



Analysis of the square wave voltammetry for reversible metal deposition on a foreign substrate – Experimental study of silver deposition on gold



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ABSTRACT

The behaviour of square wave voltammetry for a reversible metal deposition was investigated through a model involving underpotential adsorption of metal ions. A quantitative description of the response was performed using three dimensionless key quantities. It was found that the IR-drop can play an important role even in very conductive media. The half-width at half-height of the peak in the overpotential range was approximated by a simple expression leading to the determination of the number of electrons exchanged. On this point, a critical assessment of the method based on an analogy with the case of soluble redox species was presented. A very good correlation was obtained between model predictions and experimental data for the silver deposition on a polycrystalline gold disc electrode from HNO_3 and NaNO_3 solutions.

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1. Introduction

In recent years, square wave voltammetry (SWV) is increasingly employed as a method of investigating electrodeposition processes especially in fused salt media [1–12] (the list is non-exhaustive). Besides its outstanding analytical features, namely, high scan speed, signal to noise ratio and potential resolution, SWV also serves to determine the number of electrons exchanged in order to characterise the reduced species. In this matter, there seems to be some confusion since the results are analysed in the same way whether or not metal deposition occurs. Effects of ohmic potential drop are also quite systematically understated. In fact, there is no sufficient theoretical and methodological background to configure and interpret SWV experiments dealing with metal deposition.

Our modelling approach takes into account the charge-transfer adsorption and the amount of deposited metal in the underpotential range. To facilitate the description of the system trends, dimensionless combinations of dimensional physical constants and variables were used. Validation of the model within its domain of applicability is carried out by comparison between simulated and experimental results for the reversible deposition of silver on a plane gold electrode from electrolytes of various conductivities.

2. Theoretical section

2.1. Square waveform and associated notations

It can be considered that the waveform in SWV results from the superimposition of a potential pulse of height $|\Delta E|$ and duration Δt at the front of each step of a potential staircase of height $|\Delta E_s|$ and duration $2\Delta t$. The difference of currents sampled during each wave period near the end of two consecutive potential levels, ΔI , is plotted versus a potential E_s which is the potential of the step of the staircase plus $\Delta E/2$. The SWV waveform and the associated notations are presented in Fig. 1.

It is important to emphasise that often in commercial software “pulse height” corresponds with $|\Delta E|/2$. Furthermore, the square wave frequency, $1/2\Delta t$, may be alternatively used as input parameter.

2.2. Addressing the problem of metal deposition in SWV

The problem consists in finding a solution for the current I in SWV at a plane electrode assuming that:

- An indifferent electrolyte is present in large excess.
- The specific adsorption of metal ions in the underpotential range is the first step of the electrodeposition process.
- The activity of the deposited metal, a_{Red} , is nearly 1 when its surface concentration, Γ , reaches the value Γ_1 corresponding to one or more atomic layers of metal.

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List of principal symbols

A	electrode area
a_{Red}	activity of deposited metal (Red)
c_{Ox}	concentration of the metal ion (Ox)
c_{Ox}^*	bulk concentration of Ox
Δc_{Ox}	difference in concentration $c_{\text{Ox}}^* - c_{\text{Ox}}(x=0)$
Γ	surface concentration of Red
Γ_1	value of Γ for which a_{Red} becomes 1
D_{Ox}	diffusion coefficient of Ox
δ	diffusion layer thickness
E	applied or measured potential
E_s	potential of the step of the staircase plus $\Delta E/2$
$E(0)$	zero current equilibrium potential of the metal/metal ion electrode
E_p	vertex potential of the differential curve
$ \Delta E $	edge-to-edge pulse height
$ \Delta E_s $	step height in the potential staircase
F	Faraday constant
I	current
I_f	forward (reduction) current
I_b	backward current
I_{Lim}	limiting steady-state current
$\Delta I = I_f - I_b$	differential current
$ \Delta I_p $	peak height
κ	conductivity
n	electron-exchange number
ν	kinematic viscosity
R	universal gas constant
R_u	uncompensated total residual resistance

R_s	uncompensated solution resistance
T	absolute temperature
Δt	pulse duration
w	peak width at half-height
w_2	second half-width at half-height of the peak in the negative direction
x	distance from the electrode
ω	angular velocity

Dimensionless numbers

$$\mathcal{E} = nF(E_s - E(0))/RT$$

$$\mathcal{E}_p = nF(E_p - E(0))/RT$$

$$\Delta \mathcal{E} = -nF\Delta E/RT\Delta \mathcal{E}_s = -nF\Delta E_s/RT$$

$$\theta = \Gamma/\Gamma_1$$

$$\rho = \frac{n^2 F^2 A R_u c_{\text{Ox}}^* \sqrt{D_{\text{Ox}}}}{RT \sqrt{\Delta t}}$$

$$\chi = c_{\text{Ox}}^* \sqrt{D_{\text{Ox}} \Delta t} / \Gamma_1$$

$$\psi = \frac{I \sqrt{\pi \Delta t}}{n F A c_{\text{Ox}}^* \sqrt{D_{\text{Ox}}}}, \psi_f \text{ and } \psi_b \text{ refer to } I = I_f \text{ and } I = I_b$$

$$\Delta \psi = \frac{\Delta I \sqrt{\pi \Delta t}}{n F A c_{\text{Ox}}^* \sqrt{D_{\text{Ox}}}}$$

$$\Delta \psi_p = \frac{\Delta I_p \sqrt{\pi \Delta t}}{n F A c_{\text{Ox}}^* \sqrt{D_{\text{Ox}}}}$$

$$\mathcal{W} = n F w / RT \quad \mathcal{W}_2 = n F w_2 / RT$$

– All chemical processes including the crystallisation process and also the charge-transfer reaction, are in equilibrium so that the current flowing through the cell is diffusion controlled.

Therefore the model can be summarized by the equilibrium equation



where M^{n+} is the dissolved metal ion and $S - M(\theta)$ the atom M adsorbed on the substrate S at the coverage degree θ .

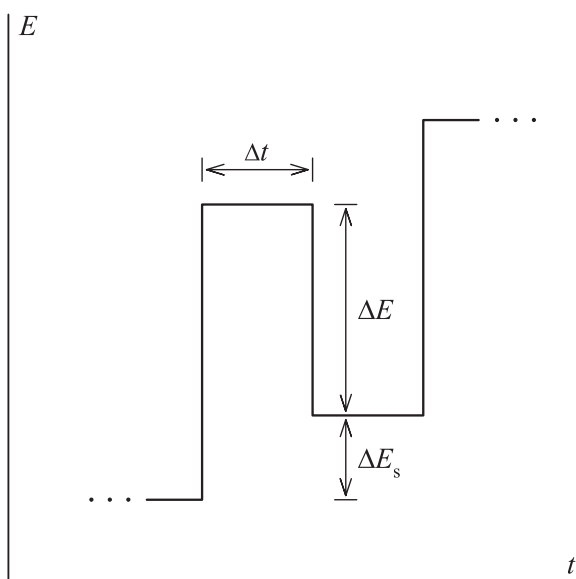


Fig. 1. SWV waveform and associated notations.

We shall denote by x the distance from the electrode, t the time, $c_{\text{Ox}}(x, t)$ the molar concentration of the metal ion, γ_{Ox} and D_{Ox} its activity and diffusion coefficients, c_{Ox}^* the initial concentration, n the number of electrons involved in the electrochemical reaction, A the area of the electrode, E the applied potential, R_u the residual uncompensated series resistance, $E(0)$ and E^0 the zero current equilibrium potential and the standard potential of the metal/metal ion electrode. Other symbols have their usual meanings. $E(0)$ is expressed by

$$E(0) = E^0 + \frac{RT}{nF} \ln(\gamma_{\text{Ox}} c_{\text{Ox}}^*) \quad (2)$$

At $t > 0$, the current is given by

$$-\frac{I}{nFA} = D_{\text{Ox}} \left(\frac{\partial c_{\text{Ox}}}{\partial x} \right)_{x=0} = \frac{d\Gamma}{dt} \quad (3)$$

and the electrode potential by the unabridged Nernst equation [13] which, taking E^0 equal to that for the bulk metal, can be written as

$$\exp \frac{nF(E - IR_u - E(0))}{RT} = \frac{c_{\text{Ox}}(0, t)}{c_{\text{Ox}}^* a_{\text{Red}}} \quad (4)$$

Using the dimensionless quantities

$$C = c_{\text{Ox}}/c_{\text{Ox}}^*, \quad \theta = \Gamma/\Gamma_1, \quad X = x/\sqrt{D_{\text{Ox}} \Delta t}, \quad T = t/\Delta t \quad (5)$$

$$\psi = \frac{I \sqrt{\pi \Delta t}}{n F A c_{\text{Ox}}^* \sqrt{D_{\text{Ox}}}} \quad (6)$$

$$\chi = c_{\text{Ox}}^* \sqrt{D_{\text{Ox}} \Delta t} / \Gamma_1 \quad (7)$$

$$\rho = \frac{n^2 F^2 A R_u c_{\text{Ox}}^* \sqrt{D_{\text{Ox}}}}{RT \sqrt{\Delta t}} \quad (8)$$

The initial and boundary value problem under conditions of semi-infinite diffusion can be put in the form:

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