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## On the mechanism initiating bursting oscillatory patterns during the pitting corrosion of a passive rotating iron-disc electrode in halide-containing sulphuric acid solutions

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**Abstract** Bursting current oscillations (trains of current spikes interrupted by a steady-state passive current) were found to occur during the iron anodic polarization in halide-containing sulphuric acid solutions. These oscillations occur at potentials located within a partially passive state of the iron. The partially passive state appears at potentials more positive than the unstable passive-active transition region of the current-potential curve of the Fe|2 M H<sub>2</sub>SO<sub>4</sub> system for halide concentrations approximately ranged between 20 and 50 mM. The bursting oscillations appear after a certain induction period which ranged from minutes to several hours. Experiments were conducted in which an external resistance was connected in series between the ground and the working electrode for the Fe|2 M H<sub>2</sub>SO<sub>4</sub> + 30 mM Br<sup>-</sup> system. The results demonstrate that the appearance of oscillations is closely related to an *IR*-drop mechanism operating during the pitting corrosion of Fe induced by halides. When an appropriate value of the external resistance was imposed in the system the induction period was entirely eliminated. Bursting oscillations appear at once after setting the potential at the desired value. These results provide strong evidence that during the anodic electrodisolution of iron in halide-containing sulphuric acid solutions bursting current oscillations will be induced even though the electrode seems to be in the partially passive state. This is expected to occur after the passage of an induction period during which the system acquires a critical value of the ohmic potential drop.

**Key words** Iron|sulphuric acid + bromides · Pitting corrosion · *IR* drop · Bursting current oscillations · External resistance

### Introduction

Oscillation phenomena are observed in many physical, chemical and biological systems. In chemical systems in particular, interesting dynamical behaviour has been observed in both homogeneous [1] and heterogeneous catalytic [2] reactions as well as in various electrochemical processes [3–6]. Among the various types of interesting oscillation phenomena in electrochemical systems is that of bursting oscillations observed during the pitting corrosion of iron in halide-containing sulphuric acid solutions [7–9]. The bursting oscillatory patterns consist of trains of spikes that are interrupted by periods of passivity. These oscillatory patterns are closely related to the electrode and physicochemical processes underlying iron pitting corrosion, a phenomenon of great technological and economical importance [10–13]. The special significance of bursting oscillation is also related to the behaviour of excitable membranes during activation and a large number of other biophysical systems [14–19].

As has been shown previously, during anodic polarization of a rotating iron-disc electrode at potentials more positive than the active-passive region in halide-containing sulphuric acid solutions, bursting oscillations emerge after the passage of a certain induction period [9]. In other words, within the entire “passive” region in the current-potential (*I-E*) curve of the Fe|2 M H<sub>2</sub>SO<sub>4</sub> + *x* M X<sup>-</sup> system a stable-in-time steady state is never established under rotational conditions of the Fe-disc electrode. The correlation between the surface processes and the surface morphology at the plateau and this partially passive region of the *I-E* curve revealed clues to the mechanism of bursting oscillations. In particular, it was assumed that two competitive processes occur during the induction period; the formation of a

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protective oxide film and the pitting corrosion induced by  $\text{Br}^-$ . After some time, during which repetitive film breakdown and repairing occurs, the dominant process seems to be the corrosion, since the electrodisolution current increases. Thus the appearance of bursting after the induction period was attributed to an increased  $IR$  drop up to a critical value, so that the true potential of the electrode shifts to less positive values. The latter potential values correspond to the beginning of the oscillatory region when the  $I$ - $E$  curve is traced on varying the potential cathodically.

In this work, the bursting oscillations observed within the partially passive region of the  $\text{Fe}|2\text{ M H}_2\text{SO}_4 + 30\text{ mM Br}^-$  system are considered. The purpose of this study is to support the assumption that an  $IR$ -drop mechanism operates during the induction period for bursting oscillations to occur. This  $IR$ -drop mechanism is supported by new experimental results and is discussed in correlation with the Fe pitting corrosion induced by halides. The present experimental results show that there is a correspondence between the type of bursting oscillations obtained after the induction period and the  $I$ - $E$  polarization curve, as this is modified by the  $IR$  drop developed during the induction period.

## Experimental

Voltammetric measurements were carried out using a potentiostatic Wenking POS 73 coupled with a Houston Instrument 2000 X-Y-t recorder.

The disc electrode was the cross section of an iron rod of 3 mm diameter embedded in a 10 mm diameter Teflon cylinder. The electrode surface was in a horizontal position facing downward. The electrochemical cell had three compartments separated by glassy diaphragms. A volume of 150 ml was maintained in the compartment containing the working electrode. A Pt sheet and a standard calomel electrode (SCE) in a saturated KCl solution were used as counter and reference electrodes, respectively. A Luggin-Haber capillary was used between the compartments of the reference and working electrodes. The rotating electrode was from Tacussel (EDI 76987) accompanied by a speed controller (Controvit) giving a maximum speed of 5000 rpm.

Before each experiment, the Fe electrode was polished by a series of wet sandings using different grit sizes (100, 180, 320, 500, 800, 1000, 1200 and superfine grit sandpaper). After polishing, the electrode was cleaned with double-distilled water. Then and prior to the potentiostatic  $I$ - $t$  experiments, the electrode surface was prepared by sweeping forward and backward between  $-0.5$  and  $1.6\text{ V}$  with a potential scan rate  $dE/dt = 10\text{ mV s}^{-1}$ . After this treatment the behaviour of the electrode was reproducible.

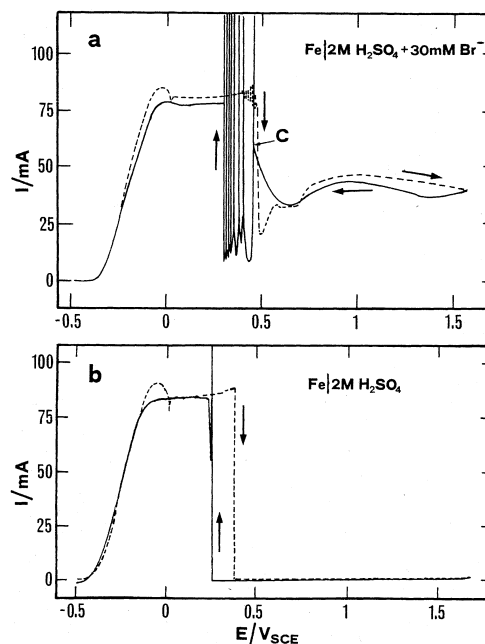
The electrolyte solution was prepared from double-distilled water,  $\text{H}_2\text{SO}_4$  (Merck pro analysis) and  $\text{NaBr}$  (Carlo Erba 99% w/w). The iron, purchased from Goodfellow Metals, was 99.99% w/w in purity. The solution was deaerated with purified nitrogen for 15–20 min before the beginning of each experiment. During the measurements nitrogen was passed over the solution. All measurements were carried out at  $T = 293\text{ K}$ .

Data acquisition was conducted by means of a PC computer interfaced with the electrochemical set-up. An SMM 386, IBM-compatible computer equipped with a 12-channel analogue-to-digital converter PCL-812PG enhanced multi-Lab. Card (Advantech) was coupled with a potentiostatic.

## Results and discussion

A brief survey of the dynamical behaviour of the  $\text{Fe}|2\text{ M H}_2\text{SO}_4 + 30\text{ mM Br}^-$  system

The current-potential ( $I$ - $E$ ) curve for the  $\text{Fe}|2\text{ M H}_2\text{SO}_4$  system in the presence of  $30\text{ mM Br}^-$  is shown in Fig. 1a. This curve was traced by scanning the potential range from  $-0.5$  to  $1.6\text{ V}$  at a rate of  $5\text{ mV s}^{-1}$  in both the anodic and cathodic directions. The shape of the  $I$ - $E$  curve is typical for a rotating Fe-disc electrode at relatively high rotation speeds ( $>2000\text{ rpm}$ ) in the presence of halides ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) within a concentration range 20–50 mM. Of course, the current values obtained at the different potential regions (Tafel, plateau, oscillatory and partially passive) are dependent on the nature of the halide, namely on its ‘‘aggressiveness’’. The corresponding curve in the halide-free  $2\text{ M H}_2\text{SO}_4$  solution is shown in Fig. 1b. A comparison of curves a and b of Fig. 1 indicates that the presence of halides causes noticeable changes in the shape of the  $I$ - $E$  curve, especially in the active-passive transition and the passive region. The presence of halides contributes to an increase of the passive current and the appearance of an oscillatory region instead of the bistability region observed in the absence of halides. At more positive potentials than the oscillatory potential region the current diminishes, giving rise to a partially passive region. These phenomena are intensified on increasing the halide concentration. Beyond a certain concentration of halides the  $I$ - $E$  curve



**Fig. 1a, b**  $I$ - $E$  polarization curves of the (a)  $\text{Fe}|2\text{ M H}_2\text{SO}_4 + 30\text{ mM Br}^-$  system obtained during both the anodic (dashed line) and cathodic (solid line) scans ( $dE/dt = 5\text{ mV s}^{-1}$ ) at  $\omega = 3000\text{ rpm}$  and (b)  $\text{Fe}|2\text{ M H}_2\text{SO}_4$  system under the same conditions as a

of the  $\text{Fe}|\text{2 M H}_2\text{SO}_4 + x \text{ M X}^-$  system shows a continuous plateau region up to 1.6 V [7–9].

Across the active-passive transition of the  $\text{Fe}|\text{2 M H}_2\text{SO}_4$  system, simple periodic relaxation oscillations of the current occur under potentiostatic conditions for  $\omega = 0$  rpm [20], while for  $\omega = 3000$  rpm only bistability, without oscillatory phenomena, is observed (Fig. 1b). On the contrary, in the presence of halides the observed current oscillations are complex, consisting of both periodic and aperiodic or chaotic patterns, depending on the potential of the Fe-disc, rotation speed and the halide concentration. The dominant patterns are the beating and bursting ones, examples of which are illustrated in Fig. 2. The beating oscillations consist of relaxation spikes with small period and occur at the least positive potentials (0.29–0.31 V) of the oscillatory region (Fig. 2a). On the other hand, the bursting oscillations consist of trains of relaxation spikes that are alternated by long periods of steady-state passivity and occur at the most positive potentials (0.35–0.46 V) of the oscillatory region (Fig. 2b). The transition between these two main types of oscillations is associated with aperiodic or chaotic patterns, in agreement with the behaviour observed for the activation potential of excitable membranes and for models of various biophysical systems [18, 19].

However, bursting oscillations appear also in the partially passive region ( $E \geq 0.46$  V) of the  $I$ - $E$  curve of Fig. 1a, although this region seems to correspond to a stable steady state at  $dE/dt = 5 \text{ mV s}^{-1}$ . These bursting oscillations appear after a certain induction period. This behaviour, in principle, indicates that the action of the

“aggressive” halides on the Fe passive oxide film is a slow process, and, in the time scale of tracing the  $I$ - $E$  curve, these oscillations are not observed.

Bursting oscillations occurring after a certain induction period

A potentiostatic  $I$ - $t$  transient curve obtained for the  $\text{Fe}|\text{2 M H}_2\text{SO}_4 + 30 \text{ mM Br}^-$  system after applying the desired potential ( $E \geq 0.46$  V) from open-circuit conditions shows at first a current drop to a small value that corresponds to a passive state in the absence of  $\text{Br}^-$ . Then a couple of current oscillations occur and the current reaches a value that corresponds to the passive state in the presence of  $\text{Br}^-$  at  $\omega = 3000$  rpm. Microscopic observations of the Fe-disc surface during the rest of the induction period show that pits are formed and repeated film breakdown and repairing processes take place [9]. The net result of these competitive processes is the increase of the electrodisolution rate up to a critical value required for bursts to occur. This current value corresponds to the point C of the  $I$ - $E$  curve of the system (Fig. 1a). The existence of an induction period for  $E \geq 0.46$  V is attributed to the fact that the passive film at more positive potentials is more resistant to the  $\text{Br}^-$  attack in contrast to the film at less positive potentials where oscillations appear without an induction period.

Several types of bursting oscillations that appear after a certain induction period are illustrated in Fig. 3 at various applied potentials. As can be seen in this figure, both the number of spikes and the amplitude of the burst decrease on increasing the potential. This effect is indicative of the operating mechanism for bursting to occur.

Because of the pitting induced by bromides, an  $IR$ -drop mechanism was previously assumed to operate during the induction period, leading to the development of a critical value of the  $IR$  term [9]. At this critical value of the  $IR$  term, a shift of the true electrode potential to less positive values (point C in Fig. 1a) occurs. The applied  $E$  and the true  $V$  electrode potential are correlated to the  $IR$  drop through the relationship  $E = V + IR$ , where  $I$  is the total current flowing through the electrochemical cell. The shift of the potential  $V$  to less positive values, towards the unstable active-passive transition region, was indicated by comparing the surface morphology at the end of the induction period with that observed across the active-passive transition [9]. If an  $IR$  drop is developed during induction period, the  $I$ - $E$  curve of the system should also be affected by this  $IR$  drop. Thus the oscillatory potential region should be shifted by the term  $IR$ . As will be shown below, this mechanism certainly seems to be valid. Indeed, when the  $IR$  drop becomes equal to a critical value  $(IR)_{\text{crit}}$ , through an external resistance, the shape of the  $I$ - $E$  curve is such that the electrode potential corresponds to the point C (Fig. 1a) which is the upper  $E$ -boundary of the oscillatory region.

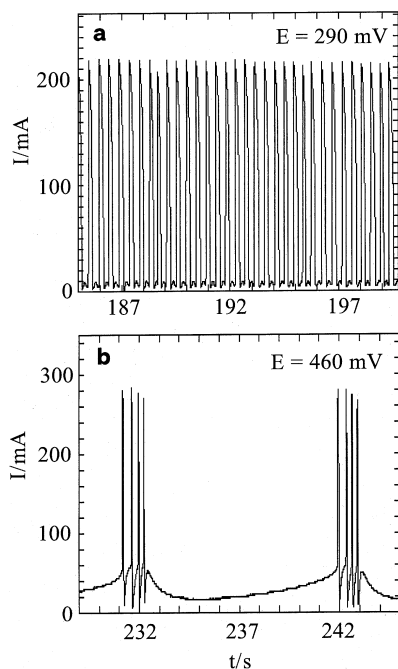
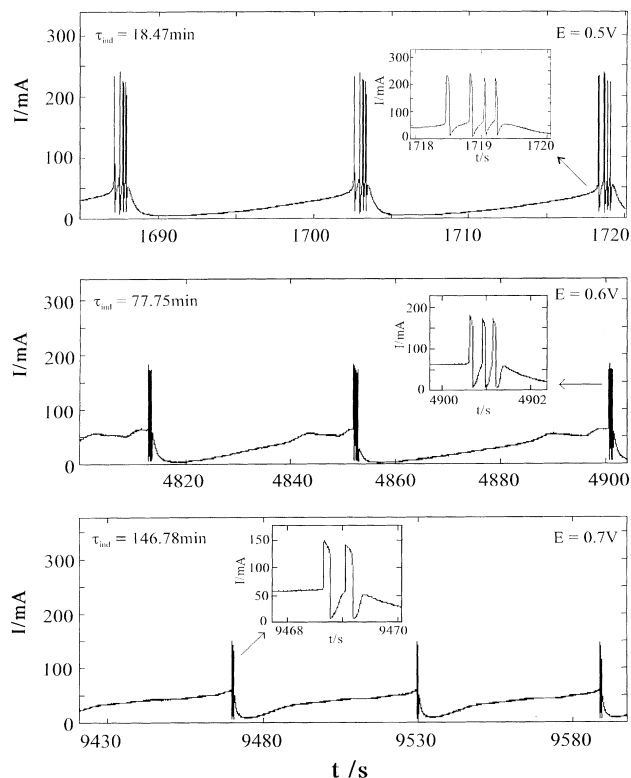


Fig. 2a, b Examples of beating and bursting oscillatory patterns occurring at potentials located within the oscillatory region observed in the  $I$ - $E$  curve of Fig. 1a

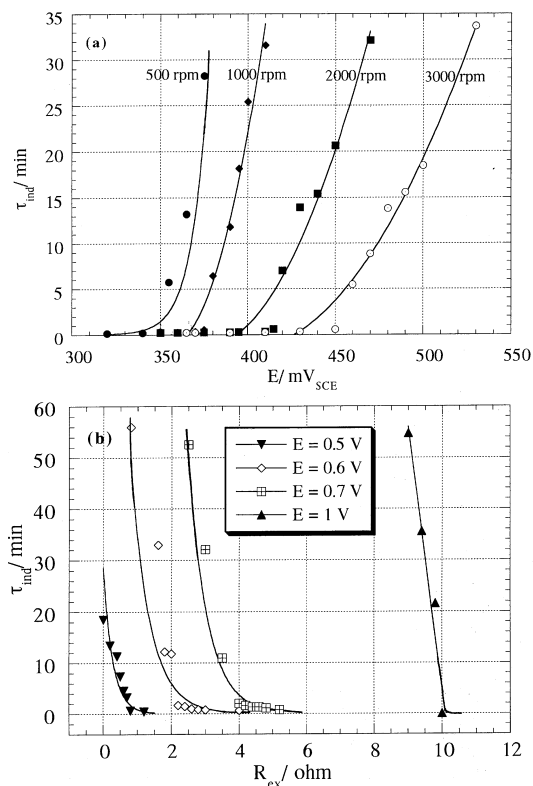


**Fig. 3** Bursting oscillatory patterns occurring after a certain induction period at  $E \geq 0.46$  V. The number of spikes and the amplitude of bursting oscillations decrease as the applied potential increases

The effect of a series external resistance connected between the ground and the working electrode

In order to show the development of  $IR = (IR)_{\text{crit}}$  during the induction period and to compare the  $I-E$  curves which correspond to the  $(IR)_{\text{crit}}$ , we use an external resistance,  $R_{\text{ex}}$ , which is connected in series between the ground and the working electrode. If the assumed mechanism is valid, then by adding an appropriate value of  $R_{\text{ex}}$ , the elimination of the induction period should be possible. This is expected since the required value of the  $IR$  for the bursting oscillations to appear is now imposed externally.

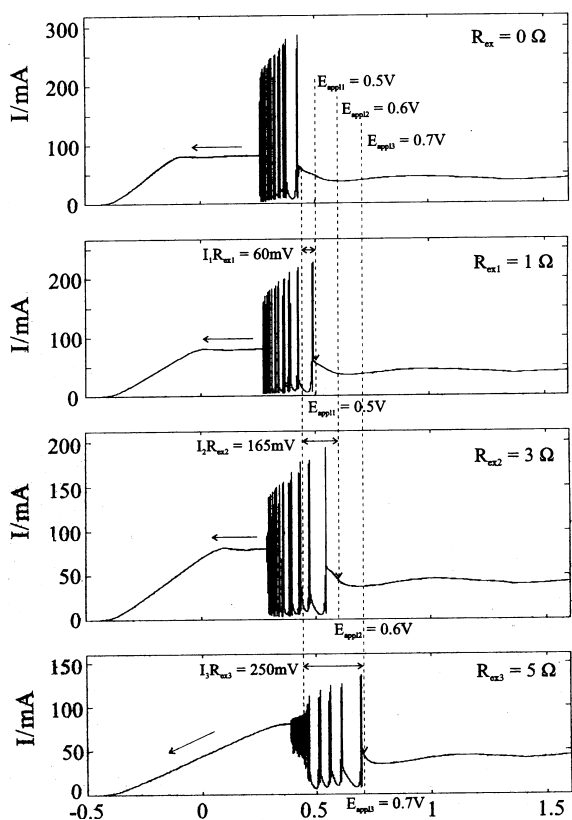
The induction period for  $R_{\text{ex}} = 0$  increases on increasing the applied potential, as illustrated in Fig. 4a for various rotation speeds of the Fe-disc electrode. Thus, for a constant value of the rotation speed, at every applied potential a different  $R_{\text{ex}}$  will be required for the elimination of the induction period. The results of the experiments in the presence of the  $R_{\text{ex}}$  show that indeed by a gradual increase of the  $R_{\text{ex}}$  the induction period decreases gradually, as seen in the plot of Fig. 4b. At a certain critical value,  $(R_{\text{ex}})_{\text{crit}}$ , the induction period is eliminated. Then the system gives rise to a sustained oscillatory behaviour without an induction period. The bursting oscillations occur immediately from the passive state, into which the electrode goes after applying a potential value higher than 0.46 V.



**Fig. 4a, b** Dependence of the induction period ( $\tau_{\text{ind}}$ ) for oscillations to occur for the  $\text{Fe}|2\text{ M H}_2\text{SO}_4 + 30\text{ mM Br}^-$  system on  $E$  at various rotation speeds,  $\omega$  (a) and on  $R_{\text{ex}}$  at various applied potentials for  $\omega = 3000$  rpm (b)

This effect can be explained by considering the  $I-E$  curve for  $R_{\text{ex}} = 0$  in comparison with the  $I-E$  curves obtained at the critical values of  $R_{\text{ex}}$  for which the induction period is eliminated (Fig. 5). As expected, the increase of the ohmic potential drop due to the  $R_{\text{ex}}$  causes changes in the polarization curve. In particular, from the curves of Fig. 5 it is seen that in the presence of the  $(R_{\text{ex}})_{\text{crit}}$  the applied potential is located close to the upper  $E$ -boundary of the oscillatory region observed in the  $I-E$  curve. The shift of the oscillatory region (equal to  $IR_{\text{ex}}$ ) corresponds to the  $IR$  drop which the system develops during the induction period (for  $R_{\text{ex}} = 0$ ) in order for bursting oscillations to occur. The current values  $I$  for the calculation of the  $IR_{\text{ex}}$  drop (shown in Fig. 5) can be obtained from the  $I-E$  curve for each  $R_{\text{ex}}$ , as indicated by dashed arrows in Fig. 5. These current values can also be taken from the  $I-t$  transients prior the burst. The various values of the  $IR_{\text{ex}}$  term represent the potential distance of the various applied potentials from the oscillatory region when  $R_{\text{ex}} = 0$ . At the same time these  $IR_{\text{ex}}$  values represent the potential shift of the  $I-E$  curve in order for the upper  $E$ -boundary of the oscillatory region to correspond to the applied potential at each  $R_{\text{ex}}$ .

The main features of the bursting oscillations occurring at  $E = 0.5, 0.6$  and  $0.7$  V at certain values of  $R_{\text{ex}}$  are presented in Table 1. By comparing the oscillation



**Fig. 5**  $I$ - $E$  polarization curves of the Fe/2 M  $\text{H}_2\text{SO}_4$  + 30 mM  $\text{Br}^-$  system during the cathodic potential scan ( $dE/dt = 5 \text{ mV s}^{-1}$ ) at  $\omega = 3000 \text{ rpm}$  for the values of  $R_{\text{ex}}$  necessary for the elimination of the induction period in comparison with the corresponding curve for  $R_{\text{ex}} = 0$ . The values of  $I R_{\text{ex}}$  indicated in the curves correspond to the ohmic potential drop developed during the induction period for oscillations to occur when  $R_{\text{ex}} = 0$

amplitude ( $A$ ) taken from the time series and the maximum oscillating current ( $I_{\text{max}}$ ) taken from the  $I$ - $E$  polarization curves an interesting result is obtained. For  $R_{\text{ex}} = 0$ , the above two quantities seem to diverge, in particular for the more positive potentials. On increasing

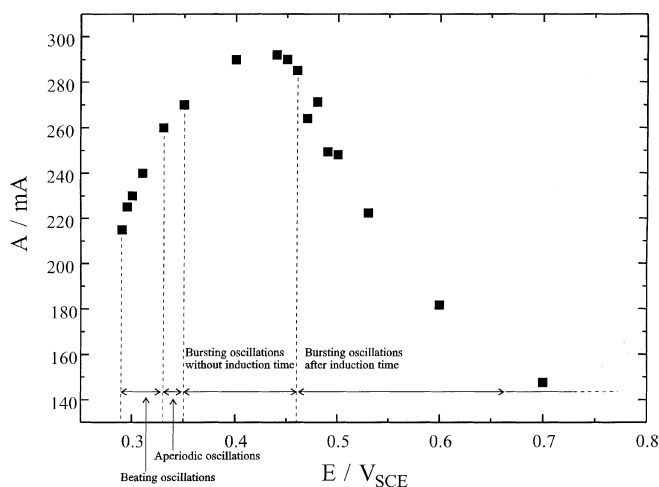
**Table 1** Effect of the value of  $R_{\text{ex}}$  on the main features of the bursting oscillations: the induction period ( $\tau_{\text{ind}}$ ), the amplitude ( $A$ ), the maximum current obtained from the corresponding  $I$ - $E$  curve ( $I_{\text{max}}$ ), the oscillation period ( $T$ ) and the number of spikes

$E_{\text{appl}}/\text{V}$	$R_{\text{ex}}/\Omega$	$\tau_{\text{ind}}/\text{s}$	$A/\text{mA}$	$I_{\text{max}}/\text{mA}$	$T/\text{s}$	Number of spikes
0.5	0	1108	240	248	15	4
	0.6	274	231	236	14	4
	1.0	27	230	225	15	5
	2.0	25	186	193	14	6
0.6	0	3645	184	248	40	3
	2.0	708	187	193	48	3
	3.0	46	169	162	16	4
	4.0	36	144	152	18	5
0.7	0	8807	146	248	58	2
	3.0	1923	150	162	55	2
	5.0	49	140	138	22	4
	5.6	43	129		20	5

the  $R_{\text{ex}}$  towards the  $(R_{\text{ex}})_{\text{crit}}$  [ $(R_{\text{ex}})_{\text{crit}} = 1, 3$  and  $5 \Omega$  for  $E_{\text{appl}} = 0.5, 0.6$  and  $0.7 \text{ V}$ , respectively], the  $A$  and  $I_{\text{max}}$  values converge. It is noted that at these critical values of  $R_{\text{ex}}$  the induction period of oscillations is eliminated (or better it becomes of the same order as the oscillation period). For the whole range of  $R_{\text{ex}}$  up to  $(R_{\text{ex}})_{\text{crit}}$  the values of  $A$  seems to correspond to the  $I_{\text{max}}$  taken from the  $I$ - $E$  polarization curve traced at the above-critical values of  $R_{\text{ex}}$ . In addition, the period and the number of spikes of the bursting oscillations remain constant up to the critical values of  $R_{\text{ex}}$ . However, when  $R_{\text{ex}} \geq (R_{\text{ex}})_{\text{crit}}$ , for each of the applied potentials, the period decreases whereas the number of spikes increases. This behaviour is closely related to the  $I$ - $E$  curve at the same  $R_{\text{ex}}$ . That is, it seems that the electrode potential shifts into the oscillatory region of the  $I$ - $E$  curves (Fig. 5) and not only up to the upper  $E$ -boundary (point C of Fig. 1a).

It is now seen from the foregoing results that during the induction period, observed for  $R_{\text{ex}} = 0$  at each applied potential, the system develops internally an ohmic potential drop giving rise to bursting patterns. These patterns are identical as far as  $R_{\text{ex}} < (R_{\text{ex}})_{\text{crit}}$ . For  $0 \leq R_{\text{ex}} < (R_{\text{ex}})_{\text{crit}}$  a complementary value of the ohmic potential drop is developed in order for the  $(IR)_{\text{crit}}$  to be attained, and for this reason the induction period is shorter than that for  $R_{\text{ex}} = 0$ . The mechanism responsible for the development of the critical ohmic potential drop is presumably the pitting corrosion of Fe due to the aggressive action of  $\text{Br}^-$ . As far as an induction period is observed, a critical  $IR$  drop is developed internally through repeated breakdown-repairing processes. This process results in a modified  $I$ - $E$  curve where the electrode potential corresponds to the upper  $E$ -boundary (point C in Fig. 1a) of the oscillatory region but not to more cathodic values. Only if the externally imposed resistance is equal to or larger than the critical  $R_{\text{ex}}$  can the potential shift into the oscillatory region, resulting in an increase of the number of spikes as can be seen in Table 1.

Further support for the build-up of the  $IR$  drop during the induction period and its effect on the  $I$ - $E$  polarization curve comes from the relationships between the oscillation amplitude and the applied potential for  $R_{\text{ex}} = 0$  (Fig. 6). As seen in Fig. 6, for all the potentials at which oscillations occur without induction period the amplitude increases on increasing the potential in accordance with the active Tafel region. However, for the potentials at which oscillations occur with an induction period, a decrease of the amplitude is observed on increasing  $E$ . These values of the amplitude are not consistent with the active current values for  $R_{\text{ex}} = 0$ , although microscopic observations at the maximum of the spikes do show active surfaces. Therefore these diminished values of the oscillation amplitude should correspond to different  $I$ - $E$  polarization curves (Fig. 5) due to the existence of the  $IR$  drop. Finally, this conclusion is also in agreement with the decrease in the number of spikes observed on increasing the potential for  $R_{\text{ex}} = 0$  (Fig. 3, Table 1).



**Fig. 6** Effect of the applied potential (for  $R_{ex} = 0$ ) on the amplitude of the current oscillations occurring within both the oscillatory and the passive-like regions for the Fe|2 M  $H_2SO_4 + 30$  mM  $Br^-$  system at  $\omega = 3000$  rpm

### Bursting oscillation mechanism and pitting corrosion

Potentiostatic anodic current transients occurring during the induction period and oscillatory patterns (Fig. 3) observed for the Fe|2 M  $H_2SO_4 + 30$  mM  $Br^-$  system are linked to the nucleation and repassivation of pits on the iron surface due to the presence of the aggressive halides. Contrary to the well-known current fluctuations of the order of pA or  $\mu A$  which originate from random events (film breakdown and repassivation), these oscillatory phenomena are quite periodic and fully reproducible.

The initiation of pitting must include the development of a concentrated halide solution at the site of the pit growth. The dissolution rate and repassivation of the pit are affected by the concentration of dissolution products within pits. The metal dissolves at a high rate in the pit but only at a very low rate on the outer passive surface. Because of this separation (pitting site and outer passive surface), there is a potential drop which is the product of the dissolution current flowing out of the pits and the resistance of the electrolyte path to current flow ( $IR = E_{surf} - E_{pit}$ ). Therefore an  $IR$ -drop mechanism operates during pitting corrosion which shifts the electrode potential to the active region of the  $I$ - $E$  curve of the metal/electrolyte system, provided that there is an active peak in the  $I$ - $E$  curve of the cavity electrolyte. This mechanism has been supported both experimentally and theoretically by Pickering et al. [21–24] for iron, stainless steel and nickel electrodisolution in halide-containing acidic solutions.

The experimental results presented in this study are also consistent with an  $IR$ -drop mechanism. In the present case, the measured current expresses the overall rate of the pitting corrosion processes and not of the processes regarding only one pit, since the local current densities are assumed and averaged in the Fe disc surface. In addition, it should be noted that, because of the

existence of an unstable region in the  $I$ - $E$  curve of the Fe|2 M  $H_2SO_4 + 30$  mM  $Br^-$  system, the  $IR$  drop causes a shift of the potential into this unstable region. In the case of the metal/electrolyte systems which have a  $I$ - $E$  curve without instabilities, the potential shifts into the active region. However, the maximum oscillatory current does correspond to the current of the active region, since the current oscillates between values that correspond to totally active and passive states. Thus, when the  $I$ - $E$  polarization curve of the metal/electrolyte system has a region of a negative impedance and a sufficiently large  $IR$  drop is promoted through repeated breakdown-repairing processes due to the halide action, the potential shifts and is trapped into the unstable region, giving rise to bursting oscillations. The same result is also obtained if the necessary  $IR$  drop is imposed externally in the electrochemical cell through a variable series resistance.

For bursting oscillations to occur, one of the two states in the bistability region is a rapid oscillation state (left branch) and the other is the passive steady state (right branch). Thus trajectories visit both the left branch (periodic current spiking) and the lower flat right portion (passive current) (Fig. 1a). This results in the appearance of a periodic burst, in contrast to the monoperiodic relaxation oscillations where both branches correspond to steady states [19]. The bursting behaviour observed for the Fe|2 M  $H_2SO_4 + 30$  mM  $Br^-$  system is quite similar to the response of the Fe|2 M  $H_2SO_4$  system when a sinusoidal component was added to the applied potential such that during each period of the perturbed potential the system entered once into the passive region (positive component, sinewave upwards) and then into the plateau region (negative component, sinewave downwards) [25].

### Conclusion

By connecting an external resistance in series between the ground and the rotating Fe-disc electrode, an elimination of the induction period required for bursting oscillations to occur is accomplished. The elimination takes place at different values of the  $R_{ex}$ , depending on the applied potential  $E$  ( $E \geq 0.46$  V). This effect supports quite well an  $IR$ -drop mechanism operating during pitting corrosion of the passive Fe-disc electrode in the bromide-containing 2 M  $H_2SO_4$  solution, hence substantiating the generally accepted principle that relatively large  $IR$  drops are necessary for localized corrosion in iron to occur. The net result of repeated film breakdown-repairing processes during the induction period is the build-up of a critical value of the ohmic potential drop, necessary for bursting oscillations to occur. This ohmic potential drop results in a shift of the oscillatory region due to the modification of the  $I$ - $E$  curve. This modification is equivalent to a shift of the system potential towards the unstable oscillatory state.

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**References**

1. Zhabotinsky AM (1991) *Chaos* 1: 379
2. Cray P, Scott SK (1990) *Chemical oscillations and instabilities*. Oxford University Press, Oxford
3. Wojtowicz J (1972) In: Bockris JO'M, Conway BE (eds) *Modern aspects of electrochemistry*, vol 8. Plenum, New York, pp 47–120
4. Franck UF (1978) *Angew Chem* 17: 1
5. Hudson JL, Tsotsis TT (1994) *Chem Eng Sci* 49: 1493
6. Koper MTM (1996) In: Prigogine I, Rice SA (eds) *Advances in chemical physics*, vol 92. Wiley, New York, pp 161–298
7. Sazou D, Pagitsas M, Georgolios C (1992) *Electrochim Acta* 37: 2067
8. Sazou D, Pagitsas M, Georgolios C (1993) *Electrochim Acta* 38: 2321
9. Sazou D, Georgolios C (1996) *Electrochim Acta* 41: 147
10. Kaesche H (1985) *Metallic corrosion*. National Association of Corrosion, Houston
11. Lorenz WJ, Heusler KE (1987) In: Mansfeld F (ed) *Corrosion mechanisms*. Dekker, New York, pp 1–83
12. Sharland SM (1987) *Corros Sci* 27: 289
13. Böhni H (1987) In: Mansfeld F (ed) *Corrosion mechanisms*. Dekker, New York, pp 285–327
14. Chay TR, Lee YS (1990) *Annals NY Acad Sci* 591: 328
15. Holden AV, Lab MJ (1990) *Annals NY Acad Sci* 591: 302
16. Pinsker HM (1977) *J Neurophysiol* 40: 544
17. Honerkamp J, Mutschler G, Seitz R (1985) *Bull Math Biol* 47: 1
18. Chay TR, Rinzel J (1985) *Biophys J* 47: 357
19. Rinzel J (1987) *Lect Notes Biomath* 71: 267
20. Sazou D, Karantonis A, Pagitsas M (1993) *Int J Bifurcation & Chaos* 3: 981
21. Pickering HW, Frankenthal R (1972) *J Electrochem Soc* 119: 1297
22. Frankenthal R, Pickering HW (1972) *J Electrochem Soc* 119: 1304
23. Xu Y, Wang M, Pickering HW (1993) *J Electrochem Soc* 140: 3448
24. Wang M, Pickering HW, Xu Y (1995) *J Electrochem Soc* 142: 2986
25. Karantonis A, Pagitsas M, Sazou D (1993) *Chaos* 3: 243