

## A study of periodic current oscillations of iron in nitric acid solutions

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(Received 4 April 2001)

The periodic current oscillations of Fe/HNO<sub>3</sub> are presented in this paper. The effects of HNO<sub>3</sub> concentration and imposed potential were investigated. The dropping method was used to change the local pH of the Fe/electrolyte interface, creating environments that favor the occurrence of current oscillations. Some interesting results were obtained and an explanation of the current oscillations is suggested.

*Keywords:* iron, nitric acid, current oscillations, electrodisolution.

### INTRODUCTION

The periodic oscillatory behavior at the transition region from the active state to the passive state of certain metals has always been an area of research interest,<sup>1–14</sup> not only because of its potential importance in corrosion and protection of metals, but also because of its role in attempts to understand the oscillation phenomena occurring in interfacial processes.<sup>2–4</sup> The most extensively studied electrochemical oscillator is the Fe/H<sub>2</sub>SO<sub>4</sub> system. However, as the metal active dissolution-passivation is a very complicated process, the oscillation mechanism of Fe/H<sub>2</sub>SO<sub>4</sub> system is still far from clear.<sup>5–8</sup>

Beck found the formation of a ferrous salt film in the prepassive potential region in the Fe/H<sub>2</sub>SO<sub>4</sub> system.<sup>10</sup> Then current oscillation phenomena were attributed to periodic changes in the salt film porosity or in the exposed area under the salt form.<sup>11,12</sup> However, many authors believe that the formation of an oxide film is the reason of current oscillation.<sup>3,4,9,13</sup> Pigeaud and Kirkpatrick thought that, before the formation of a stable passive film, precipitation of colloidal dispersed Fe(OH)<sub>2</sub> occurs.<sup>13</sup> Wang and Chen obtained some interesting results using the holographic microphotographic technique at the interface of an Fe/0.5 M H<sub>2</sub>SO<sub>4</sub> oscillatory system.<sup>3</sup> The results support the temporal formation of Fe(OH)<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> during the current oscillations. They

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thought that the temporal formation of  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}_3\text{O}_4$  is the cause of the current oscillations. With the dissolution of Fe, the  $\text{Fe}^{2+}$  is accumulated at the interface causing a decrease of the  $\text{H}^+$  concentration due to the migration of  $\text{H}^+$  ions away from the vicinity of the electrode. The local increase of pH leads to a temporal precipitation of  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}_3\text{O}_4$  which block the Fe surface. The back diffusion of  $\text{H}^+$  ions from the bulk to the interface causes the dissolution of the  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}_3\text{O}_4$  and a reactivation of the electrode.<sup>3,4</sup>

In this paper, some experimental results concerning electrochemical oscillation in the Fe/ $\text{HNO}_3$  system are presented. The effects of  $\text{HNO}_3$  concentration and imposed anode potential were investigated. Particularly, in order to investigate the electrochemical oscillation mechanism, a dropping method was used to change the local pH of the Fe/electrolyte interface, creating environments that favor the occurrence of current oscillations. Some interesting results were obtained.

#### EXPERIMENTAL

The 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, 2.5 mm in diameter, 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  $\text{Hg}/\text{Hg}_2\text{SO}_4/0.5 \text{ M H}_2\text{SO}_4$  electrode was used as a reference electrode, with its Luggin capillary probe located 2 mm below the working electrode. The electrolytes were prepared from analytical grade reagents and triply distilled water. The working electrode was polished with 600 and 1200 grade emery paper and washed with water, triply distilled water in an ultrasonic bath prior to each experiment. All measurements were performed at  $25 \pm 2^\circ\text{C}$ .

#### RESULTS AND DISCUSSION

##### *Anodic $i$ - $E$ polarization curves in $\text{HNO}_3$ solutions of various concentrations*

The current-potential ( $i$ - $E$ ) polarization curve of the Fe/ $\text{HNO}_3$  system are shown in Fig. 1. The potential scan rate was  $2 \text{ mV s}^{-1}$ . When the  $\text{HNO}_3$  concentration is very low (0.05 M), a well-defined  $i$ - $E$  curve is traced, as is shown in Fig. 1a, no current oscillation was found. With increasing  $\text{HNO}_3$  concentration, current oscillations occur over a wide range of  $\text{HNO}_3$  concentrations (0.1 M – 8 M). In the range  $0.1 \text{ M} \leq c_{\text{HNO}_3} \leq 8 \text{ M}$ , the  $i$ - $E$  curves can be divided into two types according to the  $\text{HNO}_3$  concentration. The first type is in the range  $0.1 \text{ M} \leq c_{\text{HNO}_3} \leq 1 \text{ M}$ , where by scanning the potential from  $-700 \text{ mV}$  to  $500 \text{ mV}$ , the current increases continuously until oscillations take place, then passivation is achieved. The second type is in concentrated  $\text{HNO}_3$  solutions (2 M – 8 M). With increasing potential, the current first increases and then decreases over a wide potential range, after which current oscillations occur within a certain potential range where the iron electrode is in transition from the prepassive to the passive state.

Podesta *et al.* studied current oscillations in the Fe/ $\text{H}_2\text{SO}_4$  system.<sup>14</sup> They pointed out that a  $c_{\text{H}_2\text{SO}_4} > 1 \text{ M}$ , a ferrous sulphate salt film forms on the surface of the Fe electrode, while at  $c_{\text{H}_2\text{SO}_4} < 1 \text{ M}$ , a  $\text{Fe}(\text{OH})_2$  film maybe forms. In the Fe/ $\text{HNO}_3$  sys-

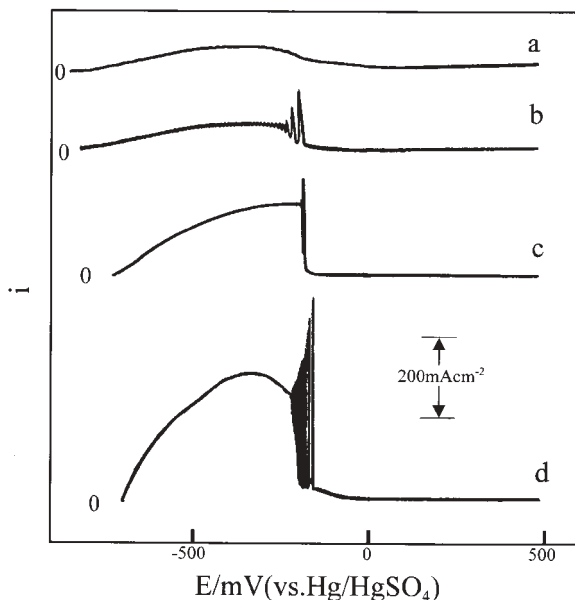


Fig. 1. Effect of the nitric acid concentration on the polarization behavior of the Fe/HNO<sub>3</sub> system.  $c_{\text{HNO}_3}$ : a, 0.05 M; b, 0.1 M; c, 0.5 M; d, 2.0 M.

tem, the solubility of  $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is 83.5 g/100 ml  $\text{H}_2\text{O}$  at 20 °C,<sup>15</sup> hence a  $\text{Fe}(\text{NO}_3)_2$  salt film can not form on the Fe electrode surface. On the other hand, taking into account the increase of the interface pH, caused by a migration of  $\text{H}^+$  away from the vicinity of the electrode, a  $\text{Fe}(\text{OH})_2$  film maybe forms at the Fe electrode surface. With decreasing  $\text{HNO}_3$  concentration, the  $\text{Fe}(\text{OH})_2$  film becomes thicker and thicker, and the amplitude of the current oscillations becomes smaller and smaller.

It can be seen from Fig. 1a that in 0.05 M  $\text{HNO}_3$  solution when the potential is scanned in a positive direction, the anodic dissolution current of Fe is very small. The amount of  $\text{Fe}^{2+}$  produced by the anodic dissolution of Fe is small, and the decrease of the  $\text{H}^+$  concentration due to the migration of  $\text{H}^+$  ions away from the vicinity of the electrode is slowed down. It is difficult to form the certain thickness of a  $\text{Fe}(\text{OH})_2$  film which is necessary for the occurrence of current oscillations. Hence, no current oscillations are observed.

#### *The effect of the HNO<sub>3</sub> concentration on current oscillations*

Figure 2 shows typical potentiostatic current/time curves at  $E = -210$  mV for the Fe/ $x$ M  $\text{HNO}_3$  systems. For 0.05 M  $\text{HNO}_3$ , the  $i-t$  curve (Fig. 2a) shows clearly that the current decreases to a very low value within a few seconds of the onset of polarization, the Fe electrode enters a passive state. No current oscillations are observed. When the  $\text{HNO}_3$  concentration is 0.1 M, current oscillations occur 54 s after the formation of the passive state. However, when the  $\text{HNO}_3$  concentration is 0.5 M, current oscillations occur immediately the polarization is commenced. For  $\text{HNO}_3$  concentration  $\geq 1.0$  M, the  $i-t$  curves are obviously different compare with that obtained with 0.5 M  $\text{HNO}_3$  as shown in Fig. 2d and Fig. 2e. When the potential of the Fe electrode is suddenly changed from the open-circuit value to  $-290$  mV, the current decreases gradually for a few seconds, and then current oscillations are observed. In 5.0 M  $\text{HNO}_3$  solution, the

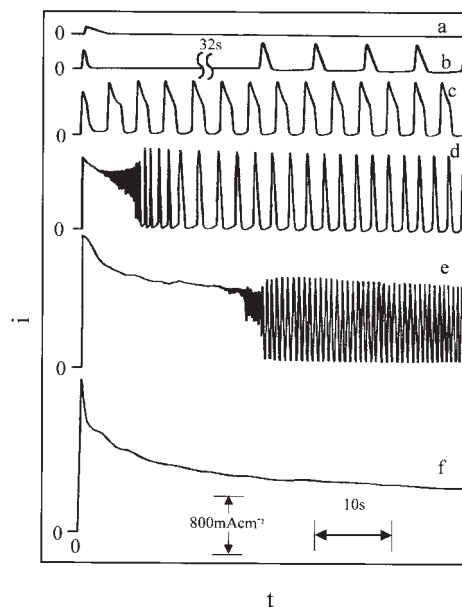


Fig. 2.  $i-t$  transients of the Fe/HNO<sub>3</sub> system as a function of the nitric acid concentration.  $c_{\text{HNO}_3}$ : a, 0.05 M; b, 0.2 M; c, 0.5 M; d, 1.0 M; e, 3.0 M; f, 5.0 M.

current decreases gradually to a relatively steady value and no oscillations are observed, as shown in Fig. 2f. In this concentration of HNO<sub>3</sub>, even if the electrode is polarized for a long time (for example, 30 min), no current oscillations are found.

#### *The effect of the imposed potential on the current oscillations*

The potentiostatic  $i-t$  curves of a Fe/0.5 M HNO<sub>3</sub> system with different imposed potentials are shown in Fig. 3. It can be seen that changing the anode potential results in different types of  $i-t$  curves. When  $E = -190$  mV, the current is very low, the electrode is in the passive state and current oscillations are not observed, as shown in Fig. 3a. With

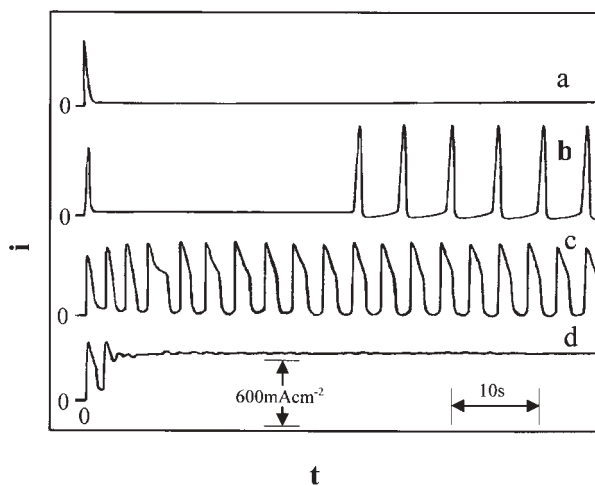


Fig. 3.  $i-t$  transients of the Fe/0.5 M HNO<sub>3</sub> system as a function of the potential. a:  $E = -190$  mV; b:  $E = -200$  mV; c:  $E = -220$  mV; d:  $E = -240$  mV.

this potential, even if the electrode is polarized for a long time (for example, 30 min), no current oscillations are found. The current oscillations appear in the potential range  $-200 \text{ mV} \approx -230 \text{ mV}$ . In this potential range when  $E = -200 \text{ mV}$ , current oscillations appear after some period of time, while when  $E = -220 \text{ mV}$ , current oscillations occur immediately after commencement of polarization, as shown in Fig. 3b and Fig. 3c. On further increasing the potential to  $-240 \text{ mV}$ , no current oscillations are observed.

#### *Explanation of the current oscillation phenomena in 0.5 M HNO<sub>3</sub>*

As occurs in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution,<sup>3</sup> it can be inferred that a change of pH in the Fe/electrolyte interface would influence the formation and dissolution of a Fe(OH)<sub>2</sub> film and a Fe<sub>3</sub>O<sub>4</sub> film, as well as the occurrence, development and ceasement of current oscillations. In the other word, if current oscillations can be induced by changing the pH in the Fe/electrolyte interface artificially, the current oscillation mechanism based on the temporal formation of Fe(OH)<sub>2</sub> films and Fe<sub>3</sub>O<sub>4</sub> films would be supported. In this section, a dropping method was used to change the local pH of the Fe/0.5 M HNO<sub>3</sub> interface, creating environments that favor the occurrence of current oscillations.

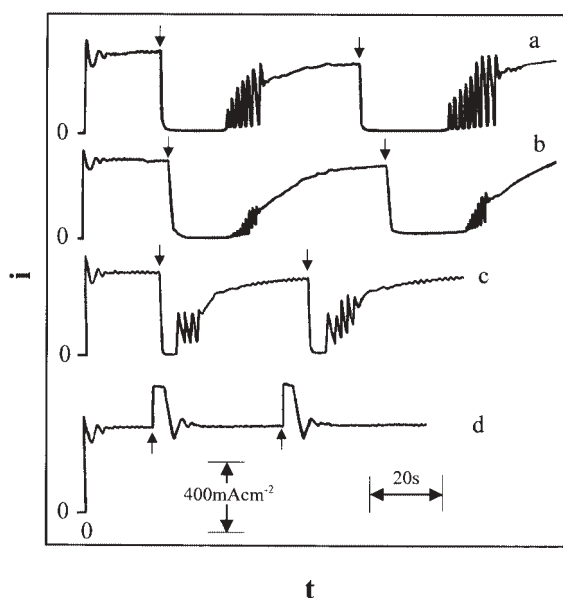


Fig. 4. Effect of dropping on the potentiostatic current oscillations of the Fe/0.5 M HNO<sub>3</sub> system. a:  $E = -290 \text{ mV}$ , 0.5 M NaOH; b:  $E = -320 \text{ mV}$ , 0.5 M NaOH; c:  $E = -290 \text{ mV}$ , H<sub>2</sub>O; d:  $E = -290 \text{ mV}$ , 0.5 M HNO<sub>3</sub> dropping.

(1) *Effect of dropping NaOH solution.* The effect of dropping a 0.5 M NaOH solution when the Fe electrode is polarized at  $-290 \text{ mV}$  in 0.5 M HNO<sub>3</sub> solution is shown in Fig 4a. As the potential is changed suddenly from the open-circuit value ( $-700 \text{ mV}$ ) to  $-290 \text{ mV}$ , the polarization current decreases gradually and finally regains a steady value, no oscillation are observed. When 0.2 ml of a 0.5 M NaOH solution is dropped through a needle (internal diameter 0.2 mm) into the electrolyte 2 mm below the surface of the Fe electrode, the current decreases suddenly and reaches a very low, indicating that the Fe electrode enters into a passive state. These effects can be attributed to a thickening of the Fe(OH)<sub>2</sub> film and the formation of a Fe<sub>3</sub>O<sub>4</sub> film. The passive state is main-

tained for 16 s, then current oscillations occur. However, these last for only 10 s, when the current resumes its original steady value. Similar phenomena are observed when the dropping is repeated once again.

For a given potential, a suitable pH value in the Fe/electrolyte is necessary for the formation of  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}_3\text{O}_4$  films. If the pH value can not be achieved only by the migration of  $\text{H}^+$  ions caused by the accumulation of  $\text{Fe}^{2+}$  ions, usually, current oscillations can not occur. Through the dropping of the NaOH solution, the pH value can be artificially attained and a  $\text{Fe}(\text{OH})_2$  film is formed which results in the current decrease. At the end of the dropping, the diffusion of  $\text{H}^+$  ions from the bulk solution to the interface causes the dissolution of the  $\text{Fe}(\text{OH})_2$  and then the  $\text{Fe}_3\text{O}_4$  film. The Fe electrode is reactivated and the current becomes larger. The  $\text{Fe}^{2+}$  ions, produced by the electro-dissolution of iron, cause migration the  $\text{H}^+$  ions away from the vicinity of the Fe electrode. The increase of pH in of the Fe/electrolyte interface leads to the formation of  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}_3\text{O}_4$  films once again. Thus, current oscillations appear.

As the amount of NaOH dropped is small compare to the bulk solution, as soon as the dropping is stopped, the Fe/electrolyte interface is restored to its original state as is the effect of diffusion before dropping. So the current oscillations can not continue for very long.

The effect of dropping a 0.5 M NaOH solution when Fe electrode is potentiostatic polarized at  $-320$  mV in 0.5 M  $\text{HNO}_3$  solution is shown in Fig. 4b. Phenomena similar to those at  $-290$  mV are observed. After dropping 0.2 ml of a 0.5 M NaOH solution, the Fe electrode enters a passive state, and then current oscillations occur. Only the oscillation amplitude is smaller and the time of oscillations is shorter than at  $-290$  mV. In fact, when  $E \leq -240$  mV, no current oscillations are found in a 0.5 M  $\text{HNO}_3$  solution, but the dropping a 0.5 M NaOH solution can introduce current oscillations until  $E = -320$  mV. At  $E < -320$  mV, current oscillations can no longer be introduced by dropping a 0.5 M NaOH solution. Maybe at this potential it is not possible to form the  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}_3\text{O}_4$  films essential for current oscillations even by the dropping of a 0.5 M NaOH solution.

(2) *Effect of dropping  $\text{H}_2\text{O}$ .* The effect of dropping 0.2 ml of  $\text{H}_2\text{O}$  when the Fe electrode is polarized at  $-290$  mV in 0.5 M  $\text{HNO}_3$  solution is shown in Fig. 4c. Before dropping  $\text{H}_2\text{O}$ , no current oscillations are observed. When  $\text{H}_2\text{O}$  is dropped, the phenomena similar to those induced by dropping a NaOH solution follow: the current decreases suddenly to a very low value. The low current is maintained for 6 s, when current oscillations occur. The change of the pH of the interface caused by dropping  $\text{H}_2\text{O}$  is less than that caused by dropping a NaOH solution, as can be seen from Fig. 4c and Fig. 4a, and the continuous time of current oscillation is shorter also.

(3) *Effect of dropping a 0.5 M  $\text{HNO}_3$  solution.* Taking into account the fact that a disturbance of the electrolyte could affect the current oscillations, a 0.5 M  $\text{HNO}_3$  was also dropped into the electrolyte as a control experiment. The  $i-t$  curve of an Fe electrode polarized at  $-290$  mV on dropping 0.2 ml of a 0.5 M  $\text{HNO}_3$  solution into a 0.5 M  $\text{HNO}_3$  solution is shown in Fig. 4d. A completely different result is obtained compared with that obtained by dropping NaOH and  $\text{H}_2\text{O}$ . Immediately after the dropping, the dissolution of  $\text{Fe}(\text{OH})_2$  is accelerated by  $\text{H}^+$  ions, so the current increases violently. Once the dropping is stopped, diffusion makes the pH of the Fe/electrolyte interace in-

crease, and the current restores its original value quickly. The above experimental results indicate that the cause of current oscillations is mainly the change of pH at the Fe/electrolyte interface.

#### CONCLUSIONS

Current oscillations occur in the Fe/ $x$ M HNO<sub>3</sub> system ( $0.1 \leq x \leq 8$ ) within a certain potential range. According to the experimental results of dropping a NaOH solution, H<sub>2</sub>O or a HNO<sub>3</sub> solution at the Fe/electrolyte interface, a change of pH at the Fe/electrolyte interface is the main cause of current oscillations. The formation of a Fe(OH)<sub>2</sub> film at the electrode surface is the essential condition for current oscillations in the Fe/HNO<sub>3</sub> system.

*Acknowledgements:* This work was subsidized by the Special Funds for the Major State Basic Research Projects G19990650 and the Chinese National Science Fund No.29873028.

#### ИЗВОД

##### ПРОУЧАВАЊЕ ПЕРИОДИЧНИХ СТРУЈНИХ ОСЦИЛАЦИЈА НА ГВОЖЂУ У РАСТВОРИМА АЗОТНЕ КИСЕЛИНЕ

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У раду су приказане периодичне струјне осцилације за систем Fe/HNO<sub>3</sub>. Проучавани су утицаји концентрације HNO<sub>3</sub> и наметнутог потенцијала. За промену локалног pH на површини Fe/електролит коришћена је метода докапавања, при чему је стварано окружење које је фаворизовало појаву струјних осцилација. Добијени су интересантни резултати, а предложено је и објашњење узрока појаве струјних осцилација.

(Примљено 4. априла 2001)

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