

Research Article

Theory of Square-Wave Voltammetry of Two-Electron Reduction with the Adsorption of Intermediate

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Thermodynamically unstable intermediate of fast and reversible two-electron electrode reaction can be stabilized by the adsorption to the electrode surface. In square-wave voltammetry of this reaction mechanism, the split response may appear if the electrode surface is not completely covered by the adsorbed intermediate. The dependence of the difference between the net peak potentials of the prepeak and postpeak on the square-wave frequency is analyzed theoretically. This relationship can be used for the estimation of adsorption constant.

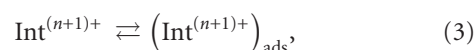
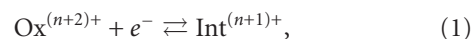
1. Introduction

In polarography and voltammetry of electrode reactions consisting of two-electron transfers, the responses depend on the stability of intermediates [1–6]. In the case of fast and reversible electroreduction, two waves or peaks appear if the standard potential of the second electron transfer is two hundred millivolts or more lower than the standard potential of the first electron transfer [2, 3]. For the difference in standard potentials higher than -0.1 V, the response is a single wave or peak [6]. Thermodynamically unstable intermediate can be kinetically stabilized if the second charge transfer is slow [1, 3, 4]. Furthermore, the intermediate can be stabilized by the adsorption to the electrode surface [7–11]. This phenomenon was observed in electroreduction of hydrogen [8, 9], chloropyridines [12], and paraquat [13], in electrooxidation of bismuth [7], aluminum [14], and methanol [15], in the passivation of cobalt electrode [16], and in the anodic evolution of oxygen [17]. The theory of two-electron reaction complicated by the adsorption of intermediate is developed for pulse and differential pulse polarography [18–23] and for impedance measurements [24–26], and in this paper the theory is extended to square-wave voltammetry [27–29]. For this technique there are theories for two-step simple and catalytic surface reactions

in which all electroactive species are strongly adsorbed to the electrode surface [30–33].

2. The Model

The following reaction mechanism is analyzed:



where $n = 0, 1, 2$, or more. It is assumed that only the reactant $\text{Ox}^{(n+2)+}$ is initially present in the solution, that the mass transfer occurs through the stationary, planar, semi-infinite diffusion, that both electron transfers are fast and reversible, that all diffusion coefficients are equal, that the adsorption can be described by Langmuir isotherm, and that there are no interactions between molecules in the adsorbed monolayer. The system of differential equations for three electroactive species:

$$\frac{\partial c_Y}{\partial t} = D \frac{\partial^2 c_Y}{\partial x^2}, \quad (4)$$

(where $Y = \text{Ox}^{(n+2)+}$, $\text{Int}^{(n+1)+}$, and Red^{n+}) is solved for the initial and boundary conditions:

$$t = 0, \quad x \geq 0 : c_{\text{Ox}} = c_{\text{Ox}}^*, \quad c_{\text{Int}} = 0, \quad c_{\text{Red}} = 0, \quad \Gamma_{\text{Int}} = 0, \quad (5)$$

$$t > 0, \quad x \rightarrow \infty : c_{\text{Ox}} \rightarrow c_{\text{Ox}}^*, \quad c_{\text{Int}} \rightarrow 0, \quad c_{\text{Red}} \rightarrow 0, \quad (6)$$

$$x = 0 : D \left(\frac{\partial c_{\text{Ox}}}{\partial x} \right)_{x=0} = -\frac{I_1}{FS}, \quad (7)$$

$$D \left(\frac{\partial c_{\text{Int}}}{\partial x} \right)_{x=0} = \frac{d\Gamma_{\text{Int}}}{dt} + \frac{I_1 - I_2}{FS}, \quad (8)$$

$$D \left(\frac{\partial c_{\text{Red}}}{\partial x} \right)_{x=0} = \frac{I_2}{FS}, \quad (9)$$

$$I = I_1 + I_2, \quad (10)$$

$$(c_{\text{Ox}})_{x=0} = (c_{\text{Int}})_{x=0} \exp(\varphi_1), \quad (11)$$

$$(c_{\text{Int}})_{x=0} = (c_{\text{Red}})_{x=0} \exp(\varphi_2), \quad (12)$$

$$\varphi_1 = \frac{F}{RT} (E - E_1^0), \quad (13)$$

$$\varphi_2 = \frac{F}{RT} (E - E_2^0), \quad (14)$$

$$\beta (c_{\text{Int}})_{x=0} = \frac{\Gamma_{\text{Int}}}{\Gamma_{\text{max}} - \Gamma_{\text{Int}}}. \quad (15)$$

The meanings of all symbols are given in Table 1. Equation (4) is transformed into the system of integral equations and solved by the numerical method of Olmstead and Nicholson [34]. A dimensionless current $\Phi = I(FSc_{\text{Ox}}^*)^{-1}(Df)^{-1/2}$ is calculated as a function of electrode potential. The solutions are reported in the appendix.

3. Results and Discussion

Theoretical square-wave voltammogram of simple, reversible two-electron reaction depends on the difference in standard potentials of two charge transfers ($E_2^0 - E_1^0$), on square-wave amplitude (E_{SW}), and on potential increment (dE). If $E_1^0 = E_2^0$, $E_{\text{SW}} = 50$ mV, and $dE = -5$ mV, the voltammogram is a single peak with the maximum at the standard potential and the dimensionless net peak current $-\Delta\Phi_p = 1.6835$. The characteristics of the forward, reductive and the backward, oxidative components are the following: $\Phi_{p,f} = -1.0483$, $E_{p,f} = E_1^0$, $\Phi_{p,b} = 0.6352$, and $E_{p,b} = E_1^0$. Under the influence of adsorption of intermediate, the voltammogram depends

TABLE 1: Meanings of symbols.

β	Adsorption constant
$c_{\text{Ox}}, c_{\text{Int}}, c_{\text{Red}}$	Concentrations of the reactant, intermediate and the product
c_{Ox}^*	Concentrations 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	Standard potentials of the first and the second electron transfers
E_{SW}	Square-wave amplitude
E_p	Peak potential
$E_{p,1}, E_{p,2}$	Peak potentials of the prepeak and postpeak
$E_{p,f}, E_{p,b}$	Peak potentials of the forward and backward components
E_{st}	Starting potential
F	Faraday constant
f	Square-wave frequency
φ	Dimensionless potential difference
Φ	Dimensionless current
Φ_f, Φ_b	Dimensionless currents of the forward and backward components
$-\Delta\Phi_p$	Dimensionless net peak current
$\Phi_{p,f}, \Phi_{p,b}$	Dimensionless peak currents of the forward and backward components
Γ_{Int}	Surface concentration of adsorbed intermediate
Γ_{max}	Maximum surface concentration of adsorbed intermediate
R	Gas constant
S	Electrode surface area
t	Time
T	Temperature
θ	Surface coverage
x	Distance perpendicular to the electrode surface

on two additional parameters: the dimensionless reactant concentration (βc_{Ox}^*) and the dimensionless adsorption constant ($\beta\Gamma_{\text{max}}\sqrt{f/D}$). Note that the adsorption constant of Henry isotherm is equal to the product $\beta\Gamma_{\text{max}}$.

Figure 1 shows the influence of the product βc_{Ox}^* . If this product is smaller than 25, the response is split into two peaks with the maxima at 0.075 V and -0.070 V versus E_1^0 . The net peak currents in Figure 1(a) are 0.88 and 1.36, respectively. These values change from 0.90 and 1.51, for $\beta c_{\text{Ox}}^* = 0.1$, to 0.86 and 1.17 for $\beta c_{\text{Ox}}^* = 25$. The splitting appears because the adsorption of intermediate facilitates the transfer of the first electron but requires an additional energy for the reduction of adsorbed intermediate [18, 20, 22]. So, the peaks 1 and 2 in Figure 1(a) are the prepeak and postpeak, respectively. The condition for the split response is that the electrode surface is not fully covered by the adsorbed monolayer. Assuming that $\beta = 10^8$ cm³/mol, as it was observed

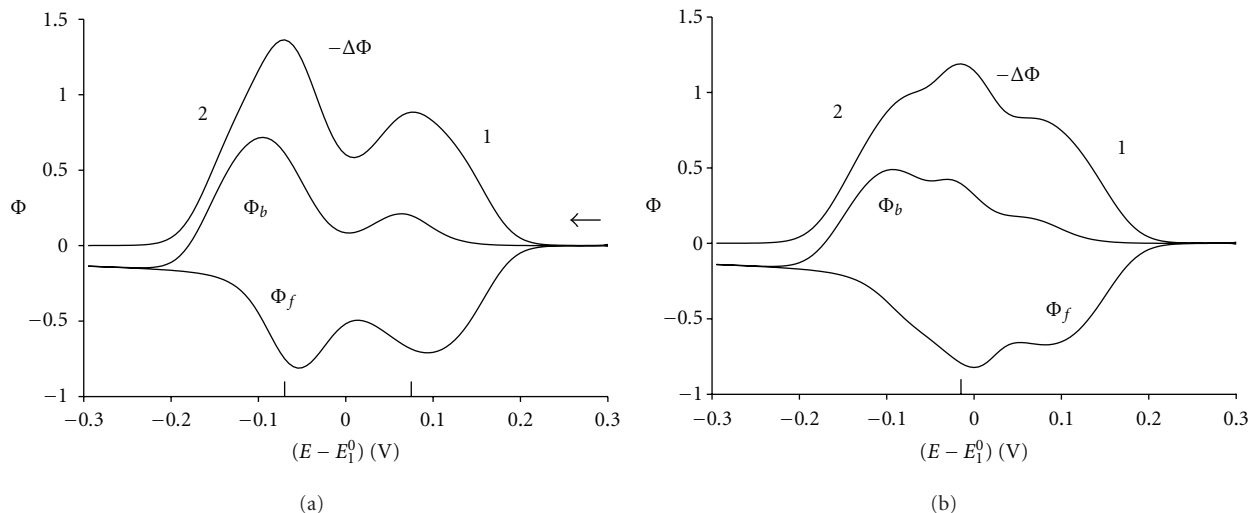


FIGURE 1: Square-wave voltammetry (SWV) of electrode reactions (1)–(3). $E_2^0 = E_1^0$, $E_{SW} = 50$ mV, $dE = -5$ mV, $E_{st} = 0.3$ V versus E_1^0 , $\beta\Gamma_{\max}\sqrt{(f/D)} = 100$, and $\beta c_{Ox}^* = 10$ (a) and 40 (b). The net peak potentials are marked by the short vertical lines above the abscissa.

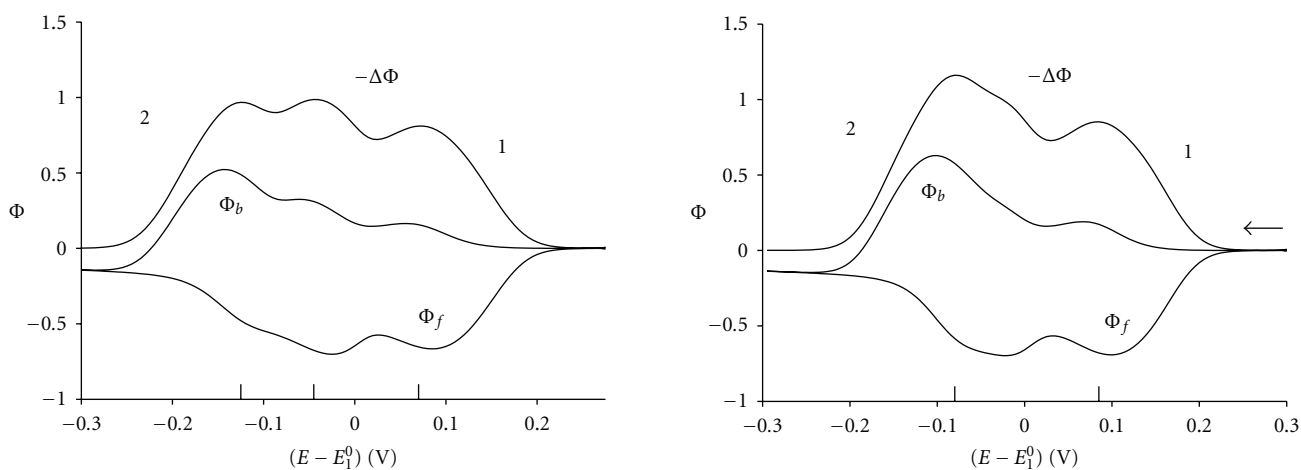


FIGURE 2: SWV of the reactions (1)–(3). $E_2^0 - E_1^0 = -0.050$ V and $\beta c_{Ox}^* = 40$. All other parameters are as in Figure 1.

FIGURE 3: SWV of the reactions (1)–(3). $\beta c_{Ox}^* = 40$ and $\beta\Gamma_{\max}\sqrt{(f/D)} = 150$. All other parameters are as in Figure 1.

in the anion-induced adsorption of some metal ions [35–37], this condition is satisfied for $c_{Ox}^* < 2.5 \times 10^{-4}$ mol/L. At higher concentrations the main peak develops, as can be seen in Figure 1(b). Its net peak potential is -0.015 V versus E_1^0 . The minimum in the forward component and the maximum in the backward component that correspond to the main peak appear at E_1^0 and -0.030 V versus E_1^0 , respectively. If $\beta c_{Ox}^* = 150$, the maximum of the main peak appears at E_1^0 , and the potentials of minimum and maximum of the forward and backward components are 0.005 V and -0.005 V versus E_1^0 , respectively.

The separation between net peak potentials of the split response is independent of the reactant concentration but depends on the square-wave amplitude. If $E_{SW} = 20$ mV, $E_{p,1} - E_{p,2} = 175$ mV, and if $E_{SW} = 70$ mV,

$E_{p,1} - E_{p,2} = 110$ mV. For this reason all analyses in this work are performed with the amplitude of 50 mV.

Figure 2 shows the voltammogram calculated for $E_2^0 - E_1^0 = -0.050$ V. All other conditions are as in Figure 1(b). It can be noted that the prepeak and the postpeak are more pronounced than in Figure 1(b). The difference in their net peak potentials is 195 mV, and if $E_2^0 - E_1^0 = -0.100$ V, this difference increases to 250 mV. Oppositely, if $E_2^0 - E_1^0 \geq 0.050$ V, the prepeak and postpeak disappear under the conditions of Figure 1(b), which means that they are less separated than for $E_1^0 = E_2^0$. These results suggest that the difference $E_{p,1} - E_{p,2}$ is an indicator of thermodynamic property of the reaction mechanism (1)–(3).

The influence of adsorption constant is shown in Figure 3, which is to be compared with Figure 1(b). If neither β nor the reactant concentration are changed, the parameter

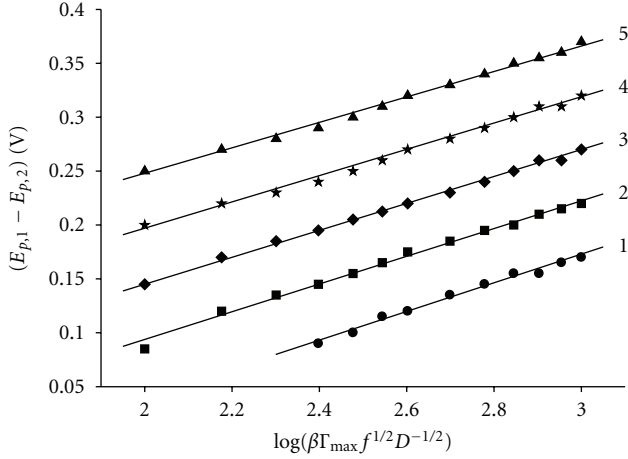


FIGURE 4: Dependence of the difference in net peak potentials of the prepeak and postpeak on the logarithm of dimensionless adsorption parameter (the symbols). $\beta c_{\text{Ox}}^* = 10$ and $(E_2^0 - E_1^0)/V = 0.100$ (1), 0.050 (2), 0.000 (3), -0.050 (4), and -0.100 (5). The lines are linear approximations. All other parameters are as in Figure 1.

$\beta\Gamma_{\text{max}}\sqrt{f/D}$ can be augmented by increasing either Γ_{max} or frequency. In the first case the surface coverage is diminished, which explains why in Figure 3 the main peak is much smaller than in Figure 1(b). Also, the difference $E_{p,1} - E_{p,2}$ increases to 165 mV, compared to 145 mV in Figure 1(a). The same can be achieved by the variation of frequency, which can be changed between 10 Hz and 2000 Hz.

The relationships between the difference $E_{p,1} - E_{p,2}$ and the logarithm of parameter $\beta\Gamma_{\text{max}}\sqrt{f/D}$ are shown in Figure 4 for various standard potentials and for the unsaturated electrode surface ($\beta c_{\text{Ox}}^* = 10$). All these functions are straight lines with the slopes and intercepts that depend on the difference in standard potentials. Figure 5 shows that these dependences are also linear: slope = $0.075 \times (E_2^0 - E_1^0) + 0.1255$ V and intercept = $-1.19 \times (E_2^0 - E_1^0) - 0.107$ V. So, the relationships in Figure 4 can be described by the following formulae:

$$\begin{aligned} E_{p,1} - E_{p,2} &= [0.075 \times (E_2^0 - E_1^0) + 0.1255] \\ &\times \log(\beta\Gamma_{\text{max}}\sqrt{f/D}) \\ &- 1.19 \times (E_2^0 - E_1^0) - 0.107 \text{ V.} \end{aligned} \quad (16)$$

However, as the difference $E_2^0 - E_1^0$ is generally unknown, the average values of the slope and the intercept can be used for the estimation of adsorption constant:

$$\begin{aligned} E_{p,1} - E_{p,2} &= (0.1255 \pm 0.0075) \\ &\times \left[\log\left(\frac{\beta\Gamma_{\text{max}}}{\sqrt{D}}\right) + \frac{1}{2} \log f \right] \\ &- 0.107 \pm 0.119 \text{ V.} \end{aligned} \quad (17)$$

For instance, if the difference $E_{p,1} - E_{p,2} = 0.220$ V is measured at $f = 144$ Hz, the parameter $\beta\Gamma_{\text{max}}/\sqrt{D}$ can be cal-

culated using (17): $\log(\beta\Gamma_{\text{max}}/\sqrt{D}) = 1.5 \pm 1.0$. The precision of this estimation is obviously very modest.

Finally, our calculations show that the maximal currents of prepeak and postpeak depend linearly on the square-root of frequency and on $f^{0.583}$, respectively.

4. Conclusion

These results show that the adsorption of thermodynamically unstable intermediate can cause the splitting of square-wave voltammogram of two-electron electrode reaction. If $\beta c_{\text{Ox}}^* < 25$, the difference between net peak potentials of the prepeak and postpeak is independent of reactant concentration and depends on the difference in standard potentials of two electron transfers and on the logarithm of the dimensionless adsorption parameter $\beta\Gamma_{\text{max}}\sqrt{f/D}$ as defined by (16). This equation applies for reversible charge transfers, equal diffusion coefficients, $E_{\text{SW}} = 50$ mV, $dE = -5$ mV, $-0.1 \text{ V} \leq E_2^0 - E_1^0 < 0.1$ V, and $\beta\Gamma_{\text{max}}\sqrt{(f/D)} \geq 100$. If $E_2^0 - E_1^0 = 0.1$ V, the splitting occurs for $\beta\Gamma_{\text{max}}\sqrt{(f/D)} > 200$.

Appendix

By the substitution $\psi = c_{\text{Ox}} + c_{\text{Int}} + c_{\text{Red}}$, the system of differential equations (4) is reduced to the single differential equation

$$\frac{\partial \psi}{\partial t} = D \frac{\partial^2 \psi}{\partial x^2} \quad (A.1)$$

with the following initial and boundary conditions:

$$t = 0, x \geq 0 : \psi = c_{\text{Ox}}^*, \Gamma_{\text{Int}} = 0, \quad (A.2)$$

$$t > 0, x \rightarrow \infty : \psi \rightarrow c_{\text{Ox}}^*, \quad (A.3)$$

$$x = 0 : D \left(\frac{\partial \psi}{\partial x} \right)_{x=0} = \frac{d\Gamma_{\text{Int}}}{dt}, \quad (A.4)$$

$$\psi_{x=0} = (c_{\text{Int}})_{x=0} [\exp(\varphi_1) + 1 + \exp(-\varphi_2)], \quad (A.5)$$

$$\frac{\beta\psi_{x=0}}{1 + \exp(\varphi_1) + \exp(-\varphi_2)} = \frac{\Gamma_{\text{Int}}}{\Gamma_{\text{max}} - \Gamma_{\text{Int}}}. \quad (A.6)$$

Using Laplace transforms, (A.1) is transformed into integral equation

$$\psi_{x=0} = c_{\text{Ox}}^* - (D\pi)^{-1/2} \frac{\partial}{\partial t} \int_0^t \frac{\Gamma_{\text{Int}} d\tau}{\sqrt{t-\tau}}. \quad (A.7)$$

The time t is divided into m increments ($t = md$), and it is assumed that within each increment the function Γ_{Int} can be replaced by the average value $\Gamma_{\text{Int},j}$ [34]. Furthermore, it is defined that each square-wave half-period is divided into 25

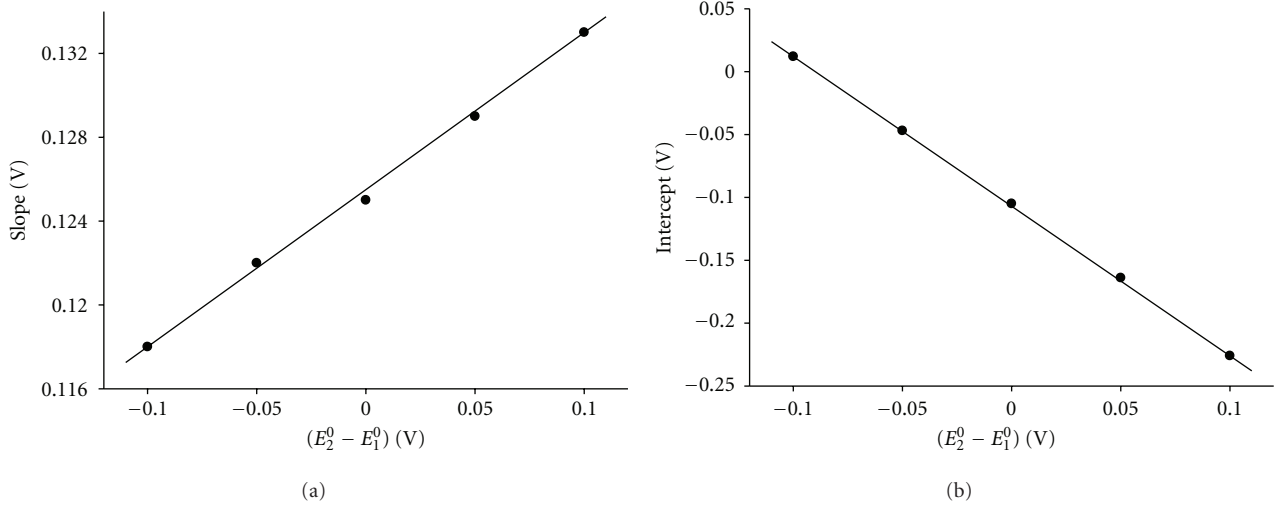


FIGURE 5: Dependence of the slopes (a) and the intercepts (b) of straight lines shown in Figure 4 on the difference in standard potentials of the second and the first electron transfers (the symbols). The lines are linear approximations.

time increments: $d = (50f)^{-1}$. In this way the solution of (A.7) is obtained:

$$\psi_{x=0,m} = c_{\text{Ox}}^* - \frac{10\sqrt{2f}}{\sqrt{D\pi}} \left(\Gamma_{\text{Int},m} + \sum_{j=1}^{m-1} \Gamma_{\text{Int},j} (S_{m-j+1} - S_{m-j}) \right), \quad (\text{A.8})$$

where $m = 1, 2, 3, \dots$ and $S_k = \sqrt{k} - \sqrt{k-1}$. Equation (A.8) is introduced into (A.6) to obtain the solution for the surface coverage $\theta_{\text{Int},m} = \Gamma_{\text{Int},m}/\Gamma_{\text{max}}$:

$$\theta_{\text{Int},m} = -\frac{z_{1,m}}{2} - \frac{\sqrt{z_{1,m}^2 - 4z_{2,m}}}{2}, \quad (\text{A.9})$$

$$z_{1,m} = -1 - \frac{\beta c_{\text{Ox}}^* + [1 + \exp(\varphi_{1,m}) + \exp(-\varphi_{2,m})]}{10\sqrt{2}/\sqrt{\pi} \cdot (\beta\sqrt{f}/\sqrt{D})\Gamma_{\text{max}}} \quad (\text{A.10})$$

$$+ \sum_{j=1}^{m-1} \theta_j (S_{m-j+1} - S_{m-j}),$$

$$z_{2,m} = \frac{\beta c_{\text{Ox}}^*}{10\sqrt{2}/\sqrt{\pi} \cdot (\beta\sqrt{f}/\sqrt{D})\Gamma_{\text{max}}} - \sum_{j=1}^{m-1} \theta_j (S_{m-j+1} - S_{m-j}), \quad (\text{A.11})$$

$$\varphi_{l,m} = \frac{F}{RT} (E_m - E_l^0), \quad (\text{A.12})$$

(where $l = 1$ and 2). The surface concentrations of electroactive species are defined by (11), (12), (15), and (A.9):

$$(c_{\text{Int}})_{x=0,m} = \frac{1}{\beta} \cdot \frac{\theta_{\text{Int},m}}{1 - \theta_{\text{Int},m}}, \quad (\text{A.13})$$

$$(c_{\text{Ox}})_{x=0,m} = \frac{\exp(\varphi_{1,m})}{\beta} \cdot \frac{\theta_{\text{Int},m}}{1 - \theta_{\text{Int},m}}, \quad (\text{A.14})$$

$$(c_{\text{Red}})_{x=0,m} = \frac{\exp(-\varphi_{2,m})}{\beta} \cdot \frac{\theta_{\text{Int},m}}{1 - \theta_{\text{Int},m}}. \quad (\text{A.15})$$

The currents I_1 and I_2 are determined by solving (4) for $Y = \text{Ox}^{(n+2)+}$ and $Y = \text{Red}^{n+}$, respectively:

$$\frac{I_1}{FS\sqrt{D}} = -\frac{c_{\text{Ox}}^*}{\sqrt{\pi t}} + \frac{\partial}{\partial t} \int_0^t \frac{(c_{\text{Ox}})_{x=0}}{\sqrt{\pi(t-\tau)}} d\tau, \quad (\text{A.16})$$

$$\frac{I_2}{FS\sqrt{D}} = -\frac{\partial}{\partial t} \int_0^t \frac{(c_{\text{Red}})_{x=0}}{\sqrt{\pi(t-\tau)}} d\tau. \quad (\text{A.17})$$

Using (A.14) and (A.15) and the numerical method described previously, the solution for the dimensionless current $\Phi_m = (I_{1,m} + I_{2,m})(FS c_{\text{Ox}}^*)^{-1} (Df)^{-1/2}$ is obtained:

$$\Phi_{1,m} = -\frac{5\sqrt{2}}{\sqrt{m\pi}} + \frac{10\sqrt{2}}{\sqrt{\pi}} \left[\frac{(c_{\text{Ox}})_{x=0,m}}{c_{\text{Ox}}^*} + \sum_{j=1}^{m-1} \frac{(c_{\text{Ox}})_{x=0,j}}{c_{\text{Ox}}^*} (S_{m-j+1} - S_{m-j}) \right], \quad (\text{A.18})$$

$$\Phi_{2,m} = -\frac{10\sqrt{2}}{\sqrt{\pi}} \left[\frac{(c_{\text{Red}})_{x=0,m}}{c_{\text{Ox}}^*} + \sum_{j=1}^{m-1} \frac{(c_{\text{Red}})_{x=0,j}}{c_{\text{Ox}}^*} (S_{m-j+1} - S_{m-j}) \right]. \quad (\text{A.19})$$

The forward and backward components of square-wave voltammogram and their difference ($-\Delta\Phi = -(\Phi_f - \Phi_b)$) are calculated.

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