Int. J. Electrochem. Sci., 15 **(2020)** 3315 – 3326, doi: 10.20964/2020.04.47

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

In situ Monitoring of pH at the Electrode|Electrolyte Interface During the Anodic Dissolution of Iron in Acidic Solutions

*Weiyan Ni, Yu shao, Jiaojiao Qi, Boyu Yuan, Liang Li**, *Chao Wang* *

Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou, 221116, China
*E-mail: lil@jsnu.edu.cn(Liang Li), wangc@jsnu.edu.cn(Chao Wang)

Received: 2 December 2019 / *Accepted:* 20 Janaury 2020 / *Published:* 10 March 2020

The anodic dissolution of iron in H_2SO_4 and HNO_3 solutions was studied by using scanning electrochemical microscopy (SECM) with a Pt ultramicroelectrode modified with polyaniline and by *in situ* monitoring of pH at the electrode|electrolyte interface. In each acidic solution, pH at the interface changed periodically during the observed current oscillations of iron, indicating that the oscillatory mechanism had some connection with pH. During the oscillatory processes, there were two layers of the film on the surface of the iron electrode: a loose outer layer ($Fe(OH)_2$ and the salt film) and a dense inner layer (Fe_3O_4). First, the outer layer was formed gradually, and then the inner layer was formed under the protection of the outer layer. With the back diffusion of H^+, the outer layer was dissolved gradually, indicating that the outer layer was mainly the $Fe(OH)_2$ film; however, the inner layer was broken immediately after the dissolution of the outer layer. The results showed that pH of the solution played a key role and that the anions played a minor role during the current oscillations. It was reasonable to deduce that the oscillations were mainly caused by a periodic formation and dissolution of the oxide film. Furthermore, the salt film played a minor role even though the acid concentrations were high.

Keywords: current oscillations; pH; oxide film; iron; acid.

1. INTRODUCTION

Complex kinetic behaviour is very common in an electrochemical reaction [1]. Under a non-equilibrium state, an electrochemical system shows instability. During the anodic dissolution of the metallic materials, electrochemical oscillations are often observed. The oscillatory processes include many nonlinear dynamic processes, such as the formation and dissolution of surface films, mass transfer, and surface chemical reactions. Because oscillation is one of the most common dynamic self-organization phenomena [2], studying nonlinear dynamic processes is of great significance in the field of metal corrosion [3]. Electrochemical oscillations have been studied since the beginning of the 19th century [4]. Although the Fe|H_2SO_4 system was one of the earliest electrochemical oscillations, there is still controversy about the composition of the surface film during current oscillations due to the complex processes of the oscillations.

It is well known that the current oscillations are caused by periodic formation and dissolution of the surface film during the anodic dissolution of the metallic materials. Understanding the structure and composition of the surface film is a key to studying the oscillatory processes. There are different opinions about the composition of the surface film during the current oscillations of iron in acidic solutions. Some researchers [5,6] believed that it was a salt film, while others [7,8] proposed that it was an oxide film or mixed film. Podesta [9] put forward two different views, and they proposed that it was an oxide film if the concentration of H_2SO_4 (c_{H2SO4}) was lower than 1 M, and it was a salt film ($FeSO_4$) if c_{H2SO4} was higher than 1 M.

Hydrogen ions are particularly important for studying the structure and composition of surface films. If it is a salt film, pH will change little; if it is an oxide film, pH will change accordingly. It is easy to monitor pH at the bulk solution; however, the electrochemical reaction, which is a heterogeneous reaction, occurs at the interface, and pH at the interface is quite different from that of the bulk solution due to the concentration polarization. It is difficult to monitor pH at the interface by using a general electrode because the scale of the interface is too small.

Because scanning electrochemical microscopy (SECM) has the advantages of real-time, high spatial resolution, and high sensitivity in the redox process at the interface, it is a powerful technique to observe electrochemical processes *in situ* [10]. It has been successfully used to observe the dynamic processes of anodic dissolution, cathode deposition, and pitting corrosion, etc., *in situ*. [11-20]. Revealing the nature of local corrosion of metal provides an increasingly convincing experimental basis. Recently, our group monitored pH at the Fe|H_2SO_4 interface *in situ* by using SECM with a Pt ultramicroelectrode modified with polyaniline, and it was found that the electrode had good selectivity for hydrogen ions [21]. As a result, it was proposed that the surface film was the oxide film (Fe_3O_4) because pH at the electrode|electrolyte interface changed in pace with the anodic current [21].

In this paper, SECM was conducted with a Pt ultramicroelectrode modified with polyaniline to study the anodic dissolution of iron in H_2SO_4 and HNO_3 solutions. During the oscillatory processes of iron in different acidic solutions, pH at the interface was monitored *in situ*. Based on the observed results, the oscillatory mechanisms of iron in the acidic solutions were discussed.

2. EXPERIMENTAL

A four-electrode system was used for the SECM (CHI 900D, CHI Instruments) measurements. The working electrode (the substrate electrode) was made of iron wire (d = 2.0 mm, 99.95%, Johnson Matthey Company). The iron wire was embedded in epoxy resin, only exposing the end of the wire to the solution. A Pt (d=10 μm) ultramicroelectrode was electrochemically polymerized with polyaniline in 0.5 M $C_6H_5NH_2 \cdot HCl$ + 1.5 M HCl solution at 0.70 V for 10 min, and it was used as the SECM tip, which was another working electrode, to monitor pH at the iron|acid interface at E'_{tip}=-0.60 V [21]. The I'_{tip} (tip current) vs the acid concentration curve at -0.60 V (not shown) was measured using the SECM tip. The higher the reduction current of H^+ (I'_{tip}), the lower the pH. In each test, the substrate electrode faced upwards, and the distance between the tip and the substrate electrode (dtip-Fe) was set at 200 μm unless otherwise noted. A platinum plate was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. All potentials reported in this work were referenced in relation to the SCE. To decrease the IR drop, a Luggin capillary was placed between the substrate electrode and the reference electrode. Before each experiment, the substrate electrode was ground with 600# and 1200# metallographic sandpaper and then cleaned in an ultrasonic bath with anhydrous ethanol and twice distilled water. All the solutions used in the experiment were prepared with analytical reagents and twice distilled water. All of the experiments were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1. Cyclic voltammetry curves of iron in acidic solutions

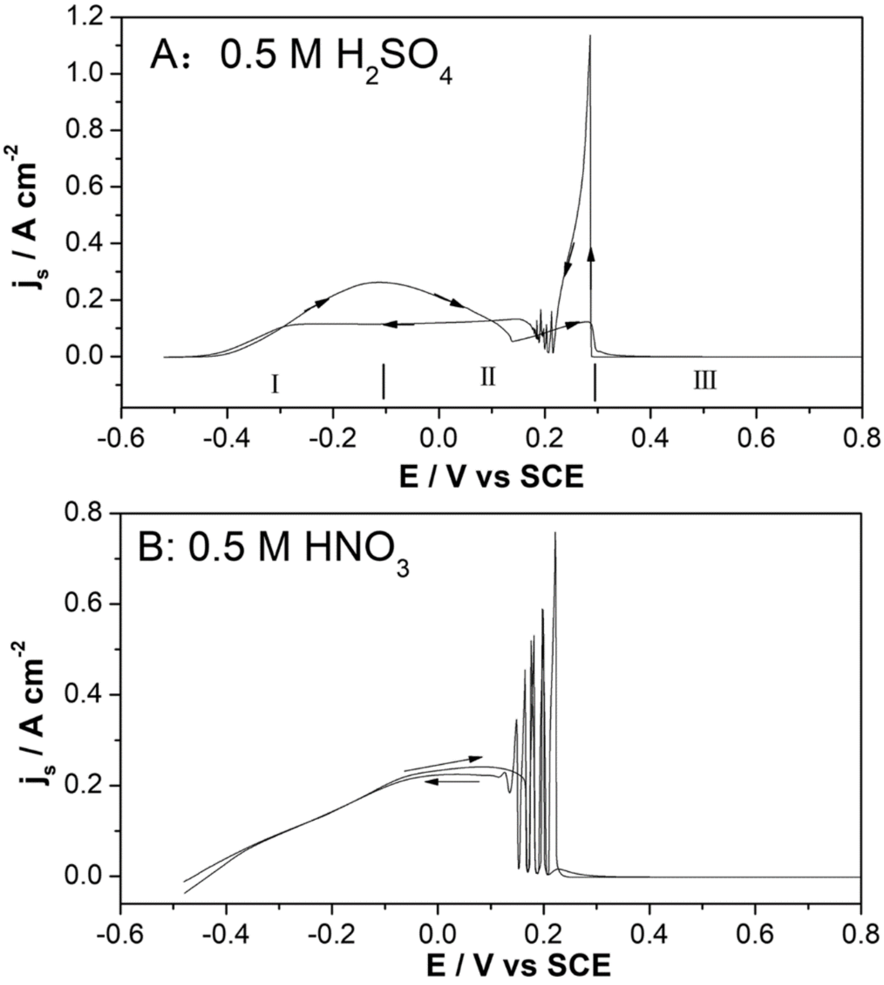

Figure 1. Cyclic voltammetry curves of Fe in 0.5 M H_2SO_4 (A) and 0.5 M HNO_3 (B) at 10 mV/s.

Fig. 1 shows the cyclic voltammetry curves of iron in 0.5 M H_2SO_4 (A) and 0.5 M HNO_3 (B) solutions at 10 mV/s. First, the potential scans positively from the open circuit potential (OCP) to 0.8 V and then negatively from 0.8 V to the OCP in each test. In each acidic solution, there are three potential regions in the positive scan: the active region, the prepassive region, and the passive region (Fig. 1a). In the active region (I), the current increases with the potential, and the rate-determining step is an electrochemical step. After a current peak appears, the current decreases as the potential shifts positively, indicating that a surface film is formed in the prepassive region (II), and the rate-determining step is a mass-transfer step. After the current oscillations are observed, the electrode becomes passive in the passive region (III), indicating that a passive film is formed. In the reverse scan, the electrode is reactivated, and current oscillations are observed.

Wang *et al* [6, 22] studied the anodic dissolution of iron in H_2SO_4 solution with the digital holography and the flow injection methods, respectively. In the cyclic voltammetry curves of iron in 0.5 M H_2SO_4 solution, the platform currents in References [6, 22] were much higher than those shown in Fig. 1A in this paper. Cui *et al* [23] studied the current oscillations of iron in the nitric acid solutions. In the polarization curves of iron in 0.5 M HNO_3 solution, the oscillatory potential region was much narrower in Reference [24] than that in this paper.

3.2. The j–t Curves of iron in H_2SO_4 and HNO_3 solutions

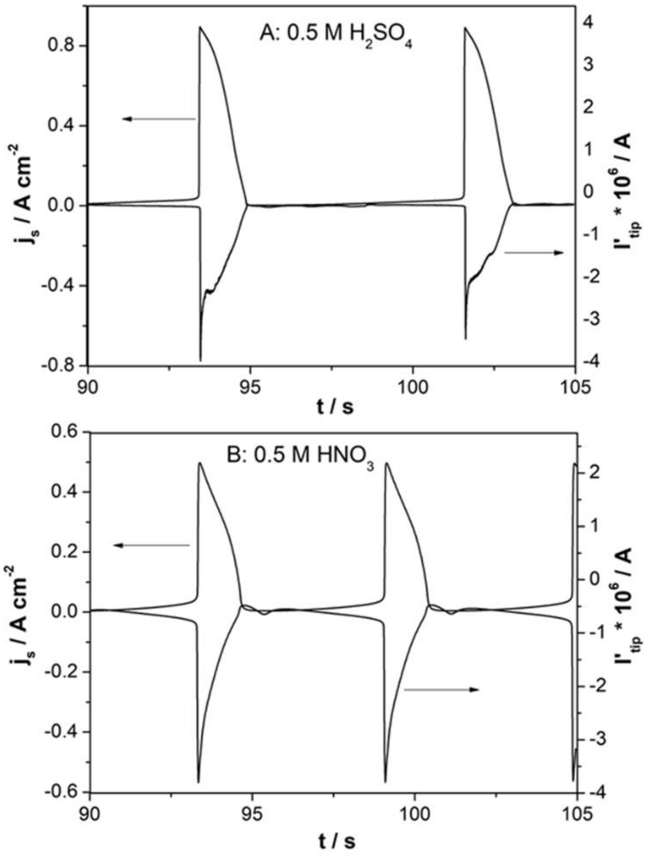

Figure 2. Superposition parts of I'_{tip} - t curves of the polyaniline modified Pt tip and j_s – t curves of the substrate electrode in 0.5 M H_2SO_4 at E_s = 0.22 V (A) and 0.5 M HNO_3 at E_s = 0.17 V (B).

Fig. 2 shows parts of the *I'*$_{tip}$ *-t* curves of the Pt ultramicroelectrode modified with polyaniline at E'$_{tip}$=-0.60 V superimposed with the anodic current of the substrate electrode (j_s) vs time (t) curves in 0.5 M H_2SO_4 (A) at 0.22 V and 0.5 M HNO_3 (B) at 0.17 V. In each solution, *I'*$_{tip}$ changes in step with j_s, indicating that the oscillations of pH at the interface were monitored *in situ* during the current oscillations of iron.

Podesta [9] proposed that the surface film was a salt film if the concentration of H_2SO_4 solution (c_{H2SO4}) was relatively high. To further study the composition of the surface film, pH at the interface was also monitored *in situ* during the anodic dissolution of iron in relatively high concentrations of two different acids.

Fig. 3 shows parts of the *I'*$_{tip}$ *-t* curves superimposed with the j_s-t curves in 1.5 M H_2SO_4 (A) at 0.27 V and 1.5 M HNO_3 (B) at 0.21 V. Even though the salt film seems to be formed more easily due to the high concentrations of anions, pH oscillations at the interface are also observed *in situ* during the current oscillations of iron in relatively high concentrations of the acids. If the oscillations were caused by periodic formation and dissolution of the salt film, the anodic current would be low in high concentrations of the acids. However, both *I'*$_{tip}$ and j_s are much higher in high concentrations of the acids (Fig. 3) than in low concentrations of the acids (Fig. 2), indicating that the current oscillations are still caused by the periodic dissolution of the oxide film in high concentrations of the acids.

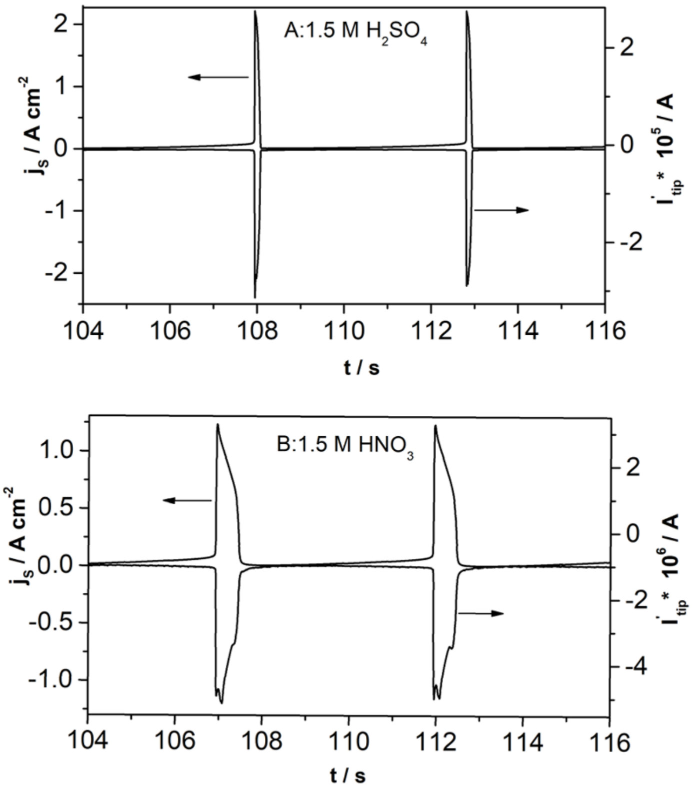

Figure 3. Superposition parts of I'$_{tip}$ - t and j_s - t curves in 1.5 M H_2SO_4 at E_s = 0.27 V (A) and 1.5 M HNO_3 at E_s = 0.21 V (B).

3.3 Effects of Fe^{2+} on pH measurement

Because pH and Fe^{2+} concentration [21] changes dynamically during the current oscillations of the iron electrode in acidic solutions, the changes in Fe^{2+} concentration may affect pH measurements. To verify whether the changes in Fe^{2+} concentration may affect pH, the effects of Fe^{2+} ions on pH have been studied.

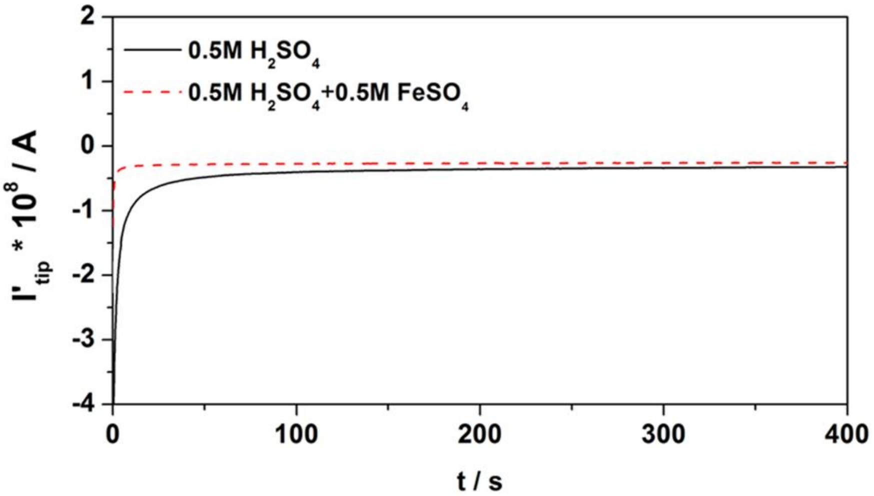

Figure 4. The I'_{tip}-t curves in 0.5 M H_2SO_4 solution without and with the addition of 0.5 M $FeSO_4$, E'_{tip} = -0.60 V.

A polyaniline film has high permeability towards hydrogen ions but inhibits the diffusion of large, highly charged ions (e.g., Fe^{2+}, Eu^{3+}) to the electrode surface [24]. As shown in Fig. 4, when 0.5 M Fe^{2+} ions were added in the 0.5 M H_2SO_4 solution, the current was minimally affected, and thus, it is confirmed that the reduction current of H^+ can hardly be affected by Fe^{2+}.

3.4 Effects of d_{tip-Fe} on I'_{tip}

Because pH at the interface is quite different from that in the bulk solution, it is reasonable to deduce that there is a gradient of H^+ near the surface. To verify this proposal, the effects of the distance between the microelectrode and the substrate electrode (d_{tip-Fe}) on I'_{tip} were studied.

Fig. 5 shows the effects of d_{tip-Fe} on the I'_{tip}-t curves at E'_{tip} = -0.60 V during the current oscillations of iron in the 0.5 M H_2SO_4 solution at E_s = 0.22 V. It is interesting to find that I'_{tip} depends on d_{tip-Fe}. The tip current oscillations are observed when d_{tip-Fe} changes from 50 μm to 200 μm and then to 600 μm (Figs. 5A-5C), and the oscillatory amplitude decreases as d_{tip-Fe} increases. However, the tip current minimally changes when the tip is set in the bulk solution (Fig. 5D). In other words, the longer the d_{tip-Fe} is, the lower the tip current is, which indicates that there is a concentration gradient of H^+ at the interface. It is further proof that the current oscillations of the iron in the acidic solutions are mainly caused by the periodic formation and dissolution of the oxide film rather than the salt film.

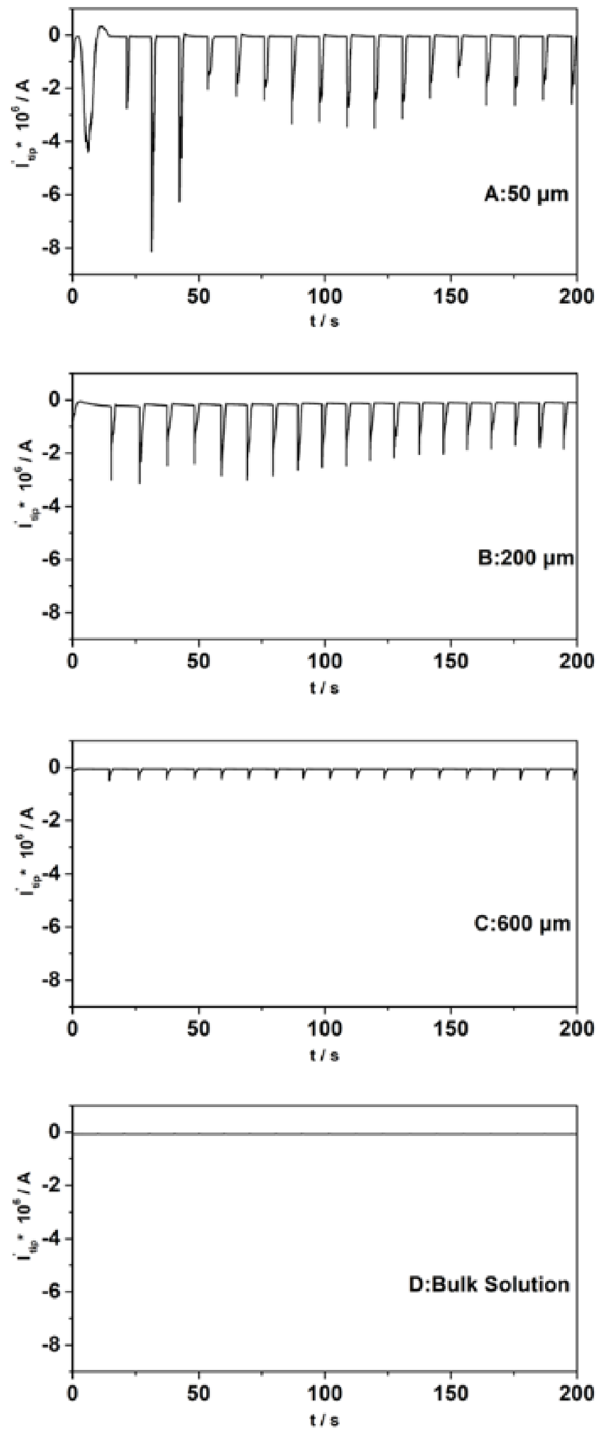

Figure 5. Effects of $d_{tip\text{-}Fe}$ (the distance between tip and the substrate electrode) on the I'_{tip}-t curves in 0.5 M H_2SO_4 solution at E_s =0.22 V. A: 50 μm; B: 200 μm; c: 500 μm; D: in the bulk solution.

3.5. Discussion

Oscillatory processes of iron in the acidic solutions

During the anodic dissolution of iron in the acidic solutions, oscillations of pH were observed during the anodic dissolution of iron in each acidic solution. Fig. 6 shows the schematic map of the oscillatory processes corresponding to a period of the current oscillation (j_s - t curve). As shown in the j_s - t curve, the period of the current oscillation includes the active period (t_a) from point a to point c and the passive period (t_p) from point c to point e. The oscillatory processes of iron in the acidic solutions can be illustrated as follows.

(1) At point a, pH decreases slightly, and the current increases slowly, and a few Fe^{2+} ions are produced.

(2) At point b, the current rises immediately after the inner layer (the dense oxide film) is broken, indicating that the electrode is activated and many Fe^{2+} ions are produced. To maintain neutrality, the Fe^{2+} ions repel the surrounding H^+ ions to increase pH at the interface. At the same time, Fe^{2+} attracts anions (such as SO_4^{2-}). Then, an $FeX_{2/n}$ ($X = SO_4^{2-}$ and NO_3^-; n: valence of anion) and $Fe(OH)_2$ film (the outer layer) is formed. This kind of film is relatively loose and not protective.

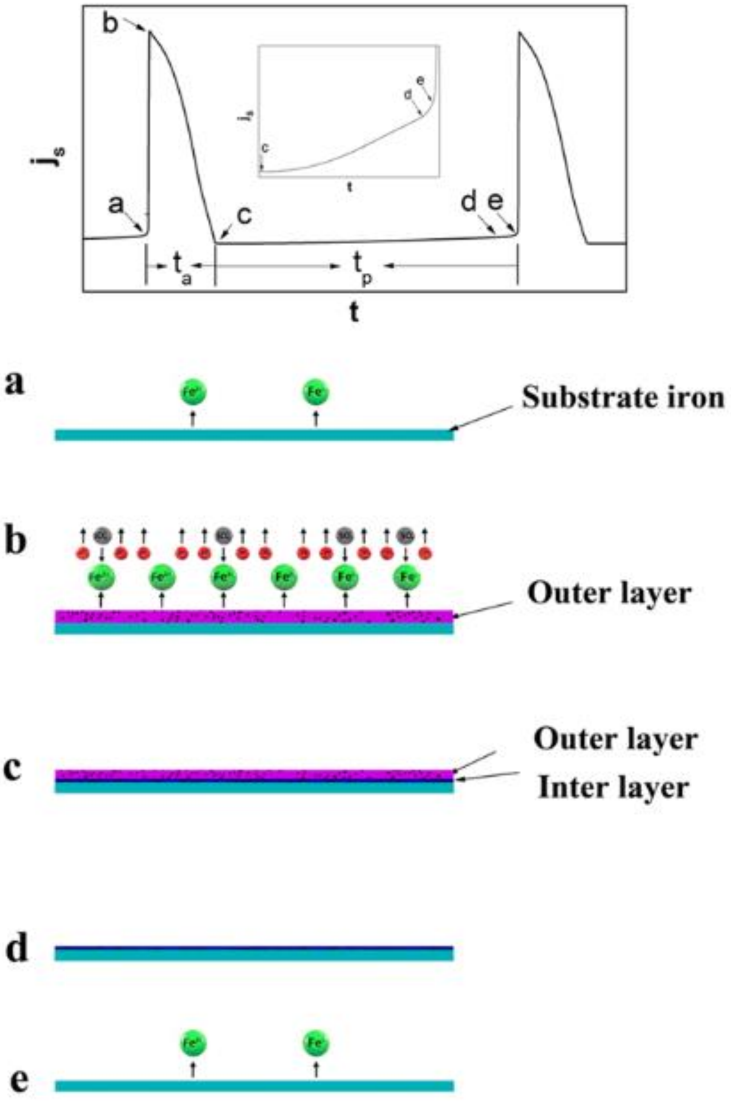

Figure 6. A period of the current oscillation (j_s - t curve, upper part) and the schematic map (lower part) of the oscillatory processes of iron in the acidic solutions, a-e in j_s - t curve corresponding to those shown in the lower part. The inserted part: enlarged part of c-e shown in j_s - t curves.

(3) At point c, the current is almost zero because the dense inner layer (Fe_3O_4) is formed on the electrode surface with the protection of the outer layer, indicating that the electrode is passive.

(4) At point d, after the electrode is passive, H^+ ions diffuse back to dissolve the film. As shown in the inserted part of Fig. 6A, the dissolution of the film can be divided into two processes. In the first process (from point c to d), the current increases slowly with the dissolution of the outer layer because it is not protective and the inner layer is not destroyed. In the second process after point d, the inner layer is broken immediately after the outer layer is removed, and the current increases to enter the next cycle of the oscillation (point e).

There is a question arising: why was the outer layer dissolved gradually but the inner layer broken quickly? This can be explained as follows: because the outer layer was loose and distributed in the solution near the surface, its dissolution was controlled by mass-transport processes. It is generally accepted that the inner layer (Fe_3O_4) is only several nanometres thick, so it is broken immediately with the presence of the back diffusion of H^+ ions.

In this paper, the electrode faces upwards. In other papers [6, 22, 23], the electrode faces sideward during the electrochemical experiments. No matter the electrode faces sideward [6, 22, 23] or upwards (this paper), there are three potential regions: active region, prepassive region, and passive region, indicating that the direction of electrode surface does not affect the electrochemical processes. However, the platform current is higher and the oscillatory region is narrower because the corrosion products was dissolved more easily when the electrode surface faced sideward than it faced upwards in this paper.

Role of anions during current oscillations

Although pH plays a key role during the current oscillations of iron in the acidic solutions, it does not imply that anions affect the current oscillations. Because the oscillatory periods and potentials are different in different acidic solutions, it is reasonable to deduce that this difference was caused by anions. The main effects of anions on the current oscillations are described in the following two ways.

(1) During current oscillations, $Fe(OH)_2$ is also formed because a large amount of Fe^{2+} ions are produced at the interface, which repel H^+ ions and increase pH at the interface. At the same time, many anions move to the interface to maintain electric neutrality at the interface. As a result, a salt film may also be formed if the solubility of the salt is not high enough.

(2) The anions easily adsorb to the surface, and the anions have different adsorption abilities. This is why the oscillatory potential regions are different in different acids (Fig. 1).

To verify this proposal further, the effects of the salts on the current oscillations of iron in the acidic solutions are studied. Fig. 7 shows parts of the I'_{tip} -t curves superimposed with the j_s-t curves in 0.5 M H_2SO_4 + 0.1 M Na_2SO_4 (A) at 0.22 V and 0.5 M HNO_3 + 0.1 M $NaNO_3$ (B) at 0.17 V, respectively. In the acidic solutions with the presence of salts, the salt film seems to be formed more easily because of the high concentrations of anions; however, oscillations of pH at the interface are also observed *in situ* during the current oscillations of iron. The oscillatory parameters with and without the added salts in the acidic solutions (Figs. 1 and 7) are shown in Table 1. The effects of the salts on the current oscillations can be illustrated as follows:

(1) With the presence of the added salts, the active time (t_a) and t_a/t_p decrease, indicating that

the outer layer is formed more quickly and then the inner layer is formed more easily with the protection of the outer layer. It is reasonable to deduce that the outer layer is composed of the salt film.

(2) With the presence of 0.1 M Na_2SO_4, the t_p decreases. The ratio of the salt film in the outer layer increases, and the dissolution of the salt film is easier because the solubility of the salt film is much higher than that of the $Fe(OH)_2$ film. However, t_p increases in 0.5 M HNO_3 + 0.1 M $NaNO_3$ solution because the inner layer becomes denser due to the increased oxidation ability of the solution with an increasing NO_3^- concentration.

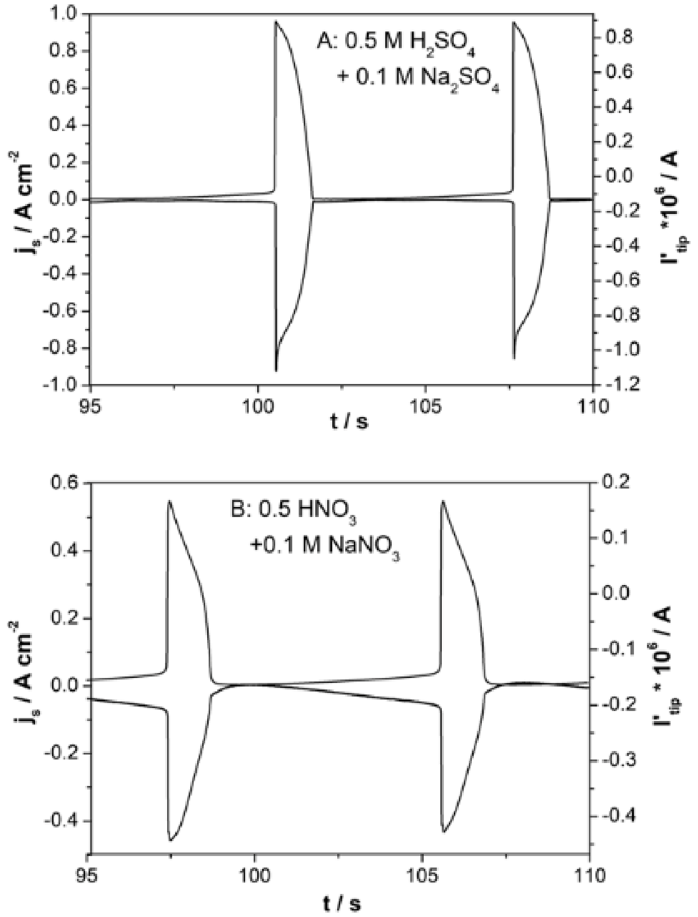

Figure 7. Superposition parts of I'_{tip} - t curves and j_s – t curves in 0.5 M H_2SO_4 + 0.1 M Na_2SO_4 at E_s = 0.22 V (A) and 0.5 M HNO_3 + 0.1 M $NaNO_3$ at E_s = 0.17 V (B).

Table 1. The oscillatory parameters of iron in different solutions

Solution	t_{period} / s	t_a / s	t_p / s	t_a / t_p
0.5 M H_2SO_4	8.13	1.5	6.63	0.226
0.5 M H_2SO_4 + 0.1 M Na_2SO_4	7.10	1.2	5.90	0.203
0.5 M HNO_3	5.77	1.47	4.30	0.342
0.5 M HNO_3 + 0.1 M $NaNO_3$	7.91	1.41	6.50	0.217

4. CONCLUSIONS

In this paper, the current oscillations of iron in H_2SO_4 and HNO_3 solutions were studied by SECM combined with a polyaniline modified probe. Oscillations of pH at the interface were monitored *in situ* during the current oscillations of iron in different acidic solutions. It was also verified that there was a gradient of H^+ ions between the surface and the bulk solution. The conclusions can be drawn as follows.

(1) During the current oscillations, there were two layers on the surface of the film: the outer layer ($FeX_{n/2}$ and $Fe(OH)_2$) and the inner layer (Fe_3O_4). The oscillations were caused by periodic formation and dissolution of the surface film. Both layers were gradually formed, and similarly, the outer layer was also gradually dissolved; however, the inner layer was broken suddenly because the inner layer was only several nanometres thick, and it dissolved quickly with the back diffusion of H^+ ions.

(2) Because the H^+ ions played a key role, the outer layer was mainly the $Fe(OH)_2$ film. Anions played a minor role by forming a salt film and adsorbing on the surface of the electrode during the oscillatory processes.

ACKNOWLEDGEMENTS
This research was supported by the National Natural Science Foundation of China (No. 21972059) and the Priority Academic Programme Development of the Jiangsu Higher Education Institutions (PAPD).

References

1. D.Y. Hua, J.L. Luo, *Chemical. Phys. Lett.*, 299 (1999) 345.
2. Nebojsa I. Potkonjak, *Reac. Kinet. Mech. Cat.*, 123 (2018) 155.
3. Dimitra Sazou, Michael Pagitsas, *Electrochim. Acta*, 51 (2006) 6281.
4. Hiroshi Okamoto, Naoki Tanaka, Masayoshi Naito, *J. Phys. Chem. A.*, 102 (1998) 7343.
5. Michael Pagitsas, Dimitra Sazou, *J. Electroanal. Chem.*, 471 (1999) 132.
6. B.Y. Yuan, J.L. Zhang, G.F. Gao, L. Li, C. Wang, *Electrochem. Commun.,* 27 (2013) 116.
7. C. Wang, S.H. Chen, X.L. Yu, *Electrochim. Acta*, 39 (1994) 4.
8. A. Karantonis, D. Koutsaftis, M. Bredaki, N. Kouloumbi, *Chem. Phys. Lett.*, 460 (2008) 182.
9. J. J. Podesta, R. C. V. Piatti, A. J. Arvia, *J. EIectrochem. Soc.*, 126 (1979) 8.
10. Y.H. Yin, L. Niu, M. Lu, W.K. Guo, S.H. Chen, *Appl. Surf. Sci.*, 255 (2009) 9193.
11. Tirdad Nickchi, Paul Rostron, Imad Barsoum, Akram Alfantazi, *J. Mater. Sci.*, 54 (2019) 9213.
12. S.Y. Zou, X.L. Zhou, Y.H. Rao, X.Z. Hua, X. Cui, *J. Alloys Compd.*, 780 (2019) 937.
13. Q.H. Zhang, P. Liu, Z.J. Zhu, Z.N. Ye, J.Q. Zhang, F.H. Cao, X.G. Li, *Electrochem. Commun.*, 93 (2018) 143.
14. A.C. Bastos, A.M. Simoes, S. Gonzalez, Y. Gonzalez-Garcia, R.M. Souto, *Electrochem. Commun.*, 6 (2004) 1212.
15. Koji Fushimi, Masahiro Seo, *Electrochim. Acta*, 47 (2001) 121.
16. A.G. Marques, J. Izquierdo, R.M. Souto, A.M. Simões, *Electrochim. Acta*, 153 (2015) 238.
17. Edgar Volker, Carlota Gonzalez Inchauspe, Ernesto J. Calvo, *Electrochem. Commun.,* 8 (2006) 179–183.
18. C. Gabrielli, S. Joiret, M. Keddam, H. Perrot, N. Portail, P. Rousseau, V. Vivier, *Electrochim. Acta*, 52 (2007) 7706.
19. Z.J. Zhu, Z.N. Ye, Q.H. Zhang, J.Q. Zhang, F.H. Cao, *Electrochem. Commun.*, 88 (2018) 47.
20. J. Izquierdo, L. Martín-Ruíz, B.M. Fernández-Pérez, R. Rodríguez-Raposo, J.J. Santana, R.M. Souto, *J. Electroanal. Chem.*, 728 (2014) 148.
21. R. Liu, M. Zhang, Q.H. Meng, B.Y. Yuan, Y.Y. Zhu, L. Li, C. Wang, *Electrochem. Commun.*, 82

(2017) 103.
22. M. Zeng, C. Wang, L. Li, *Electrochem. Commun.*, 11 (2009) 1888.
23. N. Cui, S. Y. Zhao, C. Wang, S. H. Chen, *J. Serb. Chem. Soc.*, 66 (2001) 563.
24. Yukio Ohnuki, Hiroaki Matsuda, Takeo Ohsaka, Noboru Oyama, *J. Electroanal. Chem.*, 158 (1983) 55.