS, Brazil

Estudou-se a dissolução do ferro em meio de acetato de sódio, pH = 5, na presença de perclorato na faixa de concentração entre 10^{-3} M e 0.10 M, utilizando a técnica da voltametria cíclica com eletrodo rotatório de disco e de disco e anel.

Observou-se que a velocidade de dissolução do ferro aumenta com a concentração de perclorato, sendo influenciada pelas condições hidrodinâmicas. O acetato inibe os efeitos deletérios da presença do perclorato no sistema.

Iron dissolution in acetate media, pH = 5, containing perchlorate in the range of 10^{-3} M to 0.1 M was studied. Tests on disk and ring disk electrodes using cyclic voltammetry were conducted. The presence of perchlorate increases the iron dissolution rate which is influenced by hydrodynamic conditions. The acetate inhibits the deleterious effect of perchlorate.

Keywords: *acetate, perchlorate, iron dissolution*

Introduction

The influence of anions on the dissolution of metals is very important in corrosion and in electrochemical machining, as well as in the attempts to understand some of the fundamental aspects of electrode kinetics.

The corrosion and passivation of iron in aqueous acid solutions, as well as the active to passive transition, depend on the solution composition[1,2,3]. Previous work on the electrodissolution of iron electrodes shows the direct participation of anions in this process[4,5]. The exchange currents for the Fe/Fe^{+2} system[5] proved to decrease in the series ClO$_4$-, Cl$^-$, CH$_3$COO$^-$, NO$_3$-. Foroulis[5] also observed the large variation of the exchange currents for iron with the nature of the acid anion. Bonhoeffer and Heusler[6] compared the exchange currents of the Fe/Fe^{+2} system in perchloric acid and in a mixture with formic acid at the same pH. The decrease in the exchange current when a readily adsorbed formic acid is introduced into the solution was explained as being due to the displacement of water molecules from the iron surface and a resulting decrease in the surface concentration of the OH$^-$ ions. Florianovich *et al.*[2] points out that the decrease in the iron dissolution rate could result from the displacement of ClO$_4$- ions. In fact, however, the anion actions are more complex[7]. Investigations

of the dissolution of iron in acetate media were carried out by Bech-Nielsen[8,9] who proposed a reaction mechanism involving two coupled, parallel reactions. Later, this author studied the influence of chloride, perchlorate and iodate[10] in this media and observed changes in the kinetic parameters of the dissolution reaction. Takahashi *et al.*[11] and Azambuja *et al.*[12] studied iron dissolution in acetate in the absence of other anions and concluded that the acetate takes part in the reaction mechanism by forming ferrous complexes with this anion.

The aim of this paper is to study the behavior of iron in acetate solutions containing perchlorate in a concentration ranging from 0.001 M to 0.10 M and to evaluate the kinetic parameters by using rotating disk and rotating ring disk electrodes.

Experimental

The working electrode consisted of highly pure iron (*Specpure*, Johnson Mattey Chemicals Ltd.) in the form of a rotating disk (0.07 cm^2 approximate area) embedded in epoxy resin. Before each test the electrode was mechanically polished with silicon carbide paper up to 1200 grit, and then degreased in alcohol and rinsed with twice distilled water. The electrode was cathodically polarized at -1.2 V$_{SCE}$ for 10 min in order to achieve a reproducible

electroreduced iron surface just before the electrochemical measurement was performed. Potentials were measured against a SCE provided with a Luggin capillary tip. The potentials in the text are referred to the SCE scale.

In order to detect the formation of an iron soluble species during the voltammetric sweep of the working electrode the rotating ring disk electrode (RRDE) was employed. An iron working disk platinum detector ring was made for this purpose. The geometrical characteristics of the ring-disk electrode are the following: disk radius, r_1 = 0.50 cm; ring interior radius, r_2 = 0.66 cm; and ring exterior radius, r_3 = 0.72 cm. The calculated value of the collection coefficient according to Albery and Bruckenstein[13] is N = 0.26. Solutions from analytical grade reagents and twice distilled water were prepared. The electrochemical tests were performed with two kinds of solutions with constant and variable ionic strength. The first one consisted of a mixture of $xMCH_3COONa + yMNaClO_4$ (1 < x < 0.90; 0.001 < y < 0.10), buffered with acetic acid to pH = 5. The solutions with variable ionic strength were prepared with 1 M acetate solutions, and a perchlorate concentration in the range of 0.001 to 0.1 M.

The rotation speed of the working electrode (ω) varied in the range of 0-3000 rpm. The experiments were carried out under purified N_2 gas saturation at 25 °C.

Cyclic voltammetry was performed with a Pine Instrument Bipotentiostat model RDE3.

Results and Discussion

The voltammogram of iron run in 1 M Ac + 0.10 M $NaClO_4$ from -1.0 V to 0.3 V at v = 0.1 V s^{-1} exhibits two anodic peaks at *ca.* -0.59 V (peak I) and -0.29 V (peak II), and the reverse scan presents two reactivation peaks corresponding to an intense eletrooxidation process at *ca.* -0.30 V (peak III), and a slight one at -0.63 V (peak IV) which appears only in perchlorate solutions. A comparison[14] with an iron voltammogram in 1 M acetate solution, at the same pH, shows that the height of the anodic peaks increases considerably in the presence of perchlorate, and the peak potentials are shifted to more anodic values.

According to literature data[15,16] the anodic behavior of iron in weak acid solutions which are free of oxygen, shows two anodic peaks in the potential range of the active - passive transition. El Miligy *et al.*[15] point out that these results are not dependent on the measurement technique and can be confirmed by galvanostatic and potentiostatic pulse experiments. The voltammograms (Fig. 1) indicate that the presence of perchlorate tends to stimulate the dissolution process in the active-passive transition.

The contribution of the reactivation process observed during the reverse scan depends strongly on v (Fig. 2) and ω (Fig. 3), increasing as ω increases and v decreases. These results suggest that the kinetics of the eletrooxidation proc-

ess become mass transport controlled, particularly in the potential range of peak II.

In the entire range of the solution composition tested, the height of peak I and II increases linearly with the square root of v (Fig. 2). The anodic to cathodic voltammetric charge ratio is always greater than 1 and increases with v. This behavior is similar to that found in acetate solution without perchlorate[14].

The rotation of the working electrode produces a considerable current increase in the height of the anodic peak and the Levich equation is obeyed. A comparison with the
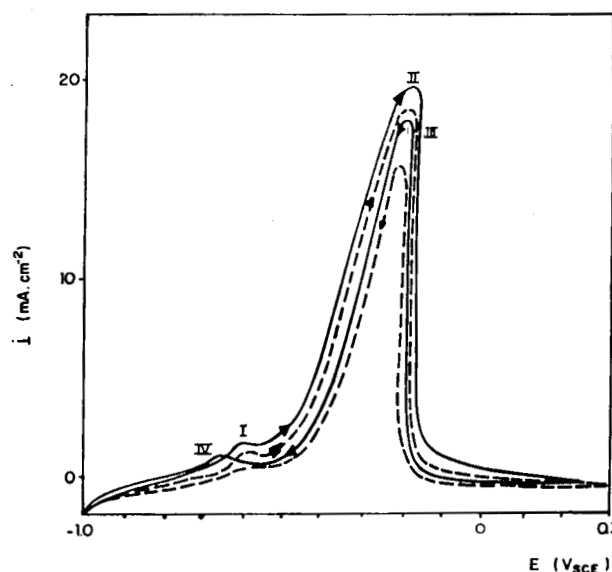

Figure 1. Cyclic voltammogram for Fe run in 1 M Ac (---) and in 1 M Ac + 0.10 M $NaClO_4$ (—), pH = 5, at 10 mV/s, ω = 1000 rpm.
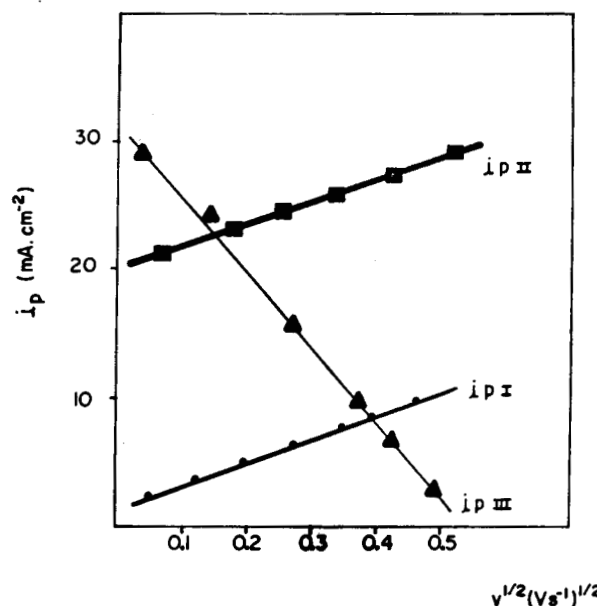

Figure 2. Dependence of the sweep rate (v) in i_{pI}, i_{pII} and i_{pIII} in 1 M Ac + 0.10 M $NaClO_4$, pH = 5 ω = 1000 rpm.

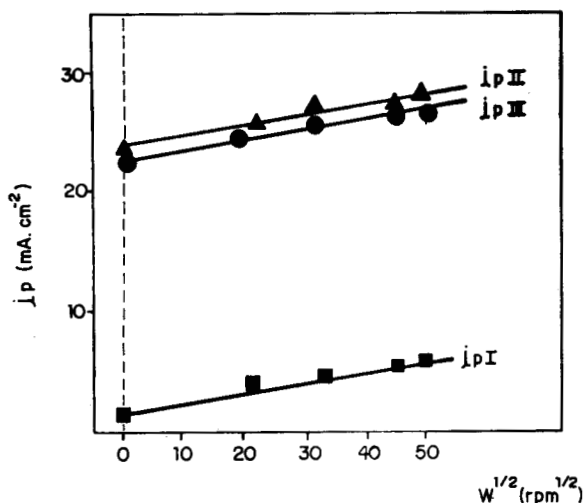**Figure 3.** Influence of the rotation speed ω on i_{pI}, i_{pII} and i_{pIII} in 0.90 M Ac + 0.10 M NaClO$_4$, pH = 5, v = 10 mV/s.

Table 1. Pseudo-reaction orders with respect to perchlorate and Tafel slopes.

$(\partial \log i/\partial \log ClO_4)E1,Ac$	0.2
$(\partial \log i/\partial \log ClO_4)E2,Ac$	≈ 0
b_1(mV/decade)	45
b_2(mV/decade)	90

literature data on acetate solutions[12] shows that with an increase of ω from 0 to 600 rpm the height of peak I changes from *ca.* 1 to 2 mA cm^{-2}, but an increase of ω from 600 to 2500 rpm does not alter the current peak. For peak II the effect of ω is similar[12] to that observed in this paper. This means that the influence of ω on the charge and height of peak I can be related to the presence of perchlorate. This anion tends to stimulate the dissolution process in the early stages of oxidation.

The charge Q corresponding to peaks I and II, at constant ω increases linearly with v^{-1} (Fig. 4). The value of Q extrapolated to v $\rightarrow \infty$ is 0.4 mC/cm^2. For peak II a charge of 10 mC/cm^2 was found. These results suggest that the anodic reactions involve at least two stages. The first one, associated with peak I, implies a dissolution reaction influ-

enced by a mass transport control which is dependent on perchlorate concentration. The small charge in this potential region can be assigned to the formation of a monolayer of Fe(OH)$_2$ species as has been suggested for iron in strongly alkaline media[17] and in slight acid solutions containing sulphate ion[18,19]. The second stage, which is related to the peak II, implies a mass transport control which is coupled to the electrochemical reaction and is mainly influenced by acetate concentration[10,12]. Previous work on acetate solution[9,14] has also found a high charge value for this peak. Bech-Nielsen[9] suggests for this peak a structure equivalent to some 30-50 atomic layers of iron. Several works[9,10,20] have postulated the participation of acetate in the iron dissolution reaction by forming acetate complexes at this potential range.

The pseudo-reaction orders[9,11,21] with respect to perchlorate are determined (Table 1) at a constant sweep rate (0.01 V/s) and in stirred solutions (ω = 1000 rpm) of variable ionic strength at E$_I$ = -0.60 V and E$_{II}$ = -0.40 V. These potentials were chosen since they were within the apparent Tafel regions of both peaks. The result found for perchlorate in the more negative potential zone agrees with the one found by Bech-Nielsen[8] through voltammetric data in slightly acid solution of perchlorate with an acetate concentration of 10^{-4} M. The reaction order in the prepassive zone presented by this author[8] is negative, and in the
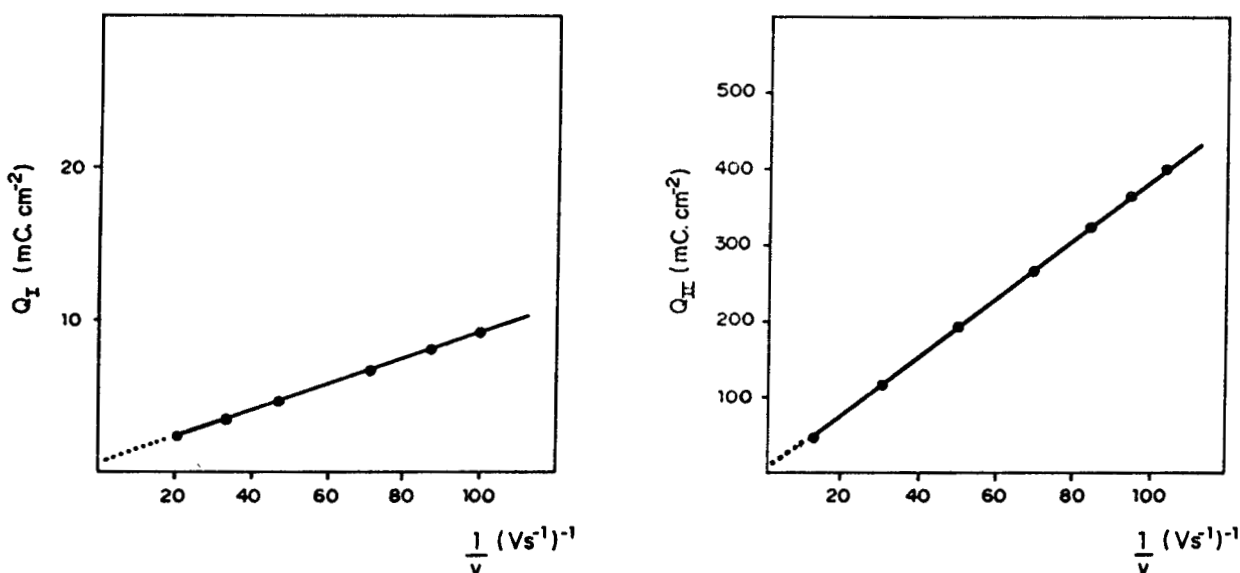
Figure 4. Effect of the sweep rate (v) on the charge Q$_I$ (a) and Q$_{II}$ (b) in 1 M Ac + 0.10 M NaClO$_4$, pH = 5, ω = 1000 rpm.
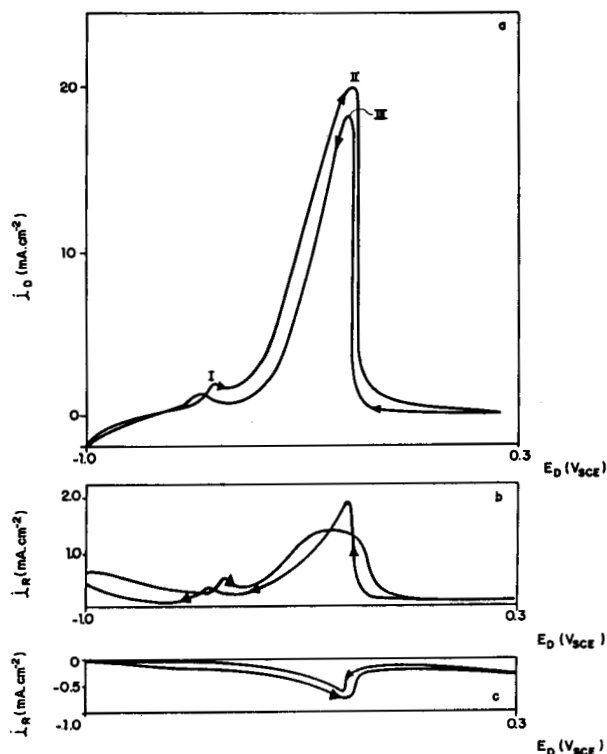
Figure 5. RRDE current *vs.* potential curves run at 10 mV/s, $\omega = 1000$ rpm in 1 M Ac + 0.10 M NaClO$_4$, pH = 5, (a) Fe disk electrode data, (b) Pt ring electrode at $E_r = 0.60$ V, (c) Pt ring electrode at $E_r = -0.60$ V.

Table 2. Effect of perchlorate concentration on the Fe(II) soluble species concentration, calculated from the ring current at $E_r = 0.6$ V, relative to peaks I (C*$_I$) and II (C*$_{II}$).

NaClO$_4$(M)	C*$_I$ (M)	C*$_{II}$(M)
10^{-3}	10^{-7}	10^{-6}
10^{-1}	10^{-6}	10^{-5}

peaks II and III can be observed on the ring. No soluble species have been detected at a more reducing potential (peak I).

From the ring current it is possible to evaluate the concentration of electroactive Fe(II) soluble species coming from the disk[23] for $E_d = E_I$ and E_{II} . Defining I_{dr} as the fraction of the disk current that is detected by the ring, we have the following relation:

$$I_{dr} = I_r / N \ (n_d/n_r) \tag{1}$$

where n_d is the number of electrons involved in the disk reaction and n_r the number of electrons in the ring reactions. Regarding the disk, one may assume:

$$Fe = Fe(II)aq + 2e^- \quad \text{with } n_d = 2$$
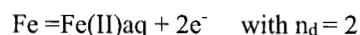
The ring reaction at $E_r = 0.60$ V is:

$$Fe(II)aq = Fe(III) + 1 \ e^- \text{ with } n_r = 1$$
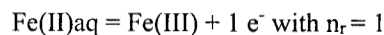
By using the Levich equation[24] one may determine the concentration of the soluble species on the disk surface in quasi-stationary conditions (v = 0.01 V/s):

$$C^* = 0.513^{1/6} I_{dr} r^2 n_d F D^{2/3} \omega^{1/2} \tag{2}$$

where v is the kinematic viscosity (0.01 cm^{2}s^{-1}), D the diffusion coefficient of Fe^{+2} (= 2.10^{-5} cm^2/s), r the disk radius, and ω is the rotation speed. The calculation was made for $E_r = 0.60$ V. Table 2 shows that the concentration (C*) of soluble Fe(II) species increases according to perchlorate concentration. In the potential zone of peak I, according to RRDE experiments and confirmed by thermodynamic[25] data, only Fe(II) species are expected as reaction products. In the potential region of peak II, Fe(II) species can be formed[25] and were detected by the ring. Fe(III) species are also observed by using RRDE at this potential (Fig. 5c). The concentration of the ferrous ion at the disk surface is determined by the solubility product of the ferrous hydroxide[25] (Kps = 8.10^{-16}). Comparing the concentration of Fe(II) species values on the disk (Table 2) with that predicted from the solubility product, it turns out that it is always lower than necessary to precipitate ferrous hydroxide.

On the other hand, the concentration of these soluble species in perchlorate concentration solution is greater than those obtained in acetate solution in the absence of per-

present paper it is approximately zero. The kinetic of the prepassive zone is mainly determined by the presence of acetate[8,9,14] which forms complexes with readily absorbed iron. Takahashi *et al.*[11] point out that the acetate is involved in the passivation process by forming numerous types of acetate-containing species, as well as hydroxil-containing species.

The Tafel slope was determined according to Thirsk and Harrison[22] using an expression for sweep voltammetry. The results for 1 M Ac + 0.10 M NaClO$_4$ are in Table 1. The Tafel constant for iron in 1 M acetate solution, at the same pH is 90 mV/decade and 160 mV/decade[14], respectively. For the solution of 1 M Ac + 0.001 M NaClO$_4$, 60 mV/decade and 80 mV/decade were obtained, respectively. For the second Tafel region the decrease observed is less pronounced. Both Tafel slopes decrease with increasing perchlorate concentration.

The RRDE data (Fig. 5) provide information about the nature and concentration of soluble Fe(II) electroactive species. When the ring potential (E_r) was set at 0.60 V only oxidation occurred on the ring, and for $E_r = -0.60$ V only reduction occurred on the ring.

For $E_r = 0.60$ V (Fig. 5b) the soluble species relative to disk peaks I and II appear on the ring voltammogram, and Fe(II) soluble species are detected as soon as Fe(II) is formed. For $E_r = -0.60$V (Fig. 5c) only the reduction of

chlorate[14]. These facts point out that perchlorate influences the nature of the products formed in the disk reaction.

The results obtained suggest that acetate inhibits the aggressive action of perchlorate. The effect of the acetate may be compared with those observed by Boenhoeffer and Heusler[6] with formic acid in the presence of perchlorate. According to these authors the presence of a strongly absorbing anion inhibits the increase in the dissolution rate caused by the presence of perchlorate. Bech-Nielsen[8] points out that anions like sulphate and perchlorate, non-specifically adsorbed, are able to influence the electrode reactions, except in the case of sulphate the change in the dissolution rate is higher than in the case of perchlorate[2]. According to MacDougall and Bardwell[23] the passivation of iron in sulfate and perchlorate solution would be inefficient because these anions, unlike those derived from borate, do not have inhibitive abilities, nor do their solutions have buffering capacity. Previous works[9,11,14] have suggested that the beneficial action of acetate in Fe passivation is due to its strongly interacting anions which give it an inhibiting capability.

Conclusions

Based on the data obtained, it appears that perchlorate acts in the iron dissolution process by increasing the dissolution rate in the early stages of oxidation, at a more negative potential. This is confirmed by kinetic data on the dependence of the dissolution rate on perchlorate concentration. This can again be related to an increase in the Fe(II) soluble species concentration in the presence of perchlorate. The acetate anion has an inhibiting ability for iron and the passivity can be achieved at more positive potentials.

References

1. D. Geana, A. El Miligy and W.J. Lorenz, *Corros. Sci.* **13**, 505 (1973).
2. G.M. Florianovich, L.A. Sokolova and Y.M. Kolortykin, *Electrochim. Acta* **12**, 879 (1967).
3. M. Keddam, O.M. Mattos and H. Takenouti, *J. Electrochem. Soc.* **128(2)**, 257 (1981).
4. J.O'M. Bockris, D. Drazic and A.R. Despic, *Electrochim. Acta* **4**, 325 (1961).
5. Z.A. Foroulis, *J. Electrochem. Soc.* **113**, 532 (1966).
6. K.F. Bonhoeffer and K.E. Heusler, *Z. Elektrochem.* **61**, 122 (1957).
7. J.G.N. Thomas and J.D. Davies, *Br. Corros. J.* **12**, 108 (1977).
8. G. Bech-Nielsen, *Electrochim. Acta* **19**, 821 (1974).
9. G. Bech-Nielsen, *Electrochim. Acta* **20**, 619 (1975).
10. G. Bech-Nielsen, *Electrochim. Acta* **23**, 425 (1978).
11. K. Takahashi, J.A. Bardwell, B.M. Dougall and M.J. Graham, *Electrochim. Acta* **37**, 477 (1992).
12. D.S. Azambuja, Thesis, Escola de Engenharia, UFRGS, Brazil (1991).
13. J. Albery and S. Bruckenstein, *Trans. Far. Soc.* **62**, 1920 (1966).
14. D.S. Azambuja and I.L. Muller, *Corros. Sci.* (accepted for publication).
15. A. El Miligy, D. Geana and W.J. Lorenz, *Electrochimica Acta* **21**, 273 (1985).
16. P. Lorbeer and W.J. Lorenz, *Electrochimica Acta* **25**, 375 (1980).
17. C.R. Valentini, C.A. Moina, J.R. Vilche, and A.J. Arvia *Corros. Sci.* **25**, 985 (1985).
18. J.O. Zerbino, J.R. Vilche and A.J. Arvia, *J. Appl. Electrochemistry* **11**, 703 (1981).
19. O. Albani, J.O. Zerbino, J.R. Vilche and A.J. Arvia, *Electrochim. Acta* **31**, 1403 (1986).
20. D.S. Azambuja, I.L. Muller, M. Keddam and H. Takenouti, Proceedings, *ISE Meeting*, Cordoba (1992).
21. F. Hilbert, Y. Miyashi, G. Eickorn and W.J. Lorenz, *J. Electrochem. Soc.* **118**, 1919 (1971).
22. H.R. Thirsk and J.A. Harrison, *A Guide to Study of Electrode Kinetics,* (Academic Press, New York, 1972), 174 p.
23. E.B. Castro, J.R. Vilche and A.J. Arvia, *Corros. Sci* **32**, 3 (1991).
24. A.J. Bard and L.R. Faulkner, *Electrochemical Methods. Fundamentals and Applications* (John Wiley & Sons, Inc. New York, 1980), 718 p.
25. M. Pourbaix, *Atlas d'Equilibres Electrochimiques.* (Gauthier-Villars, Paris, 1963) 644 p.