

CHARACTERISTICS OF THE PERIODIC FARADAIC CURRENT OSCILLATIONS OF Zn/ALKALINE SOLUTION INTERFACES UNDER POTENTIOSTATIC CONDITIONS

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Abstract — Phenomenological aspects of the current oscillation at a constant potential related to the Zn/alkaline solution interfaces are described. The results are correlated to those already reported for other metal/aqueous solution interfaces.

INTRODUCTION

The phenomenology of the periodic oscillation of the faradaic current at electrochemical interfaces reveals the influence of variables such as the electrolyte composition, the concentration of the acid, the temperature and the hydrodynamic conditions in producing the oscillatory effect [1, 2]. The pertaining data are of importance to establish a general model to explain the periodic phenomena in different electrochemical systems and to evaluate through it the concentration polarization contribution in relation to the localized corrosion of the metal electrodes. Furthermore, as the periodic current response is a characteristic of each electrochemical interface it should be possible to derive the relevant information associated with the proper electrochemical reactions.

The current/potential (I/E) curves of zinc in alkaline solutions show a region where current oscillations are usually observed [3-6] prior to passivation. These oscillations were studied under a relatively restricted range of experimental conditions [3-7]. The present paper reports data on the periodic current oscillations at the Zn/alkaline solution interfaces taking into account that according to the potential/pH equilibrium diagram, the corrosion and passivation of the metal is influenced by different complexing anions [8].

EXPERIMENTAL

The experimental set up is similar to that already described in a previous work [1]. The working electrode consisted of a polycrystalline zinc disc (0.125 cm²) made from a cylinder of pure metal (99% purity, 0.4 cm dia.), axially embedded in a larger diameter PTFE rod. The whole piece was cut in a lathe, so that the zinc disc was concentrically placed in the PTFE disc (1.6 cm dia.). The working electrode was used either motionless or under rotation. The potential of the working electrode was measured against the Hg/HgO/1 M NaOH reference electrode. A platinum counter-electrode (ca 25 cm²) was also employed in the electrolysis cell to complete the circuitry. The electrolyte solutions were made with doubly distilled

water and AR chemicals in the 1 M ≤ C ≤ 5 M NaOH concentration range. Electrolyte solutions either with the addition of KCN in the 0.1-0.9 M range, or with the addition of Na₂ZnO₂ in the 2 × 10⁻² - 5 × 10⁻² M range were used. Experiments were made in the 18-50°C range.

The following electrochemical measurements were carried out, namely, potentiostatic I/E curves covering the potential range of both the metal corrosion and passivation and the application of potential steps in the potential range where the active to passive transition takes place. The former measurement gave the potential region where the oscillatory effect is produced.

RESULTS

(1) Potentiostatic current/potential curves

Potentiostatic "stationary" I/E curves are recorded by a 50 mV stepwise increase of potential, each reading being made after the current variation has reached no more than 1% in 3 min. These records are used as a reference to correlate the periodic effect, particularly with the potential range associated to the negative resistance and passivity (Fig. 1). For any electrolyte

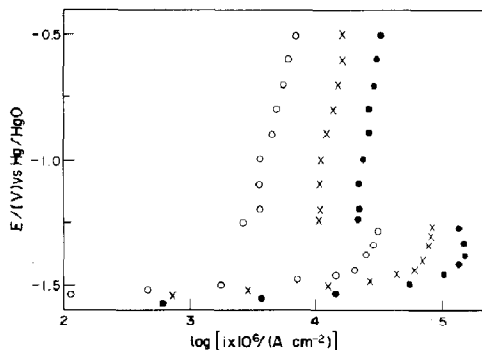


Fig. 1. Semilogarithmic plot of potentiostatic I/E curves run as described in the text, at 25°C, for NaOH solutions, (O) 1 M; (x) 2 M and (●) 4 M.

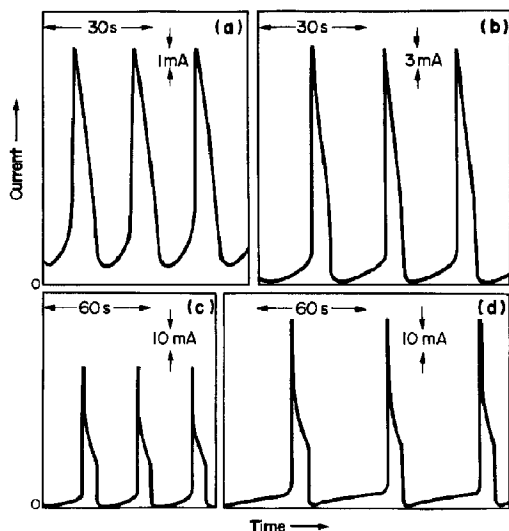


Fig. 2. Current/time displays (a) 1 M NaOH; (b) 1.5 M NaOH; (c) 2.5 M NaOH and (d) 3.5 M NaOH.

solution the active to passive transition takes place abruptly at the potential -1.27 ± 0.02 V. Therefore, the periodic current oscillation is observed only within a relatively very narrow potential range at any temperature within the range covered in the present work.

(2) Characteristics of the oscillating current

At a constant temperature and solution composition, the periodic fluctuations of the current under the -1.27 ± 0.02 V potential step are very reproducible (Fig. 2) both in their shape and frequency. The oscillating current response once initiated lasts until no metal remains in contact with the solution. For the sake of simplicity in describing the effect, each current oscillation cycle is arbitrarily divided into two main regions (Fig. 3). From A to B the anodic current increases steadily although its value is relatively low. This region is ascribed to the passive region of the current fluctuation cycle. Once point B is reached, the current spontaneously jumps to reach a maximal value (I_M) and immediately afterwards the anodic current decays to attain point C. At this point an abrupt decrease of the anodic current is produced and later the whole current oscillating cycle repeats itself again. The time involved in one cycle determines the period of

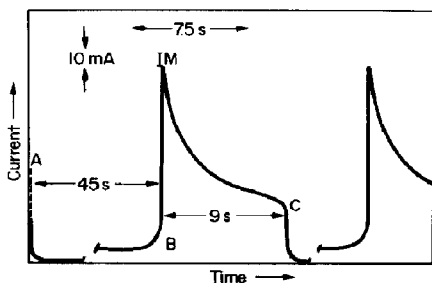


Fig. 3. Definition of parameters related to the current/time displays. 3.5 M NaOH, 25°C.

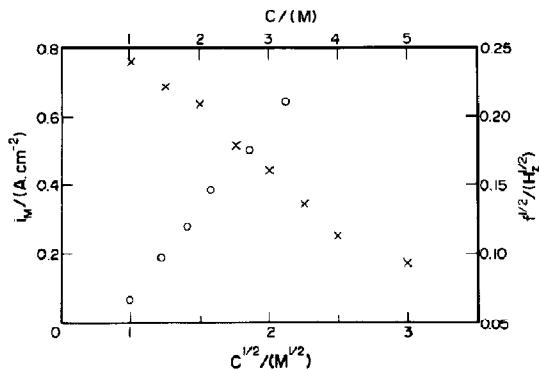


Fig. 4. Dependences of i_M on $C^{1/2}$ and of $f^{1/2}$ on C , 25°C.

the oscillating current (T). Its reciprocal is the oscillating frequency (f). Each period consists of the total of the time of the passive region (t_p) and the time of the active dissolution region (t_d), Q_p and Q_d being the corresponding charges involved. The total charge (Q_T) taking part in each oscillating cycle is equal to $Q_p + Q_d$.

The maximum current density (i_M) increases linearly with the square root of the NaOH concentration (Fig. 4). The extrapolation of the $i_M/C^{1/2}$ plot to $i_M = 0$ yields the lowest NaOH concentration value required for producing the oscillating effect. On the other hand, the square root of the frequency of the oscillating current depends linearly with the NaOH concentration (Fig. 4). Both Q_p and Q_d also increase linearly with the NaOH concentration (Fig. 5), although the linear plots are not intercepting the origin of coordinates. Both lines, however, yield through the extrapolation at $Q_d = Q_p = 0$, the NaOH concentration value obtained from the $i_M/C^{1/2}$ plot. The Q_d/Q_p ratio derived from the linear Q/C plots is always close to four.

When a complexing anion such as CN^- ion is added to the electrolyte, the I/t characteristics change accordingly (Fig. 6). Thus, in the active region, the current

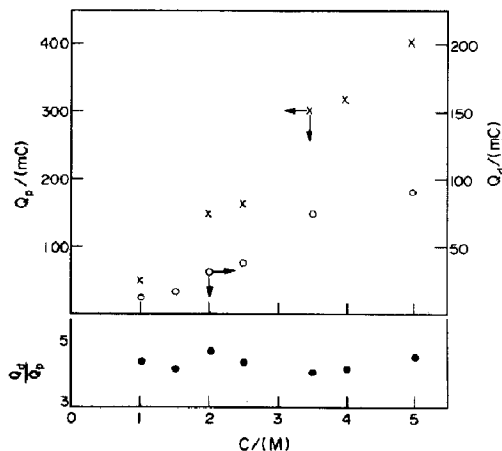


Fig. 5. Dependences of Q_p and Q_d and Q_p/Q_d ratio on the NaOH concentration, at 25°C.

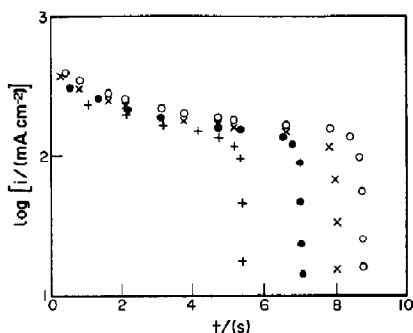


Fig. 6. Current density dependence on time at different KCN concentrations in 3.5 M NaOH solution: (O) no KCN addition; (x) 0.1 M KCN; (●) 0.2 M KCN; (+) 0.9 M KCN, 25°C.

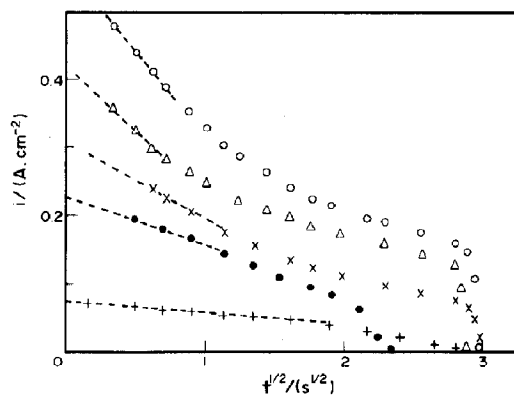


Fig. 7. Current density decay as function of $t^{1/2}$ at different NaOH concentrations at 25°C: (+) 1 M; (●) 1.5 M; (x) 2 M; (Δ) 3 M and (O) 3.5 M.

decays more rapidly as the CN^- ion concentration increases and simultaneously both i_M and Q_d decrease. When the CN^- concentration increases, at least within the range covered in this work, then the Q_d/Q_p ratio gradually exceeds the value of four. The plot of the current density decay counted from $t = 0$ at i_M , as a function of $t^{1/2}$ (Fig. 7) shows an initial linear portion which becomes more extended as the NaOH concentration decreases. The addition of ZnO_2^{2-} ions produced ambiguous results since it either tended to produce slightly the reverse effect or has no appreciable influence when compared to the CN^- ions.

(3) Temperature dependence

From the temperature dependence of both i_M and f (Figs 8 and 9), the average apparent activation energy related to the oscillating current is -2.7 ± 0.2 Kcal/mol.

(4) Influence of the hydrodynamic conditions

In the 1–5 M NaOH concentration range the electrochemical interface subjected to the potential step ceases to oscillate when the zinc disc electrode is rotated even at rotation speeds as low as 50 rev/min.

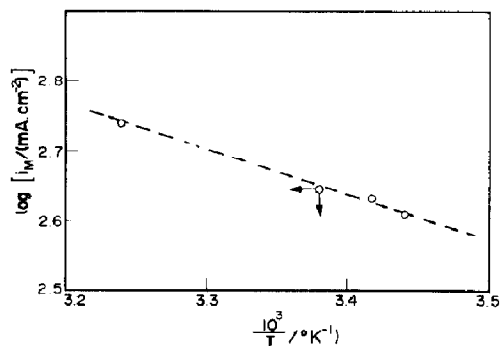


Fig. 8. Arrhenius plot for the maximum current density i_M ; 4 M NaOH.

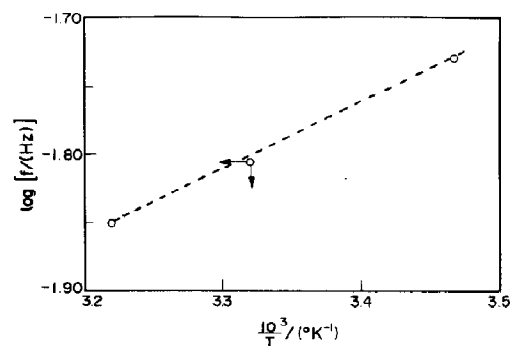


Fig. 9. Arrhenius plot for the frequency of the periodic current oscillation, 4 M NaOH.

Under these circumstances, the current flowing through the cell attained immediately a steady current which corresponds to the i_M value and the metal electrodisolution is apparently more uniform.

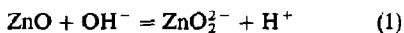
(5) Corrosion characteristics of zinc under current oscillation

During the current oscillation a net localized corrosion of zinc in the alkaline solutions is observed with the simultaneous formation of dense, shiny, bluish-black layers of ZnO containing excess zinc metal particles, which coincide with earlier reported results on zinc corrosion in these solutions[5, 9].

DISCUSSION

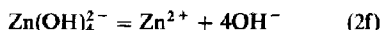
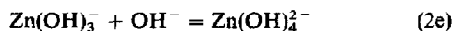
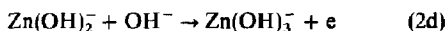
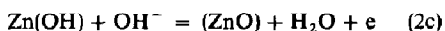
The periodic oscillation of current under a constant potential located in the active to passive transition region of the i/E display for the $\text{Zn}/\text{NaOH}(\text{aq})$ interface contains a large diffusion contribution as deduced both from the $i_M/t^{1/2}$ relationships and from the influence of stirring in the potential range defining the bistability of the electrochemical interface. The periodic oscillating current at a constant potential is associated with a net steady and localized corrosion of the metal.

It is evident that the current fluctuation takes place when the NaOH concentration is above the minimum pH associated with the following equilibrium[3]:



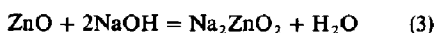
that is the electrolyte pH should be compatible with the existence of the ZnO species to passivate the electrode[8].

Despite the relatively large amount of literature concerning the anodic processes on the zinc electrode in alkaline solutions[10, 11] their interpretation is still controversial. The complex reactions related to the zinc electrode have been attributed to different consecutive reaction mechanisms which include the participation of the OH⁻ ion[12–17]. In accordance with the number of postulated steps, the reaction order with respect to the OH⁻ ion under stationary conditions is between 1 and 3. Under non-stationary conditions it apparently depends on the type of perturbation used[18]. Thus, on the basis of the following sequence of reactions the active dissolution of the metal is explained[15, 18]:



This mechanism includes the interference of the ZnO₂²⁻ ion in the anodic reaction with a simultaneous redeposition of the metal. Then, the reaction order with respect to zincate is nil under stationary conditions. Therefore, taking into account reactions (1) and (2) in the potential range associated to the periodic current, the electrode is already covered by a film of corrosion products. Three types of processes were attributed to the inhibition of zinc electrodisolution in the alkaline electrolytes. The first corresponds to a passive film of the order of one monolayer thickness which is formed at relatively low anodic over-voltages[4, 5, 18, 20]. At higher potentials the film thickness increases[21, 22] and particularly in quiescent solutions a non-adherent deposit of zinc oxide can be formed on the electrolyte side of the already formed thick film[22]. It is quite likely that the existence of the non-adherent film is related to the occurrence of the periodic oscillating current only in quiescent electrolytes.

Zn(OH)₂ and ZnO formation are accompanied by a local change of the OH⁻ ions at the reaction interface which should reflect through the kinetics of the overall anodic process. The electrochemical reactions at the potential where the current oscillates implies the participation of a non-uniform chemical dissolution process represented by:



whose major contribution should occur during the passive region of each cycle and then it is assisted by the local back diffusion of the OH⁻ ions. As soon as a free metal surface exists the electrodisolution process repeats. This qualitative description met the multiple steady states theory for the periodic fluctuations which involve a spatial distribution of reactant and products in the electrochemical interface and the simultaneous

occurrence of the active electrodisolution of the metal, the onset of the electrode passivation and the complex chemical dissolution of the passive film with the participation of various diffusional processes[23]. Accordingly the electrodisolution and passivation mechanism, the linear average i_M vs $C^{1/2}$ plot, can be, in principle, explained if the maximum current is supposed to be exclusively related to the metal corrosion, and if the transient current in the active region of each current-oscillation cycle can be compared to the response of the interface to a potentiostatic step function[19]. The dissolution of ZnO as ZnO₂²⁻ is favoured by increasing the OH⁻ ion concentration, then, the Q_a charge should also increase as the OH⁻ concentration increases. Furthermore, since the dissolution of the ZnO film is produced by the complexing OH⁻ ion, the changes of Q_a and Q_p due to the presence of CN⁻ ions system are attributed to the difference in the stability constant of the Zn(OH)₂²⁻ and Zn(CN)₄²⁻ ions which, at 25°C, are 10^{12.4} and 10²⁰, respectively[24, 25].

The occurrence of reaction (3) permits the possibility that the passivity of zinc is related to a back precipitation of Zn(OH)₂ from a local supersaturated solution and to the formation of ZnO directly from the metal lattice as previously reported[22]. The first blocks the electrode and favours the second process[26]. This explanation applies to the current oscillatory phenomenon and agrees with linear sweep voltammetry measurements and simultaneous microscopic observation at the Zn/alkaline solution interfaces. In any case the onset of the zinc electrode passivation takes place when the Zn(II) concentration at the anode equals one half the OH⁻ ion concentration in solution[27].

It is possible that the film involved during each period of the oscillating cycle is a non-equilibrated film where the electric field assists the restructuration of ZnO yielding more compact structures. But this situation which corresponds to an ageing-type process is undistinguishable under the conditions of the present work, but has to be considered in deriving structural conclusions from passive films formed under definite perturbation conditions that are involved in the periodic current oscillations.

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