MATHCAD FILE FOR SIMULATION OF DIFFUSIONAL CrevE (CrevE=Electrochemical Mechanism Coupled with Preceding Chemical Reaction) in CYCLIC VOLTAMMETRY

Rubin Gulaboski

$tac := 0.01$

$Es := -0.5 \quad Ef := 0.5 \quad \Delta E := Ef - Es \quad dE := 0.01 \quad \tau := 0.05 \quad d := \frac{\tau}{25}$

$s := 1 .. \frac{tac}{d}$

$m := \frac{tac}{d} + 1 .. \frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d}$

$n := \frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} + 1 .. \left(\frac{\Delta E}{dE} \cdot 25 \cdot 2 + \frac{tac}{d}\right)$

$\frac{\Delta E}{dE} = 100$

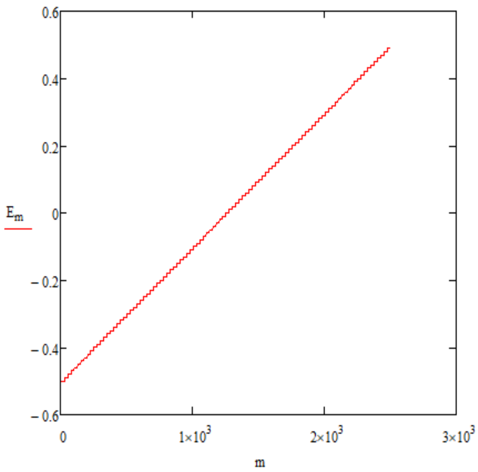
$E_m := Es + \left(\mathrm{ceil}\left(\frac{m - \frac{tac}{d}}{25}\right) \cdot dE - dE\right)$

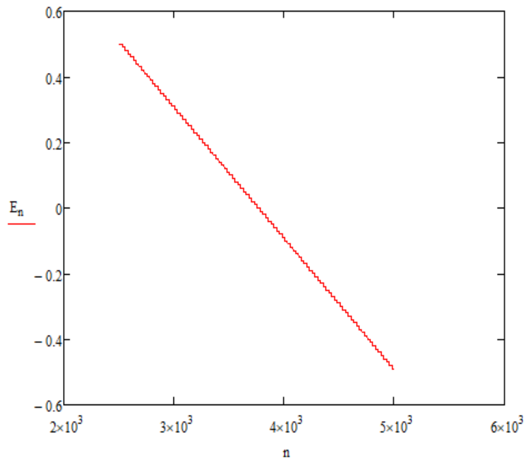
$E_n := Ef - \left[\mathrm{ceil}\left[\frac{n - \left(\frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d}\right)}{25}\right] \cdot dE - dE\right]$

$\frac{dE}{\tau} = 0.2 \qquad \frac{dE}{\tau} = 0.2$

CrevE Diffusional Mechanism
in CYCLIC VOLTAMMETRY

λ is dimensionless kinetic parameter related to electrode reaction
r is dimensionless catalytic parameter related to preceding chemical reaction
α is electron transfer coefficient
K is equilibrium constant of preceding chemical reaction
kf and kb are forward and backward rate constants of preceding chemical reaction
Es is starting potential
Ef is final potential
dE is potential step
Ψ is symbol for dimensionless current
Em is cathodic potential ramp in cyclic voltammetry
En is anodic potential ramp
Sk is integration factor
τ is duration of potential steps
D is diffusion coefficient of Ox and Red





$A := 0.28 \qquad cox := 0.0000008$

$ks := 0.0506 \qquad D := 5 \cdot 10^{-6}$

$\lambda := \frac{ks \cdot \sqrt{\tau}}{\sqrt{D}} \qquad \alpha := 0.5$

$kf := 0.1$
$kb := 0.00010000$

0.05	0.005
0.075	0.0075
0.35	0.05

$K := \frac{kf}{kb}$ Konstanta na ramnoteza

$\lambda = 5.06$

$\log(K) = 3 \qquad K$

$K := 0.1500$

$\log(\lambda) = 0.704$

$F := 96500 \quad el := 1 \quad R := 8.314 \quad T := 298.15$

$\varepsilon := kf + kb$ kineticki parametar

$k := 1 .. 2 \cdot \left(\frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d}\right)$

$\Phi_m := el \cdot \frac{F}{R \cdot T} \cdot (E_m) \quad \Phi_n := el \cdot \frac{F}{R \cdot T} \cdot (E_n)$

$\Phi ac := el \cdot \frac{F}{R \cdot T} \cdot Es$

$r := \varepsilon \cdot \tau$

$z := (kf + kb)^{0.5} \cdot \tau^{0.5}$

$z = 0.071$

$$\gamma := \frac{ks}{\varepsilon^{\frac{1}{2}} \cdot D^{\frac{1}{2}}}$$

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

$$h = 0.071$$

$$h = 0.071$$

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

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

$$\Psi_s := \frac{\frac{\lambda \cdot e^{-\alpha \cdot \Phi ac} \cdot K}{1+K} \cdot \left[1 - \frac{2}{\sqrt{50 \cdot \pi}} \cdot \sum_{j=1}^{s-1} \left(\Psi_j \cdot S1_{s-j+1}\right)\right] - \gamma \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{-\alpha \cdot \Phi ac} \cdot \sum_{j=1}^{s-1} \left(\Psi_j \cdot S_{s-j+1}\right) - \lambda \cdot \frac{2}{\sqrt{50 \cdot \pi}} \cdot e^{\Phi ac \cdot (1-\alpha)} \cdot \sum_{j=1}^{s-1} \left(\Psi_j \cdot S1_{s-j+1}\right)}{\left(\frac{\lambda \cdot e^{-\alpha \cdot \Phi ac} \cdot K}{1+K} \cdot \frac{2}{\sqrt{50 \cdot \pi}}\right) + 1 + \gamma \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{-\alpha \cdot \Phi ac} + \lambda \cdot \frac{2}{\sqrt{50 \cdot \pi}} \cdot e^{\Phi ac \cdot (1-\alpha)}}$$

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

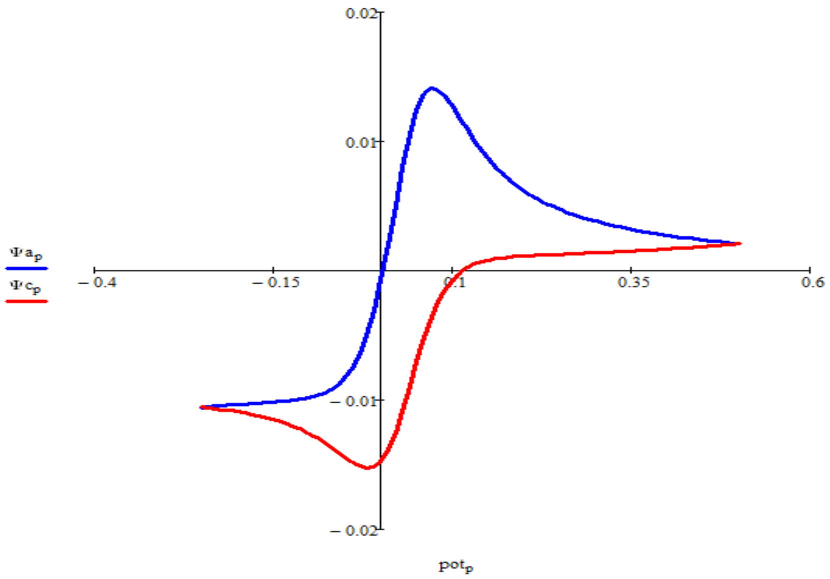
$$\Psi_n := \frac{\frac{\lambda \cdot e^{-\alpha \cdot \Phi_n} \cdot K}{1+K} \cdot \left[1 - \frac{2}{\sqrt{50 \cdot \pi}} \cdot \sum_{j=1}^{n-1} \left(\Psi_j \cdot S1_{n-j+1}\right)\right] - \gamma \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{-\alpha \cdot \Phi_n} \cdot \sum_{j=1}^{n-1} \left(\Psi_j \cdot S_{n-j+1}\right) - \lambda \cdot \frac{2}{\sqrt{50 \cdot \pi}} \cdot e^{\Phi_n \cdot (1-\alpha)} \cdot \sum_{j=1}^{n-1} \left(\Psi_j \cdot S1_{n-j+1}\right)}{\left(\frac{\lambda \cdot e^{-\alpha \cdot \Phi_n} \cdot K}{1+K} \cdot \frac{2}{\sqrt{50 \cdot \pi}}\right) + 1 + \gamma \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{-\alpha \cdot \Phi_n} + \lambda \cdot \frac{2}{\sqrt{50 \cdot \pi}} \cdot e^{\Phi_n \cdot (1-\alpha)}}$$

$$S_1 = -0.042$$

$$S1_1 = 1$$

$$\Psi_1 = 0.096$$

$$p := 25 .. \frac{\Delta E}{dE} \qquad \Psi a_p := (-\Psi)_{\left(\frac{\tau}{d \cdot 25} + p\right) \cdot 25} \qquad \Psi c_p := (-\Psi)_{\left[\left[\frac{\Delta E}{dE} \cdot 2 + \left(\frac{\tau}{25 \cdot d}\right)\right] - p\right] \cdot 25} \qquad pot_p := Es + p \cdot dE$$



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