Journal of Electroanalytical Chemistry 754 (2015) 30–39

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

A complementary survey of staircase voltammetry with metal ion deposition on macroelectrodes

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ARTICLE INFO

Article history:
Received 5 May 2015
Received in revised form 5 June 2015
Accepted 8 June 2015
Available online 9 June 2015

Keywords:
Cyclical staircase voltammetry
Metal ion deposition
Ohmic potential drop
Integration of the voltammograms
Zero-crossing
3D nucleation

ABSTRACT

Further analysis of staircase voltammetry for reversible and quasi-reversible metal ion deposition on a same metal electrode and on a foreign electrode is presented. Literal solutions and numerical simulation are used to quantify the electrochemical response under conditions of planar semi-infinite diffusion. Addressed topics include: consideration of the uncompensated resistance, comparison of the apparent charge found by integration of the voltammograms with the actual faradaic charge transferred, anodic dissolution of the deposit in a cyclical potential scan, properties and interest of the zero-crossing point, occurrence of 3D nucleation overvoltage.

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1. Introduction

In the preceding article [1], we have proposed a theoretical analysis of staircase voltammetry (SV) and of linear sweep voltammetry (LV) for reversible metal ion deposition on both native and foreign plane electrodes neglecting effects of ohmic potential drop.

In this article, after reviewing the principal elements of our previous work [1], the theoretical analysis is extended to incorporate ohmic potential drop (quite unavoidable with macroelectrodes), quasi-reversible charge transfer, anodic dissolution of the deposit and integration of the voltammograms. These topics may meet practical needs of determining kinetic parameters and of detecting surface inhibition.

LV appears as a limiting case of SV when the potential scan increment tends to zero. More emphasis is, however, laid on the discussion of SV which de facto has replaced LV in modern computer-controlled instrumentation.

Our study is conducted by dimensionless analysis of the electrochemical response. The mathematical model takes into account: under potential deposition, feedback between ohmic potential drop and current, superposition of charge-transfer and diffusion rate-control. The same model was also recently applied to the study of square wave voltammetry [2] and received experimental validation [2,3]. Finally, the occurrence of a diffusion-controlled three-dimensional nucleation in SV is also discussed.

2. Basic Theoretical Framework

This section provides a brief overview of the basic mathematical treatment previously published [1].

2.1. Notations in the SV Waveform

In the SV waveform, the potential applied at $t = 0$ is followed at $t = t_i$ $(i = 1,2,\ldots,k)$ by k potential steps of constant height $|\Delta E_s|$ and equal duration Δt. The values of the potential E by time interval are denoted as:

$$\begin{array}{lll} 0 \leqslant t < t_1 & E_1 & \\ t_i \leqslant t < t_{i+1} & E_{i+1} = E_1 + i\Delta E_s & i \in [1, k-1] \\ t_k < t & E_{k+1} = E_1 + k\Delta E_s & \end{array} \quad (1)$$

The current is sampled at $t = t_k + u$ with $u < \Delta t$.

2.2. Fast Charge Transfer

Unhindered charge-transfer on plane electrodes and an exclusive current-control by semi-infinite linear diffusion were initially regarded.

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http://dx.doi.org/10.1016/j.jelechem.2015.06.012
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List of Dimensionless Numbers and Associated Symbols

Dimensionless numbers:

$\psi = \frac{I}{nFAc^*_{\mathrm{Ox}}}\sqrt{\frac{RT}{nFvD_{\mathrm{Ox}}}}$

$\Delta\varepsilon_{\mathrm{s}} = nF|\Delta E_{\mathrm{s}}|/RT$

$\chi = \frac{c^*_{\mathrm{Ox}}}{\Gamma_1}\sqrt{\frac{D_{\mathrm{Ox}}RT}{nFv}}$

$\rho = (nF)^{5/2}R_{\mathrm{u}}\ A\ c^*_{\mathrm{Ox}}(D_{\mathrm{Ox}}v)^{1/2}/(RT)^{3/2}$

$\psi_0 = k^{\mathrm{o}}\left(\frac{RT}{D_{\mathrm{Ox}}Fv}\right)^{1/2}\left(\frac{c^*_{\mathrm{Ox}}}{c^{\mathrm{o}}}\right)^{-\alpha_{\mathrm{c}}}$

$nF\eta_{\mathrm{inv}}/RT$

$[Q] = \frac{Q\sqrt{nFv/RT}}{nFAc^*_{\mathrm{Ox}}\sqrt{D_{\mathrm{Ox}}}}$

$[Q^{-}] = \frac{Q^{-}\sqrt{nFv/RT}}{nFAc^*_{\mathrm{Ox}}\sqrt{D_{\mathrm{Ox}}}}$

Symbols:

A	electrode area
c^*_{Ox}	bulk concentration of metal ions (Ox)
c^{o}	standard amount concentration (1 mol L^{-1})
D_{Ox}	diffusion coefficient of Ox
E	potential
E_{Eq}	zero current equilibrium potential
$\|\Delta E_{\mathrm{s}}\|$	step height in the potential staircase = potential increment
I	current
k^{o}	standard rate constant
n	number of electrons
Q	dimensional faradaic charge
Q^{-}	apparent dimensional faradaic charge
R_{u}	uncompensated residual resistance
Δt	duration of the steps in SV
v	potential scan rate ($v = \|\Delta E_{\mathrm{s}}\|/\Delta t$)
α_{c}	cathodic charge transfer coefficient
Γ_1	surface concentration of the deposit for which its activity becomes 1
η	overvoltage ($\eta = E - E_{\mathrm{Eq}}$)
η_{inv}	inversion overvoltage

2.2.1. Metal ion Deposition on a Same Metal Electrode

For reversible metal ion deposition on a same metal electrode, assuming E_1 equal to the equilibrium potential, the current in SV at $t = t_k + u$ is given by:

$$\frac{I}{nFAc^*_{\mathrm{Ox}}\sqrt{D_{\mathrm{Ox}}}} = \frac{1}{\sqrt{\pi}}\sum_{i=1}^{k}\frac{\lambda_{i+1}-\lambda_i}{\sqrt{t-t_i}} \tag{2}$$

where

$$\lambda = \exp(nF\eta/RT) \tag{3}$$

$$\eta = E - E_{\mathrm{Eq}} \tag{4}$$

$$E_{\mathrm{Eq}} = E^{\mathrm{o}} + \frac{RT}{nF}\ln(\gamma_{\mathrm{Ox}}c^*_{\mathrm{Ox}}/c^{\mathrm{o}}) \tag{5}$$

In the above expressions, n is the number of exchanged electrons, A the surface area of the working electrode, c^*_{Ox} the molar bulk concentration of metal ions (Ox), $c^{\mathrm{o}} = 1$ mol L^{-1}, D_{Ox} the diffusion coefficient and γ_{Ox} the activity coefficient of Ox, E_{Eq} the equilibrium potential and E^{o} the standard potential of the metal/metal ion electrode, the remaining symbols having their usual meanings. Throughout this article the reduction current is assumed to be negative.

Letting

$$v = |\Delta E_{\mathrm{s}}|/\Delta t \tag{6}$$

$$r = u/\Delta t \tag{7}$$

$$\Delta\varepsilon_{\mathrm{s}} = nF|\Delta E_{\mathrm{s}}|/RT \text{ (denoted } \chi_1 \text{ in Ref. [1])} \tag{8}$$

and

$$\psi = \frac{I}{nFAc^*_{\mathrm{Ox}}}\sqrt{\frac{RT}{nFvD_{\mathrm{Ox}}}} \tag{9}$$

Eq. (2) is put into dimensionless form:

$$\psi = \frac{1}{\sqrt{\pi\Delta\varepsilon_{\mathrm{s}}}}\sum_{i=1}^{k}\frac{\lambda_{i+1}-\lambda_i}{\sqrt{k+r-i}} \tag{10}$$

Thereafter, r is assumed to be 1, which corresponds to a sampling of current near the end of each potential step. The curve $\psi = \mathrm{f}(nF\eta/RT)$ depends on $\Delta\varepsilon_{\mathrm{s}}$. For $0 \leqslant \Delta\varepsilon_{\mathrm{s}} < 0.4$ ($0 \leqslant -n\Delta E_{\mathrm{s}}/\mathrm{mV} < 10$ at 25 °C), where 0 applies to LV, the peak coordinates $(nF\eta_{\mathrm{p}}/RT, \psi_{\mathrm{p}})$ were very well approximated with an accuracy of three or four significant figures by:

$$\frac{nF\eta_{\mathrm{p}}}{RT} = -(0.854 + 0.866\Delta\varepsilon_{\mathrm{s}}^{0.467}) \tag{11}$$

$$\psi_{\mathrm{p}} = -\frac{0.6105}{1 + 0.5878\sqrt{\Delta\varepsilon_{\mathrm{s}}}}. \tag{12}$$

2.2.2. Metal ion Deposition on a Foreign Electrode

The reduction of metal ions M^{n+} at a foreign plane electrode in the presence of a large excess of an indifferent electrolyte was modeled with the following assumptions:

- The charge-transfer reaction $M^{n+} + S + ne^- = S - M(\theta)$, where $M(\theta)$ represents the adatoms on the substrate S at the coverage degree θ, and other chemical or crystallization reactions are in equilibrium so that the current is only controlled by diffusion.
- The activity of the deposit (Red) in the molar scale, a_{Red}, tends to 1 as its surface concentration, Γ, approaches the value Γ_1 corresponding to one or more atomic layers.

Let c_{Ox} be the concentration of Ox at distance x from the electrode and time t. Letting:

$$\mathrm{C} = c_{\mathrm{Ox}}/c^*_{\mathrm{Ox}} \tag{13}$$

$$\mathrm{X} = x\sqrt{nFv/D_{\mathrm{Ox}}RT} \tag{14}$$

$$\mathrm{T} = nFvt/RT \tag{15}$$

$$\theta = \Gamma/\Gamma_1 \tag{16}$$

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