

# A Study of the Relation Between Current Oscillations and Pitting

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Anodic polarization behaviors of iron in pure  $\text{H}_2\text{SO}_4$  and three mixed acidic solutions,  $\text{H}_2\text{SO}_4 + \text{NaCl}$ ,  $\text{H}_2\text{SO}_4 + \text{NaNO}_3$  and  $\text{H}_2\text{SO}_4 + \text{NaCl} + \text{NaNO}_3$ , were investigated. The potentiodynamic sweep curves showed that the current densities rose and dropped irregularly in  $\text{H}_2\text{SO}_4 + \text{NaCl}$  solution at the more anodic potentials since the iron surface suffered pitting attack in the solution, but the pitting corrosion was inhibited effectively in the presence of nitrate ions. The surface morphological measurements indicated that pits appeared on the iron surface in  $\text{H}_2\text{SO}_4 + \text{NaCl}$  solution and only a few unobvious corrosion spots were observed in  $\text{H}_2\text{SO}_4 + \text{NaCl} + \text{NaNO}_3$  solution after the iron electrode was potentiostatically polarized at 1.3 V. The oscillatory properties of iron are associated with the susceptibility of the iron to pitting. In  $\text{H}_2\text{SO}_4 + \text{NaCl}$  solution, the regular potentiostatic current oscillations gradually evolved into the irregular current fluctuations due to occurrence of the pitting; whereas in  $\text{H}_2\text{SO}_4 + \text{NaCl} + \text{NaNO}_3$  solution, the current oscillations took place regularly, like the oscillatory behavior in the pure  $\text{H}_2\text{SO}_4$  solution. Thus, when the higher the oscillatory frequency, the more irregular oscillatory process and the more sensitive to pitting iron occurred.

**Keywords** current oscillation, pitting, iron, oscillatory frequency, passivation

## Introduction

The current oscillation is a common phenomenon observed in the anodic polarization process of some transition metals in acidic solutions.<sup>1-3</sup> The periodic electrodisolution of iron in the sulfuric acid solution has been studied most extensively and its origin has been interpreted by different author in terms of the precipitation-dissolution model of  $\text{Fe}(\text{OH})_2\text{-Fe}_3\text{O}_4$  bilayer film<sup>4-8</sup> or the precipitation-dissolution model of  $\text{FeSO}_4$  film.<sup>9-12</sup> Anodic oscillatory behaviors of iron and its alloys in the chloride-containing solutions have also been reported by several authors.<sup>13-19</sup> The oscillations are believed to originate from alternate buildup and breakdown of a porous, nonprotective ferrous chloride salt film on the iron surface. However, there are few reports about the relation between electrochemical oscillations and the pitting corrosion although it may be inferred that elec-

trochemical oscillation behavior is inherently associated with pitting corrosion.<sup>20, 21</sup>

Studies about the inhibiting action of nitrate to the pitting corrosion caused by chloride in  $\text{Fe}/\text{H}_2\text{SO}_4$  system have received scant attention. Sazou and Pagitsas' recent results<sup>22</sup> indicate that, at lower potentials nitrates stimulate pitting acting as activators of the oxide dissolution; whereas at higher potentials nitrates act as passivators causing a sudden passivation of iron during a mass-transport controlled process across a salt film. This is in agreement with earlier studies of corrosion of different stainless steels exposed to  $\text{NO}_3^-/\text{Cl}^-$  corrosive environments carried out by Kolman *et al.*,<sup>23</sup> Greene and Fontana,<sup>24</sup> Newman and Ajjawi'.<sup>25</sup> However, how nitrate ions inhibit the pitting has been unclear so far.

In this paper, the anodic polarization and the potentiostatic current oscillations for iron in dilute  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SO}_4 + \text{NaNO}_3$ ,  $\text{H}_2\text{SO}_4 + \text{NaCl}$  and  $\text{H}_2\text{SO}_4 + \text{NaCl} + \text{NaNO}_3$  were systemically investigated, in order to get an insight into the inherent relations between the electrochemical oscillations and pitting initiation as well as to interpret better the inhibition effect of nitrate on the pitting in acidic solutions.

## Experimental

A small iron electrode was made from a 99.99% specpure iron wire of 0.5 mm diameter (Johnson Matthey Chemicals Ltd.), without any further treatment. The small electrode was used to reduce the variation of electrolyte composition. The wire specimen was embedded in the epoxy resin mold, and only its cross-section was allowed to contact the electrolyte. The electrode was polished with # 600 and # 1200 emery papers in proper order prior to each measurement, and then rinsed with alcohol and triply distilled water.

The electrolyte solutions used here,  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ),  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaNO}_3$  ( $0.1 \text{ mol} \cdot \text{L}^{-1}$ ),

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$\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaCl}$  ( $0.01 \text{ mol} \cdot \text{L}^{-1}$ ) and  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaCl}$  ( $0.01 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaNO}_3$  ( $0.1 \text{ mol} \cdot \text{L}^{-1}$ ), were prepared with analytical grade chemicals and the triply distilled water.

All experiments were conducted at room temperature ( $\sim 22 \text{ }^\circ\text{C}$ ) using a traditional three-electrode cell. The counter electrodes were two pieces of platinum and the reference electrode was a saturated calomel electrode (SCE). All potentials were measured with respect to the SCE.

The potentiodynamic and potentiostatic measurements were carried out by a CHI 650A electrochemical workstation.

## Results and discussion

### Potentiodynamic sweep curves

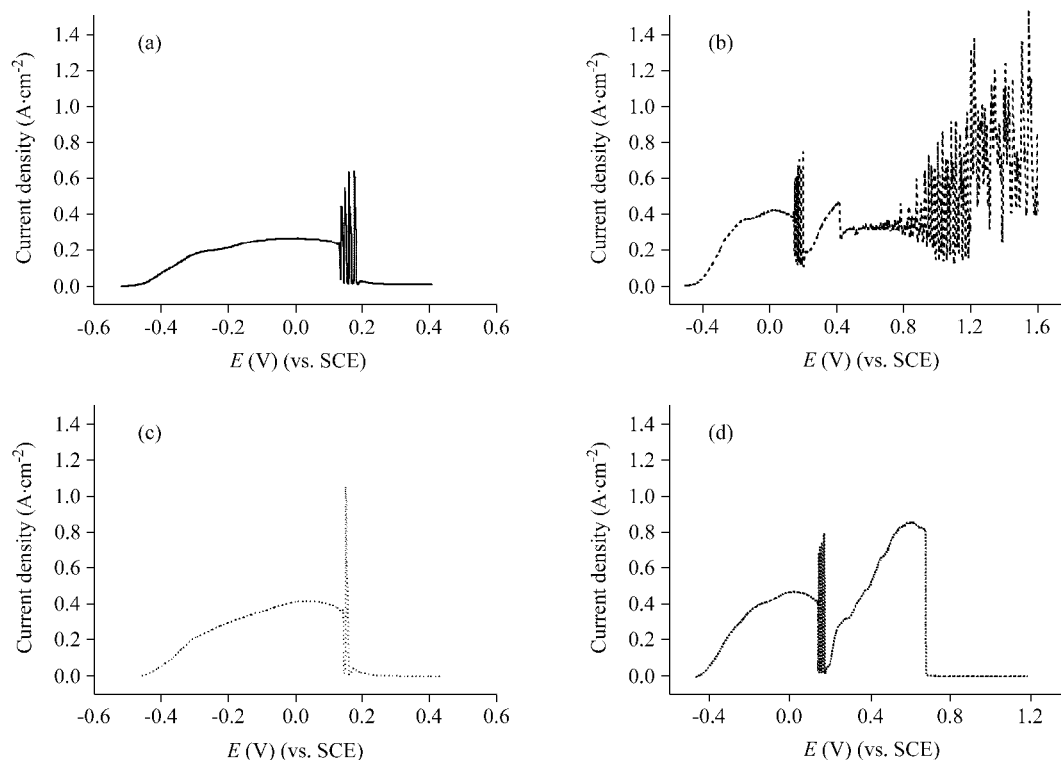
Fig. 1(a)–1(d) show a set of anodic potentiodynamic scan curves for iron in  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) solution alone and in the presence of  $\text{NaCl}$  or  $\text{NaNO}_3$  or both.

In the  $\text{H}_2\text{SO}_4$  solution ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) (Fig. 1(a)), the anodic current increased with the potential increase before  $-0.05 \text{ V}$ , and kept an approximate constant of about  $0.26 \text{ A} \cdot \text{cm}^{-2}$  in the potential range between  $-0.05$  and  $0.12 \text{ V}$ , leading to occurrence of a current plateau, and then began to oscillate strongly at  $0.12 \text{ V}$ , followed by the sharp drop, and finally reached passive state at potentials more than  $0.22 \text{ V}$ . The overall anodic process may be divided roughly into four regions, an active one, a prepassive one, a transition from prepassivation to passivation, and a passive one.<sup>5</sup>

In  $\text{H}_2\text{SO}_4$  +  $\text{NaCl}$  mixed solution, the anodic behavior of iron was similar to that in pure  $\text{H}_2\text{SO}_4$  solution before  $0.22 \text{ V}$  (Fig. 1(b)), but quite different from that of iron in  $\text{H}_2\text{SO}_4$  solution after  $0.22 \text{ V}$ . From  $0.45 \text{ V}$  towards more positive potentials, the currents started to oscillate irregularly; moreover, the oscillation amplitude became larger and larger. Theoretically, the irregular current oscillations should be related to formation of pits on the iron surface. This type of pitting probably initiates in transition region from prepassive to passive state and occurs at more noble potentials, according to Smialowska.<sup>26</sup> Although the relation between current oscillations and pitting corrosion has been unclear so far, it is possible that chlorides participates in the current oscillation process and destroy the passivating trend of the iron surface.

The presence of nitrate has no other influence on the anodic behavior of iron except promoting the current density and oscillation amplitude of current to some extent, as shown in Fig. 1(c).

In  $\text{H}_2\text{SO}_4$  +  $\text{NaNO}_3$  +  $\text{NaCl}$  mixed solution, the anodic polarization curve (Fig. 1(d)) shows the current increased with the potential and current oscillations took place at potentials lower than  $0.18 \text{ V}$ , like the anodic behavior of iron in three solutions mentioned above; however, the current increased rapidly after the strong oscillations, reaching the maximum of  $0.86 \text{ A} \cdot \text{cm}^{-2}$  at  $0.61 \text{ V}$ , and then declined sharply due to passivation of iron surface. Obvi-

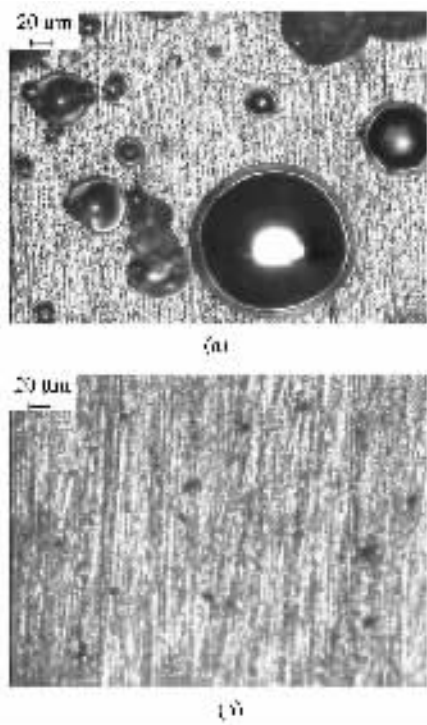


**Fig. 1** Potentiodynamic scan curves for the small iron electrode in various solutions at  $5 \text{ mV} \cdot \text{s}^{-1}$ . (a)  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ); (b)  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaCl}$  ( $0.01 \text{ mol} \cdot \text{L}^{-1}$ ); (c)  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaNO}_3$  ( $0.1 \text{ mol} \cdot \text{L}^{-1}$ ); (d)  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaNO}_3$  ( $0.1 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaCl}$  ( $0.01 \text{ mol} \cdot \text{L}^{-1}$ ).

ously, the presence of  $\text{NO}_3^-$  ions effectively prevented the iron surface from suffering pitting attack by  $\text{Cl}^-$  ions.

### Surface morphology

An iron rod of 5.0 mm diameter with the same compositions (Johnson Matthey Chemicals Ltd.) was used as substitute for the iron wire in order to carry out metallographic experiments better. Fig. 2(a) shows that there were pits or pit clusters on the iron surface after the iron electrode was polarized at 1.2 V in  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaCl}$  ( $0.01 \text{ mol} \cdot \text{L}^{-1}$ ) solution for 3 min; whereas Fig. 2(b) shows that only a few small spots appeared and rest of area was the original ground surface when the iron electrode was polarized in 1.2 V in  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaNO}_3$  ( $0.1 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaCl}$  ( $0.01 \text{ mol} \cdot \text{L}^{-1}$ ) mixed solutions under the same condition. Based on the results shown in Fig. 2(a) and 2(b), together with Fig. 1(b) and 1(d), it is confirmed that, the rise of current after current oscillations in Fig. 1(b) is attributed to the appearance of pits on the iron surface and the pitting corrosion has been inhibited to great extent by nitrate ions although the iron surface is still susceptible to pitting.



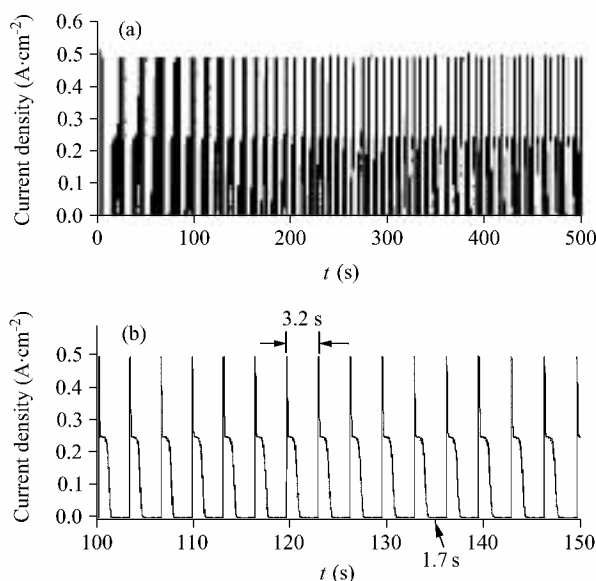
**Fig. 2** Surface morphology of the large iron electrode after being polarized at 1.2 V (vs. SCE) for 3 min: (a) in  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaCl}$  ( $0.01 \text{ mol} \cdot \text{L}^{-1}$ ) solution; (b) in  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaNO}_3$  ( $0.1 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaCl}$  ( $0.01 \text{ mol} \cdot \text{L}^{-1}$ ) solution.

### Potentiostatic current oscillations

#### $\text{H}_2\text{SO}_4$ solution

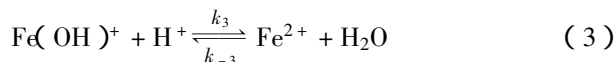
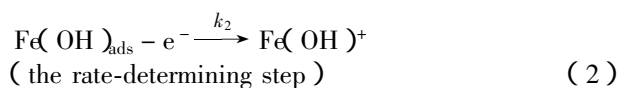
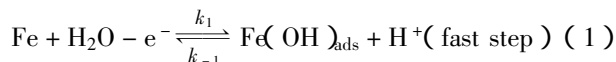
Fig. 3(a) shows the waveforms of the potentiostatic

current oscillations at 0.16 V in 500 s and Fig. 3(b) is the enlarged current density-time curve from the 100th to the 150th s. All current peaks displayed regularly the sharp rise and stepwise drops. It is determined roughly from Fig. 3(b) that the oscillatory period of current is about 3.2 s and the interval between two current oscillations is 1.7 s. In fact, the interval reflects the brief passivation time in a whole oscillation process.



**Fig. 3** (a) Current-time curve for the small iron electrode in  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) at 0.16 V (vs. SCE); (b) the enlarged waveforms of current oscillations from 100 to 150 s.

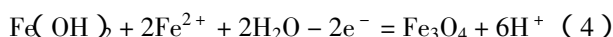
The precipitation-dissolution mechanism of  $\text{Fe}(\text{OH})_2$ - $\text{Fe}_3\text{O}_4$  bilayer film is more suitable for explaining the current oscillatory behavior in dilute solutions ( $< 1.0 \text{ mol} \cdot \text{L}^{-1}$ ) according to the viewpoint of Podesta *et al.*<sup>27</sup> The rapid rise of current is associated with the two fast consecutive dissolution processes, chemical dissolution of the  $\text{Fe}(\text{OH})_2$ - $\text{Fe}_3\text{O}_4$  bilayer film and the subsequent electrodis-solution of the iron. The maximum current should be the anodic current produced by the electrodis-solution of iron, according to the Bockris-Drazic-Despic (BDD) mechanism:<sup>28</sup>



where  $\text{Fe}(\text{OH})_{\text{ads}}$  is an adsorbed species at the iron surface and  $\text{Fe}(\text{OH})^+$  is an intermediate in the solution.  $\text{Fe}(\text{OH})_2$  precipitations cannot form on the iron surface in the period

of current rise, since the electrodisolution process of iron is so fast that no pH change occurs at the iron/solution interface.<sup>27</sup>

Once the current reaches the maximum, such high electrodisolution rate will lead to the accumulation of  $\text{Fe}^{2+}$  in the vicinity of the iron surface and the migration of hydrogen ions out of this region in an amount equivalent to the  $\text{Fe}^{2+}$  produced.<sup>5, 27</sup> The two actions cause an increase of local  $\text{OH}^-$  concentration close to the iron surface, making the hydrolysis of  $\text{Fe}^{2+}$  and the formation of  $\text{Fe}(\text{OH})_2$  precipitation possible.<sup>27</sup> Subsequently, the compact  $\text{Fe}_3\text{O}_4$  thin film forms inside  $\text{Fe}(\text{OH})_2$  film through Eq. (4).<sup>4, 5</sup>



Formation of  $\text{Fe}(\text{OH})_2$ - $\text{Fe}_3\text{O}_4$  bilayer film is relatively slow, which is reflected from the stepwise drop of current. It is estimated from Fig. 3(b) that the drop time in each oscillation is about 1.5 s.

The current oscillations occur regularly. When one oscillatory period finishes, a new one will restart.

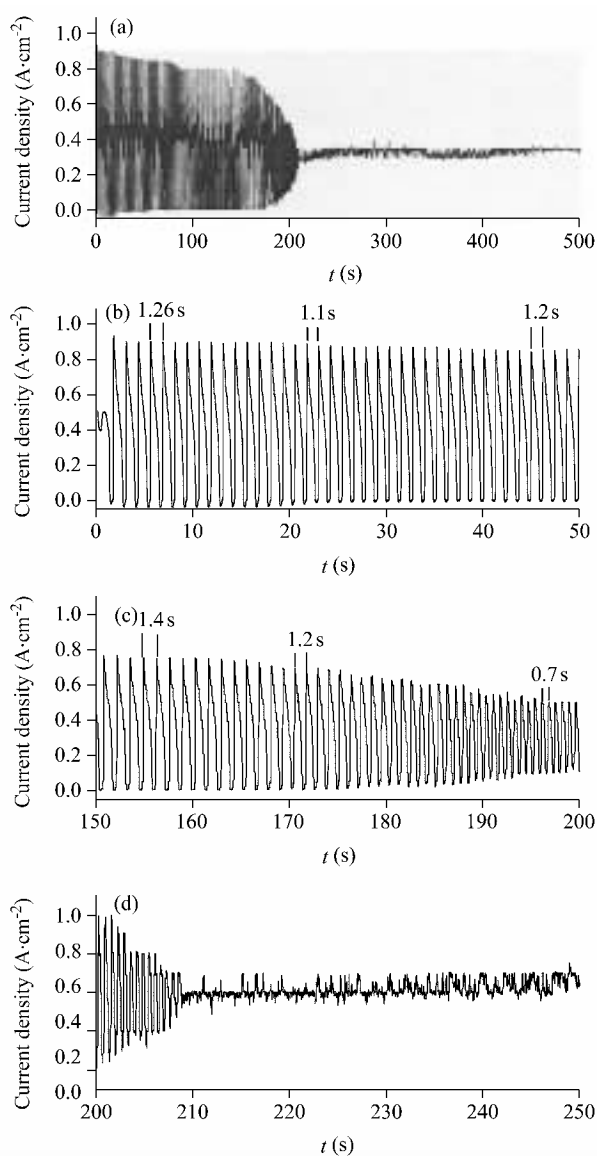
#### $\text{H}_2\text{SO}_4 + \text{NaCl}$ mixed solution

Different from the current oscillation characteristics of iron in  $\text{H}_2\text{SO}_4$  solution, Fig. 4(a)–4(d) shows that the current oscillations for iron in  $\text{H}_2\text{SO}_4 + \text{NaCl}$  mixed solution at 0.16 V can be divided into three different phases: (i) relatively regular current oscillations in the first 180 s; (ii) irregular current oscillations from the 180th to the 208th s; (iii) irregular current fluctuations since the 208th s.

In the first 180 s, although each peak displayed sharp rise and stepwise drops in most cases, the rising rate slowed and the dropping rate quickened to some extent, compared to the current oscillations of iron in  $\text{H}_2\text{SO}_4$  solution. It is worth noticing that the oscillation frequency increased and the interval between two current oscillations almost disappeared; in addition, the oscillation periodicity and the symmetry of current peak became worse. From the 180th to the 208th s, the oscillation periodicity and the symmetry of current peak worsened. The oscillatory frequency obviously quickened and oscillatory amplitude gradually decreased. The oscillations completely developed into the irregular fluctuations in 208 s, like the current noise signals although the amplitude was much larger.

Rosenfeld *et al.*<sup>20, 21</sup> have proposed an assumption that the more prone to pitting a metal, the higher the oscillation frequency, and suggested that oscillation may serve as a test of susceptibility of a metal to pitting in a given solution. Variation of current oscillation behavior with time shown in Fig. 4(a)–4(d) indicates that oscillations are inherently associated with the pitting corrosion.

Our recent investigation has shown that oscillatory behavior of the iron in dilute  $\text{H}_2\text{SO}_4$  solution is closely related to the electrolyte microenvironments adjacent to the iron surface, including the composition and pH value and other



**Fig. 4** (a) Current-time curve for the small iron electrode in  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaCl}$  ( $0.01 \text{ mol} \cdot \text{L}^{-1}$ ) solution at 0.16 V (vs. SCE). (b) The enlarged waveforms of current oscillations from 0 to 50 s. (c) The enlarged waveforms of current oscillations from 150 to 200 s. (d) The enlarged waveforms of current oscillations from 250 to 300 s.

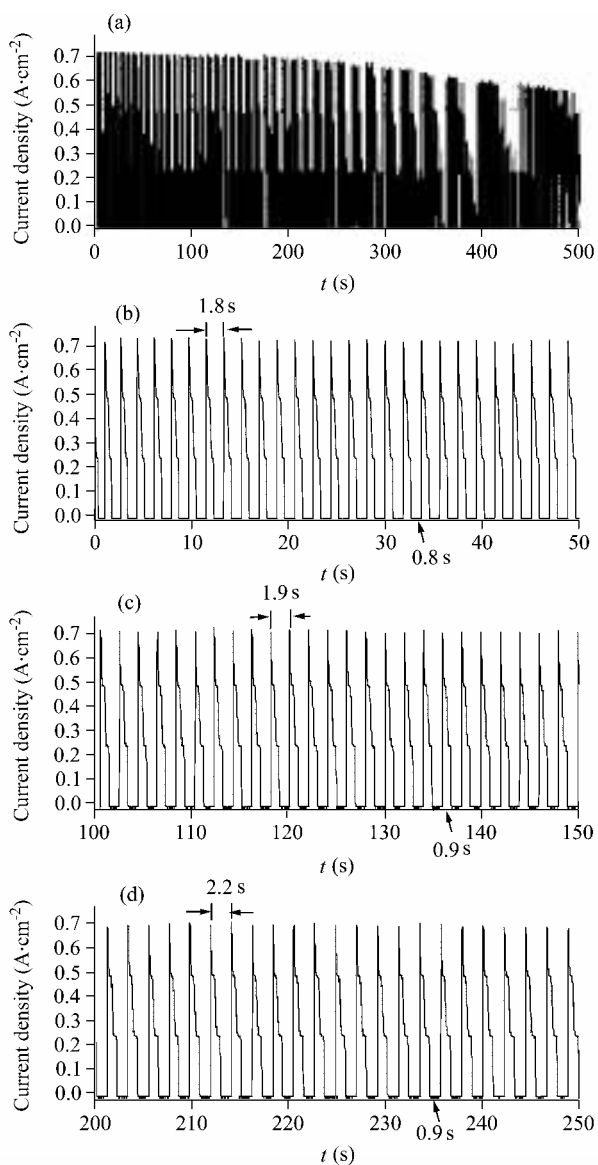
factors.<sup>29</sup> Current or potential oscillations occurring in the iron/chloride systems are attributed to the alternate buildup and breakdown of an unstable porous  $\text{FeCl}_2$  salt film on the iron surface by some authors.<sup>13, 17-19</sup>

Through analyzing the characteristics of current oscillations for the iron/ $\text{H}_2\text{SO}_4 + \text{NaCl}$  system in different phases, it is believed that the oscillations originate from the alternate formation and dissolution of the  $\text{Fe}(\text{OH})_2$ - $\text{Fe}_3\text{O}_4$  bilayer films at the beginning stage; the participation of  $\text{Cl}^-$  ions in the oscillatory process changes the original oscillation characteristics for the iron/ $\text{H}_2\text{SO}_4$  system. Driven by the applied anodic potential, chloride ions will migrate to the iron electrode and form the  $\text{FeCl}_2$  salt precipitation by reacting with ferrous ions, which is either on surface of

$\text{Fe}(\text{OH})_2\text{-Fe}_3\text{O}_4$  precipitations or insert into the precipitations. As chloride is a corrosive ion, its presence in the  $\text{Fe}(\text{OH})_2\text{-Fe}_3\text{O}_4$  bilayer film not only will affect the regular formation and dissolution process of the bilayer film, but also will destroy the passivating trend of iron surface and induce initiation of pitting. The metallographic observation proved that there existed small pits on the iron surface.

#### $\text{H}_2\text{SO}_4 + \text{NaNO}_3 + \text{NaCl}$ solution

Fig. 5(a)–(d) show the oscillatory behavior of iron at 0.16 V in  $\text{H}_2\text{SO}_4 + \text{NaNO}_3 + \text{NaCl}$  solution is similar to



**Fig. 5** (a) Current-time curve for the small iron electrode in  $\text{H}_2\text{SO}_4$  ( $0.2 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaNO}_3$  ( $0.1 \text{ mol} \cdot \text{L}^{-1}$ ) +  $\text{NaCl}$  ( $0.01 \text{ mol} \cdot \text{L}^{-1}$ ) solutions at 0.16 V (vs. SCE). (b) The enlarged waveforms of current oscillations from 0 to 50 s. (c) The enlarged waveforms of current oscillations from 100 to 150 s. (d) The enlarged waveforms of current oscillations from 200 to 250 s.

that in  $\text{H}_2\text{SO}_4$  and quite different from that in  $\text{H}_2\text{SO}_4 + \text{NaCl}$  solution. The oscillation frequency was higher than that of iron in  $\text{H}_2\text{SO}_4$  solution and the symmetry of current peak was not as good as that for the iron/ $\text{H}_2\text{SO}_4$  system. The oscillation period increased with the time extension, and the interval of two current oscillations approximately kept constant (0.8–0.9 s), lower than the value (1.7 s) in Fe/ $\text{H}_2\text{SO}_4$  system.

Generally, salt films are nonprotective films and can not lead to passivation of metal surface. Passivation of the iron surface at 0.20 V (Fig. 1(d)) suggests that  $\gamma\text{-Fe}_2\text{O}_3$  films has been formed on the iron surface in  $\text{H}_2\text{SO}_4 + \text{NaNO}_3 + \text{NaCl}$  mixed solution at higher anodic potentials, without question. In this sense, nitrates and chlorides have completely opposite effects.<sup>23</sup> The former is a powerful passivating agent and the latter is a powerful depassivating agent.

The current oscillations at Fe/ $\text{H}_2\text{SO}_4 + \text{NaNO}_3 + \text{NaCl}$  solution interface probably involve formation of both salt films and oxide film. The film formed during current oscillations is probably a mixed-type film composed of  $\text{Fe}(\text{OH})_2$ ,  $\text{Fe}_3\text{O}_4$ , ferrous chloride and ferrous nitrate. The competitive adsorption of  $\text{Cl}^-$  and  $\text{NO}_3^-$  on the surface has begun during the current oscillations; moreover, the  $\text{NO}_3^-$  should dominate over  $\text{Cl}^-$  in the competition. Otherwise, the irregular current fluctuations like Fig. 4(d) will occur. Although the pitting corrosion of iron is inhibited effectively by nitrate ions in  $\text{H}_2\text{SO}_4 + \text{NaNO}_3 + \text{NaCl}$  mixed solution, the system itself is susceptible to pitting corrosion. The susceptibility of this system to the pitting is related to the fact that this system has the higher oscillation frequency and the shorter passivation time, as compared with the iron/ $\text{H}_2\text{SO}_4$  system.

## Summary

Nitrates behave like passivators and chlorides act as depassivators. Nitrates are able to protect the iron surface from the pitting attack by chlorides to great extent and ensure the iron surface to be passivated. The metallographic measurements confirmed that the pitting corrosion on the iron was inhibited effectively by nitrates.

The current oscillations for the iron in the solutions displayed rapid rise and stepwise drop. The former is attributed to two rapid consecutive dissolution reactions, the dissolution of the  $\text{Fe}(\text{OH})_2\text{-Fe}_3\text{O}_4$  bilayer film and the electrodisolution of the iron. The latter is due to the formation of  $\text{Fe}(\text{OH})_2\text{-Fe}_3\text{O}_4$  bilayer film or mixed films composed of the  $\text{Fe}(\text{OH})_2\text{-Fe}_3\text{O}_4$  bilayer film and salt film.

The oscillatory behavior is closely related to the susceptibility of the iron to the pitting. When the higher the oscillatory frequency, the more irregularly oscillatory process take place and the more prone to the pitting corrosion of iron.

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