

Nonlinear Dynamical Behavior Observed During Later Stages of Localized Corrosion of Iron in Chloride-containing Sulfuric Acid Solutions
 Dimitra Sazou, Michael Pagitsas
 Laboratory of Physical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, 54 006 Thessaloniki, Greece

Spontaneous oscillations of current and potential as well as spatiotemporal dynamics were observed in a large number of electrochemical systems [1-3]. During the past decade and after the progress in the theory of nonlinear dynamical systems, oscillatory metal electrodisso- lution-passivation and electrocatalytic reactions attracted special interest by many researchers. Aside from the scientific point of view of exploring the dynamics of physico- chemical systems, formation/dissolution of anodic films on metals and alloys acquire a practical significance due to their applications in processes of technological importance such as pitting corrosion and electropolishing.

Anodic dissolution of Fe in chloride-containing sulfuric acid solutions leads to a rich nonlinear dynamical behavior, characterized mainly by complex current oscillations [4, 5]. In general, the origin of this dynamical behavior lies on electron transfer kinetics coupled with transport processes in the bulk electrolyte. In terms of reaction mechanisms, the particular process involves the breakdown of the passive iron oxide film, the localized corrosion of Fe, and the formation-dissolution of anodic salt films associated with a high rate metal dissolution at individuals areas of attack of the Fe passive surface by chlorides. It is found that by studying the dynamical response of the system, information on the processes involved at various stages of pitting corrosion can be obtained [6].

In the present work the factors controlling the onset of current oscillations during passivity breakdown of Fe by chlorides are further explored. Various types of electrochemical experiments were conducted towards this goal by using: (1) A downward-facing Fe-disc electrode under stationary conditions; (2) an upward-facing Fe-disc electrode and (3) a rotating Fe-disc electrode. In addition, potential-perturbation experiments were carried out.

Figure 1a shows the current-potential (I - E) anodic polarization curve of a downward-facing Fe electrode in chloride-containing 0.75 M H_2SO_4 under stationary conditions. These conditions are beneficial for the nucleation of a large number of pits but not for pit repassivation. By varying the potential between 0.3 and 1.3 V different oscillatory states occur. On the basis of the type of current oscillations and the morphological features of the Fe surface, as were observed by a scanning electron microscope, the oscillatory region is divided to three regions. (a) Region I where oscillations of a bursting type occur, referred to a passive-to-active transition (Fig. 1b at $E=0.45$ V). (b) Region II, a transitory region, where aperiodic oscillations of a small amplitude occur (Fig. 1b, at $E=0.65$ V), referred to imperfect electropolishing. (c) Region III, where aperiodic (chaotic) current oscillations occur (Fig. 1b, at $E=1.3$ V), referred to electropolishing.

The experimental results provide evidence that the oscillatory regions I-III are associated with different types of anodic films. The type of oscillation changes according to the nature of the anodic Fe-oxide films. Aside the potential, the chloride concentration, and hydrodynamic conditions pertaining to Fe|film|solution interfaces influence significantly the type of the induced dynamical instabilities. By increasing the chloride concentration and the potential, repassivation, due to the oxide formation, becomes gradually unlikely giving rise to the formation of ferrous salt layers in front of the Fe electrode. A viscous layer appears near the Fe surface. The average oscillation frequency reflects the change in the nature of the salt film, from ferrous sulfate to ferrous chloride. Using a rotating Fe-disc electrode at sufficiently high rotation speeds formation of the oxide film is favored. Moreover, oscillatory states I-III change to current fluctuations of low amplitude if an upward-facing Fe electrode is used. These conditions favor stabilization of pits due to the fact that accumulated chloride ions and corrosion products are kept inside the pit. The effect of the potential is less pronounced in this case.

The mechanism of the onset of current oscillations and the correlation between bifurcation diagrams and pitting corrosion states are discussed.

References

- [1] J.L. Hudson, T.T. Tsotsis, Chem. Eng. Sci. 49 (1994) 1493.
- [2] M.T.M. Koper, Adv. Chem. Phys. 92 (1996) 161.
- [3] K. Krischer, in: R.E. White, J.O'.M. Bockris, B.E. Conway (Eds.), Modern Aspects of Electrochemistry, vol. 32, Kluwer Academic/Plenum Publishers, N. Y., 1999, p. 1.
- [4] M. Pagitsas, D. Sazou, J. Electroanal. Chem. 471 (1999) 132.
- [5] D. Sazou, A. Diamantopoulou, M. Pagitsas, Electrochim. Acta 45 (2000) 2753.
- [6] D. Sazou, A. Diamantopoulou, M. Pagitsas, J. Electroanal. Chem. 489 (2000) 1.

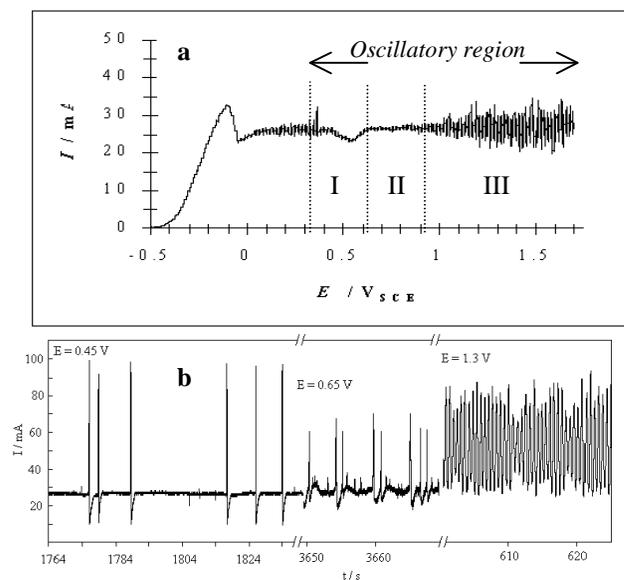


Fig. 1: (a) Anodic I - E polarization curve of a downward-facing Fe electrode in 0.75 M H_2SO_4 +25 mM Cl^- ; (b) examples of current oscillations at potential regions I-III.