



# Theory of square wave voltammetry of three step electrode reaction



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## ABSTRACT

A theory of square wave voltammetry of three step electrode reaction of amalgam forming ions is developed for a thin mercury film electrode. It is assumed that the first and the second electron transfers are kinetically controlled while the third one is reversible and that the intermediates are thermodynamically unstable. The responses to the cathodic and anodic scan directions are analyzed.

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## 1. Introduction

The exchange of three electrons between an electrode and a redox center can occur in three consecutive steps if the center contains three electronic levels that can accommodate one electron each [1–3]. In voltammetry the response may consist of one, two or three peaks, depending on the stability of intermediates [4,5]. The theory of this type of reactions is developed for the single and double pulse chronoamperometry [6–8], chronopotentiometry [9,10], polarography [11–13], cyclic voltammetry [14–16] and square wave voltammetry [17]. Electrode reactions of bismuth [18–26] and antimony [27] were analyzed. The responses of charge transfers that are kinetically controlled depend on the standard rate constants and transfer coefficients of all slow steps [6,11,12,15,17]. Under these conditions the intermediates could be additionally stabilized by the electrode kinetics and the form of response may change with the frequency or scan rate [17]. In this paper electrode reactions that are influenced by the kinetics of the first and the second step are analyzed theoretically for the direct and reverse square wave voltammetry. In the latter technique the scan starts at the potential at which the reactant is not stable at the electrode surface [28,29]. The possibility to determine the second transfer coefficient is investigated.

## 2. The model

An electrode reaction that occurs through three consecutive steps is analyzed. It is assumed that the final product is an atom

that is dissolved into a thin mercury film that covers a stationary working electrode surface and that only the reactant  $M^{3+}$  is initially present in the solution. Furthermore, we assume that the first two charge transfers are kinetically controlled while the third one is fast and reversible. The rates of electron transfers are described by well established Butler–Volmer equation, assuming that transfer coefficients may vary between 0.25 and 0.75 [1,6,12,15,16].



The uniform concentration of atoms in the thin film is assumed. For the stationary, semi-infinite diffusion of ions, the following system of differential equations has to be solved:

$$\partial c_{M^{3+}} / \partial t = D(\partial^2 c_{M^{3+}} / \partial x^2) \quad (4)$$

$$\partial c_{M^{2+}} / \partial t = D(\partial^2 c_{M^{2+}} / \partial x^2) \quad (5)$$

$$\partial c_{M^+} / \partial t = D(\partial^2 c_{M^+} / \partial x^2) \quad (6)$$

$$t = 0, x \geq 0: c_{M^{3+}} = c_{M^{3+}}^*, c_{M^{2+}} = c_{M^+} = c_{M^0} = 0 \quad (7)$$

$$t > 0, x \rightarrow \infty: c_{M^{3+}} \rightarrow c_{M^{3+}}^*, c_{M^{2+}} \rightarrow 0, c_{M^+} \rightarrow 0 \quad (8)$$

$$x = 0: D(\partial c_{M^{3+}} / \partial x)_{x=0} = -I_1 / FS \quad (9)$$

$$D(\partial c_{M^{2+}} / \partial x)_{x=0} = (I_1 - I_2) / FS \quad (10)$$

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$$D(\partial C_{M^+}/\partial x)_{x=0} = (I_2 - I_3)/FS \quad (11)$$

$$C_{M^0} = -L^{-1} \int_0^t (I_3/FS) d\tau \quad (12)$$

$$I_1/FS = -k_{s1} \exp(-\alpha_1 \varphi_1) [(C_{M^{3+}})_{x=0} - (C_{M^{2+}})_{x=0} \exp(\varphi_1)] \quad (13)$$

$$I_2/FS = -k_{s2} \exp(-\alpha_2 \varphi_2) [(C_{M^{2+}})_{x=0} - (C_{M^+})_{x=0} \exp(\varphi_2)] \quad (14)$$

$$(C_{M^+})_{x=0} = C_{M^0} \exp(\varphi_3) \quad (15)$$

$$\varphi_1 = (F/RT)(E - E_1^0) \quad (16)$$

$$\varphi_2 = (F/RT)(E - E_2^0) \quad (17)$$

$$\varphi_3 = (F/RT)(E - E_3^0) \quad (18)$$

The meanings of all symbols are reported in Table 1. Differential Eqs. (4)–(6) are solved by Laplace transformations and by the method of numerical integration proposed by Olmstead and Nicholson [30]. The solution is the system of recursive formulae for the dimensionless current,  $\Phi_i = I_i(FSC_{M^{3+}}^*)^{-1}(Df)^{-1/2}$ , where  $i = 1, 2$  or 3. The sum,  $\Phi = \Phi_1 + \Phi_2 + \Phi_3$  is reported as a function of electrode potential.

$$\Phi_{1,1} = -5\sqrt{\pi/2}\kappa_1 \exp(-\alpha_1 \varphi_{1,1}) [5\sqrt{\pi/2} + Z_3]^{-1} \quad (19)$$

$$\Phi_{1,m} = \left[ -5\sqrt{\pi/2}\kappa_1 \exp(-\alpha_1 \varphi_{1,m}) - Z_3 \sum_{j=1}^{m-1} \Phi_{1j} s_{m-j+1} + Z_4 \sum_{j=1}^{m-1} \Phi_{2j} s_{m-j+1} + Z_5 \left( \sum_{j=1}^{m-1} \Phi_{3j} s_{m-j+1} - \sum_{j=1}^{m-1} \Phi_{3j} \right) \right] (5\sqrt{\pi/2} + Z_3)^{-1} \quad (20)$$

$$\Phi_{2,1} = \kappa_2 \exp(-\alpha_2 \varphi_{2,1}) Z_2^{-1} \Phi_{1,1} \quad (21)$$

$$\Phi_{2,m} = \kappa_2 \exp(-\alpha_2 \varphi_{2,m}) Z_2^{-1} \left( \Phi_{1,m} + \sum_{j=1}^{m-1} \Phi_{1j} s_{m-j+1} \right) - Z_6 \sum_{j=1}^{m-1} \Phi_{2j} s_{m-j+1} + Z_7 \left( \sum_{j=1}^{m-1} \Phi_{3j} s_{m-j+1} - \sum_{j=1}^{m-1} \Phi_{3j} \right) \quad (22)$$

$$\Phi_{3,1} = \Phi_{2,1} (1 + Z_1)^{-1} \quad (23)$$

$$\Phi_{3,m} = \left[ \Phi_{2,m} + \sum_{j=1}^{m-1} \Phi_{2j} s_{m-j+1} - \sum_{j=1}^{m-1} \Phi_{3j} s_{m-j+1} - Z_1 \sum_{j=1}^{m-1} \Phi_{3j} \right] (1 + Z_1)^{-1} \quad (24)$$

$$Z_1 = \lambda \sqrt{\pi/200} \exp(\varphi_{3,m}) \quad (25)$$

$$Z_2 = 5\sqrt{\pi/2} + \kappa_2 \exp(-\alpha_2 \varphi_{2,m}) [1 + Z_1 \exp(\varphi_{2,m}) (1 + Z_1)^{-1}] \quad (26)$$

$$Z_3 = \kappa_1 \exp(-\alpha_1 \varphi_{1,m}) [1 + \exp(\varphi_{1,m}) (1 - \kappa_2 \exp(-\alpha_2 \varphi_{2,m}) Z_2^{-1})] \quad (27)$$

$$Z_4 = \kappa_1 \exp((1 - \alpha_1) \varphi_{1,m}) [1 - \kappa_2 Z_2^{-1} \exp(-\alpha_2 \varphi_{2,m}) (1 + Z_1 \exp(\varphi_{2,m}) (1 + Z_1)^{-1})] \quad (28)$$

$$Z_5 = \kappa_1 \kappa_2 Z_1 Z_2^{-1} \exp((1 - \alpha_1) \varphi_{1,m}) \exp((1 - \alpha_2) \varphi_{2,m}) (1 + Z_1)^{-1} \quad (29)$$

$$Z_6 = \kappa_2 Z_2^{-1} \exp(-\alpha_2 \varphi_{2,m}) [1 + \exp(\varphi_{2,m}) Z_1 (1 + Z_1)^{-1}] \quad (30)$$

$$Z_7 = \kappa_2 \exp((1 - \alpha_2) \varphi_{2,m}) Z_1 Z_2^{-1} (1 + Z_1)^{-1} \quad (31)$$

$$\lambda = L^{-1} \sqrt{D/f} \quad (32)$$

$$\kappa_i = k_{s,i} (Df)^{-1/2} \quad (i = 1, 2) \quad (33)$$

$$s_k = \sqrt{k} - \sqrt{k-1} \quad (34)$$

$$2 \leq m \leq M \quad (35)$$

$$M = 50(E_{st} - E_{fin})/dE \quad (36)$$

**Table 1**  
Meanings of symbols.

$\alpha_1, \alpha_2$	Transfer coefficients of the first and the second electron transfer steps
$C_{M^{3+}}, C_{M^{2+}}, C_{M^+}, C_{M^0}$	Concentrations of the reactant, intermediates and the product
$C_{M^{3+}}^*$	Concentration of the reactant in the bulk of solution
$D$	Common diffusion coefficient
$dE$	Square wave potential increment
$E$	Electrode potential
$E_1^0, E_2^0, E_3^0$	Standard potentials of the first, the second and the third electron transfer steps
$E_{sw}$	Square wave amplitude
$E_{st}$	Square wave starting potential
$E_p$	Peak potential
$F$	Faraday constant
$f$	Square wave frequency
$\Phi$	Dimensionless current
$I_1, I_2, I_3$	Currents of the first, the second and the third electron transfers
$k_{s,1}, k_{s,2}$	Standard rate constants of the first and the second electron transfers
$\kappa_2, \kappa_1$	Dimensionless kinetic parameters of the first and the second electron transfers
$L$	Mercury film thickness
$\lambda$	Dimensionless mercury film thickness
$R$	Gas constant
$S$	Electrode surface area
$T$	Temperature
$t$	Time
$x$	Distance perpendicular to the electrode surface

### 3. Results and discussion

If all three electron transfers are fast and reversible, the net response in square wave voltammetry may consist of either one peak, or two peaks, or three peaks. The single peak appears if  $E_2^0 - E_1^0 > -0.1$  V and  $E_3^0 - E_1^0 > -0.1$  V. This means that both intermediates are thermodynamically unstable. In the second case either the first, or the second intermediate is stable. These responses occur if  $-0.2 < E_2^0 - E_1^0 < -0.1$  V and  $-0.3 < E_3^0 - E_1^0 \leq 0$  V, or  $E_2^0 - E_1^0 > -0.1$  V and  $E_3^0 - E_1^0 < -0.1$  V. The last type of voltammogram arise if  $E_2^0 - E_1^0 < -0.2$  V and  $E_3^0 - E_2^0 < -0.1$  V. The peak potentials are equal to the standard potentials, except for the third one that depends on the logarithm of dimensionless mercury film thickness:  $E_{p,3} = E_3^0 - 0.040 - (RT/F) \ln(\lambda)$  (V). For this reason the potential of a single peak is also the function of the parameter  $\lambda$ :  $E_p = (E_1^0 + E_2^0 + E_3^0)/3 - 0.040 - (RT/3F) \ln(\lambda)$  (V). All these responses do not depend on the scan direction and the starting potential. In this paper it is assumed that standard potentials are equal:  $E_1^0 = E_2^0 = E_3^0$ .

Fig. 1 shows the voltammogram influenced by the kinetics of the first electron transfer. For the cathodic scan direction the response is dominated by the forward, reductive component, while the backward component gradually vanishes. The dependence of net peak potentials on the logarithm of the first dimensionless kinetic parameter is shown in Fig. 2A. If  $\log(\kappa_1) < -2$  this relationship is

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