MATHCAD ПЛАТФОРМА ЗА СИМУЛАЦИЈА НА ЦИКЛИЧНИ ВОЛТАМОГРАМИ ЗА “CE” ЕЛЕКТРОХЕМИСКИ МЕХАНИЗАМ

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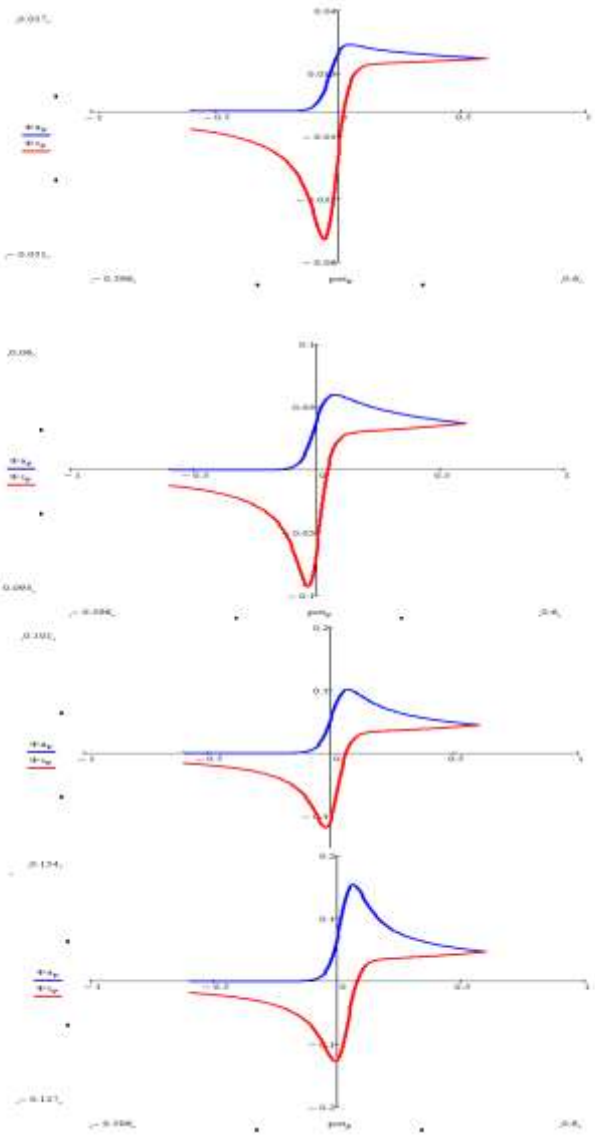
Abstract: Електрохемискиот механизам во кој електроактивниот реактант се добива преку хомогена хемиска реакција се нарекува “CE” (Chemical-Electrochemical) механизам. Во овој фајл, дадена е сиулациска платформа во MATHCAD што овозможува симулирање на циклични волтамограми за овој исклучително важен механизам. Симулираните одговори се функција од параметри поврзани со чекорот на електронски трансфер, но и со параметри поврзани со кинетиката и термодинамиката на претходната хемиска реакција. Фајлот е достапен **во слободна форма.**



DIFFUSIONAL CE MECHANISM
in CYCLIC VOLTAMMETRY 2024

$tac := 0.01$

$Es := -0.6 \quad Ef := 0.6 \quad \Delta E := Ef - Es \quad dE := 0.004 \quad \tau := 0.05 \quad d := \frac{\tau}{25}$

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

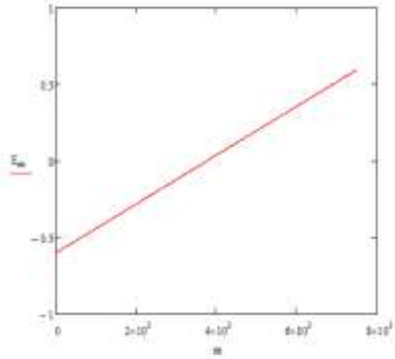
$m := \frac{tac}{d} + 1 .. \frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} \qquad n := \frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} + 1 .. \left(\frac{\Delta E}{dE} \cdot 25 \cdot 2 + \frac{tac}{d}\right)$

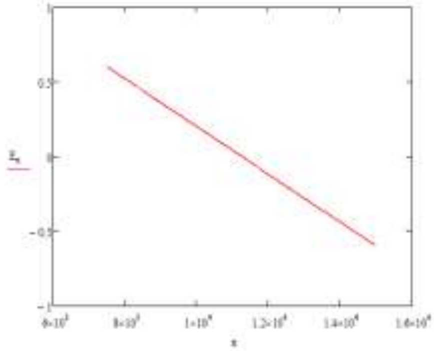
$\frac{\Delta E}{dE} = 300$

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

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

$\frac{dE}{\tau} = 0.08 \qquad \frac{dE}{\tau} = 0.08$





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

$ks := 0.506 \qquad D := 5 \cdot 10^{-6}$

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

$kf := .38626$
$kb := .38626300000000$

0.05	0.005
0.075	0.0075
0.15	0.05

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

$\lambda = 50.6$

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

$\log(\lambda) = 1.704$

$K := .505772000001500$

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

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

$\varepsilon := kf + kb$ kineticki parametar

$t := \varepsilon \cdot \tau$

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

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

$\varepsilon = 0.197$

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

$h = 0.197$

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

$h = 0.197$

$S1_k := \sqrt{k} - \sqrt{k-1}$

$S_k := \mathrm{erfc}\left[\left(\varepsilon \cdot \frac{k}{25}\right)^{0.5}\right] - \mathrm{erfc}\left[\left[\varepsilon \cdot \frac{(k-1)}{25}\right]^{0.5}\right]$

$$\Psi_1 := \lambda \cdot e^{\alpha \cdot \Phi_1} \cdot \frac{K}{1+K} \cdot \left[1 + \lambda \cdot e^{\alpha \cdot \Phi_1} \cdot \frac{K}{(1+K)} \cdot \frac{2}{\sqrt{25 \cdot \pi}} - \frac{\lambda \cdot e^{\alpha \cdot \Phi_1} \cdot S_1}{(K+1) \cdot \varepsilon} \cdot (1) + \lambda \cdot e^{-(1-\alpha) \cdot \Phi_1} \cdot \frac{2}{\sqrt{25 \cdot \pi}}\right]^{-1}$$

$$\Psi_x := \frac{\frac{\lambda \cdot e^{\alpha \cdot \Phi ac} \cdot K}{1+K} \cdot \left[1 - \frac{2}{\sqrt{25 \cdot \pi}} \sum_{j=1}^{x-1} \left(\Psi_j \cdot S1_{x-j+1}\right)\right] - \gamma \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{\alpha \cdot \Phi ac} \sum_{j=1}^{x-1} \left(\Psi_j \cdot S_{x-j+1}\right) - \lambda \cdot \frac{2}{\sqrt{25 \cdot \pi}} \cdot e^{-[\Phi ac \cdot (1-\alpha)]} \sum_{j=1}^{x-1} \left(\Psi_j \cdot S1_{x-j+1}\right)}{\left(\frac{\lambda \cdot e^{\alpha \cdot \Phi ac} \cdot K}{1+K} \cdot \frac{2}{\sqrt{25 \cdot \pi}}\right) + 1 + \gamma \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{\alpha \cdot \Phi ac} + \lambda \cdot \frac{2}{\sqrt{25 \cdot \pi}} \cdot e^{-[\Phi ac \cdot (1-\alpha)]}}$$

$$\Psi_m := \frac{\frac{\lambda \cdot e^{\alpha \cdot \Phi_m} \cdot K}{1+K} \cdot \left[1 - \frac{2}{\sqrt{25 \cdot \pi}} \sum_{j=1}^{m-1} \left(\Psi_j \cdot S1_{m-j+1}\right)\right] - \gamma \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{\alpha \cdot \Phi_m} \sum_{j=1}^{m-1} \left(\Psi_j \cdot S_{m-j+1}\right) - \lambda \cdot \frac{2}{\sqrt{25 \cdot \pi}} \cdot e^{-[\Phi_m \cdot (1-\alpha)]} \sum_{j=1}^{m-1} \left(\Psi_j \cdot S1_{m-j+1}\right)}{\left(\frac{\lambda \cdot e^{\alpha \cdot \Phi_m} \cdot K}{1+K} \cdot \frac{2}{\sqrt{25 \cdot \pi}}\right) + 1 + \gamma \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{\alpha \cdot \Phi_m} + \lambda \cdot \frac{2}{\sqrt{25 \cdot \pi}} \cdot e^{-[\Phi_m \cdot (1-\alpha)]}}$$

$$\Psi_n := \frac{\frac{\lambda \cdot e^{\alpha \cdot \Phi_n} \cdot K}{1+K} \cdot \left[1 - \frac{2}{\sqrt{25 \cdot \pi}} \sum_{j=1}^{n-1} \left(\Psi_j \cdot S1_{n-j+1}\right)\right] - \gamma \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{\alpha \cdot \Phi_n} \sum_{j=1}^{n-1} \left(\Psi_j \cdot S_{n-j+1}\right) - \lambda \cdot \frac{2}{\sqrt{25 \cdot \pi}} \cdot e^{-[\Phi_n \cdot (1-\alpha)]} \sum_{j=1}^{n-1} \left(\Psi_j \cdot S1_{n-j+1}\right)}{\left(\frac{\lambda \cdot e^{\alpha \cdot \Phi_n} \cdot K}{1+K} \cdot \frac{2}{\sqrt{25 \cdot \pi}}\right) + 1 + \gamma \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{\alpha \cdot \Phi_n} + \lambda \cdot \frac{2}{\sqrt{25 \cdot \pi}} \cdot e^{-[\Phi_n \cdot (1-\alpha)]}}$$

$S_1 := -0.1$

$Si_1 := 1$

$\Psi_1 := -0.381$

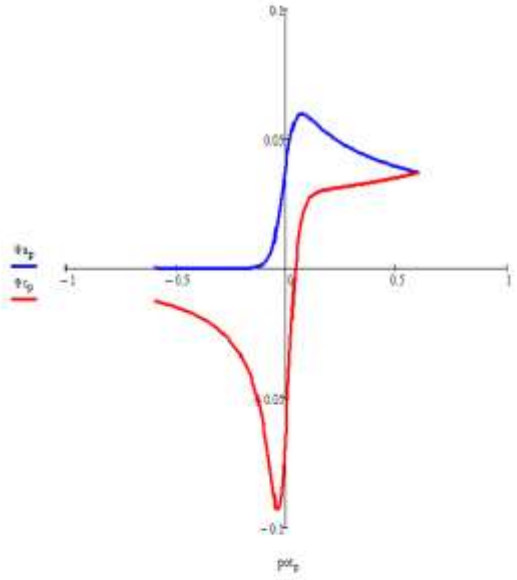
$p := 1, \frac{\Delta E}{dE}$ $\quad \Psi a_p := (\Psi)^{\left(\frac{\tau}{4.25}+p\right).25}$ $\quad \Psi c_p := (\Psi)^{\left[\left[\frac{\Delta E}{dE}\right]\cdot\left(\frac{\tau}{23.d}\right)\right]-p.25}$ $\quad pot_p := Es + p \cdot dE$

$R_n := s$

20za3000
20 za 20 000

20 za 20
5 za 1

0 za 0.2



slope na Ep od epsilon =K/25(1+K)

$\Psi a_p =$

pot_p

$\Psi c_p := \Psi c_p$

$D := 0.000002$

$$Ic_p := \Psi c_p \cdot 1 \cdot F \cdot A \cdot 0.446 \cdot \sqrt[2]{D} \cdot \frac{cox}{\sqrt[2]{\tau}}$$

$$Ia_p := \Psi a_p \cdot F \cdot 1 \cdot A \cdot 0.446 \cdot \sqrt[2]{D} \cdot \frac{cox}{\sqrt[2]{\tau}}$$

$Ic_{70} = -1.91 \times 10^{-6}$

$Ic_{70} \cdot R = -1.588 \times 10^{-5}$

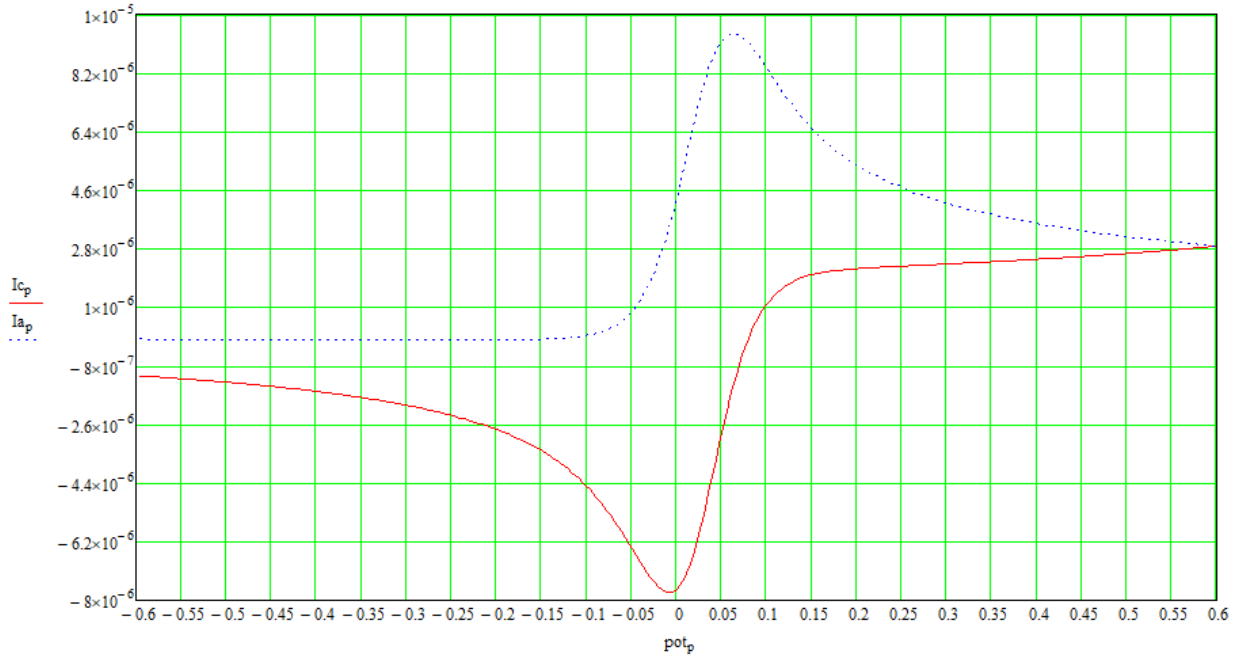
$Ro := 10000$

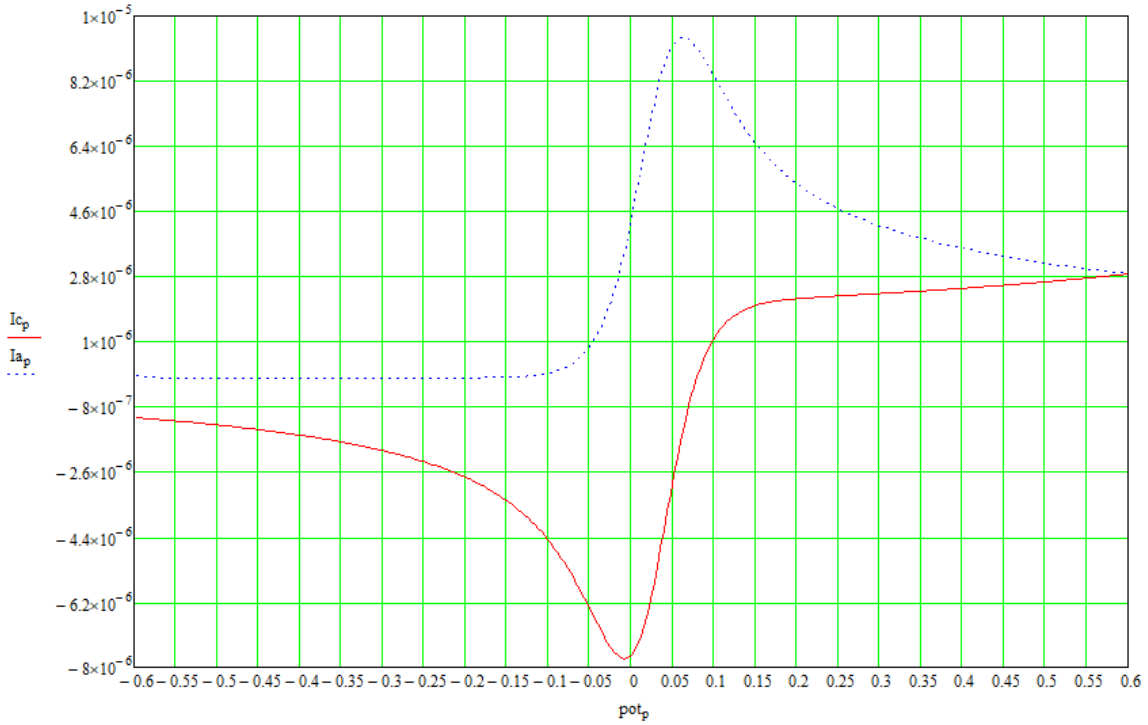
$\frac{1.2}{1.6} = 0.75$

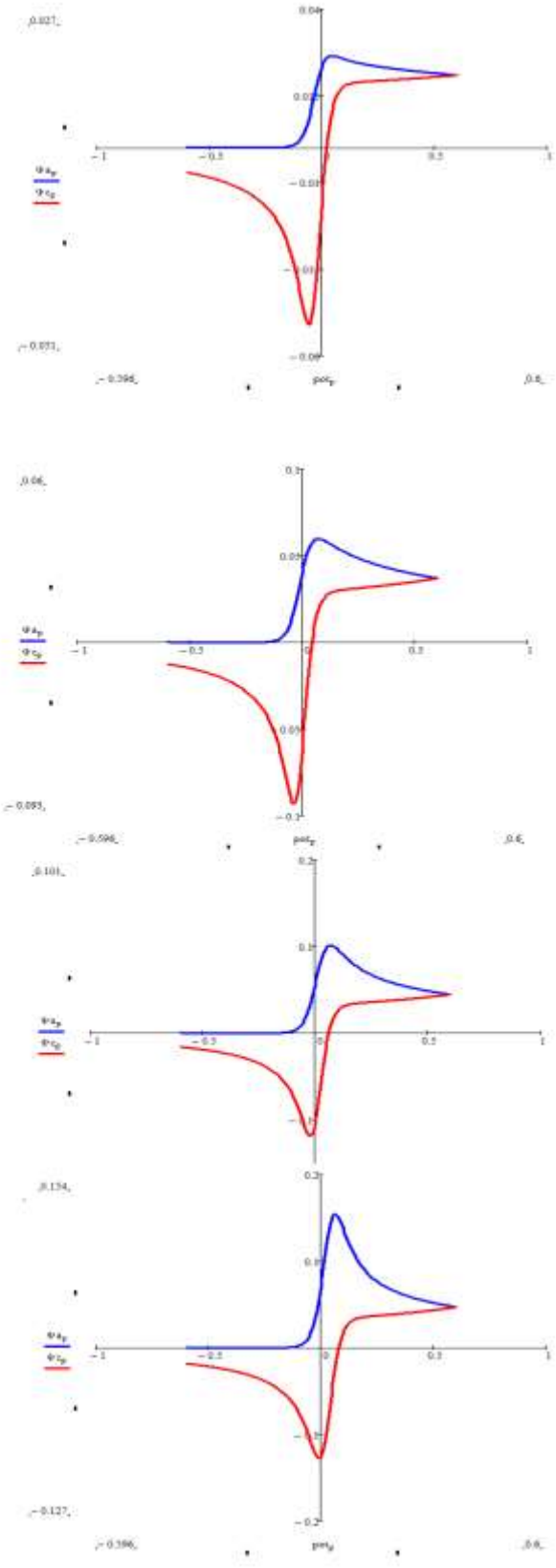
$piot_p := Es + p \cdot dE - \left(Ic_p - Ia_p\right) \cdot Ro$

$\frac{1.45}{2.2} = 0.659$

$\sqrt[2]{-1} \cdot -1 = -i$







Влијание на кинетиката на хемиската реакција врз својства на циклични волтамограми

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