

MATHCAD FILE FOR SIMULATION OF DIFFUSIONAL ECreV (ECreV=Electrochemical Mechanism Coupled with FOLLOW UP Chemical Reaction) in CYCLIC VOLTAMMETRY

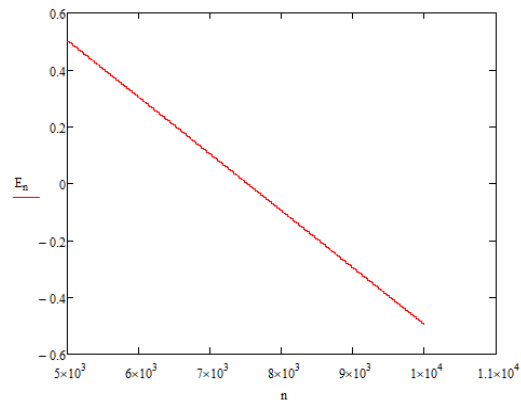
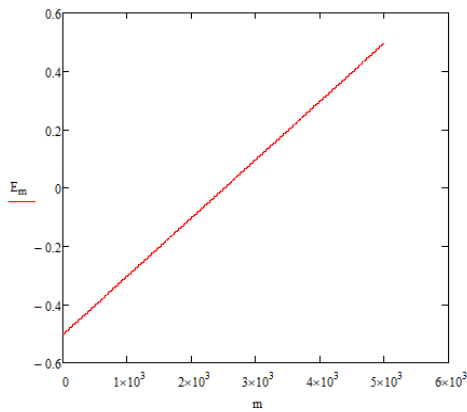
Rubin Gulaboski

$$\begin{aligned}
 & \text{tac} := 0.01 \\
 & E_s := -0.5 \quad E_f := 0.5 \quad \Delta E := E_f - E_s \quad dE := 0.005 \quad \tau := 0.05 \quad d := \frac{\tau}{25} \\
 & m := \frac{\text{tac}}{d} + 1 \cdot \frac{\Delta E}{dE} \cdot 25 + \frac{\text{tac}}{d} \quad n := \frac{\Delta E}{dE} \cdot 25 + \frac{\text{tac}}{d} + 1 \cdot \left(\frac{\Delta E}{dE} \cdot 25 \cdot 2 + \frac{\text{tac}}{d} \right) \\
 & E_m := E_s + \left[\text{ceil} \left(\frac{m - \frac{\text{tac}}{d}}{25} \right) \cdot dE - dE \right] \\
 & E_n := E_f - \left[\text{ceil} \left(\frac{n - \left(\frac{\Delta E}{dE} \cdot 25 + \frac{\text{tac}}{d} \right)}{25} \right) \cdot dE - dE \right]
 \end{aligned}$$

$$\begin{aligned}
 \tilde{\omega} &:= 1 \cdot \frac{\text{tac}}{d} \\
 \frac{\Delta E}{dE} &= 200
 \end{aligned}$$

ECreV Diffusional Mechanism
in Cyclic Voltammetry

Λ is dimensionless kinetic parameter related to electrode reaction
 γ is dimensionless catalytic parameter related to preceding chemical reaction
 α is electron transfer coefficient
 M is equilibrium constant of preceding chemical reaction
 k_f and k_b are forward and backward rate constants of preceding chemical reaction
 E_s is starting potential
 E_f is final potential
 dE is potential step
 Ψ is symbol for dimensionless current
 E_m is cathodic potential ramp in cyclic voltammetry
 E_n is anodic potential ramp
 S_k is integration factor
 τ is duration of potential steps
 D is diffusion coefficient of Ox and Red



$$\begin{aligned}
 \Lambda &:= 0.28 \quad \text{cox} := 0.0000008
 \end{aligned}$$

$$\begin{aligned}
 k_s &:= 0.05 \quad D := 3 \cdot 10^{-6} \quad k_f := 1000 \quad 0.05 \quad 0.005 \\
 K_{\tilde{\omega}} &:= \frac{k_s \sqrt{\tau}}{\sqrt{D}} \quad \alpha := 0.5 \quad k_b := 1000 \quad 0.075 \quad 0.0075 \\
 M &:= \frac{k_f}{k_b} \quad \text{Konstanta na ramnoteza} \quad 0.35 \quad 0.05
 \end{aligned}$$

$$\log(K) = 0.81 \quad K \quad M_{\tilde{\omega}} := 0.1500000$$

$$E_s := 96500 \quad e_l := 3 \quad R_{\tilde{\omega}} := 8.314 \quad T_{\tilde{\omega}} := 298.15$$

$$\Phi_{em} := e_l \cdot \frac{F}{R \cdot T} \cdot (E_m) \quad b_n := e_l \cdot \frac{F}{R \cdot T} \cdot (E_n)$$

$$\tilde{\omega} := k_f + k_b \quad \text{kineticki parametar} \quad k := 1 \cdot 2 \left(\frac{\Delta E}{dE} \cdot 25 + \frac{\text{tac}}{d} \right)$$

$$r := e \cdot \tau$$

$$S1_k := \sqrt{\frac{k}{50}} - \sqrt{\frac{k-1}{50}} \quad S1_3 := \bullet$$

$$\begin{aligned}
 z &:= (k_f + k_b)^{0.5} \cdot \tau^{0.5} \\
 z &= 10
 \end{aligned}$$

$$\Phi_{ac} := e_l \cdot \frac{F}{R \cdot T} \cdot E_s$$

$$\gamma := \frac{k_s}{e^2 \cdot D^2}$$

$$h := \sqrt{E} \cdot \sqrt{\tau}$$

$$h = 10$$

$$S_k := \left(1 - \text{erfc} \left(\sqrt{\frac{E \cdot \tau}{50}} \cdot k \right) \right) - \left[1 - \text{erfc} \left(\sqrt{\frac{E \cdot \tau}{50}} \cdot (k-1) \right) \right]$$

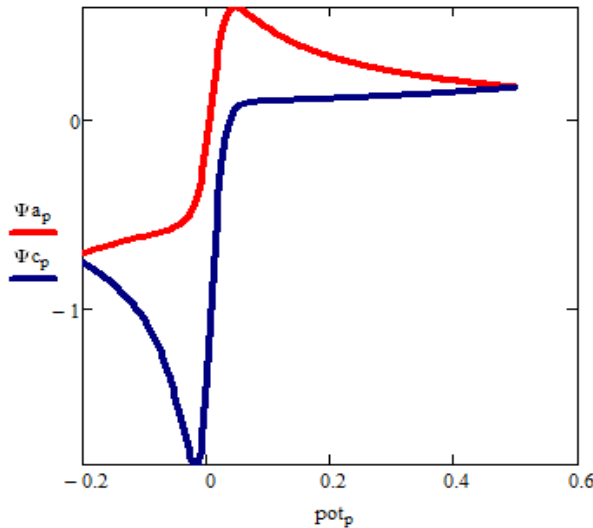
$$\Psi_1 := \frac{K \cdot e^{-\alpha \cdot \Phi_1}}{\left[1 + \frac{2 \cdot K \cdot e^{(1-\alpha) \cdot \Phi_1}}{\sqrt{\pi \cdot 50}} + \frac{2 \cdot K \cdot e^{(1-\alpha) \cdot \Phi_1}}{\sqrt{\pi \cdot 50}} \cdot \frac{M}{1+M} \right] + \frac{\gamma}{1+M} \cdot e^{(1-\alpha) \cdot \Phi_1} \cdot S_1}$$

$$\Psi_s := \frac{K \cdot e^{-\alpha \cdot \Phi_{ac}} - \frac{2 \cdot K \cdot e^{-\alpha \cdot \Phi_{ac}}}{\sqrt{\pi \cdot 50}} \cdot \sum_{j=1}^{s-1} (\Psi_j \cdot S1_{s-j+1}) - \frac{2 \cdot K \cdot e^{(1-\alpha) \cdot \Phi_{ac}}}{\sqrt{\pi \cdot 50}} \cdot \frac{M}{1+M} \cdot \sum_{j=1}^{s-1} (\Psi_j \cdot S1_{s-j+1}) - \frac{\gamma}{1+M} \cdot e^{(1-\alpha) \cdot \Phi_{ac}} \cdot \sum_{j=1}^{s-1} (\Psi_j \cdot S_{s-j+1})}{1 + \frac{2 \cdot K \cdot e^{-\alpha \cdot \Phi_{ac}}}{\sqrt{\pi \cdot 50}} + \frac{2 \cdot K \cdot e^{(1-\alpha) \cdot \Phi_{ac}}}{\sqrt{\pi \cdot 50}} \cdot \frac{M}{1+M} + \frac{\gamma}{1+M} \cdot e^{(1-\alpha) \cdot \Phi_{ac}} \cdot S_1}$$

$$\Psi_m := \frac{K \cdot e^{-\alpha \cdot \Phi_m} - \frac{2 \cdot K \cdot e^{-\alpha \cdot \Phi_m}}{\sqrt{\pi \cdot 50}} \cdot \sum_{j=1}^{m-1} (\Psi_j \cdot S1_{m-j+1}) - \frac{2 \cdot K \cdot e^{(1-\alpha) \cdot \Phi_m}}{\sqrt{\pi \cdot 50}} \cdot \frac{M}{1+M} \cdot \sum_{j=1}^{m-1} (\Psi_j \cdot S1_{m-j+1}) - \frac{\gamma}{1+M} \cdot e^{(1-\alpha) \cdot \Phi_m} \cdot \sum_{j=1}^{m-1} (\Psi_j \cdot S_{m-j+1})}{1 + \frac{2 \cdot K \cdot e^{-\alpha \cdot \Phi_m}}{\sqrt{\pi \cdot 50}} + \frac{2 \cdot K \cdot e^{(1-\alpha) \cdot \Phi_m}}{\sqrt{\pi \cdot 50}} \cdot \frac{M}{1+M} + \frac{\gamma}{1+M} \cdot e^{(1-\alpha) \cdot \Phi_m} \cdot S_1}$$

$$\Psi_n := \frac{K \cdot e^{-\alpha \cdot b_n} - \frac{2 \cdot K \cdot e^{-\alpha \cdot b_n}}{\sqrt{\pi \cdot 50}} \cdot \sum_{j=1}^{n-1} (\Psi_j \cdot S1_{n-j+1}) - \frac{2 \cdot K \cdot e^{(1-\alpha) \cdot b_n}}{\sqrt{\pi \cdot 50}} \cdot \frac{M}{1+M} \cdot \sum_{j=1}^{n-1} (\Psi_j \cdot S1_{n-j+1}) - \frac{\gamma}{1+M} \cdot e^{(1-\alpha) \cdot b_n} \cdot \sum_{j=1}^{n-1} (\Psi_j \cdot S_{n-j+1})}{1 + \frac{2 \cdot K \cdot e^{-\alpha \cdot b_n}}{\sqrt{\pi \cdot 50}} + \frac{2 \cdot K \cdot e^{(1-\alpha) \cdot b_n}}{\sqrt{\pi \cdot 50}} \cdot \frac{M}{1+M} + \frac{\gamma}{1+M} \cdot e^{(1-\alpha) \cdot b_n} \cdot S_1}$$

$$p := 60 \cdot \frac{\Delta E}{dE} \quad \Psi_{a_p} := (-\Psi) \left(\frac{\tau}{d \cdot 25} + p \right) \cdot 25 \quad \Psi_{c_p} := (-\Psi) \left[\left[\frac{\Delta E}{dE} \cdot 2 + \left(\frac{\tau}{25 \cdot d} \right) \right] - p \right] \cdot 25 \quad \text{pot}_p := Es + p \cdot dE$$



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