Corrosion Science 83 (2014) 355–358

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Electrochemical oscillations during copper electrodissolution/passivation in trifluoroacetic acid induced by current interrupt method

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ARTICLE INFO

Article history:
Received 16 September 2013
Accepted 22 February 2014
Available online 3 March 2014

Keywords:
A. Copper
B. Polarization
C. Acid corrosion
C. Anodic dissolution
C. Negative difference effect
C. Passive films

ABSTRACT

Complex oscillatory behavior of electric current and electrode potential were observed during potentiodynamic anodic polarization of Cu in 1 M TFA, applying the current interrupt method for *IR* drop compensation. This oscillatory behavior was found to give an electrochemical response in the form of a polarization curve with continuous loop. The results presented show that the current interrupt method is capable of eliminating the entire *IR* drop. Under such conditions, oscillations of the applied potential are in fact those of the double-layer potential. Theoretically predicted interplay between oscillatory behavior of the double-layer potential and the electric current is experimentally demonstrated.

1. Introduction

Electrochemical oscillations can spontaneously emerge during metal electrodissolution/passivation processes [1]. To better understand fundamental principles that govern such nonlinear phenomena, a metal/electrolyte interface (a distinctive system capable of exchanging energy and matter with its environment) has been recognized as a central issue [2–4]. Electrochemical oscillations are generally seen as the interplay of electrode kinetics, mass transfer processes and electric circuit effect [3].

Electrochemical systems that exhibit an explicit negative differential resistance (NDR) in the current–potential (I–E) characteristic (N-shaped I–E polarization curve), sustainable current oscillatory behavior may appear due to complex interaction between the NDR region and the ohmic (IR) drop throughout potentiostatic mode of operation [3–7]. As the result of this interaction, the potential drop across the double-layer (ϕ_{DL}), an essential dynamic variable of positive (destabilizing) feedback loop in the NDR region, acts as a fast activator [2,5,6]. The potential drop across the double-layer can also be called interfacial potential or double-layer potential; in this study, the latter term will be used [5]. Current oscillations, in the N-NDR electrochemical systems, emerge due to the coupling of the positive feedback loop with ϕ_{DL} being autocatalytically involved and the negative (stabilizing) feedback loop where slow mass transport-limited processes of electroactive species act as inhibitors [5,6]. Generally considered unwanted in electrochemical experiments, the *IR* drop was found to be essential for the occurrence of sustained current oscillations [7,8]. Electrochemical oscillating systems of this type are often called N-NDR electrochemical oscillators [5,6,8].

Interconnection between double-layer potential and current oscillations is only theoretically predicted [2–6,8]. When current oscillations are followed potentiodynamically, the instrument detects the applied potential (E) between the working and the reference electrode, displaying I–E characteristics. The “real” potential of the working electrode, i.e., the double-layer potential, differs from the applied potential due to existence of the *IR* drop ($E = \phi_{DL} + IR$) [2,5]. Dynamic distribution of E on ϕ_{DL} and *IR* drop, in the NDR region, is significant for a better understanding of electrochemical oscillations [2,6–8]. It will be of great interest to performer experiments on an electrochemical oscillatory system, but now under conditions where the *IR* drop is zero.

Current oscillations are widespread nonlinear phenomenon in electrodissolution–passivation processes [9–16]. Recently, self-organized phenomena arisen in both time and space are exploited for its practical application in the field of material science [17–19]. Specially, the oscillatory dynamics of these reactions is proven to be a promising topic in investigation of corrosion/passivation processes, which are followed by localized breakdown of passive film [20–26].

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http://dx.doi.org/10.1016/j.corsci.2014.02.034
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In this study, the used electrochemical system consisted of a copper (Cu) electrode, as the working electrode, and 1 M trifluroacetic acid (TFA) as an electrolyte. The electrochemical system Cu/TFA is a known electrochemical oscillator, which exhibits rather interesting nonlinear dynamics mostly in the form of current oscillations [12–14]. The copper electrode was anodically polarized by means of linear sweep voltammetry with/without current interrupt (CI) method applied for *IR* drop compensation.

2. Experimental

All experiments were carried out in a thermostated three-electrode electrolytic cell at 293 K, with a copper rod (Goodfellow, 99.99% purity, 2 mm in diameter) as the working electrode, Pt foil as the counter electrode, and a saturated calomel electrode (SCE) as the reference one. The working electrode was embedded in a plastic capillary leaving only the rod cross-section (0.0314 cm^2) exposed to the electrolyte solution. A Luggin capillary was used between the reference electrode and the working electrode; the tip of the capillary was set 2 mm away from the working electrode surface. Electrolyte solution, 1 M TFA, was prepared from spectroscopic grade TFA (Sigma, T-6340) and deionized water (18.2 MΩ cm at 25 °C). The volume of electrolyte solution in the cell was 100 ml. Electrochemical experiments were carried out using a Gamry PCI4/750 electrochemical workstation. In order to remove dissolved oxygen, 1 M TFA solution in the electrolytic cell was deaerated with gaseous nitrogen (>99.995 vol.% N_2, Messer, Serbia) for 10 min, before each electrochemical measurement. Linear sweep voltammetry was performed using anodic potential scan starting from 0.0 V_{SCE}, at a rate of 10 mV s^{-1}, and a step size of 0.01 mV per point. Electrochemical impedance spectroscopy (EIS) measurement was performed at 0.550 V_{SCE}, in the frequency range from 250 kHz to 0.10 Hz, with AC voltage amplitude of ±20 mV (rms). All reported potentials in this study are given with the respect to the SCE.

3. Results and discussion

Current density–potential (*i*–*E*) polarization curves obtained during anodic dissolution of Cu electrode in 1 M TFA, with and without CI method applied, are shown in Fig. 1. During the electrochemical experiment, the CI method uses a very brief interruption of the electric current to measure and compensate for *IR* drop errors (in the case of Gamry PCI4/750 electrochemical workstation, the electrode potential was corrected from point to point, with the current interruption period between 15 μs and 1 ms). This requires that potentiostat momentarily drop the cell current to zero and then to measure the electrode potential. If there is no current flow ($I = 0$ A), the IR drop between the reference electrode and the working electrode will be zero ($IR = 0$ V), allowing measurement of a "true" electrode potential, that is the double-layer potential (ϕ_{DL}). The applied potential (E) between the working and the reference electrode is corrected until the interrupted-measured value agrees with the desired potential.

The *i*–*E* polarization curve, with applied CI method, displays highly complex electrochemical response, with an atypical voltammetric profile. Clearer picture of this response can be perceived if electrochemical oscillatory response is extracted in the vicinity of bifurcation points, Fig. 2. As presented, the investigated system undergoes synchronized oscillations of the current and applied potential, in-between these points (potentials), forming a continuous loop. Spiral, continuous loop emerges at the bifurcation potential $E_{B1}^{ci} = 0.298\ V_{SCE}$ and disappears at $E_{B2}^{ci} = 0.517\ V_{SCE}$. Outside these bifurcation points the system is in a stable stationary state. Since the direction of anodic polarization goes from less positive to more positive potentials, E_{B1}^{ci} and E_{B2}^{ci} are the entry and the exit bifurcation point, respectively. Between these points, the system displays complex current/potential oscillatory behavior. In the case when the polarization was performed without CI method, the bifurcation points were observed at $E_{B1} = 0.644\ V_{SCE}$ and $E_{B2} = 0.694\ V_{SCE}$.

In order to understand this complex electrochemical response, electric current and applied potential values from the *i*–*E* polarization curve (Fig. 1, CI method applied) are presented in the time scale in Fig. 3. This temporal presentation revealed simultaneous oscillatory behavior of both parameters. Thus, the shape of the original *i*–*E* polarization curve, with applied CI method, is in fact a result of the oscillatory behavior of both parameters. It appears that the oscillatory behavior of applied potentials occurs only in-between bifurcation points. It means that the applied potential linearly increases outside of the oscillatory region, while the current density is a monotonic function of the applied potential. If the oscillatory region is excluded, then we can say that the electrochemical instrument displays an *i*–*E* polarization curve with "normal" shape. The discrepancy in "normal" behavior was observed only in-between bifurcation points. The onset of the oscillations

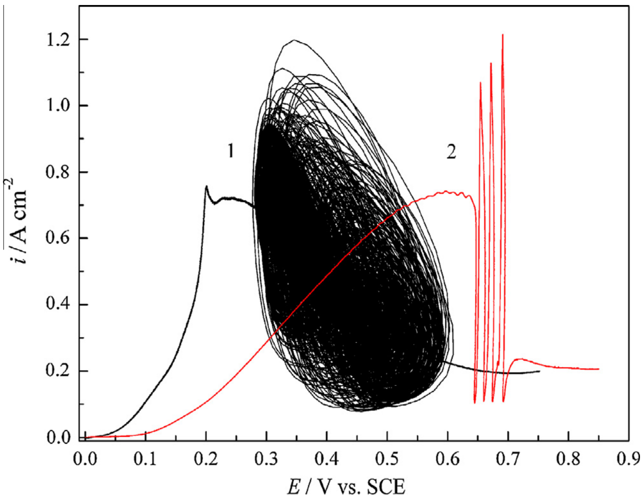

Fig. 1. Anodic *i*–*E* polarization curve of Cu in 1 M TFA: (1) with CI method (2) without CI method.

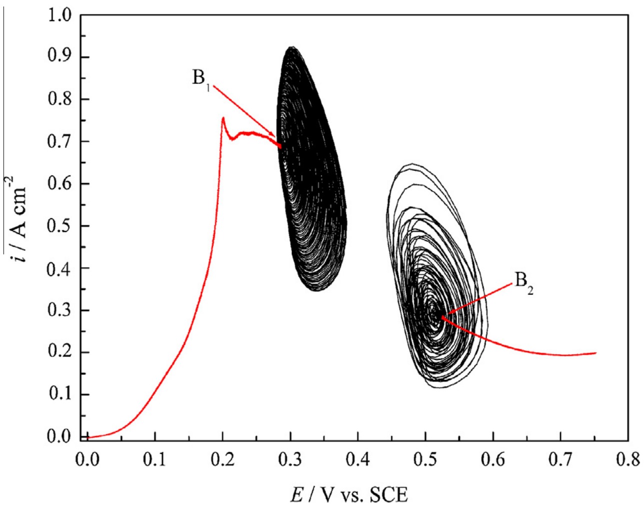

Fig. 2. Oscillatory behavior in the vicinity of bifurcation points on the anodic polarization curve of Cu in 1 M TFA with CI method, extracted from Fig. 1. Two attractors correspond to the states close to the bifurcation points for the onset (B_1) and decay (B_2) of the oscillations.