MATHCAD FILE FOR SIMULATION OF SIMPLE DIFFUSIONAL $C_{rev}E$ MECHANISM IN SQUARE WAVE VOLTAMMETRY

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Abstract

Reaction of disproportionation or degradation of given compound „A" leads to generation of reactive species "Ox" that can undergo electron transfer at the working electrode surface. The mechnism known as Diffusional CE or simply CE Mechanism is considered under conditions of square-wave voltammetry. The reaction scheme of this mechanism met in many physiological systems is as follow

A --→ Ox(water) + ne- = Red(water)

SW voltammetric patterns are function of the electron transfer parameter related to the electrode reaction, but they also depend on the kinetic and thermodynamic parameters related to the chemical step. The entire interplay of all parameters leads to very specific voltammograms, whose feature can reveal important kinetic and thermodynamic parameters relevant to the physiological systems of interest. Electrode transformation of many transient metal ion, drugs, enzymes, neutrotransmiters, vitamins and metal-Ligand complexes follow this pathway.

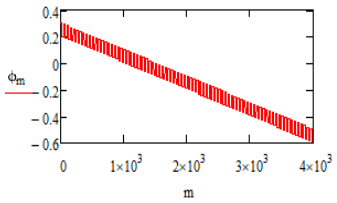
THEORETICAL MODEL IN SQUARE-WAVE VOLTAMMETRY
of a DIFFUSIONAL CE (Chemical-Electrochemical) Mechanism

$dE := 0.01$ $Esw := 0.05$ $\Delta E := 0.8$ $m := 1..\frac{\Delta E}{dE} \cdot 50$ $Es := 0.25$ $i := 1..1$

$f := 20$

$$relativepot_m := \left(ceil\left(\frac{m}{25}\cdot\frac{1}{2}\right)\cdot dE + if\left(\frac{ceil\left(\frac{m}{25}\right)}{2} = ceil\left(\frac{m}{25}\cdot\frac{1}{2}\right), 1, -1\right)\right)\cdot Esw + \phi_m := Es + Esw - relativepot_m$$

$ks := 0.200$ $D := 5\cdot 10^{-6}$ $kf := 0.000001$



$\lambda := \frac{ks}{\sqrt{D\cdot f}}$ .1 $\alpha := 0.5$ $kb := 0.0001$

$\lambda = 20$ $K := \frac{kf}{kb}$ Equilibrium constant

$\log(\lambda) = 1.301$ $K = 0.01$

$F := 96500$ $n := 1$ $R := 8.314$ $T := 298.15$ $\Phi_m := n\cdot\frac{F}{R\cdot T}\cdot\phi_m$ $\varepsilon := kf + kb$ kineticki parametar $k := 1..\frac{\Delta E}{dE}\cdot 50$

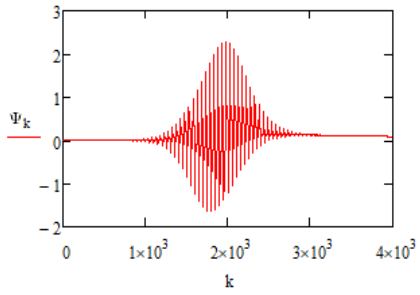
$z := \frac{\varepsilon}{f}$

$Sl_k := \sqrt{k} - \sqrt{k-1}$ $Sl_3 = 0.318$

$$S_k := erfc\left[\left(z\cdot\frac{k}{50}\right)^{0.5}\right] - erfc\left[\left[z\cdot\frac{(k-1)}{50}\right]^{0.5}\right]$$

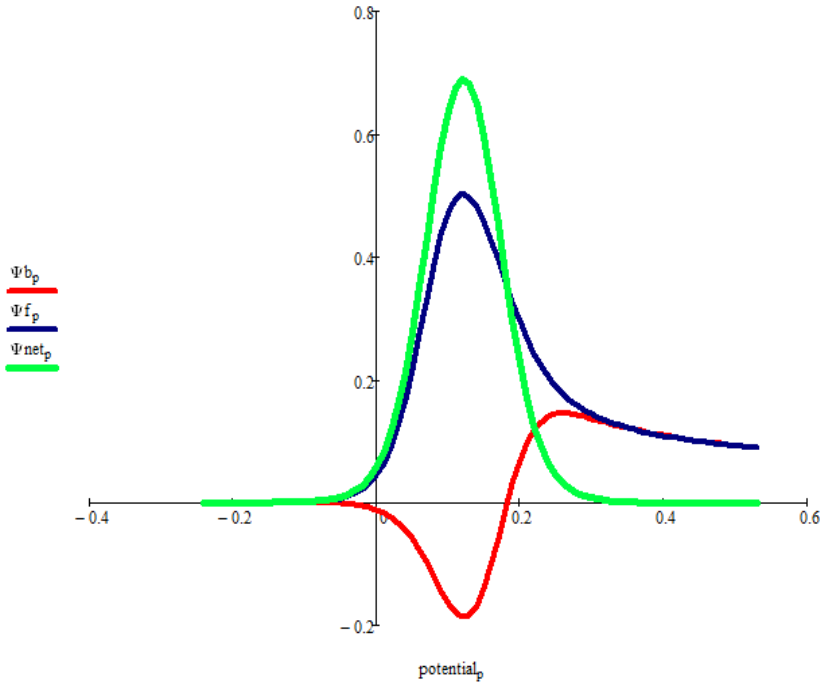
$$\Psi_1 := \lambda\cdot e^{-\alpha\cdot\Phi_1}\cdot\frac{K}{1+K}\cdot\left[1+\lambda\cdot e^{-\alpha\cdot\Phi_1}\cdot\frac{K}{(1+K)\cdot 50} - \frac{\lambda\cdot e^{-\alpha\cdot\Phi_1}\cdot S_1}{(K+1)\cdot z}\cdot(1) + \frac{\lambda\cdot e^{(1-\alpha)\cdot\Phi_1}}{50}\right]^{-1}$$

$$\Psi_k := \frac{\frac{\lambda\cdot e^{-\alpha\cdot\Phi_k}\cdot K}{1+K}\cdot\left[1-\frac{2}{\sqrt{50\cdot\pi}}\cdot\sum_{j=1}^{k-1}\left(\Psi_j\cdot Sl_{k-j+1}\right)\right] - \gamma\cdot\left(\frac{1}{1+K}\right)\cdot(-1)\cdot e^{-\alpha\cdot\Phi_k}\cdot\sum_{j=1}^{k-1}\left(\Psi_j\cdot S_{k-j+1}\right) - \lambda\cdot\frac{2}{\sqrt{50\cdot\pi}}\cdot e^{\Phi_k\cdot(1-\alpha)}\cdot\sum_{j=1}^{k-1}\left(\Psi_j\cdot Sl_{k-j+1}\right)}{\left(\frac{\lambda\cdot e^{-\alpha\cdot\Phi_k}\cdot K}{1+K}\cdot\frac{2}{\sqrt{50\cdot\pi}}\right) + 1 + \gamma\cdot(-1)\cdot\left(\frac{1}{1+K}\right)\cdot S_1\cdot e^{-\alpha\cdot\Phi_k} + \lambda\cdot\frac{2}{\sqrt{50\cdot\pi}}\cdot e^{\Phi_k\cdot(1-\alpha)}}$$



$p := 1..\frac{\Delta E}{dE} - 2$ $\Psi f_p := (\Psi)_{(p+1)\cdot 50}$ $\Psi b_p := (\Psi)_{50\cdot p+25}$ $\Psi net_p := \Psi f_p - \Psi b_p$

$potential_p := -Es + (p)\cdot dE$



kf and kb are rate constants of forward and backward chemical steps
K is the equilibrium constant of chemical step
D is the diffusion coefficient
ks is standard rate constant of electrode reaction
λ is dimensionless kinetic parameter related to electron transfer step
z is dimensionless chemical kinetic parameter
S is integration factor
F is Faraday constant
R is universal gas constant
Φ is dimnesionless potential
dE is potential step
Es is starting potential
f is SW frequency
Ψ is dimensionless current
α is electron transfer coefficient
Esw is the square-wave amplitude

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