MATHCAD FILE FOR SIMULATION OF DIFFUSIONAL CATALYTIC REGENERATIVE MECHANISM IN

CYCLIC VOLTAMMETRY (with IREEVERSIBLE CHEMICAL STEP)

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Cyclic staircase voltammetry

DIFFUSIONAL CATALYTIC MECHANISM in CYCLIC VOLTAMMETRY

$tac := 0.01$

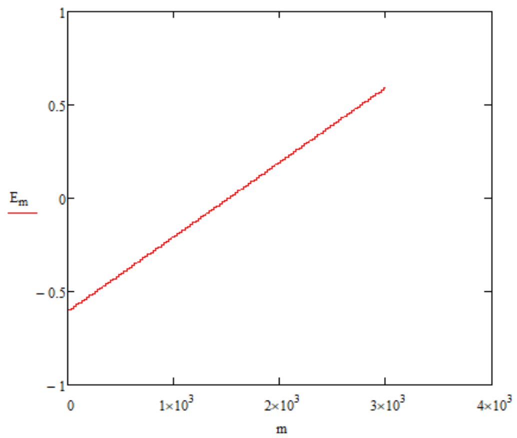
$Es := -0.6$ $\quad Ef := 0.6$ $\quad \Delta E := Ef - Es$ $\quad dE := 0.01$ $\quad \tau := 0.05$ $\quad d := \frac{\tau}{25}$ $\quad s := 1..\frac{tac}{d}$

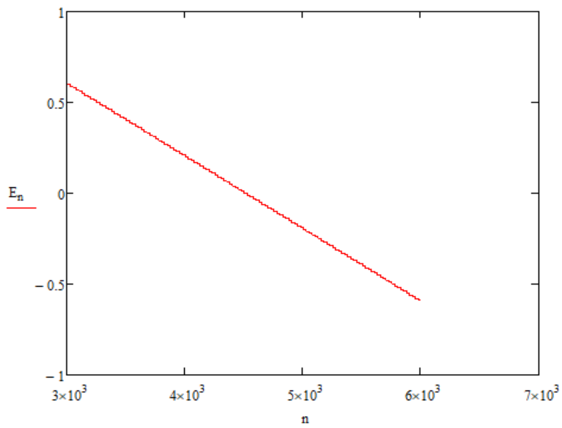
$m := \frac{tac}{d} + 1..\frac{\Delta E}{dE}\cdot 25 + \frac{tac}{d}$ $\quad n := \frac{\Delta E}{dE}\cdot 25 + \frac{tac}{d} + 1..\left(\frac{\Delta E}{dE}\cdot 25\cdot 2 + \frac{tac}{d}\right)$ $\quad \frac{\Delta E}{dE} = 120$

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

$E_n := Ef - \left[\mathrm{ceil}\left[\frac{n - \left(\frac{\Delta E}{dE}\cdot 25 + \frac{tac}{d}\right)}{25}\right]\cdot dE - dE\right]$ $\quad \frac{25}{0.04} = 625$ $\quad \frac{dE}{\tau} = 0.2$ $\quad \frac{dE}{\tau} = 0.2$

λ is dimensionless kinetic parameter related to electrode reaction
z is dimensionless catalytic parameter related to regenerative reactions
α is electron transfer coefficient
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





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

$ks := 0.0245$ $\quad D := 5\cdot 10^{-6}$

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

$\lambda = 2.45$ $\quad \alpha := 0.5$

$\log(\lambda) = 0.389$ $\quad kc := 10^{-1.15}$ $\quad$ kc-konstanta na kataliza

1

$z := (kc\cdot\tau)$

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

$z = 3.54\times 10^{-3}$ $\quad \frac{\lambda}{z} = 692.143$

$\Phi_m := el\cdot\frac{F}{R\cdot T}\cdot(E_m)$ $\quad b_n := el\cdot\frac{F}{R\cdot T}\cdot(E_n)$ $\quad \Phi ac := el\cdot\frac{F}{R\cdot T}\cdot Es$

$\log(z) = -2.451$ $\quad \frac{z}{\lambda} = 1.445\times 10^{-3}$

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

$S_k := \mathrm{erf}\left(\sqrt{z}\cdot\sqrt{k}\right) - \mathrm{erf}\left(\sqrt{z}\cdot\sqrt{k-1}\right)$

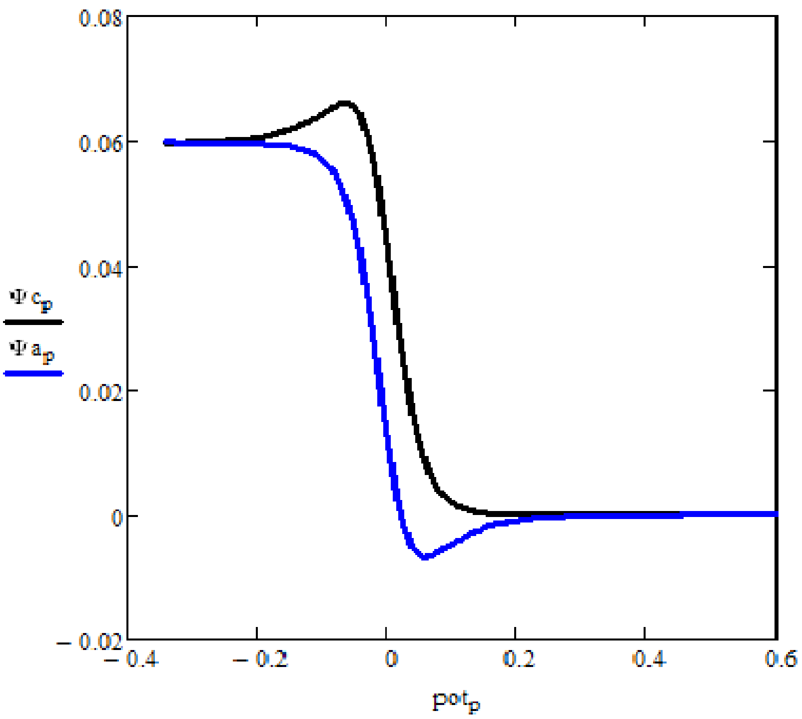
$$\Psi_1 := \lambda \cdot e^{-\alpha \cdot \Phi_1} \cdot \left[1 + \frac{\lambda \cdot S_1}{\sqrt{z}} + \frac{e^{(1-\alpha)\cdot \Phi_1} \cdot S_1}{\sqrt{z}} \right]^{-1}$$

$$\Psi_s := \frac{\lambda \cdot e^{-\alpha \cdot \Phi ac} - \frac{\lambda \cdot e^{-\alpha \cdot \Phi ac}}{\sqrt{z}} \cdot \sum_{j=1}^{s-1} \left(\Psi_j \cdot S_{s-j+1} \right) - e^{\Phi ac \cdot (1-\alpha)} \cdot \lambda \cdot \frac{1}{\sqrt{z}} \cdot \sum_{j=1}^{s-1} \left(\Psi_j \cdot S_{s-j+1} \right)}{1 + \frac{\lambda \cdot e^{-\alpha \cdot \Phi ac} \cdot S_1}{\sqrt{z}} + \frac{\lambda \cdot e^{(1-\alpha)\cdot \Phi ac} \cdot S_1}{\sqrt{z}}}$$

$$\Psi_m := \frac{\lambda \cdot e^{-\alpha \cdot \Phi_m} - \frac{\lambda \cdot e^{-\alpha \cdot \Phi_m}}{\sqrt{z}} \cdot \sum_{j=1}^{m-1} \left(\Psi_j \cdot S_{m-j+1} \right) - e^{\Phi_m \cdot (1-\alpha)} \cdot \lambda \cdot \frac{1}{\sqrt{z}} \cdot \sum_{j=1}^{m-1} \left(\Psi_j \cdot S_{m-j+1} \right)}{1 + \frac{\lambda \cdot e^{-\alpha \cdot \Phi_m} \cdot S_1}{\sqrt{z}} + \frac{\lambda \cdot e^{(1-\alpha)\cdot \Phi_m} \cdot S_1}{\sqrt{z}}}$$

$$\Psi_n := \frac{\lambda \cdot e^{-\alpha \cdot b_n} - \frac{\lambda \cdot e^{-\alpha \cdot b_n}}{\sqrt{z}} \cdot \sum_{j=1}^{n-1} \left(\Psi_j \cdot S_{n-j+1} \right) - e^{b_n \cdot (1-\alpha)} \cdot \lambda \cdot \frac{1}{\sqrt{z}} \cdot \sum_{j=1}^{n-1} \left(\Psi_j \cdot S_{n-j+1} \right)}{1 + \frac{\lambda \cdot e^{-\alpha \cdot b_n} \cdot S_1}{\sqrt{z}} + \frac{\lambda \cdot e^{(1-\alpha)\cdot b_n} \cdot S_1}{\sqrt{z}}}$$

$p := 26 .. \frac{\Delta E}{dE}$ $\quad \Psi a_p := (\Psi)_{\left(\frac{\tau}{d \cdot 25} + p\right) \cdot 25}$ $\quad \Psi c_p := (\Psi)_{\left[\left[\frac{\Delta E}{dE} \cdot 2 + \left(\frac{\tau}{25 \cdot d}\right)\right] - p\right] \cdot 25}$ $\quad pot_p := Es + p \cdot dE$



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