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Periodic current oscillations of zinc in nitric acid solutions

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Abstract: This paper presents current oscillations of a Zn anode in solutions of nitric acid and potassium dichromate. The effects of the nitric acid concentration were investigated. The system was analyzed using cyclic voltammetry, current–time plots and attractors. It was found that the concentration of nitric acid has a major effect on the behavior of the system and it is proposed that zinc hydroxide precipitation–dissolution processes are responsible for the current oscillations.

Keywords: zinc; corrosion; dynamic behavior; current oscillations; attractor.

INTRODUCTION

The dynamic behavior of some metals in the transition region from the active to the passive state, from the steady state to simple, double or chaotic oscillations, presents a large area of research interest in the corrosion and protection of metals and, also, for an understanding of oscillatory phenomena which occur during solid/liquid interface processes.[1–16]

Self-organization of electrochemical systems is not limited to temporal phenomena but can also involve spatial pattern formation.[2,9,11,13] The most studied electrochemical system, from the point of view of dynamic behavior, is the anodization of iron in sulfuric acid media.[2,4,6,9] In addition to iron, there are many other metals which exhibit current or potential oscillations (Ni, Cu, Co, Pb, Ag, Zn, alloys) in certain media (acid, alkaline or solutions of salts). The behavior of zinc electrodes were studied in alkaline solutions as cathodes but their behavior is almost unknown in acidic media.[14,15]

Current oscillations are explained by a precipitation–dissolution mechanism or chemical reactions having an autocatalytic step.[3,15] The precipitation–dissolution mechanism is the most extensive mechanism and it seems to be the closest to the real phenomena of current oscillations. This mechanism presumes that chemical species (salt, hydroxide or oxide) are precipitated at the electrode surface.

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It is well known that zinc, as well as certain other metals and alloys, exhibit the phenomenon of metallic passivity, *i.e.*, the metal becomes inert under certain environmental conditions since its surface is covered by a thin oxide film. In the passive state, defects in the protective film may induce propagating reaction zones, which lead to the dissolution of the pacifying layer and transform the electrode into its active state.

For iron in acidic media, an increase of the dissolution rate with increasing electrode potential is observed. At the passivation potential, the dissolution rate decreases dramatically and the electrode surface becomes passive again. Under these conditions, the system forms an excitable medium where passivation–activation phenomena occur successively, leading to current oscillations.

This paper presents the dynamic behavior of a zinc anode in nitric acid-oxidizing media and the influence of the acidity and the electrode potential on this behavior. In addition, the attractors generated by current–time series are presented. The dynamic behavior of zinc was studied in solutions of nitric acid (0.2−1.6 M) containing 0.15 M of potassium dichromate.

EXPERIMENTAL

The experiments were performed using a three-electrode system in a non-stirred electrolyte. The potential of the zinc electrode was controlled by a Voltalab 40 PGZ 301 potentiostat and the response current was monitored by Voltamaster 7.08 software. The working electrode was a zinc rod (8 mm diameter) of 99.9 % purity (Merck) embedded in an isolating muff, so that only the end of the rod was exposed to the solution. The counter electrode was a Pt wire and a saturated calomel electrode (SCE) was used as the reference electrode. The electrolytes were prepared with purified Millipore water (> 18 MΩ cm resistivity) and analytical grade potassium dichromate (Riedel-de-Haën, 99.8 % purity) and nitric acid (Fluka, 65 %). The total volume of the solution in each experiment was 100 ml. The working electrode was polished with 600 and 1000 grade emery paper, washed with water and wiped prior to each experiment. All experiments were performed at room temperature.

RESULTS AND DISCUSSION

Cyclic voltammetry

The four cyclic voltammograms for the four nitric acid concentrations (0.2, 0.3, 0.6 and 1.6 M), at the same potassium dichromate concentration (0.15 M), recorded at a potential scan rate, are presented in Fig. 1. For all of the voltammograms, in the positive sweep, a slow increase of the current, followed by a plateau at around zero current, then an abrupt increase of the current at ≈ 0.2 V, accompanied by gas evolution at the counter electrode, can be observed. The width of the plateau zone decreased as the nitric acid concentration increased, so that at a nitric acid concentration of 1.6 M, the plateau was very small. Nevertheless, a maximum of the current appeared and then the electrode passivates.

For the negative sweep, the current decreased continuously but presents higher values than in the positive sweep. At around −0.2 V, the current oscillated, which is marked in Fig. 1 by A. The potential domain in which oscillations occurred increased up to a nitric acid concentration of 0.6 M and then decreased. Current oscillations seem to appear only after the passive layer had attained a critical thickness and the potential attained a certain value. At this moment, the system became unstable and transitions between the passive and active state occurred. If both conditions (film thickness and potential value) exist, oscillations may appear.

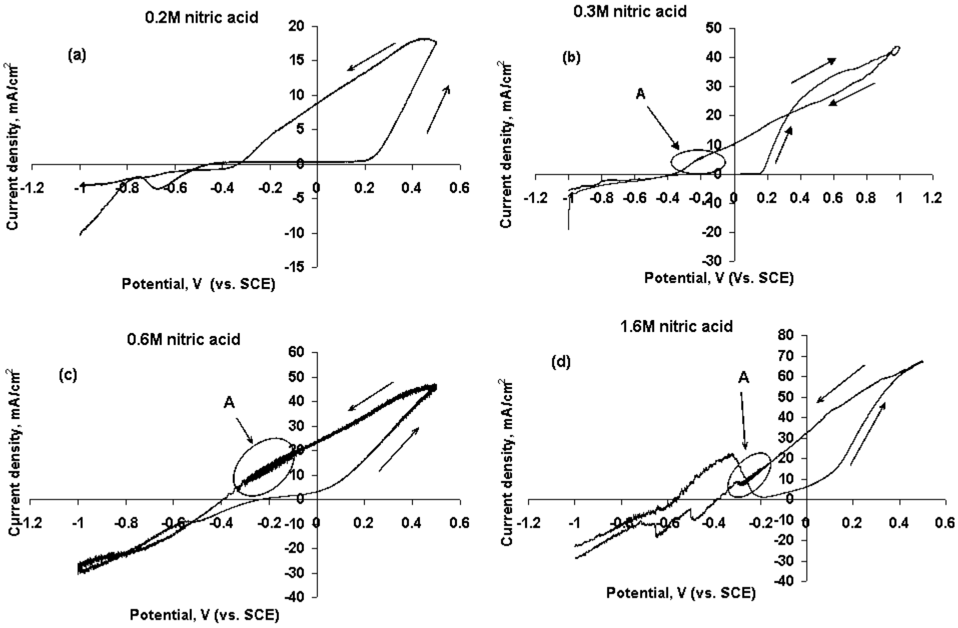

Fig. 1. Cyclic voltammograms recorded in a) 0.2 M HNO_3, b) 0.3 M HNO_3, c) 0.6 M HNO_3 and d) 1.6 M HNO_3. The zones indicated with A denote oscillatory regions. The arrows indicate the direction of potential sweeping.

In the passive state, defects in the protective film may induce propagating reaction zones and electrode surface becomes active.[13] Zinc dissolution leads to an accumulation of zinc ions and a migration of H^+ ions away from the vicinity of the electrode. Consequently, the pH increases and a temporary precipitation of zinc hydroxide may occur, whereby zinc dissolution ceases. The electrode surface becomes passive and the current decreases. Due to the precipitation of zinc ions, H^+ ions migrate back from the bulk to the surface of the electrode, leading to dissolution of the hydroxide layer, whereby the electrode reverts to its active state, the current increases and cycle repeats itself.

In order to obtain current oscillations, the electrode potential was swept from −1.0 V to 0.50 V then back to the potential value where oscillations occur (around −0.2 V). No oscillations were observed for a concentration of nitric acid of 0.2 M or lower.

Current–time series

The current *vs.* time plots for nitric acid concentrations of 0.3, 0.6 and 1.6 M at −0.20, −0.10 and −0.05 V are presented in Fig. 2. The dynamic behavior of system changed, depending on the nitric acid concentration.

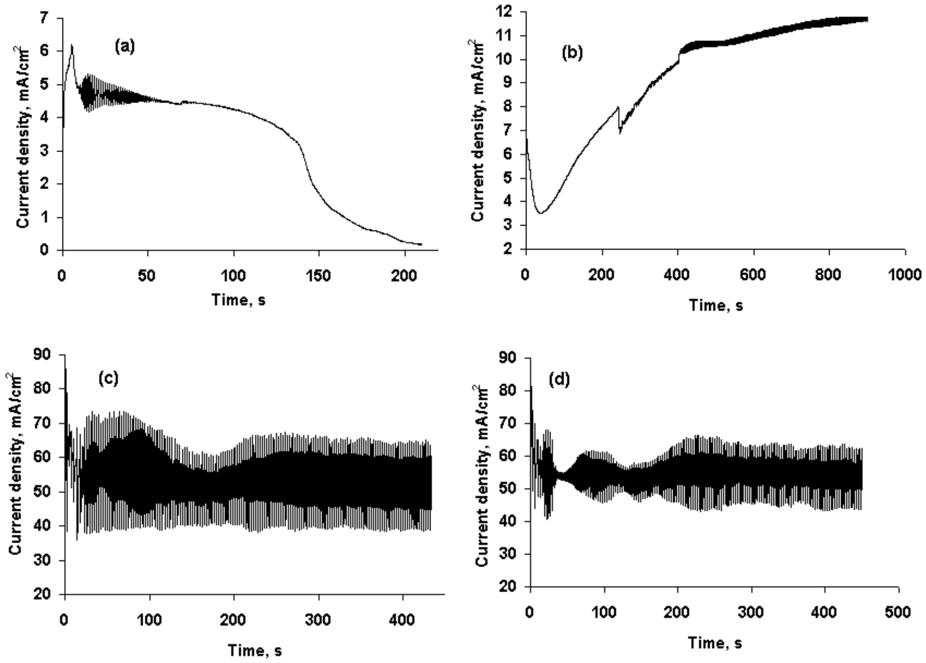

Fig. 2. Current–time series registered in a) 0.3 M HNO_3 at $E = -0.2$ V, b) 0.6 M HNO_3 at $E = -0.2$ V, c) 1.6 M HNO_3 at $E = -0.1$ V and d) 1.6 M HNO_3 at $E = -0.05$ V.

For 0.3 M nitric acid (Fig. 2a), the current passed through a maximum and oscillations appear after about 10 s but they rapidly ceased, then the current decreased to zero. For 0.6 M nitric acid (Fig. 2b), the current exhibited a minimum but oscillations did not appear even after 4 min. A short stir of the solution resulted in oscillations which occurred for 10 min. In this case, one period of oscillations could be observed but the amplitude was not very constant. For 1.6 M nitric acid (Figs. 2c and 2d), oscillations appeared immediately which become regular, with a double-period, after 4 min.

As observed, for 1.6M nitric acid solution, the oscillations were similar for different potential values (Figs. 2c and 2d,) but the amplitude was smaller at the lower potential (−0.05 V), than at the higher potential (− 0.10 V) and the frequency increased.

Attractors

The attractors for the time series in Fig. 2 and the shape of the oscillations are presented in Fig. 3. Attractors 3a and 3b correspond to one period oscillation

(Figs. 2a and 2b, respectively) and 3c to double-period oscillation (2c), from which it can be concluded that as the concentration of nitric acid increased, the complexity of the oscillations increased and their shape changed. The oscillations for 0.3 and 0.6 M nitric acid are perfectly sinusoidal, while for 1.6 M nitric acid, the oscillations seem to be of the relaxation type.

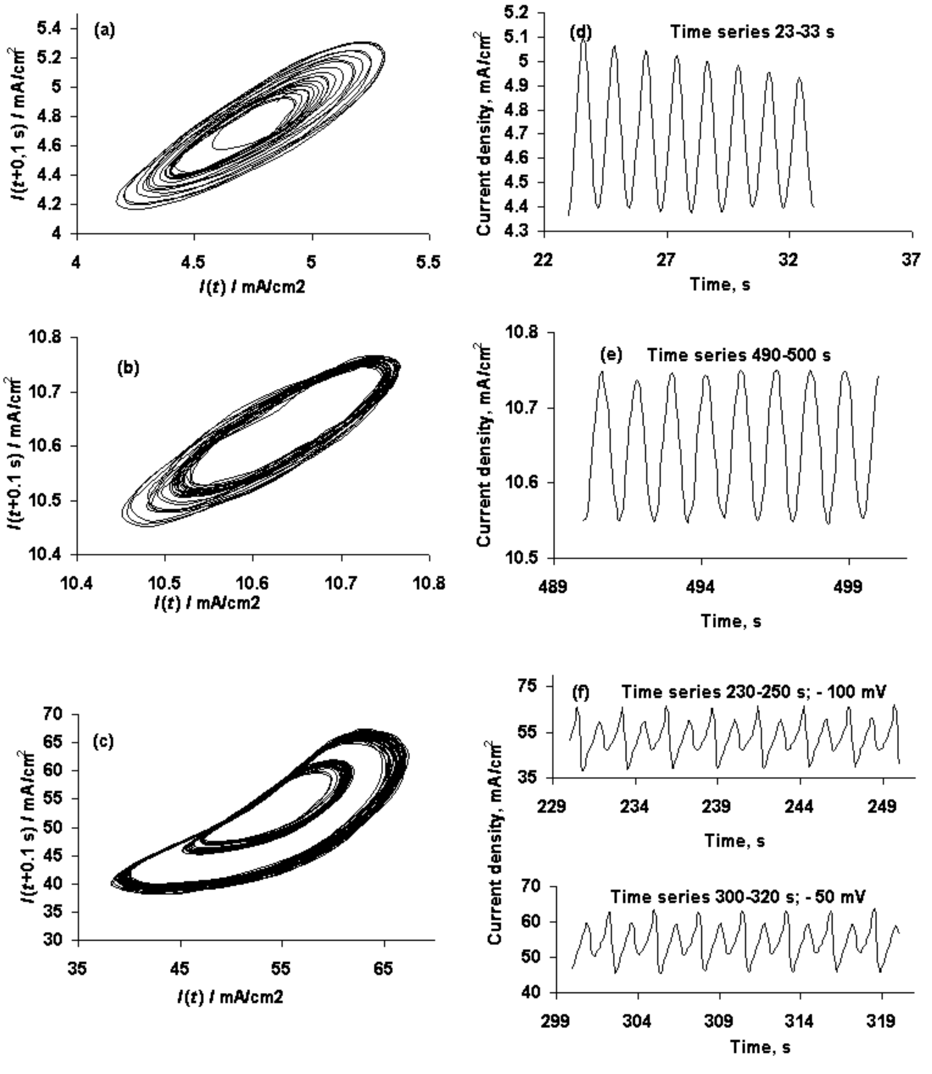

Fig. 3. Attractors and part of the time-series. a) 0.3 M HNO_3 (for 2a); b) 0.6 M HNO_3 (for 2b); c) 1.6 M HNO_3 (for 2c). The diagrams d–f present the shape of the oscillations for 2a–2d, respectively.

It is possible to find chaotic behavior for higher concentrations of nitric acid and the route to chaos is likely to be a period-doubling one. Further investigation is necessary to elucidate this mechanism and the role of potassium dichromate in it.

CONCLUSIONS

According to the experimental results, current oscillations in the Zn–nitric acid–potassium dichromate system occur within a certain potential range. In addition, the oscillations are strongly influenced by the nitric acid concentration but not enough information is available to explain the role of the potassium dichromate. The oscillations may be explained by the precipitation–dissolution mechanism and it is possible that a chemical reactions mechanism with participation of the potassium dichromate exists, which can lead to self-organization of the system.

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ИЗВОД

ПЕРИОДИЧНЕ СТРУЈНЕ ОСЦИЛАЦИЈЕ ЦИНКА У РАСТВОРИМА АЗОТНЕ КИСЕЛИНЕ

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Овај рад приказује струјне осцилације аноде од цинка у растворима азотне киселине уз додатак калијум-бихромата. Испитиван је утицај концентрације азотне киселине на ову појаву. Систем је анализиран коришћењем цикличних волтамограма, графика зависности струје од времена и атрактора. Нађено је да концентрација азотне киселине има одлучујући утицај на понашање система и претпостављено да је процес таложења и растварања цинк-хидроксида одговоран за струјне осцилације.

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