Theory of Square-Wave Voltammetry of Two-Step Diffusional EC'EC' Mechanism with Regenerative Chemical Reactions Coupled to the Products of Both Electron Transfer Steps

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Abstract

The two-step successive electrochemical diffusional mechanism, coupled with two regenerative irreversible chemical steps to both electrochemically generated products is solved for the first time under conditions of square-wave voltammetry. While the entire simulation protocol to calculate voltammograms of this complex mechanism is given in MATHCAD, hints are given to perform calculations related to electrochemical systems complying to this electrochemical mechanism.

TWO STEP DIFFUSIONAL EC'EC'cat Mechanism in SWV---Tocen 21 sept 2023

$EsI := 0.35 \quad \Delta E := 1 \quad dE := 0.01 \quad Esw := 0.05 \quad EsII := 0.65 \quad r := 1..1$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad KI_r := 10^{-.75 \cdot r} \quad KII := 10^{-.75}$

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

$\alpha 2 := 0.5 \quad \alpha 1 := 0.5 \quad \log(KI_r) =$ 0.75

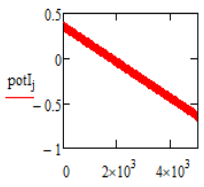
$potI_j := EsI + Esw - \left[\left(ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$

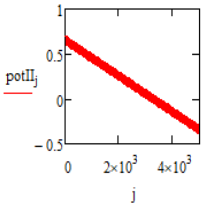
$potII_j := EsII + Esw - \left[\left(ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$

$KI_1 = 5.623$

$\lambda := 100.0000$

λ e kineticki parametar na ireverzibilna hemiska reakcija
povrzana so prv elektroden cekor





$M1_j := \sqrt{\frac{j}{1}} - \sqrt{\frac{j-1}{1}}$

$A_j := \left(1 - erfc\left(\sqrt{\frac{\lambda}{50\times 1}}\cdot j\right)\right) - \left[1 - erfc\left[\sqrt{\frac{\lambda}{50\times 1}}\cdot(j-1)\right]\right]$

$B_j := \left(1 - erfc\left(\sqrt{\frac{z}{50\times 1}}\cdot j\right)\right) - \left[1 - erfc\left[\sqrt{\frac{z}{50\times 1}}\cdot(j-1)\right]\right]$

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

$x := 0.001$

z := 100.00
z e kataliticki parametar vo ovoj model povrzan so vtor cekor

L e konst na ramnoteza na hem follow up (na e za ovoj model)
$L := 100.000001000$

$$\Psi I_{1,r} := \frac{\frac{KI_r}{1}\cdot e^{-\alpha 1\cdot\Phi I_1} - 0}{1 + KI_r\cdot\lambda^{-.5}\cdot A_1\cdot e^{-\alpha 1\cdot\Phi I_1} + 1\lambda^{-.5}\cdot e^{\Phi I_1\cdot(1-\alpha 1)}\cdot A_1}$$

$$\Psi II_{1,r} := \frac{\frac{2}{\sqrt{\pi\cdot 50}}KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{1 + \frac{KII\cdot M1_1\cdot 2}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot\Phi II_1}\cdot\left(1 + e^{\Phi II_1}\right)}\cdot\Psi I_{1,r}\cdot A_1 + \frac{KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{1 + \frac{2\cdot KII\cdot M1_1\cdot e^{-\alpha 2\cdot\Phi II_1}}{\sqrt{\pi\cdot 50}} + \frac{2\cdot KII\cdot e^{(1-\alpha 2)\cdot\Phi II_1}}{\sqrt{\pi\cdot 50}}}\cdot 1$$

$\Psi I_{1,1} = 1.013\times 10^{-5}$

$\Psi II_{1,1} = 9.165\times 10^{-12}$

$$\Psi I_{j,r} := \frac{KI_r\cdot e^{-\alpha 1\cdot\Phi I_j} - KI_r\cdot\frac{1}{\sqrt{\lambda}}\cdot e^{-\alpha 1\cdot\Phi I_j}\cdot\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot A_{j-i+1}\right) - KI_r\lambda^{-0.5}\cdot e^{\Phi I_j\cdot(1-\alpha 1)}\cdot\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot A_{j-i+1}\right)}{1 + KI_r\frac{2}{\sqrt{\lambda}}\cdot A_1\cdot e^{-\alpha 1\cdot\Phi I_j} + \lambda^{-0.5}\cdot e^{\Phi I_j\cdot(1-\alpha 1)}\cdot A_1\cdot KI_r}$$

$$\Psi II_{j,r} := \frac{KII\frac{1}{\sqrt{\lambda}}\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot\sum_{i=1}^{j}\left(\Psi I_{1,r}\cdot A_{j-i+1}\right) - KII\frac{0}{\sqrt{\lambda}}\cdot e^{(-\alpha 2)\cdot \Phi II_j}\cdot\sum_{i=1}^{j}\left(\Psi I_{1,r}\cdot A_{j-i+1}\right) - \frac{0}{\sqrt{\pi\cdot 50}}\frac{KII}{1+0}\cdot e^{1\cdot \Phi II_j\cdot(-\alpha 2)}\cdot(1)\cdot\sum_{i=1}^{j-1}\left(\Psi II_{1,r}\cdot M1_{j-i+1}\right) - \frac{1}{(\sqrt{2})\cdot(1+0)}KII\cdot e^{1\cdot \Phi II_j\cdot(-\alpha 2)}\cdot(1)\cdot\sum_{i=1}^{j-1}\left(\Psi II_{1,r}\cdot B_{j-i+1}\right) - \frac{1}{(\sqrt{2})\cdot(1+0)}KII\cdot e^{1\cdot \Phi II_j\cdot(1-\alpha 2)}\cdot(1)\cdot\sum_{i=1}^{j-1}\left(\Psi II_{1,r}\cdot B_{j-i+1}\right)}{1 + KII\frac{A_1\cdot 0}{\sqrt{\lambda}}\cdot e^{(-\alpha 2)\cdot \Phi II_j} + \frac{0\cdot M1_1}{\sqrt{\pi\cdot 50}}\frac{KII}{1+0}\cdot e^{1\cdot \Phi II_j\cdot(-\alpha 2)} + \frac{1\cdot B_1}{(\sqrt{2})\cdot(1+0)}KII\cdot e^{1\cdot \Phi II_j\cdot(-\alpha 2)} + \frac{1\cdot B_1}{(\sqrt{2})\cdot(1+0)}KII\cdot e^{1\cdot \Phi II_j\cdot(1-\alpha 2)}}$$

$$\Psi_{j,r} := \Psi I_{j,r} + \Psi II_{j,r}$$

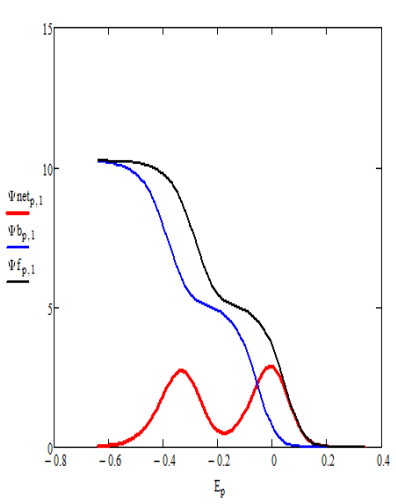
$$p := 1..\left(\frac{\Delta E}{dE}\right) - 1$$

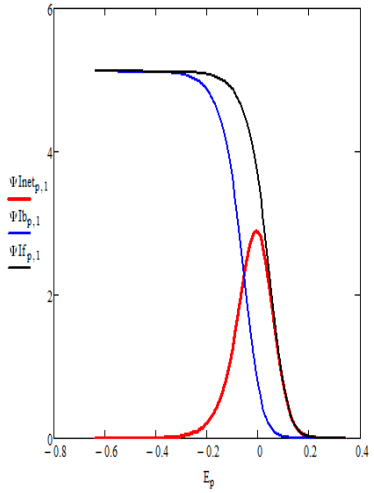
$$\Psi If_{p,r} := \Psi I_{(p+1)\cdot 50,r} \quad \Psi Ib_{p,r} := \Psi I_{50\cdot p+2} \quad \Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$$

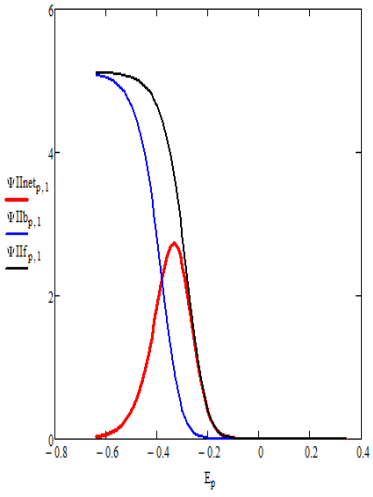
$$\Psi IIb_{p,r} := \Psi II_{50\cdot p+25,1} \quad \Psi IIf_{p,r} := \Psi II_{(p+1)\cdot 50,1} \quad \Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$$

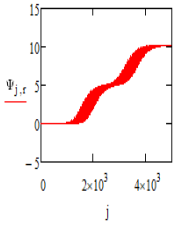
$$E_p := EsI - p\cdot dE$$

$$\Psi b_{p,r} := \Psi_{50\cdot p+25,r} \quad \Psi f_{p,r} := \Psi_{(p+1)\cdot 50,r} \quad \Psi net_{p,r} := \Psi f_{p,r} - \Psi b_{p,r}$$









$\Psi f_{p,1}$ =

$1.242\cdot10^{-4}$
$1.831\cdot10^{-4}$
$2.698\cdot10^{-4}$
$3.974\cdot10^{-4}$
$5.852\cdot10^{-4}$
$8.611\cdot10^{-4}$
$1.266\cdot10^{-3}$
$1.861\cdot10^{-3}$
$2.732\cdot10^{-3}$
$4.007\cdot10^{-3}$
$5.868\cdot10^{-3}$
$8.578\cdot10^{-3}$

$\Psi b_{p,1}$ =

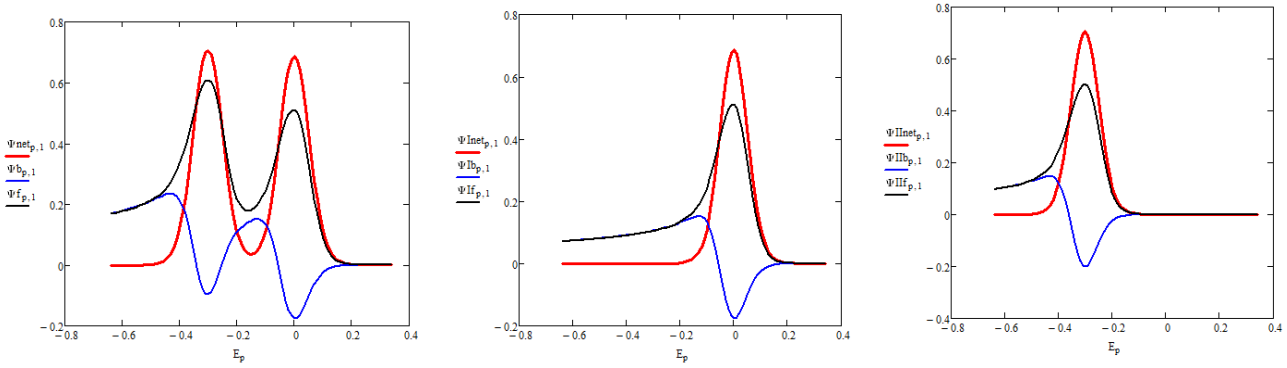
$2.546\cdot10^{-6}$
$3.757\cdot10^{-6}$
$5.544\cdot10^{-6}$
$8.18\cdot10^{-6}$
$1.207\cdot10^{-5}$
$1.781\cdot10^{-5}$
$2.627\cdot10^{-5}$
$3.875\cdot10^{-5}$
$5.714\cdot10^{-5}$
$8.427\cdot10^{-5}$
$1.242\cdot10^{-4}$
$1.831\cdot10^{-4}$

$\Psi net_{p,1}$ =

$1.217\cdot10^{-4}$
$1.794\cdot10^{-4}$
$2.643\cdot10^{-4}$
$3.893\cdot10^{-4}$
$5.731\cdot10^{-4}$
$8.433\cdot10^{-4}$
$1.24\cdot10^{-3}$
$1.822\cdot10^{-3}$
$2.675\cdot10^{-3}$
$3.922\cdot10^{-3}$
$5.743\cdot10^{-3}$

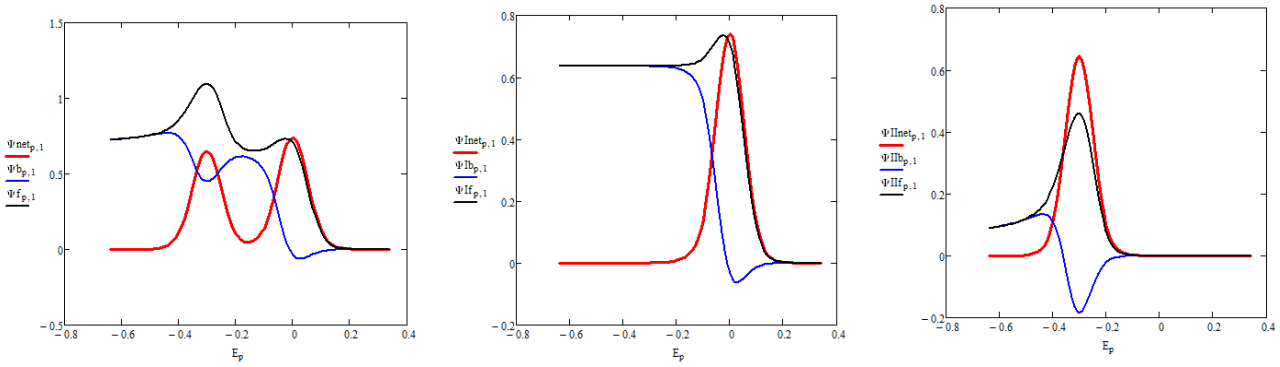
E_p =

0.34
0.33
0.32
0.31
0.3
0.29
0.28
0.27
0.26
0.25
0.24



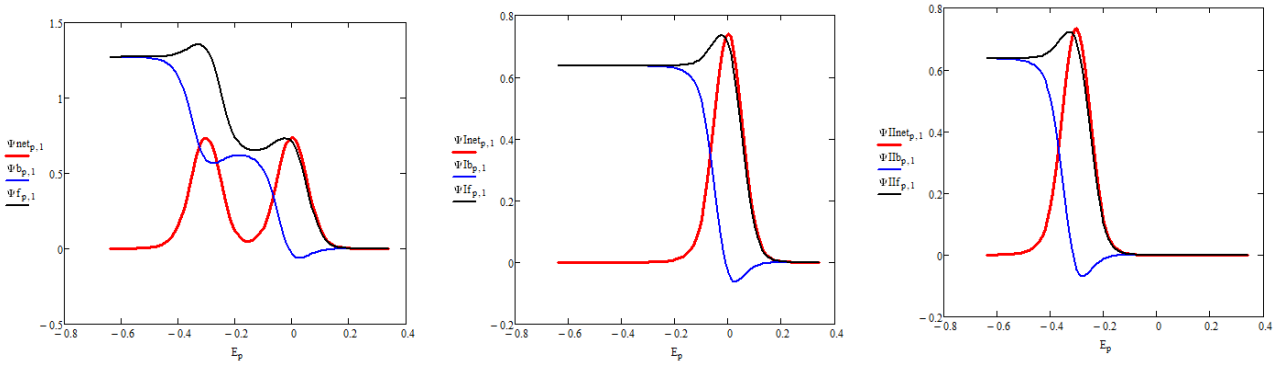
Simulation Conditions

Kcat1=Kcat2=0.00005; Ket1=Ket2=5.62

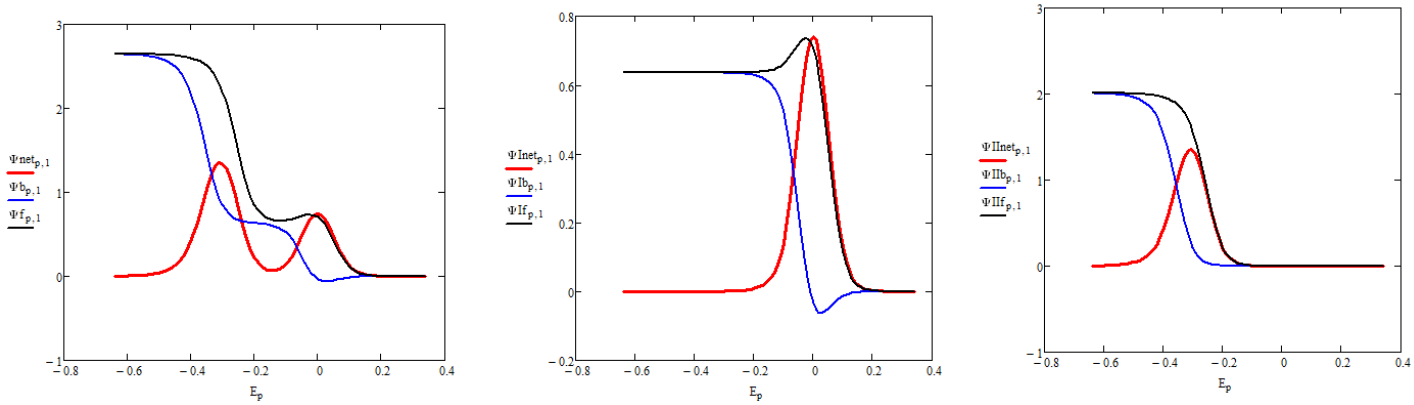


Kcat1=0.5: Kcat2=0.00005

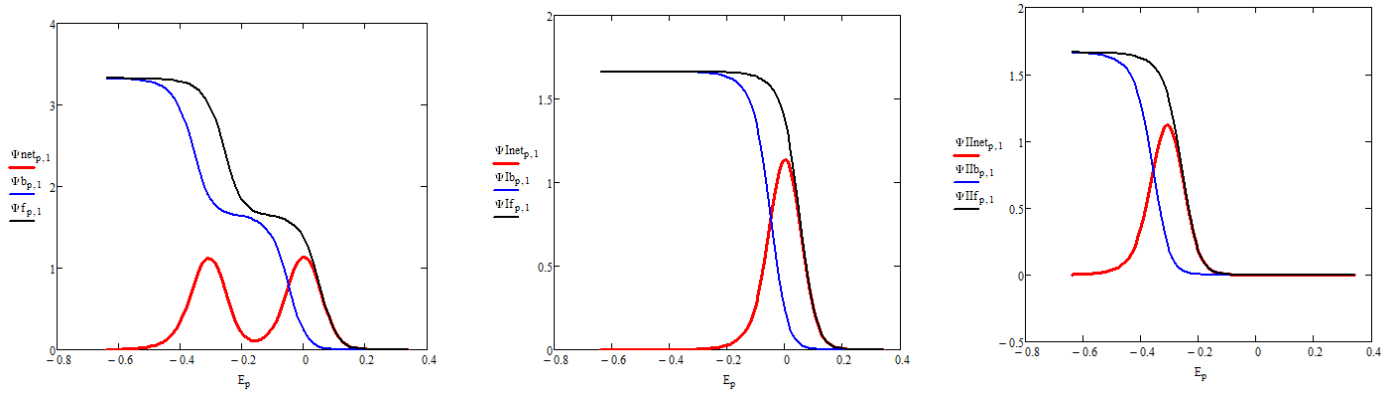
Kcat1=0.5: Kcat2=0.5



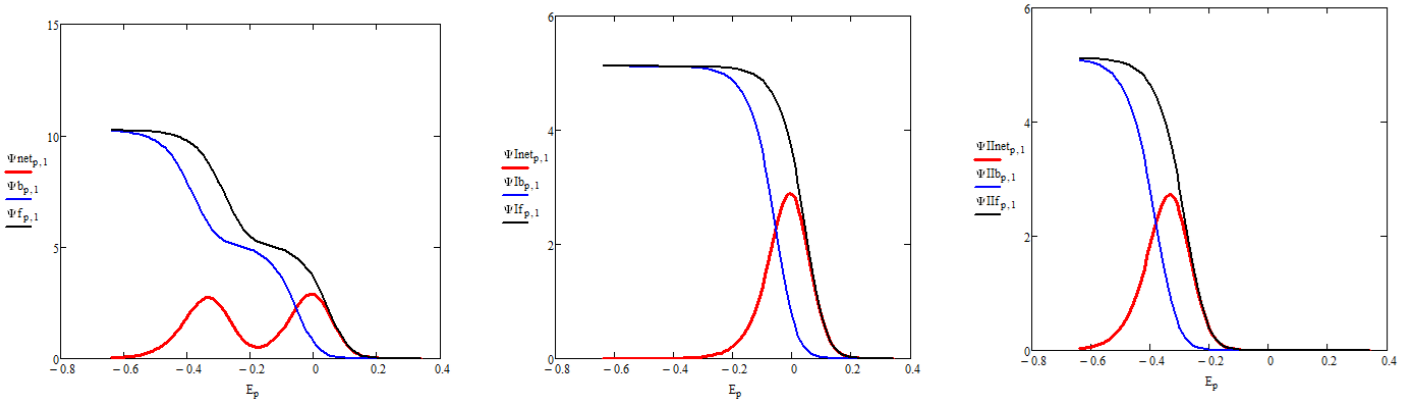
Kcat1=0.5: Kcat2=5.0



Kcat1=5.0: Kcat2=5.0



Kcat1=100.0: Kcat2=100.0



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