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Short communication

Current oscillations during electrodissolution of iron in perchloric acid solutions

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1. Introduction

Numerous examples of current or potential oscillations during electrodissolution [1–15] and deposition of metals [16–19] have been reported. The understanding of electrochemical oscillation mechanism offers insights into the fundamental processes involved in passivation, breakdown and repassivation of metals in corrosive media. The most extensively studied electrochemical oscillator is the Fe/H_2SO_4 system. There are two distinct current oscillations in this system. One appears at the beginning of the limiting current plateau of polarization curve and the other appears at the end of the plateau before the transition to passivity, close to the Flade potential. The Flade potential is the potential at which transition occurs for passivation by an iron oxide film, and is found to have a strong dependence on pH [20]

$$V_F = 0.58 - 0.058\,\mathrm{pH}\ (V \text{ vs NHE})$$

Franck and FitzHugh attributed periodic behaviour to the spontaneous formation and dissolution of a passivating iron oxide film [21]. Wang and coworkers studied the anodic behaviour of Fe in 0.5 mol dm^{-3} H_2SO_4 using holographic microphotography [22]. They considered that the temporal formation of $Fe(OH)_2$ and Fe_3O_4 is the cause of current oscillations. With the dissolution of Fe, the Fe^{2+} accumulates at the interface causing a decrease in H^+ due to their migration away from the electrode vicinity. The local increase in pH leads to a temporal precipitation of $Fe(OH)_2$ and Fe_3O_4, as well as blocking of the Fe surface. The backward diffusion of H^+ from the bulk to the interface causes dissolution of the $Fe(OH)_2$ and Fe_3O_4 and reactivation of the electrode. Sazou [23] reported that the current oscillatory phenomena of Fe in $4\ \mathrm{mol\,dm^{-3}} \leqslant C_{H_3PO_4} \leqslant 10\ \mathrm{mol\,dm^{-3}}$ occur across the transition from the limiting current to the passive state. Beck [24] studied the formation of salt films during passivation of Fe in 5 mol dm^{-3} $HClO_4$. He attributed the oscillatory phenomena, observed during passivation of iron, to formation and dissolution of salt films coupled to changes in pH under the salt films, due to mass transport. Details on the current oscillation of the $Fe/HClO_4$ system were not reported.

In this paper we present experimental results of current oscillations of the Fe electrode in $HClO_4$ solution. The effect of $HClO_4$ concentration, temperature and imposed anode potential was investigated. Particularly, in order to investigate the electrochemical oscillation mechanism, an injection method was used to change the local pH at the Fe/electrolyte interface, to create environments that favor or inhibit the occurrence and progress of current oscillations.

2. Experimental details

Electrochemical experiments were carried out in a three-electrode system. The electrode potential was controlled by a PAR M173 potentiostat and a PAR M175 function generator. The response current was monitored by a YEW 3086 X-Y-t recorder. The working electrode (dia. 0.5 mm) was prepared from an iron rod of 99.99% purity (Johnson Matthey Chemicals). The electrode was carefully sealed with epoxy resin in a glass tube, leaving only the working surface exposed to the solution. The counter electrode was a Pt sheet, and a saturated calomel electrode (SCE) was used as a reference, with its Luggin capillary probe located at 2 mm below the working electrode (all electrical potentials are reported with reference to the SCE). The electrolytes were prepared from analytical grade reagents and triply distilled water. The working electrode was polished using 600 and 1200 grade emery paper and washed with water, triply distilled water prior to each experiment. The temperature was controlled using a superthermostat.

3. Results and discussion

3.1. *Anodic i/E polarization curves in various $HClO_4$ concentrations*

Figure 1 shows polarization curves for the $Fe/HClO_4$ system with various $HClO_4$ concentrations. The temperature was 25 °C, and the potential scan rate 1 mV s^{-1} which implies almost steady-state conditions rather than fully steady-state conditions. Current oscillations take place over a wide $HClO_4$ concentration range ($0.07\ \mathrm{mol\,dm^{-3}} \leqslant C_{HClO_4} \leqslant 7\ \mathrm{mol\,dm^{-3}}$). These i/E curves can be divided into two types according to the $HClO_4$ concentration. The first type is in concentrated $HClO_4$ solutions ($3.5\ \mathrm{mol\,dm^{-3}} \leqslant C_{HClO_4} \leqslant 7\ \mathrm{mol\,dm^{-3}}$), where by scanning the potential from −500 to 500 mV, the current achieves a maximum point first and then with a decrease the current plateau is continued over a wide potential range. Finally, the current becomes abruptly near zero and the iron electrode enters a passive state. The current oscillations take place within a certain potential range where the iron electrode transits from the prepassive to passive state. The second type is in the range $0.07\ \mathrm{mol\,dm^{-3}} \leqslant C_{HClO_4} \leqslant 2.8\ \mathrm{mol\,dm^{-3}}$. The key feature is that there is a decrease in current between the plateau and the current oscillations. The effect of $HClO_4$ concentration on the current oscillations is summarized in Table 1. There is a shift of the lower potential-boundaries of the oscillatory region, E_{low}, in the positive potential direction on increasing C_{HClO_4}. But the maximum oscillation amplitude ΔI_{max} and average oscillation current I_{av} have maximum values at $C_{HClO_4} = 4.2\ \mathrm{mol\,dm^{-3}}$.

When $C_{HClO_4} \leqslant 0.035\ \mathrm{mol\,dm^{-3}}$, the rate of Fe^{2+} production is very slow. The migration of H^+ is also slowed down. The formation of $Fe(OH)_2$ and Fe_3O_4 films is difficult because the pH at the Fe/electrolyte interface is not high enough. Once formed the Fe_3O_4 film is also difficult to dissolved owing to the slow backward diffusion of H^+. Thus no current oscillations are observed. It can be seen that, in order to induce the current oscillations, the local pH at the Fe/electrolyte interface must be very different to that in the electrolyte bulk. That is, the local pH must be high enough to form $Fe(OH)_2$ and Fe_3O_4 films. But the bulk pH must be low enough to dissolve the $Fe(OH)_2$ and Fe_3O_4 films.

Table 1. Summary of the effect of the $HClO_4$ concentration on current oscillation

C_{HClO_4} mol dm^{-3}	Potential-boundaries of oscillatory region/mV	Maximum oscillation amplitude ΔI_{osc}/A cm^{-2}	Average current density I_{av} /A cm^{-2}
8.0	no oscillation		
7.0	358–364	0.0967	0.122
6.3	360–366	0.148	0.151
6.0	320–349	1.68	0.765
4.9	310–373	2.86	1.48
4.2	285–330	5.10	2.65
3.5	273–297	4.03	2.14
2.8	170–240	3.27	1.53
2.1	110–180	2.50	1.38
1.4	90–140	1.68	1.02
0.70	65–117	0.910	0.434
0.35	40–85	0.420	0.281
0.070	39–85	0.142	0.0765
0.035	no oscillation		

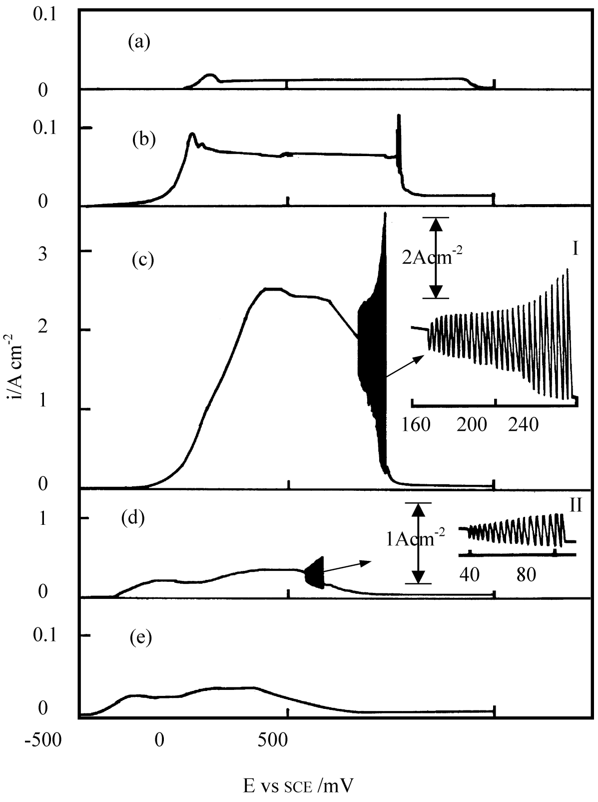

Fig. 1. Effect of the perchloric acid concentration on the polarization behaviour of the $Fe/HClO_4$ system. C_{HClO_4}: (a) 8, (b) 6.3, (c) 2.8, (d) 0.35 and (e) 0.035 mol dm^{-3}.

3.2. *Effects of temperature and the imposed anode potential*

A set of experiments was carried out, where the temperature was increased gradually from 0 °C to 50 °C. The anode potential was swept from −500 to 500 mV, the scan rate was 1 mV s^{-1} and the electrolyte was 0.7 mol dm^{-3} $HClO_4$. At 0 °C, no current oscillation was observed. As the temperature reaches 5 °C, current oscillations are observed after the current reaches the maximum point and begins to drop. The shapes of the i/E curves are similar over the whole experimental temperature range with 0.7 mol dm^{-3} $HClO_4$. This means that the concentration of $HClO_4$ is a critical factor affecting the curve shapes. Pertinent measurements of the oscillation characteristics are summarized in Table 2. With temperature increase from 5 °C to 50 °C, E_{low} shifts in the positive direction, the oscillation-potential window is widened and the maximum oscillation amplitude also becomes larger. With increase in temperature, the electrodissolution of Fe is accelerated, and the Fe^{2+} concentration near the electrode increases. The migration of H^+ is enhanced and the pH at the Fe/electrolyte interface becomes higher. Thus the $Fe(OH)_2$ and Fe_3O_4 films can be formed more easily. Moreover, the solubility of

Table 2. Summary of the effect of temperature on anodic current oscillation

Temperature /°C	Potential-boundaries of oscillatory region ΔE_{osc}/mV	Maximum oscillation amplitude ΔI_{osc}/A cm^{-2}
0	no oscillation	
5	60–85	0.41
10	65–102	0.56
20	62–115	0.81
25	65–117	0.96
30	78–155	1.47
40	85–170	1.63
50	87–183	2.29

Table 3. Summary of the effect of the imposed anode potential on current oscillation of Fe/0.7 mol dm^{-3} $HClO_4$ system

Anode potential, *E* /mV vs SCE	Oscillation period/s	Maximum oscillation amplitude ΔI_{osc}/A cm^{-2}
70	no oscillation	
80	0.65	0.71
90	0.77	0.91
100	0.77	1.22
110	1.02	1.27
120	1.03	1.33
130	irregular oscillation	1.43
140	no oscillation	

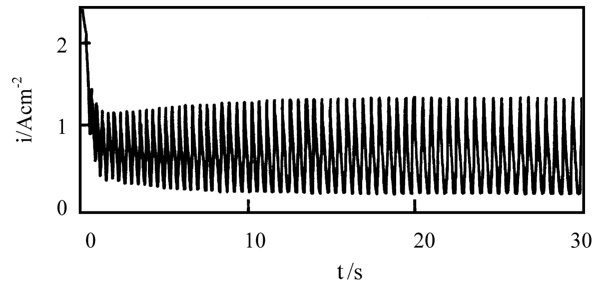

Fig. 2. *i*/*t* transients of the Fe/0.7 mol dm^{-3} $HClO_4$ system as $E = 120$ mV.

$Fe(OH)_2$ is reduced with the increase in temperature; this also favors the formation of $Fe(OH)_2$ film. So ΔE_{osc} becomes increasingly wide and ΔI_{osc} becomes larger.

Figure 2 shows the current transients of the Fe electrode in 0.7 mol dm^{-3} $HClO_4$ solution when the potential was changed suddenly from the open-circuit value to 120 mV. The temperature was 25 °C. Detail of the oscillation parameters at various potentials is summarized in Table 3. The minimum current values of the oscillations are nonzero which differs dramatically from the behaviour in the Fe/0.5 mol dm^{-3} H_2SO_4 system, in which the minimum current values of the oscillations are near zero [22], associated with a complete passivation. This nonzero current obtained from the *i*/*t* curve corresponds to the nonzero minimum current of the oscillations in the *i*/*E* curve. This indicates that the electrode is not in the completely passivation state.

3.3. *Explanation of the current oscillation mechanism in 0.7 mol dm^{-3} $HClO_4$*

If the current oscillations could be induced or prevented by changing the pH artificially, the current oscillation mechanism based on the temporal formation of $Fe(OH)_2$ and Fe_3O_4 films would be supported. In 0.7 mol dm^{-3} $HClO_4$ solution, when the Fe electrode was potentiostatic polarized at 70 mV, no current oscillations were observed. However, when 0.2 ml 0.1 mol dm^{-3} NaOH solution was injecting through a needle (int. dia. 0.2 mm) at 2 mm below the Fe electrode, the current decreased suddenly, indicating thickening of the $Fe(OH)_2$ film and formation of Fe_3O_4. As soon as the injecting was stopped, current oscillations occurred (Figure 3). Under a given potential, the condition for current oscillations is that there must be a suitable pH value at the interface of Fe/electrolyte for the formation of $Fe(OH)_2$ and Fe_3O_4 films. If the pH value cannot be achieved only by migration of H^+ caused by the accumulation of Fe^{2+}, then normally, current oscillations cannot occur. Through injecting NaOH solution, the pH value is attained artificially. After this, $Fe(OH)_2$ and Fe_3O_4 films are formed and the current decreases. At the end of injection, the diffusion

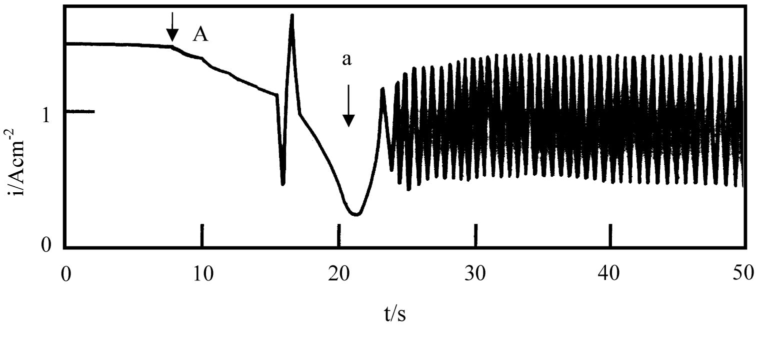

Fig. 3. Effect of injection of NaOH on potentiostatic current oscillations of Fe/0.7 mol dm^{-3} $HClO_4$ system. $E = 70$ mV, A: injection, a: end of injection.

of H^+ from the electrolyte bulk to the interface causes the dissolution of $Fe(OH)_2$ and Fe_3O_4 films in sequence. The Fe electrode is reactivated and the current becomes large. Fe^{2+}, produced by the electrodissolution of iron, leads to H^+ electromigration away from the Fe electrode. Increasing the interface pH causes $Fe(OH)_2$ and Fe_3O_4 films to be formed again. Thus, current oscillations appear. In brief, injecting NaOH solution can induce current oscillations at potentials where no current oscillation was observed before injection. This can be explained by involving a mechanism based on the temporal formation of $Fe(OH)_2$ and Fe_3O_4 films. If a $Fe(ClO_4)_2$ film were the prerequisite of current oscillations, the injection of NaOH solution would dilute the ClO_4^- concentration at the interface. The formation of $Fe(ClO_4)_2$ film would be inhibited, and current oscillations could not take place. Therefore, it is clear that the prerequisite of current oscillations is $Fe(OH)_2$ and Fe_3O_4 films rather than $Fe(ClO_4)_2$ film.

As the Fe electrode was potentiostatically polarized at 120 mV, current oscillations were observed. When 0.2 ml of 0.1 mol dm^{-3} NaOH solution was injected, the local interfacial pH increased. As a result, the $Fe(OH)_2$ film could not be dissolved and the current decreased. Oscillations disappeared for 20 s until the effect of OH^- was offset by backward diffusion of H^+ as shown in Figure 4.

H_2O can also be used in injection experiments to induce or prevent current oscillations as shown in Figure 5.

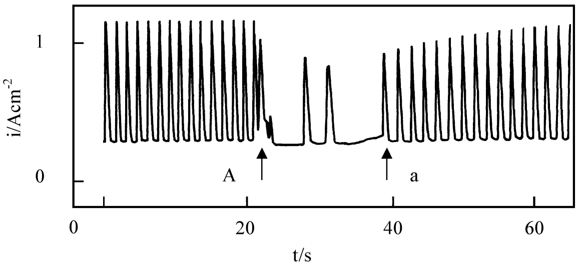

Fig. 4. Effect of injection of NaOH on potentiostatic current oscillations of Fe/0.7 mol dm^{-3} $HClO_4$ system. $E = 120$ mV, A: injection, a: end of injection.

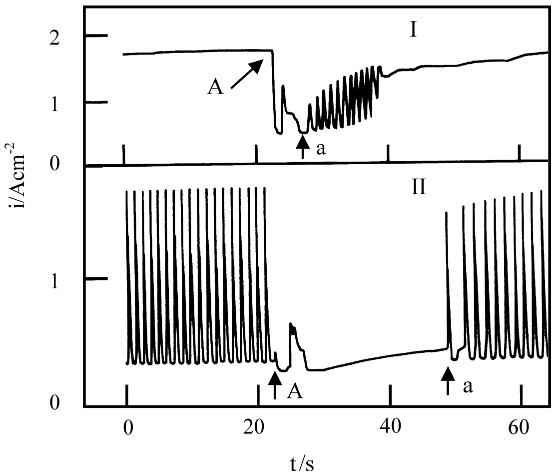

Fig. 5. Effect of injection of H_2O on potentiostatic current oscillations of Fe/0.7 mol dm^{-3} $HClO_4$ system. A: injection, a: end of injection. (I) $E = 70$ mV, (II) $E = 120$ mV.

4. Conclusions

The $Fe/HClO_4$ system exhibits current oscillations when 0.07 mol $dm^{-3} \leqslant C_{HClO_4} \leqslant 7$ mol dm^{-3}. With increase in $HClO_4$ concentration, the E_{low} of the current oscillations shifted positively. The minimum current values of the oscillations were nonzero due to incompleted passivation. The current oscillations took place over a wide temperature range and a narrow potential window. With increase in temperature from 5 to 50 °C, E_{low} shifted successively in the positive direction, the oscillation-potential window was widened, and the maximum oscillation amplitude also became larger. Current oscillations can be induced or prevented by changing the pH at the Fe/electrolyte interface artificially by injecting NaOH solution and H_2O. This further supports the current oscillation mechanism based on the temporal formation of $Fe(OH)_2$ and Fe_3O_4 films.

Acknowledgements

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