Current oscillations of iron in *p*-toluenesulfonic acid[*]

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The periodic current oscillations of an iron electrode in *p*-toluenesulfonic acid (PTSA) solutions were investigated by cyclic volatammetry and potentiostatic polarization. The Fe/PTSA system is a new electrochemical oscillator and shows some interesting phenomena. The oscillations are ascribed to the alternate buildup and breakdown of $Fe(OH)_2$ and Fe_3O_4 films.

Keywords: iron, electrodissolution, *p*-toluenesulfonic acid, current oscillation, pH dependence.

INTRODUCTION

p-Toluenesulfonic acid (PTSA) is used in many fields as a kind of strong organic acid,[1–4] but current oscillations of the Fe/*p*-toluenesulfonic acid system has not been reported until now. Otherwise, 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,[5–8] not only because of its potential important implications in corrosion and protection,[9] but also because of its role in the attempt to understand oscillation phenomena occurring in interfacial processes.[5–11] Some models of oscillators have been made to explain metal corrosion, diffusion and passivation.[10,11] However, since metal electrodisolution-passivation is a very complicated process, these models are not fully in accord with the experimental results. For example, the potentiostatic current oscillations in the Fe/sulfuric acid system during the transition from the prepassive to the passive region have been extensively studied and many mechanisms have been presented, but no satisfactory description of the periodic phenomenon has yet been produced, especially the composition of the prepassivating film.[5–11] Some investigators supported the suggestion that the film is ferrous sulfate,[7,8] while others favored the idea that it is ferrous hydroxide.[10,11]

The purpose of this paper is to summarize the results of a recent experimental investigation of the anodic dissolution of Fe in *p*-toluenesulfonic acid. It is hoped thereby

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to gain a better understanding of the dependence of the oscillatory behavior on the electrode potential, the electrolyte concentration and the hydrodynamic conditions.

EXPERIMENTAL

The electrochemical experiments were carried out in a three-compartment cell. 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 recorder. The working electrode, 2.5 mm in diameter, was prepared from an iron rod of 99.99 % purity (Johnson Mattey 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 Hg/Hg_2SO_4 electrode was used as a reference electrode, with its Luggin capillary probe located 2 mm below the working electrode. All the electrode potentials reported in this paper are referenced to the Hg/Hg_2SO_4 electrode in 0.5 M H_2SO_4. The electrolytes were prepared from analytical grade reagents and triply distilled water. The working electrode was polished by 600 and 1200 grade emery paper and washed with triply distilled water prior to each experiment. The temperature was controlled by a superthermostat. All the experiment were performed at a temperature of 25 ± 1 ºC.

RESULTS

The characteristics of i–E curves of the Fe/PTSA oscillatory system

Figure 1 shows the effect of the PTSA concentration on the cyclic voltammetry curves of the Fe/PTSA oscillatory system. The potential scan rate was 2 mV/s. The scanning potential region was from the corrosion potential to + 0.4 V. The thin dotted line represent the forward potential scan and the solid line represent the backward potential scan.

No oscillations were observed in any of the curves of the forward potential scan. In 0.1 M PTSA (Fig. 1a), from $E = -1.06$ V to $E = -0.4$ V the current first increased continuously until a maximum value appeared and then decrease gradually until a very low value was attained at $E = -0.24$ V meaning that the Fe electrode was passivated. In higher concentrations of PTSA (Fig. 1b–d), the phenomenon was different to that in 0.1 M PTSA as two oxidation peaks were visible in each case. For example, in 0.5 M PTSA (Fig. 1d) the first peak appeared at – 0.80 V and the second one at – 0.20 V. The first one represents the oxidation of Fe to Fe(II) and the second one the oxidation of Fe(II) to Fe(III).

In the curve of the backward potential scan of 0.1 M PTSA (Fig. 1a), no current oscillations were found. From $E = +0.4$ V the current initially kept a low value but increased abruptly to a large value at – 0.23 V. Then current decreased continuously (from $E = -0.23$ V to $E = -1.06$ V). With increasing PTSA concentration (0.2 M and 0.4 M), the obvious current oscillations appeared in a certain potential region. The amplitude of the current oscillations decrease gradually until the oscillations disappeared. Then the current maintained a certain value for a long time and then finally became small. In 0.5 M PTSA, the *i–E* curve showed similar phenomena as it in 0.2 M and 0.4 M PTSA, except that no oscillations were observed.

The potentiostatic i–t curves of the Fe/PTSA system

Figure 2 shows the effect of the PTSA concentration on the *i–t* curves of Fe/PTSA system. In this experiment, the applied potential was stepped from the corrosion poten-
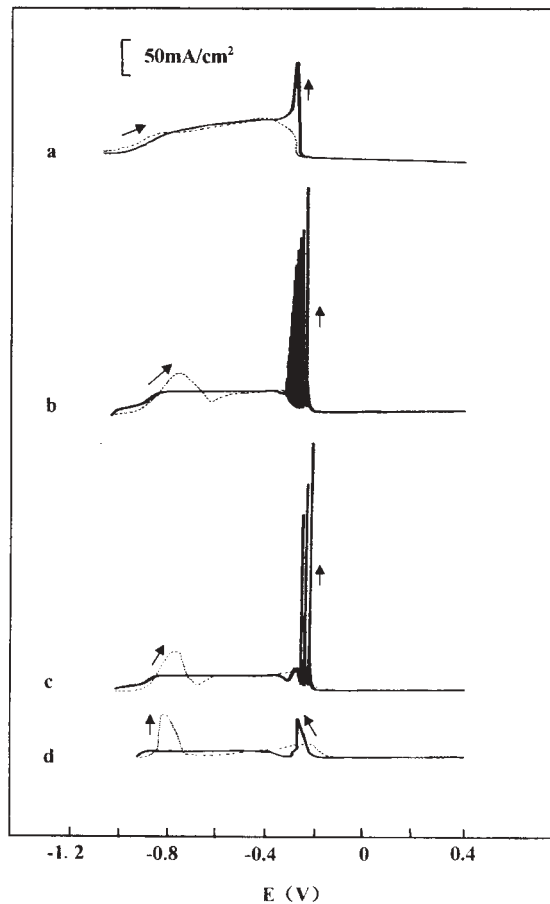
Fig. 1. Effect of the *p*-toluenesulfonic acid (PTSA) concentration on the polarization behavior of the Fe/PTSA system. (a) 0.1 M; (b) 0.2 M; (c) 0.4 M; (d) 0.5 M.

tial of the electrode to -220 mV. For 0.5 M PTSA (Fig. 2a), no current oscillations were observed. The electrode was active. With decreasing PTSA concentration, current oscillations appeared (Fig. 2b–d). For 0.4 M PTSA (Fig. 2b), the electrode was in an active state for 14 s before the current oscillations appeared. When the concentration of PTSA was 0.3 M (Fig. 2c), the active state time of the electrode became 10 s. However, for 0.2 M PTSA (Fig. 2d), after polarization of the electrode the current oscillations began immediately, but only lasted 10 s before the oscillations ceased and the current maintained a very low value. For 0.1 M PTSA (Fig. 2e), there were no current oscillations and the electrode surface was passivated.

Figure 3 shows the effect of the polarization potential on the resulting *i–t* curves of the Fe/0.2 M PTSA system. The oscillation wave forms varied with potential regions. For $E = -200$ mV, the current was very low meaning that the surface of electrode was passivated. No current oscillations were observed. In the current oscillation region
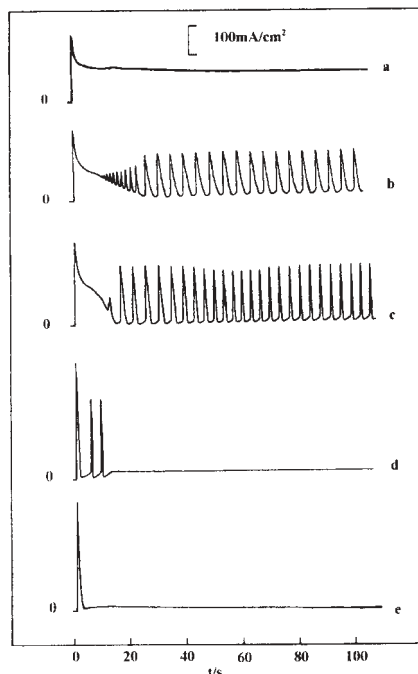
Fig. 2. *i–t* curves of the Fe/PTSA system as a function of the PTSA concentration. (a) 0.5 M; (b) 0.4 M; (c) 0.3 M; (d) 0.2 M; (e) 0.1 M.
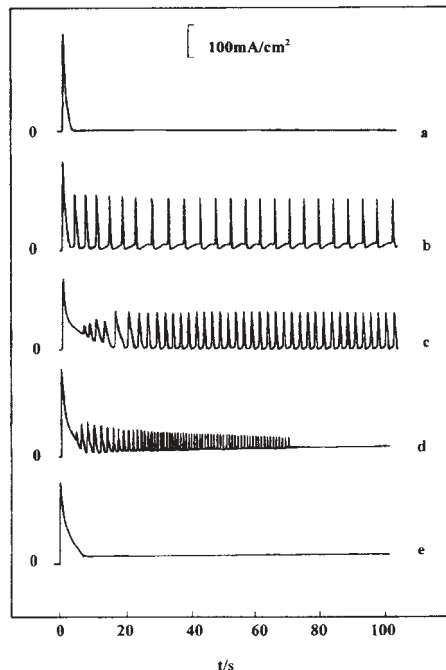
Fig. 3. *i–t* curves of the Fe/PTSA system as a function of the potential. (a) – 200 mV; (b) – 220 mV; (c) – 260 mV; (d) – 280 mV; (e) – 300 mV.

from $E = -220$ mV to -280 mV, the variation of the electrode potential affected the amplitude and the period of the oscillations. With decreasing potential, the current oscillation amplitude decreased and the period shortened. Especially when $E = -280$ mV (Fig. 3d), the current oscillation was not as regular as those when $E = -220$ mV or -260 mV. The current oscillation period is longer when $t < 20$ s than when $t > 20$ s. The oscillation amplitude became smaller and smaller and then the oscillation disappeared at $t = 72$ s. For $E = -300$ mV, no current oscillations appeared, the electrode was in an active state.

DISCUSSION

The chemical composition of surface of mild steel after passivation in 1 M PTSA solution was studied by Camalet with XPS.[1] No sulfur signals were observed on the samples and analysis of the oxygen signal confirmed the presence of metallic oxide, hydroxide and oxyhydroxide. So, it is impossible to form a salt film on the electrode surface in the Fe/PTSA system. In Fig. 1b the plateau current density is the diffusion limiting current density (i_L), which can be given as:

$$i_L = zFDc/\delta \qquad (1)$$

where D is the diffusion coefficient, δ is the thickness of diffusion layer, z is the charge involved in the reaction, F is the Faraday constant and c is the concentration

of the diffusing ions. Under stationary condition (in this study), $\delta \approx 0.05$ cm and for the majority of ions, $D = 10$ cm^2/s at 25 ºC, so that Eq. (1) can be simplified:[12]

$$i_L = 20 \, z \, c \qquad\qquad (2)$$

assuming Fe dissolves as

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad\qquad (3)$$

The solubility of Fe(OH)$_2$ is 1.5×10^{-6} g/ml at 18 ºC.[13] The ferrous ion concentration was calculated from (2) as 7.5×10^{-4} mol/cm^3 in 0.2 M PTSA near the electrode surface. This concentration is high enough for ferrous hydroxide to be precipitated, although this is only an estimate.

In the cases of oscillation, when the potential is first applied, Fe is electrochemically oxidized to Fe^{2+}. Its concentration at the Fe/solution interface rapidly increases. The formation of Fe^{2+} results in the electromigration of H$^+$ away from the vicinity of the electrode. Hence, near the electrode surface the pH increases gradually. Under this condition, it is to be expected that Fe(OH)$_2$ will precipitate as the initial surface blocking species. It is not compact and dissolves easily in acidic solution. As long as the rate of film formation is greater than the rate of its dissolution, the film thickens. When the current attains its maximum value, it is possible that an Fe$_3$O$_4$ film forms on the substrate of the iron electrode.[10] The current begins to decrease sharply and the electrode is passive. Thus, the dissolution rate of the electrode becomes low, the backward diffusion of H$^+$ from the bulk solution to the electrode will enable the Fe(OH)$_2$ to be dissolved quickly. The Fe$_3$O$_4$ film is also unstable in acidic solution and will dissolve after Fe(OH)$_2$. Thus, the iron electrode is activated again and the cycle of the same steps repeats.

In low concentrations of PTSA, the oxide film formed on the electrode surface is stable and the dissolution of Fe is slow (Fig. 2e). With increasing concentration of PTSA (Fig. 2d – b), the formation of a thick Fe(OH)$_2$ film becomes difficult. On the other hand, after the formation of Fe$_3$O$_4$, the backward diffusion of H$^+$ will result in a more rapid dissolution of the Fe(OH)$_2$ and Fe$_3$O$_4$ film. This causes the appearance of current oscillations. The time of passivation is accordingly shortened. If the concentration of PTSA is sufficiently high, the film dissoulution rate is increased to the point where there is only a very thin film, or no film at all, so that current oscillations do not commence (Fig. 2a).

At low potentials, the rate of formation of the Fe(OH)$_2$ film is relatively slow compared to the rate of film dissolution and so any film dissolves as soon as it is formed (Fig. 3e). Hence the electrode remains active and current oscillations does not appear. As the potential increases, the rate of film formation increases until it exceeds the dissolution rate and an Fe(OH)$_2$ film begins to build up on the Fe surface (Fig. 3d – b). The fraction of the anodic current which is consumed to oxidize Fe(II) to Fe(III) becomes larger with increasing potential. This probably results in the formation of a compact Fe$_3$O$_4$ film on the surface of the electrode; thus the time of passivation is increased. At the same time, the diffusion of H$^+$ results in the dissolution the Fe(OH)$_2$ and Fe$_3$O$_4$ film so that current oscillations appear. At potentials more than the Flade potential, the Fe$_3$O$_4$ will transform into γ–Fe$_2$O$_3$, and the electrode is passivated (Fig. 3a).[10]

CONCLUSIONS

A new current oscillations phenomenon was observed in the Fe/PTSA system. The oscillations have been ascribed to the cyclic formation and breakdown of an $Fe(OH)_2$ and Fe_3O_4 film. The experimental results show that the pH of the solution plays an important role in the current oscillations in the Fe/PTSA system.

И З В О Д

СТРУЈНЕ ОСЦИЛАЦИЈЕ НА ГВОЖЂУ У *p*-ТОЛУЕНСУЛФОНСКОЈ КИСЕЛИНИ

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Испитиване су струјне осцилације на електроди од гвожђа у растворима *p*-толуенсулфонске киселине (PTSA) цикличном волтаметријом и поларизацијом (потенциостатском). Систем Fe/PTSA је нови електрохемијски осцилатор који показује неке интересантне феномене. Осцилације су приписане наизменичном стварању и разлагању $Fe(OH)_2$ и Fe_3O_4.

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REFERENCES

1. J. L. Camalet, J. C. Lacroix, S. Aeiyach, P. C. Lacaze, *J. Electroanal. Chem.* **445** (1998) 117
2. I. J. Yang, M. Y. Teng, *Corros. Sci.* **33** (1992) 1915
3. N. Higashi, M. Takahashi, M. Niwa, *Langmuir* **15** (1999) 111
4. I. J. Yang, M. Y. Teng. *J. Electrochem. Soc.* **140** (1993) 1556
5. D. Sazou, *Electrochim. Acta* **42** (1997) 627
6. B. Rush, J. Newman, *J. Electrochem. Soc.* **142** (1995) 3770
7. W. J. Müller, *Trans. Faraday Soc.* **27** (1931) 737
8. R. A. Alkire, S. Perusich, *Corros. Sci.* **23** (1983) 1121
9. J. J. Podesta,, R. C. V. Piatti, A. J. Arvia, *J. Electrochem. Soc.* **126** (1979) 1363
10. S. Chen, C. Wang, X. Yu, *Electrochim. Acta* **39** (1994) 731
11. U. F. Franck, R. FitzHugh, *Z. Elektrochem.* **65** (1961) 156
12. L. L. Shreir, *Corrosion. Metal/Environment Reactions*, Butterworts, London, 1976, Vol 1, p. 9: 41
13. R. C. Weast, M. J. Astle, W. H. Beyer, *CRC Handbook of Chemistry and Physics*, CRC Press Inc., Boca Raton, Florida 1988–1989, 69th Edition, p. B–99.