Форма на Потенцијалниот Сигнал на CYCLIC SQUARE WAVE VOLTAMMETRY и дефиниции во MATHCAD

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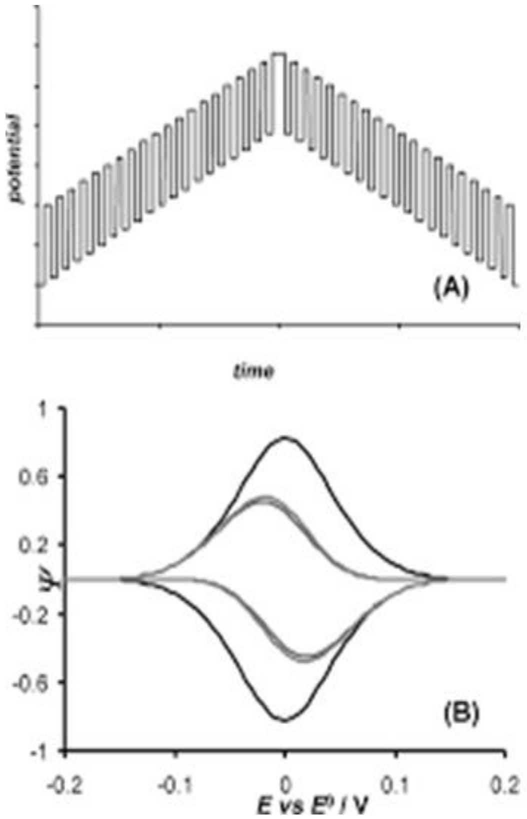
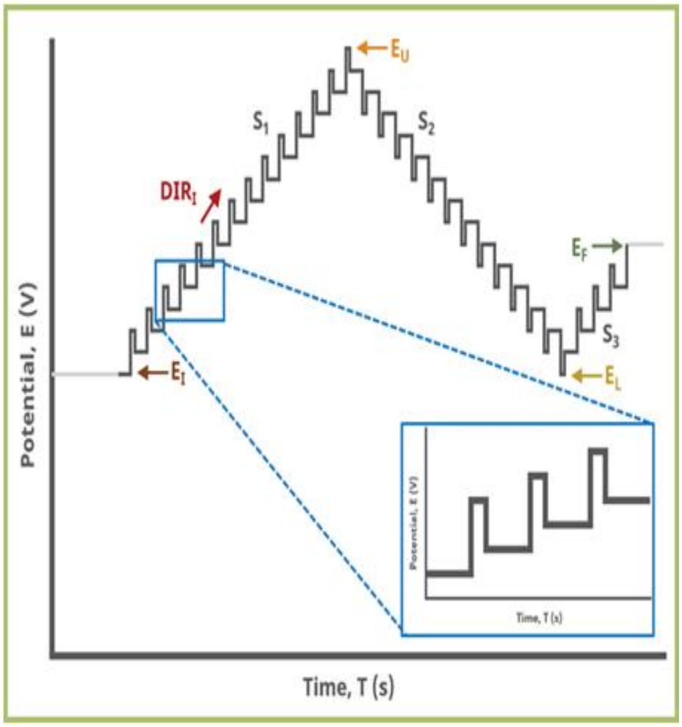
Цикличната квадратно-бранова волтаметрија е тип на хибридна техника што ги обединува потенцијалните форми на цикличната и квадратно-брановата волтаметрија. Во рамките на оваа презентација, дадени се дефинициите на сигналот во циклична квадратно-бранова волтаметрија, како и карактеристиките на овој сигнал во симулацискиот пакет MATHCAD. Дадени се и специфичните карактеристики на волтамограмите симулирани со оваа техника, што е особено ефикасна за студирање на ензимско супстратните механизми.





MATHCAD работен фајл за CYCLIC Square-wave voltammetry со Дефиниции за сите параметри за CrevE површински механизам

CYCLIC SWV MODEL
for SURFACE CE MECHANISM

$Es := 0.4$ $Ef := -0.4$ $r := 1..1$

$\Delta E := Es - Ef - Ef + Es$ $dE := 0.01$ $Esw := 0.05$ $f := 10$ $\varepsilon := kf + kb$

$n := 2$ $F := 96500$ $R := 8.314$ $T := 298.15$ $\Delta E = 1.6$ $ks_r := 10^{.65r}$

$j := 1..\frac{\frac{\Delta E}{2}}{dE} \cdot 50$ $kf := 5$ $kb := 5$

$\alpha := 0.5$

$\lambda_r := \frac{ks_r}{f}$ $K := 10^2$ $K = 100$

$$potI_j := Es + Esw - \left[\left(ceil\left(\frac{j}{25} - \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} - \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]$$

$\varepsilon := 10^{3.4}$ $\lambda_r =$ $\boxed{0.447}$ $\varepsilon = 2.512 \times 10^3$

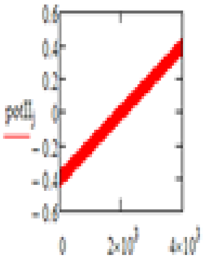
$z := \frac{\varepsilon}{f}$

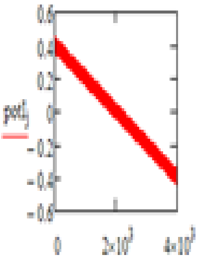
$$potII_j := Ef + Esw + \left[\left(ceil\left(\frac{j}{25} - \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} - \frac{1}{2}\right), 1, -1\right) \cdot Esw - Esw\right) - dE\right]$$

$k := 1..\frac{\frac{\Delta E}{2}}{dE} \cdot 50$ $\log\left(\frac{ks}{\varepsilon_r} \cdot K\right) =$ $z = 251.189$ $\log(z_r) =$

$S_k := e^{\frac{z}{50} \cdot (-k)} - e^{\frac{z}{50} \cdot (-k+1)}$ $\varepsilon = 2.512 \times 10^3$ $z = 251.189$ $u := \frac{\Delta E}{dE} \cdot 50..1$ $\log(\lambda_1) = -0$

$10^{1.2} = 15.849$ $L_u := e^{\frac{z}{50} \cdot (-u)} - e^{\frac{z}{50} \cdot (-u+1)}$

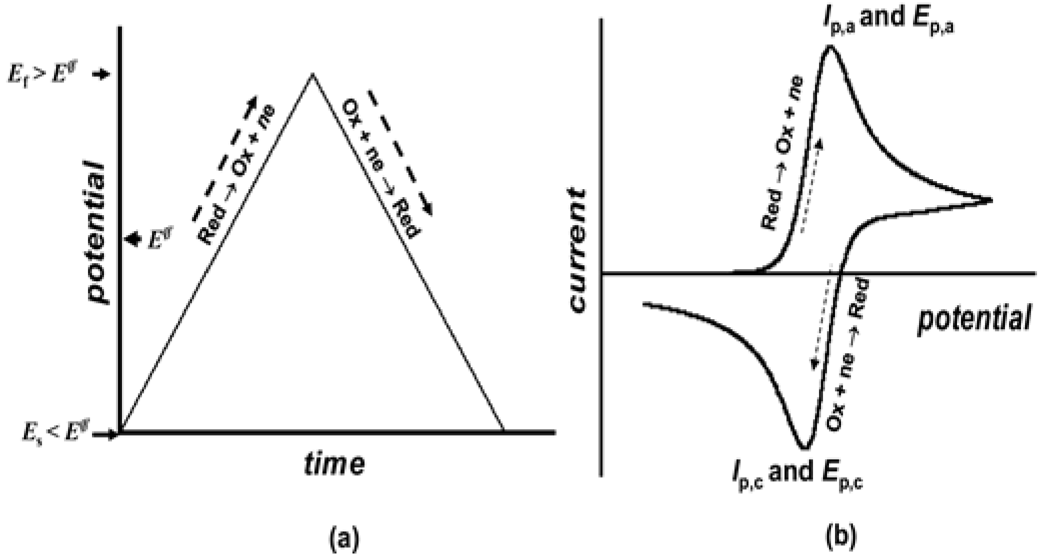




$\Phi I_j := n \cdot \frac{F}{R \cdot T} \cdot potI_j$

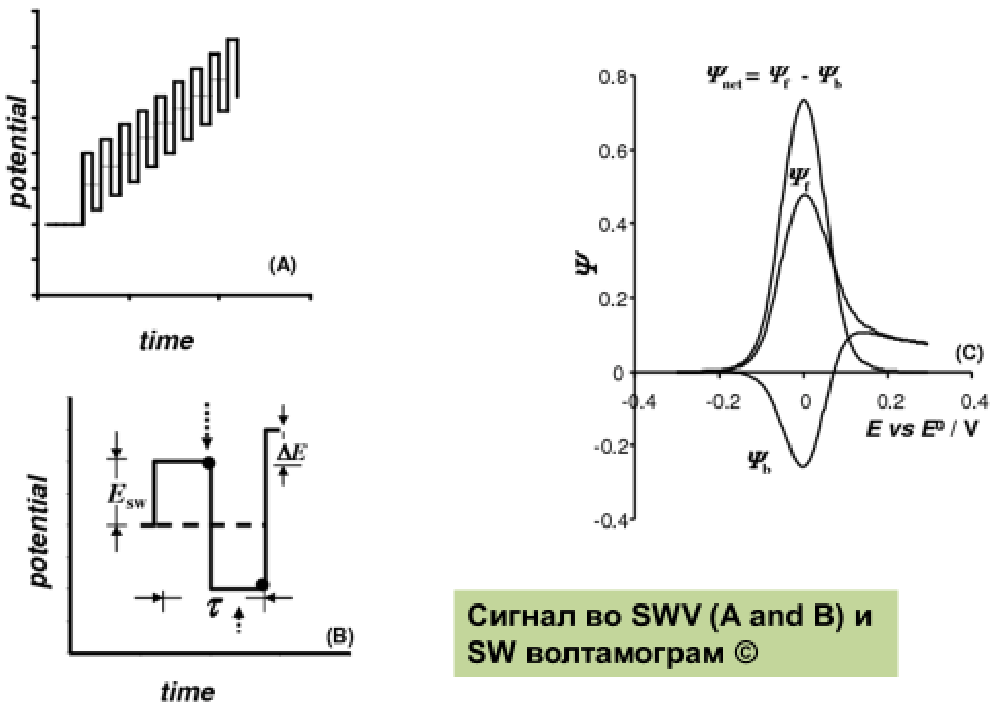
$\Phi II_j := n \cdot \frac{F}{R \cdot T} \cdot potII_j$

Цикличната волтаметрија е една од назначајните техники за
Студирање на електродните механизми кај голем број системи.
Оваа техника подразбира апликација на потенцијал од дадена почетна
До дадена крајна вредност, при што се студираат, на пример, процеси на
Редукција. Кога потенцијалот ќе стигне до крајна дефинирана вредност, тој се
Менува кон почетниот потенцијал и се студираат процесите на оксидација



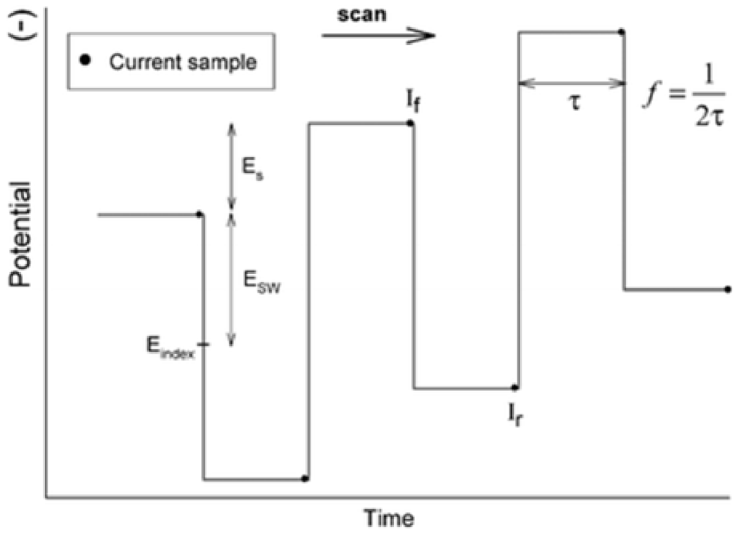
Форма на потенцијал во циклична волтаметрија (а) и цикличен волтамограм (б)

Техниката ***квадратно-бранова волтаметрија*** е пулсна волтаметриска техника
Каде во текот на секој пулс, со модификација преку дадена SW амплитуда
Се студираат процесите и на редукција и на оксидација.
Оваа техника е повеќе осетлива и побрза од циклична волтаметрија, а нуди
Истовремено увид и во процесите на оксидација и на редукција

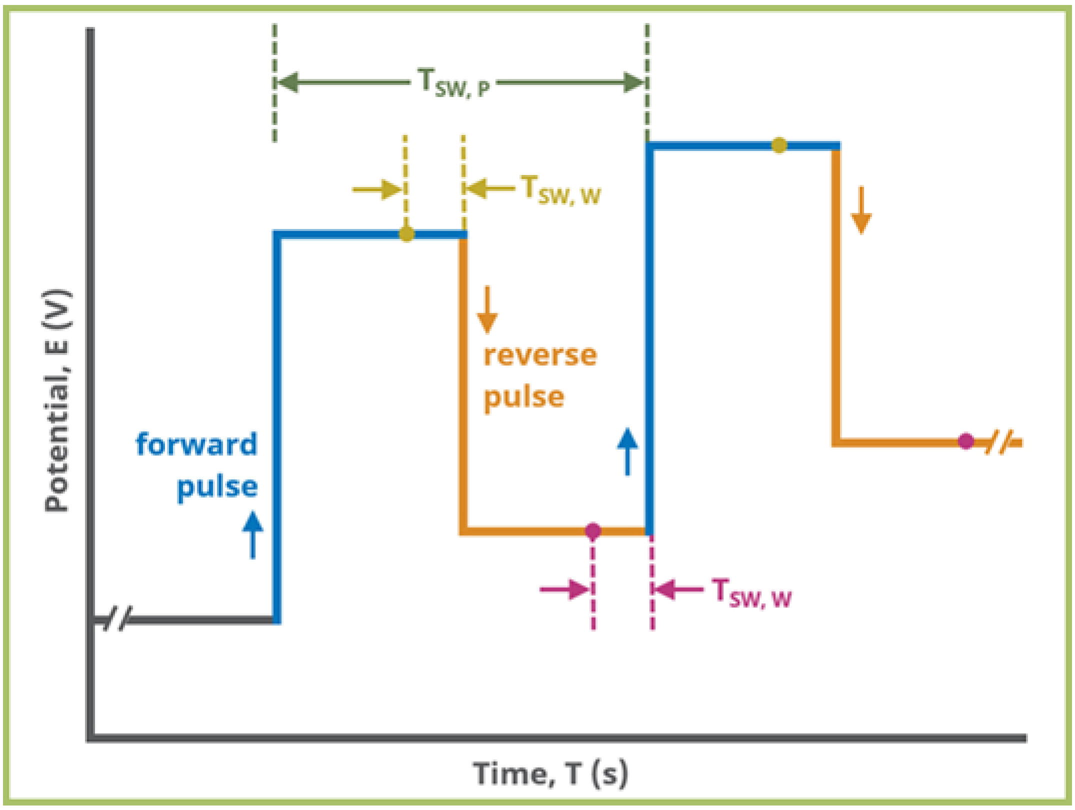


Сигнал во SWV (A and B) и SW волтамограм ©

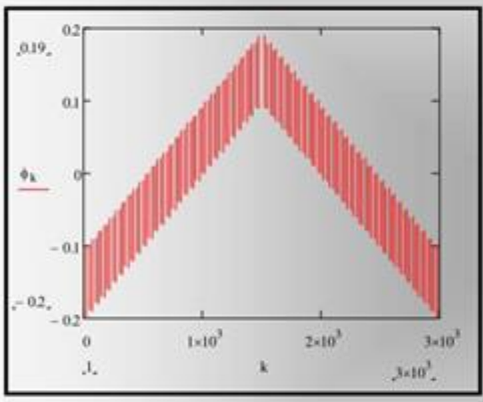
Дефиниција на параметри на даден пулс во SWV

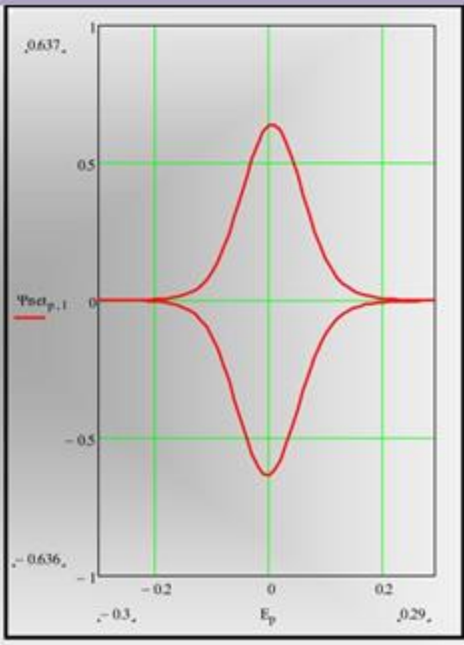


Форма на еден потенцијален пулс во SWV



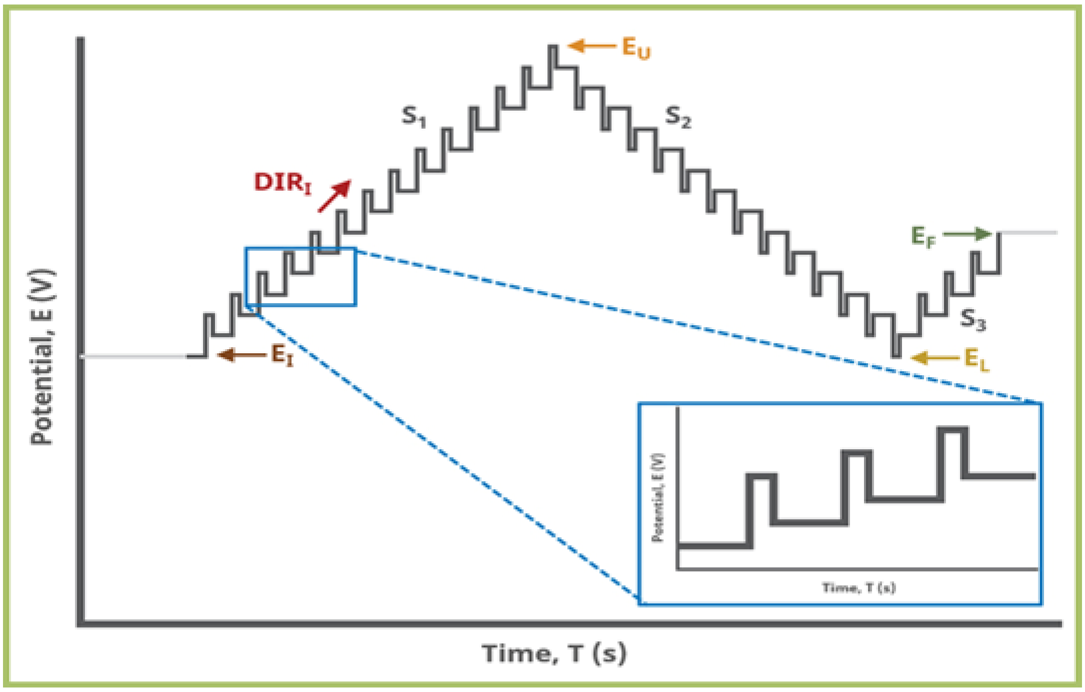
Циклична квадратно-бранова волтаметрија е ХИБРИД од Циклична и од квадратно бранова волтаметрија со потенцијален сигнал Како на сликата лево



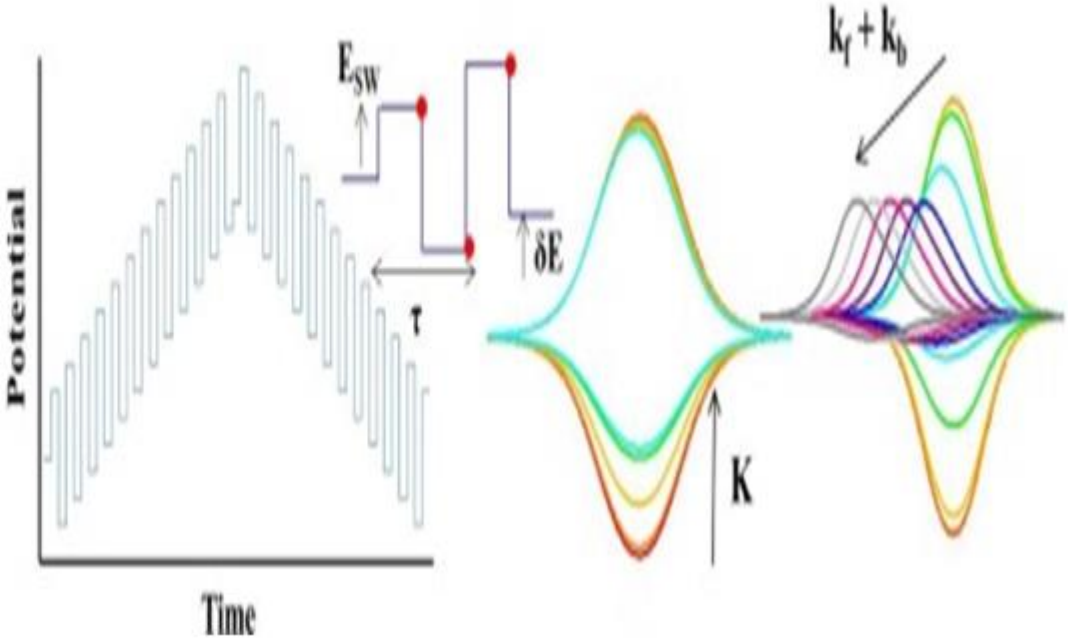


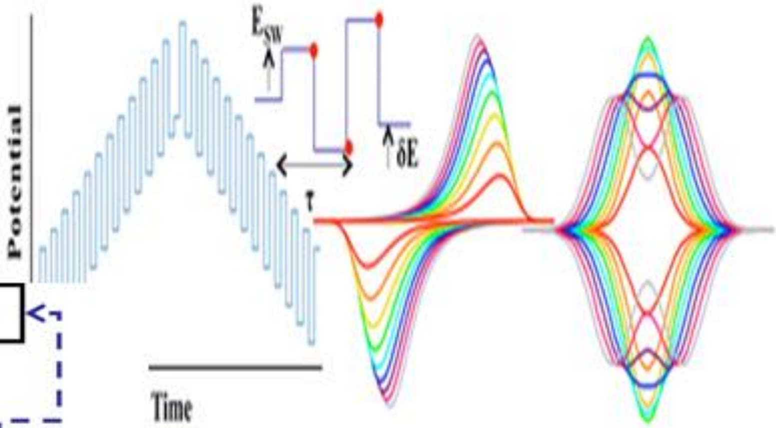
Оваа техника ги обединува Предностите и на Циклична и на SWV

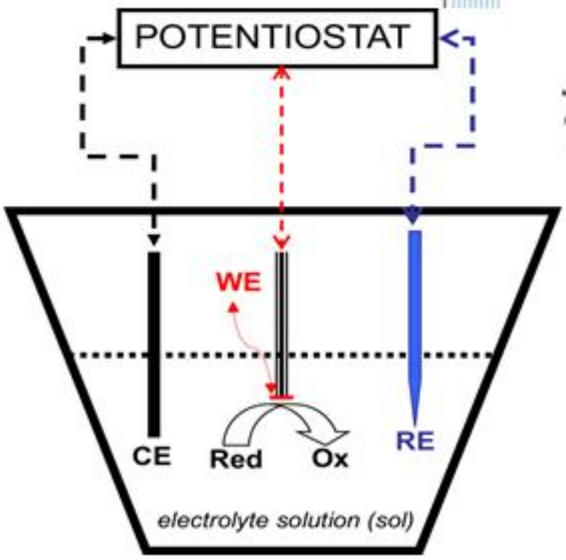
Карактеристични параметри на потенцијален пулс во техниката Циклична квадратно-бранова волтаметрија

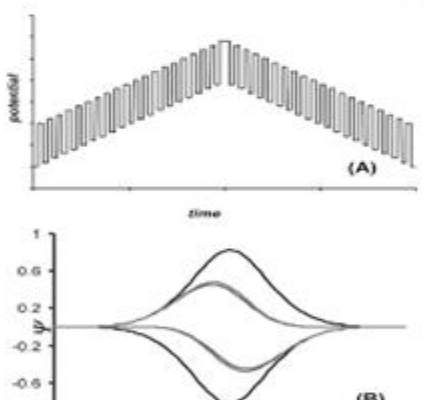


Форма на волтамограми добиени со техниката Циклична квадратно-бранова волтаметрија









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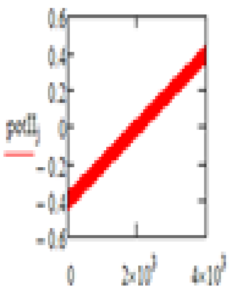
$n := 2$ $\quad F := 96500$ $\quad R := 8.314$ $\quad T := 298.15$ $\quad \Delta E = 1.6$

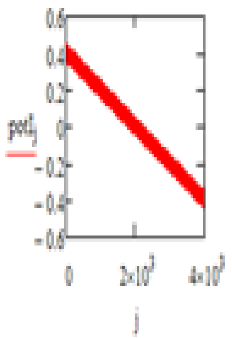
$j := 1 .. \frac{\frac{\Delta E}{2}}{dE} \cdot 50$ $\quad \alpha := 0.5$

potIj i potIIj se potencijalite

$$potI_j := Es + Esw - \left[\left[\left(ceil\left(\frac{j}{25} - \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} - \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]\right]$$

$$potII_j := Ef + Esw + \left[\left[\left(ceil\left(\frac{j}{25} - \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} - \frac{1}{2}\right), 1, -1\right) \cdot Esw - Esw\right) - dE\right]\right]$$





$$\Phi I_j := n \cdot \frac{F}{R \cdot T} \cdot potI_j$$

$$\Phi II_j := n \cdot \frac{F}{R \cdot T} \cdot potII_j$$

$\varepsilon := kf + kb$

$f := 10$ $\quad ks_r := 10^{.65r}$

$kf := 5$

$kb := 5$

$\lambda_r := \frac{ks_r}{f}$ $\quad K := 10^2$ $\quad K = 100$

$\varepsilon := 10^{3.4}$

$\lambda_r =$ $\quad \varepsilon = 2.512 \times 10^3$

0.447

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

$\log\left(\frac{ks}{\varepsilon_r} \cdot K\right) =$ $\quad z = 251.189$ $\quad \log(z_r) =$

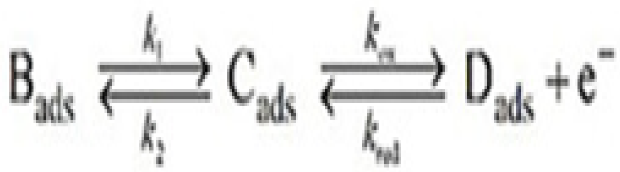
$k := 1 .. \frac{\frac{\Delta E}{2}}{dE} \cdot 50$

$$S_k := e^{\frac{z}{50}\cdot(-k)} - e^{\frac{z}{50}\cdot(-k+1)}$$

$\varepsilon = 2.512 \times 10^3$ $\quad z = 251.189$ $\quad u := \frac{\Delta E}{dE} \cdot 50 .. 1$ $\quad \log(\lambda_r) = -0$

$10^{1.2} = 15.849$

$$L_u := e^{\frac{z}{50}\cdot(-u)} - e^{\frac{z}{50}\cdot(-u+1)}$$



Дефиниции за пресметки на струите во циклична квадратно-бранова волтаметрија

$$\Psi I_{1,r} := \lambda_r \cdot e^{-\alpha \cdot \Phi I_1} \cdot \frac{K}{1+K} \cdot \left[1 + \lambda_r \cdot e^{-\alpha \cdot \Phi I_1} \cdot \frac{K}{(1+K) \cdot 50} - \frac{\lambda_r \cdot e^{-\alpha \cdot \Phi I_1} \cdot S_1}{(K+1) \cdot z} \cdot (1) + \frac{\lambda_r \cdot e^{(1-\alpha) \cdot \Phi I_1}}{50} \right]^{-1}$$

$\Psi_{1,r} =$

$$\Psi I_{k,r} := \frac{\frac{\lambda_r \cdot e^{-\alpha \cdot \Phi I_k} \cdot K}{1+K} \cdot \left(1 - \frac{1}{50} \cdot \sum_{j=1}^{k-1} \Psi I_{j,r}\right) - (z)^{-1} \cdot \lambda_r \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{-\alpha \cdot \Phi I_k} \cdot \sum_{j=1}^{k-1} \left(\Psi I_{j,r} \cdot S_{k-j+1}\right) - \frac{\lambda_r}{50} \cdot e^{\Phi I_k \cdot (1-\alpha)} \cdot \sum_{j=1}^{k-1} \Psi I_{j,r}}{\left(\frac{\lambda_r \cdot e^{-\alpha \cdot \Phi I_k} \cdot K}{1+K} \cdot \frac{1}{50}\right) + 1 + (z)^{-1} \cdot \lambda_r \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{-\alpha \cdot \Phi I_k} + \frac{\lambda_r}{50} \cdot e^{\Phi I_k \cdot (1-\alpha)}}$$

$$\Psi II_{1,r} := \lambda_r \cdot e^{-\alpha \cdot \Phi II_1} \cdot \frac{K}{1+K} \cdot \left[1 + \lambda_r \cdot e^{-\alpha \cdot \Phi II_1} \cdot \frac{K}{(1+K) \cdot 50} - \frac{\lambda_r \cdot e^{-\alpha \cdot \Phi II_1} \cdot S_1}{(K+1) \cdot z} \cdot (1) + \frac{\lambda_r \cdot e^{(1-\alpha) \cdot \Phi II_1}}{50} \right]^{-1}$$

$$\Psi II_{k,r} := \frac{\frac{\lambda_r \cdot e^{-\alpha \cdot \Phi II_k} \cdot K}{1+K} \cdot \left(1 - \frac{1}{50} \cdot \sum_{j=1}^{k-1} \Psi II_{j,r}\right) - (z)^{-1} \cdot \lambda_r \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{-\alpha \cdot \Phi II_k} \cdot \sum_{j=1}^{k-1} \left(\Psi II_{j,r} \cdot S_{k-j+1}\right) - \frac{\lambda_r}{50} \cdot e^{\Phi II_k \cdot (1-\alpha)} \cdot \sum_{j=1}^{k-1} \Psi II_{j,r}}{\left(\frac{\lambda_r \cdot e^{-\alpha \cdot \Phi II_k} \cdot K}{1+K} \cdot \frac{1}{50}\right) + 1 + (z)^{-1} \cdot \lambda_r \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{-\alpha \cdot \Phi II_k} + \frac{\lambda_r}{50} \cdot e^{\Phi II_k \cdot (1-\alpha)}}$$

$\Psi T_{k,r} := \Psi I_{k,r} + \Psi II_{k,r}$

$p := 1 .. \frac{\frac{\Delta E}{2}}{dE} - 1$

$\Psi Af_{p,r} := \Psi I_{(p+1) \cdot 50,r}$ $\quad \Psi Ab_{p,r} := \Psi I_{50 \cdot p+25,r}$

$E_p := Es - p \cdot dE$

$\Psi Bb_{p,r} := \Psi II_{50 \cdot p+25,r}$ $\quad \Psi Bf_{p,r} := \Psi II_{(p+1) \cdot 50,r}$

$\Psi Bnet_{p,r} := \Psi Ab_{p,r} - \Psi Bb_{p,r}$

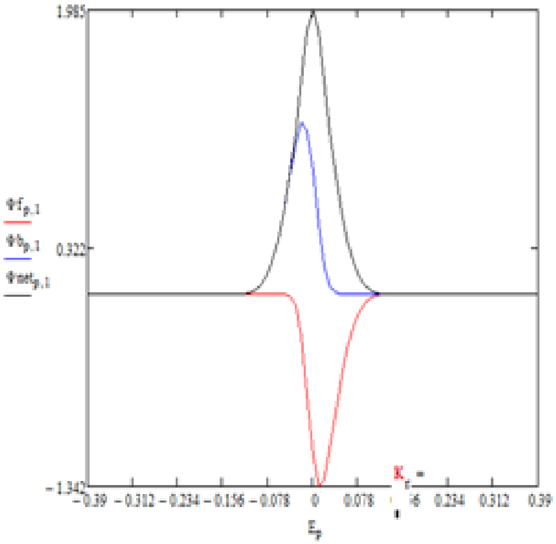
$\Psi b_{p,r} := \Psi Bb_{p,r} - \Psi Ab_{p,r}$

$\Psi f_{p,r} := \Psi Bf_{p,r} - \Psi Af_{p,r}$

$\Psi Anet_{p,r} := \Psi Af_{p,r} + \Psi Bf_{p,r}$

Волтамограм добиен со симулирање во Циклично-квадратно-бранова волтаметрија

$\Psi net_{p,r} := \Psi b_{p,r} - \Psi f_{p,r}$



$K_r =$

$E_p =$

0.39
0.38
0.37
0.36
0.35
0.34
0.33
0.32
0.31
0.3
0.29
0.28
0.27
0.26

$\Psi f_{p,1} =$

$\Psi net_{p,1} =$

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