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Intermittent turbulence and period doubling at the corrosion–passivity transition in iron

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It is shown that the transition from corrosion to passivity in iron is characterized by chaotic behaviour. Intermittent 'turbulence' period doubling and other periodic and aperiodic oscillations are observed. It is also shown that the observed sequences of oscillations can be explained in terms of a model describing the gradual transformation of an anodic film. Although the model is too simplistic to explain the complexities of passivation, it is nevertheless the first model of electrochemical oscillations which explains both their occurrence and their decay-growth patterns.

1. Introduction

Chaotic behaviour is present in a wide variety of physical phenomena [1]. Research in these phenomena has been focused on classifying irregular solutions into simple scenarios [2]. Well-understood physical systems [3, 4], have been investigated in order to understand chaotic behaviour. Conversely, in this paper, chaotic behaviour is investigated in order to understand an important electrochemical phenomenon: the passivation [5] of iron. Passivation is not yet well understood. In this paper it is shown that the transition from corrosion to passivity in iron is characterized by chaotic behaviour and intermittent turbulence*, period doubling and other periodic and aperiodic oscillations are observed. It is also shown that the observed sequences of oscillations can be explained in terms of a model describing the gradual transformation of an anodic film. Although the model is too simplistic to explain the complexities of passivation, it is nevertheless the first model of electrochemical oscillations which explains both their occurrence and their decay-growth patterns.

Oscillations of current at the corrosion–passivity transmission in potentiostatically controlled Fe/H_2SO_4 interfaces have been reported, but no satisfactory explanations have been given [6]. There have been no reports of chaotic behaviour. On the contrary, these oscillations are usually reported to be regular and undamped [7].

2. Experimental observations

This paper reports potentiostatic measurements in a three-electrode electrochemical cell containing 0.5 M H_2SO_4 electrolyte. Working, counter and reference electrodes were Fe ($\sim 0.1\ cm^2$) (ultra-pure grade), Pt and SCE (saturated calomel electrode) respectively. By varying the electrode potential (and other external parameters) different types of current oscillations were observed:

(a) Regular oscillations of constant amplitude and period (~ 1 s–5 min) in the shape of short pulses spaced by low current regions (Fig. 1a)
(b) Completely irregular (in amplitude, period and shape) oscillations
(c) Oscillations around a non-zero current value, intermittently increasing and decreasing in amplitude (Fig. 1b)
(d) Oscillations with many sub-harmonics appearing as a 'noisy' period 2 (Fig. 2)
(e) regular oscillations with sub-harmonics of period 2, 4, 8 or 16 (insert of Fig. 2)
(f) Regular oscillations decaying in time to a constant finite current value
(g) Gradual increase of current from an initially

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* 'Turbulence' is the accepted term in the 'chaos' literature. (See [1] and [2].) In this case it refers to fluctuations of electrical signals.

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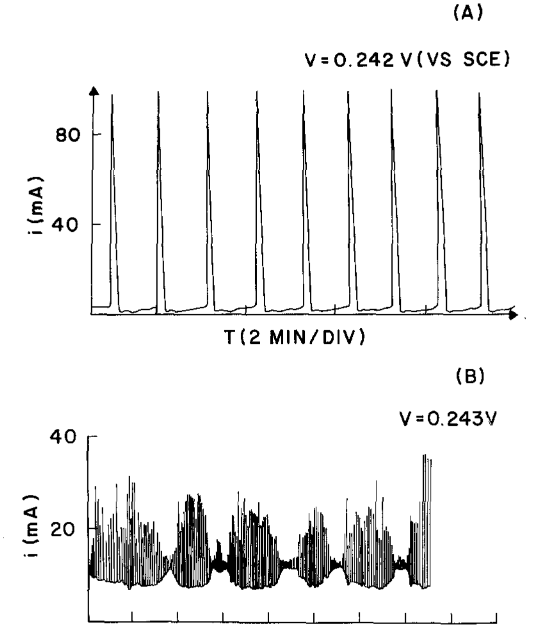

Fig. 1. (a) Self oscillations for a ~ 0.25 cm^2 iron electrode in 0.5 M H_2SO_4 at 0.242 V vs SCE. (b) Intermittently 'turbulent' self oscillations at 0.243 V vs SCE.

low value to short pulses of high amplitude and low frequency.

In an extended (over many hours) observation with constant external parameters several of these sequences appeared in succession. Briefly, the observations that suggest a 'chaotic' scenario are:

1. Period doubling and the appearance of even sub-harmonics
2. Decrease in amplitude of successive sub-harmonics with increasing order of the sub-harmonics
3. Intermittent *turbulence* in the oscillation
4. Extreme sensitivity to external parameters

Further evidence for a chaotic scenario has been gained by studying forced electrochemical oscillations. Current oscillations at an iron electrode, as described above, observed when a square wave voltage was pulsed between 0 and 1 V (versus SCE), and the solution stirred rapidly, have constant amplitude for pulses of 1.8 s. Period doubling has been observed with pulse duration of 1.7 s, period quadrupling with 0.6 s pulses and chaotic behaviour when the pulse duration was reduced to 0.2 s. These data, together with the self-oscillation data, provide strong indication of underlying chaotic dynamics, and suggest a model to explain the observed complex sequences of self oscillations and transitions between them.

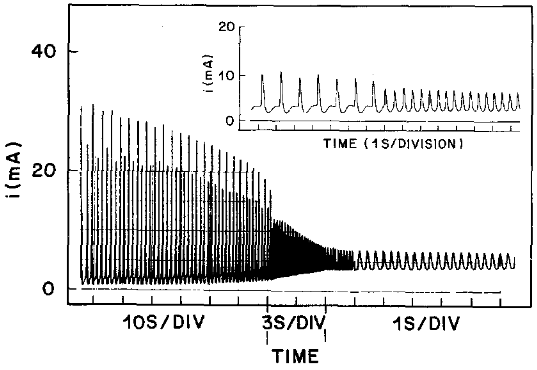

Fig. 2. Self oscillations for a ~ 0.04 cm^2 iron electrode as in Fig. 1 at ~ 0.254 V vs SCE.

3. The model

The empirical fact that a film is formed on the iron electrode during pre-passivation is taken as a starting point but no assumption with regard to the microscopic nature of this film [8, 9] is made. It is assumed that the film is a resistor with rectifying characteristics. (Although plausible for many anodic films, the assumption of rectification is not essential to the appearance of a chaotic scenario.) A second empirical fact in the model is the existence of a delay time between applied anodic voltage and formation–dissolution of the pre-passive film [10].

Apart from these assumptions the electrochemical interface is treated in the standard fashion, i.e. as a 'resistor' and a 'capacitor' in parallel [11]. The resistor is highly non-linear, as measured by voltammetry (Fig. 3). (The relationship between shape of voltammogram and external parameters, e.g. sweep rate, is discussed elsewhere [12].) The capacitor is modelled as a 'discrete' capacitor to take into account the delay time mentioned above. To clarify this crucial part of the model the concept of such a discrete capacitor is described.

Consider as the capacitor a corroding-metal/electrolyte interface, *M*/*E*. Assume

1. that by applying a voltage *V* across *M*/*E* the metal starts corroding and, simultaneously, a new distribution of charge comes into existence at *M*/*E*

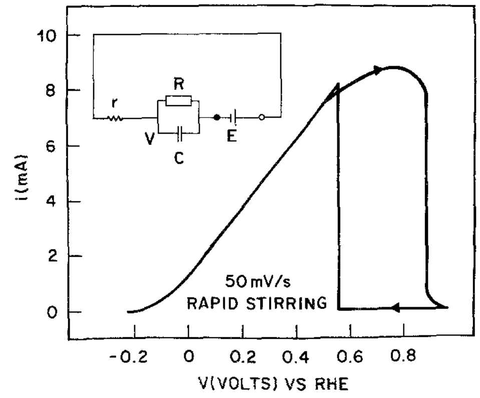

Fig. 3. Voltammogram of the iron electrode of Fig. 1 (RHE = Reversible Hydrogen Electrode).

in proportion to V, i.e. $Q = CV$ where C is the 'capacitance'

2. that after a time τ_p from the onset of corrosion a film precipitates on M so that M/E ceases to exist

3. that after a time τ ($\gg \tau_p$) from the time of film precipitation, the film is completely dissolved into the electrolyte so that the metal is re-exposed, i.e. M/E returns into existence.

In this system, any voltage applied between M and E during the interval τ has no effect on the 'capacitor', since M/E is not present. Thus, the charge Q is a function of the discrete time variable $n\tau$ ($n = 0, 1, 2, \ldots$), where τ_p has been neglected with respect to τ. Since, again for simplicity, the 'capacitance' is assumed to be constant (Assumption 1) the dynamic equation of the capacitor is written as

$$Q_{(n+1)\tau} - Q_{n\tau} = C[V_{(n+1)\tau} - V_{n\tau}] \qquad (1)$$

It is important to remark that the electrochemistry of the process prevents us from going to the limit $\tau \to 0$ and write Equation 1 as a differential, rather than a difference equation.

The electric circuit analog of the system is shown in the insert of Fig. 3. A fixed potential E is set between the electrochemical interface (closed circle) and the solution (open circle). The film is a rectifying resistor r, and the electrochemical interface is an RC parallel where R is defined by the i–V characteristics of the two-terminal voltammogram. The difference equation for the voltage V is

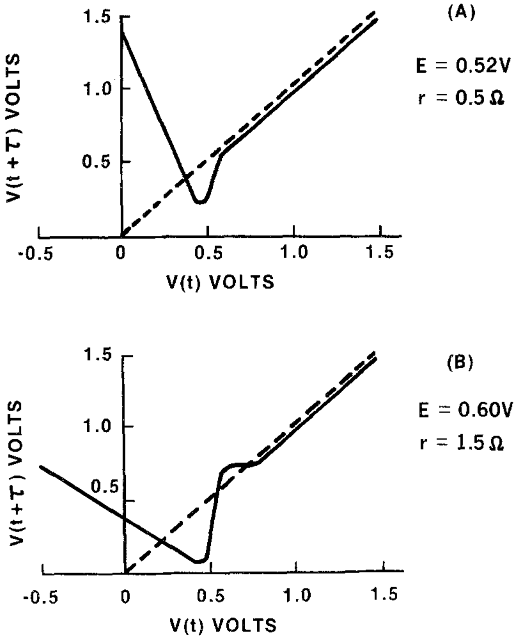

Fig. 4. Two maps from Equation 2 for $\tau/C = 1.5\ \Omega$.

$$V(t+\tau) - V(t) = \frac{\tau}{C}\left\{\frac{1}{r}[E - V(t)] - i[V(t)]\right\} \qquad (2)$$

where $i(V)$ is the i–V characteristic obtained from the two-terminal voltammogram and r is the film resistance (plus the external circuit resistance) which is modelled as $r = \infty$ for $E - V < 0$; τ/c and r are the only adjustable parameters. For numerical calculations the two-terminal voltammogram has been approximated as $i(V) = 0.003 + (0.1 + 0.5V)/[1 + \exp(40V - 20)]$ (i in amps, V in volts).

Because of the nonlinearity of $i[V(t)]$ the map (Fig. 4) described by Equation 2 can give rise to chaotic behaviour. Since the trajectory may be trapped for many cycles in the right upper portion of Fig. 4a, until it suddenly jumps into the lower region intermittent *turbulence* is expected. Because of the minimum, a Feigenbaum-type [13] scenario is also expected. Fig. 4b shows how the map can change by increasing r (left branch) and/or by increasing E. Depending on the initial conditions, a stable (high voltage) passive state or (low voltage) active state, may be achieved, as experimentally observed.

Examples of numerical solutions to the difference Equation 2 are shown in Fig. 5. In the six sequences of oscillations, for $E = 0.52$ V, $\tau/c =$

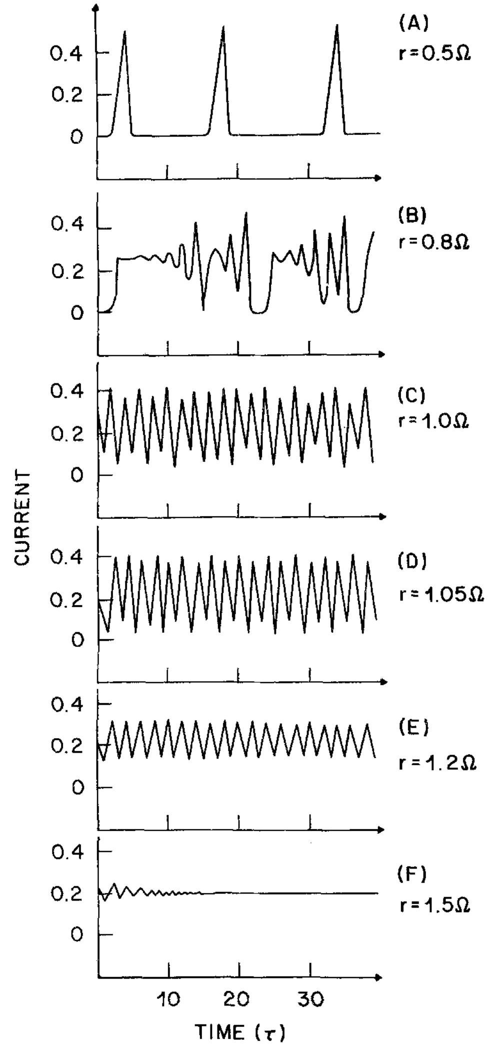

Fig. 5. Numerical solutions to Equation 2 for $E = 0.52$ V, $\tau/C = 1.5\ \Omega$.

1.5 ohm and $r = 0.5, 0.8, 1.0, 1.05, 1.2$ and 1.5 ohm, respectively, the experimentally observed sequences are clearly discernible.

4. Conclusion

In conclusion, it has been shown that the transition between corrosion and passivity in iron shows chaotic behaviour. (Rigorous proof of chaos, such as the verification of the Feigenbaum [13] number, cannot be given due to the natural evolution of the system since the parameter that controls the chaotic sequence cannot be experimentally adjusted.) Although the present model is a simplification of a complex phenomenon of which little is known in detail, it is the first example of chaos for an electrochemical system, and one of technological importance. It also provides the first quantitative explanation for the evolution of electrochemical self-oscillations, which so far has only been attempted for steady state conditions.

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