MATHCAD Working File for a two-step diffusional EECrev mechanism in Square-wave Voltammetry

Square-wave voltammetry of two-step diffusional electrode mechanism coupled with a reversible follow-up chemical reaction, *J. Solid State Electrochem* 2021

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$f := 10$

$EsI := 0.2 \quad \Delta E := .6 \quad dE := 0.01 \quad Esw := 0.05$

$EsII := 0.4 \quad r := 1..1$

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

$KI_r := 10^{0.5 \cdot r} \quad KI_1 = 3.162$

$KII := 10^{0.5} \quad KII = 3.162$

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

$\alpha 2 := 0.5$

$\alpha 1 := 0.5$

$\varepsilon := 1000000$

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

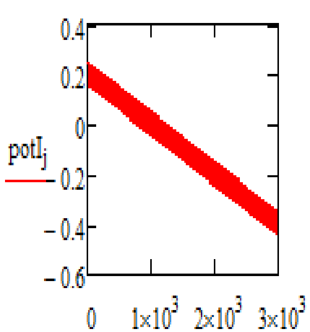
$\gamma := \frac{\varepsilon}{f}$

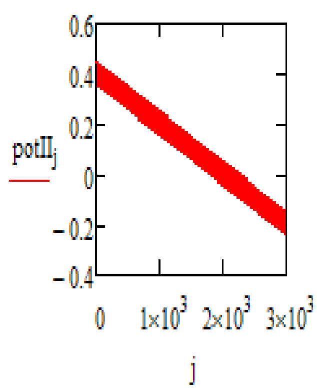
$$potII_j := EsII + Esw - \left[\left(\mathrm{ceil}\left(\frac{j}{25} \cdot \frac{1}{2}\right) \cdot dE + \mathrm{if}\left(\frac{\mathrm{ceil}\left(\frac{j}{25}\right)}{2} = \mathrm{ceil}\left(\frac{j}{25} \cdot \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]$$

$\gamma := 10.00100$

$U := 100.05000001$

EsI---is standard redox potential of first electron transfer
EsII--is standard redox potential of second electron transfer
dE is step increment
Esw is SW amplitude
f is SW frequency
ΔE is potential window
α is electron transfer coefficient
n--is number of electrons exchanged
ε is chemical rate parameter
KI = ks1/(Df)0.5 ---is dimensionless electrode parameter of first electron transfer
KII = ks2/(Df)0.5 --is dimensionless electrode parameter of second electron transfer
γ = Kchem = ε/f = (kf+kb)/f---is dimensionless chemical rate parameter
U = Keq = equilibrium constant of chemical reaction defined as = kf/kb
kf-rate constant of forward chemical step
kb-rate constant of backward chemical step
ΨI is dimensionless current of first electron transfer step
ΨII is dimensionless current of second electron transfer step
Ψ is overal dimensionless current
M1j --is numerical integration factor
Mj --is numerical integration factor
j--number of potential pulses
ΦIj and ΦIIj are dimensionless potentials
F is Faraday constant
R is universal gas constant
T is thermodynamic temperature





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

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

$$M_j := \left(1 - \mathrm{erfc}\left(\sqrt{\frac{\gamma}{\ldots} \cdot j}\right)\right) - \left[1 - \mathrm{erfc}\left[\sqrt{\frac{\gamma}{\ldots} \cdot (j-1)}\right]\right]$$

$$x := 0.001$$

$$\Psi I_{1,r} := \operatorname{root}\left[\left[1+\frac{KI_r\cdot e^{-\alpha 1\cdot \Phi I_1}}{\sqrt{\pi\cdot 50\cdot 0.5}}\cdot\left(1+e^{\Phi I_1}\right)\right]\cdot x-\frac{KI_r}{\sqrt{\pi\cdot 50\cdot 0.5}}\cdot e^{(1-\alpha 1)\cdot \Phi I_1}\cdot\left[\frac{x\cdot\frac{KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50\cdot 0.5}}}{1+\frac{KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50\cdot 0.5}}\cdot\left(1+e^{\Phi II_1}\right)}\right]-KI_r\cdot e^{-\alpha 2\cdot \Phi I_1}, x\right] \qquad \Psi I_{1,1} = 3.662\times 10^{-4}$$

$$\Psi II_{1,r} := \frac{\frac{2}{\sqrt{\pi\cdot 50}}KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{1+\frac{KII\cdot M1_1\cdot 2}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot \Phi II_1}\cdot\left(1+e^{\Phi II_1}\right)}\cdot \Psi I_{1,r}+\frac{KII\cdot e^{-\alpha 2\cdot \Phi II_1}-\frac{2\cdot KII\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}}\cdot 0-\frac{2\cdot KII\cdot e^{(1-\alpha 2)\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}}\cdot\frac{U}{(1+U)\cdot 1}\cdot 0-\frac{\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot \Phi II_1}\cdot 0}{1+\frac{2\cdot KII\cdot M1_1\cdot e^{-\alpha 2\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}}+\frac{2\cdot KII\cdot e^{(1-\alpha 2)\cdot \Phi II_1}}{\sqrt{\pi\cdot 50}}\cdot\frac{U\cdot M1_1}{(1+U)\cdot 1}+\frac{\gamma}{1+U}\cdot e^{(1-\alpha 2)\cdot \Phi II_1}\cdot M_1}\cdot 1$$

$$x := 0.001$$

$$\Psi II_{1,1} = 1.426\times 10^{-7}$$

$$\Psi I_{j,r} := \operatorname{root}\left[x-\frac{KI_r\cdot e^{-\alpha 1\cdot \Phi I_j}}{M1_1}\cdot\left[1-\left[\frac{2}{\sqrt{\pi\cdot 50}}\cdot\left(1+e^{\Phi I_j}\right)\cdot\left[x+\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)\right]+\frac{e^{\Phi I_j}}{\sqrt{\pi\cdot 50\cdot 0.5}}\cdot\left[\frac{1}{1+e^{\Phi II_j}}\cdot\left[x+\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)\right]-\frac{\sqrt{\pi\cdot 50\cdot 0.5}}{KII\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot\left(1+e^{\Phi II_j}\right)}\cdot\left[KII\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot\left[\frac{2}{\sqrt{\pi\cdot 50}}\cdot\left[x+\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)\right]-\frac{2}{\sqrt{\pi\cdot 50}}\cdot\left(1+e^{\Phi II_j}\right)\cdot\left[\frac{\sqrt{\pi\cdot 50\cdot 0.5\cdot x}}{KI_r\cdot e^{(1-\alpha 1)\cdot \Phi I_j}}-\sqrt{\pi\cdot 50}\cdot 0.5\cdot e^{-\Phi I_j}\cdot\left[1-\frac{1}{\sqrt{\pi\cdot 50\cdot 0.5}}\cdot\left(1+e^{\Phi I_j}\right)\cdot\left[x+\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)\right]\right]\right]\right]\right]\right]\right]\right], x\right]$$

$$\Psi II_{j,r} := \frac{\frac{2}{\sqrt{\pi\cdot 50}}KII\cdot e^{-\alpha 2\cdot \Phi II_j}}{1+\frac{KII\cdot 1\cdot 2}{\sqrt{\pi\cdot 50}}\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot\left(1+e^{\Phi II_j}\right)}\cdot\sum_{i=1}^{j}\left(\Psi I_{i,r}\cdot M1_{j-i+1}\right)+\frac{\frac{2}{\sqrt{\pi\cdot 50}}\cdot KII e^{-\alpha 2\cdot \Phi II_j}-\frac{2\cdot KII\cdot e^{-\alpha 2\cdot \Phi II_j}}{\sqrt{\pi\cdot 50}}\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot M1_{j-i+1}\right)-\frac{2\cdot KII\cdot e^{(1-\alpha 2)\cdot \Phi II_j}}{\sqrt{\pi\cdot 50}}\cdot\frac{1}{(1+U)\cdot 1}\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot M1_{j-i+1}\right)-\frac{KII\cdot U}{(1+U)\cdot\gamma}\cdot e^{(1-\alpha 2)\cdot \Phi II_j}\cdot\sum_{i=1}^{j-1}\left(\Psi II_{i,r}\cdot M_{j-i+1}\right)}{1+\frac{2\cdot KII\cdot e^{-\alpha 2\cdot \Phi II_j}\cdot M1_1}{\sqrt{\pi\cdot 50}}+\frac{2\cdot KII\cdot e^{(1-\alpha 2)\cdot \Phi II_j}}{\sqrt{\pi\cdot 50}}\cdot\frac{1\cdot M1_1}{(1+U)\cdot 1}+\frac{KII\cdot U}{(1+U)\cdot\gamma}\cdot e^{(1-\alpha 2)\cdot \Phi II_j}\cdot M_1}\cdot 1$$

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

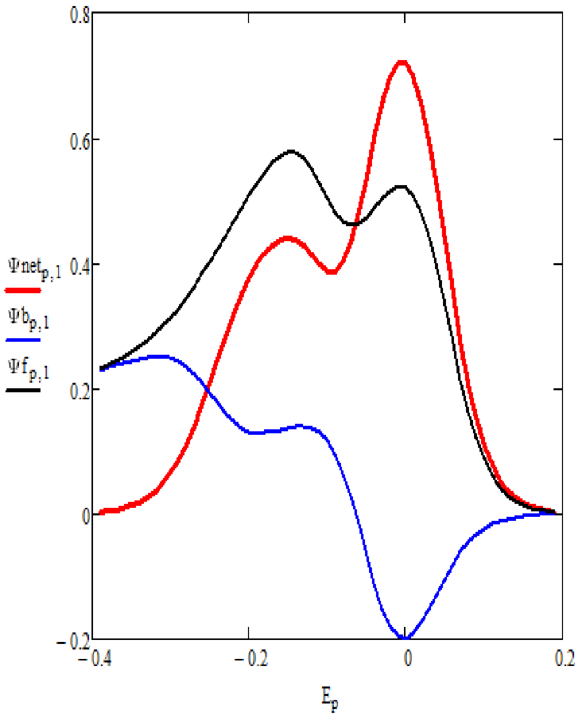
$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

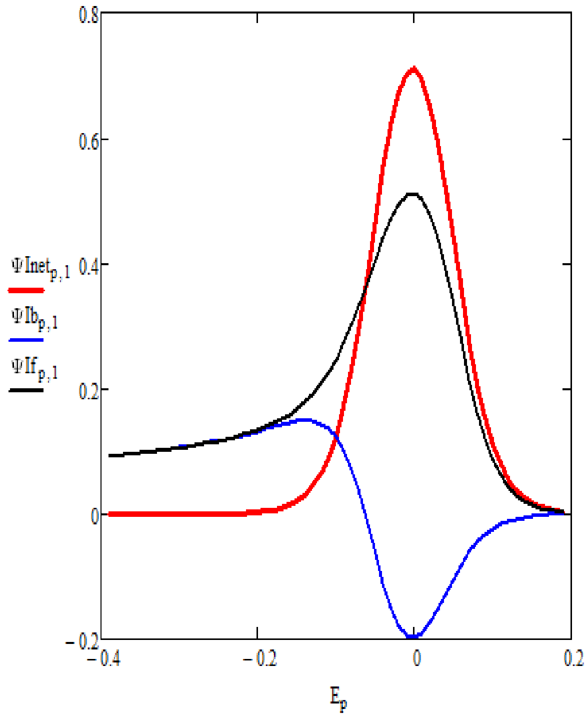
$\Psi If_{p,r} := \Psi I_{(p+1)\cdot 50,r}$ $\Psi Ib_{p,r} := \Psi I_{50\cdot p+2}$ $\Psi Inet_{p,r} := \Psi If_{p,r} - \Psi Ib_{p,r}$

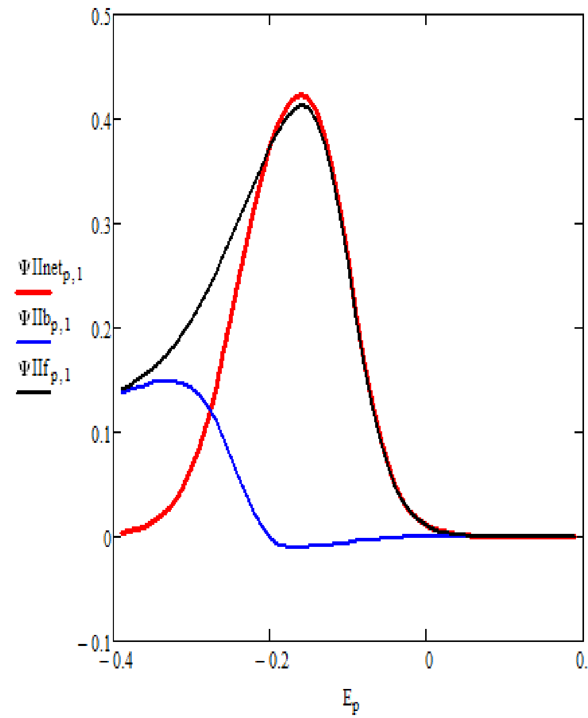
$\Psi IIb_{p,r} := \Psi II_{50\cdot p+25,r}$ $\Psi IIf_{p,r} := \Psi II_{(p+1)}$ $\Psi IInet_{p,r} := \Psi IIf_{p,r} - \Psi IIb_{p,r}$

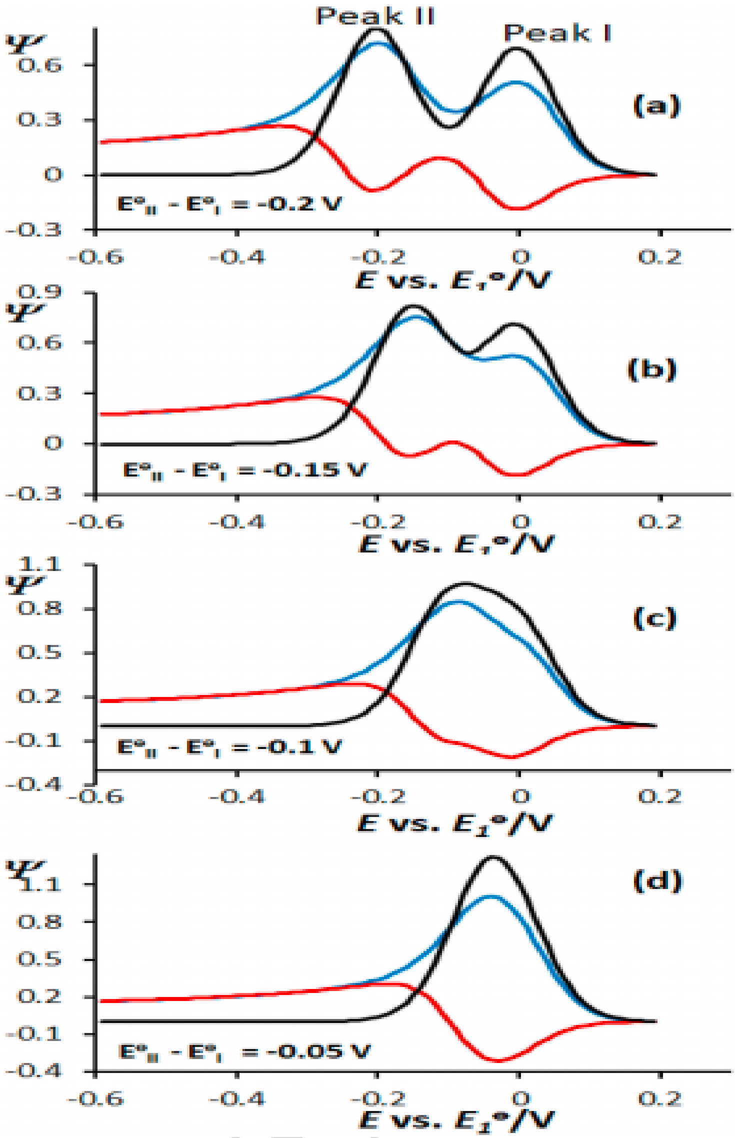
$\Psi b_{p,r} := \Psi_{50\cdot p+25,r}$ $\Psi f_{p,r} := \Psi_{(p+1)\cdot 5(}$ $\Psi net_{p,r} := \Psi f_{p,r} - \Psi b_{p,r}$

$E_p := EsI - p\cdot dE$









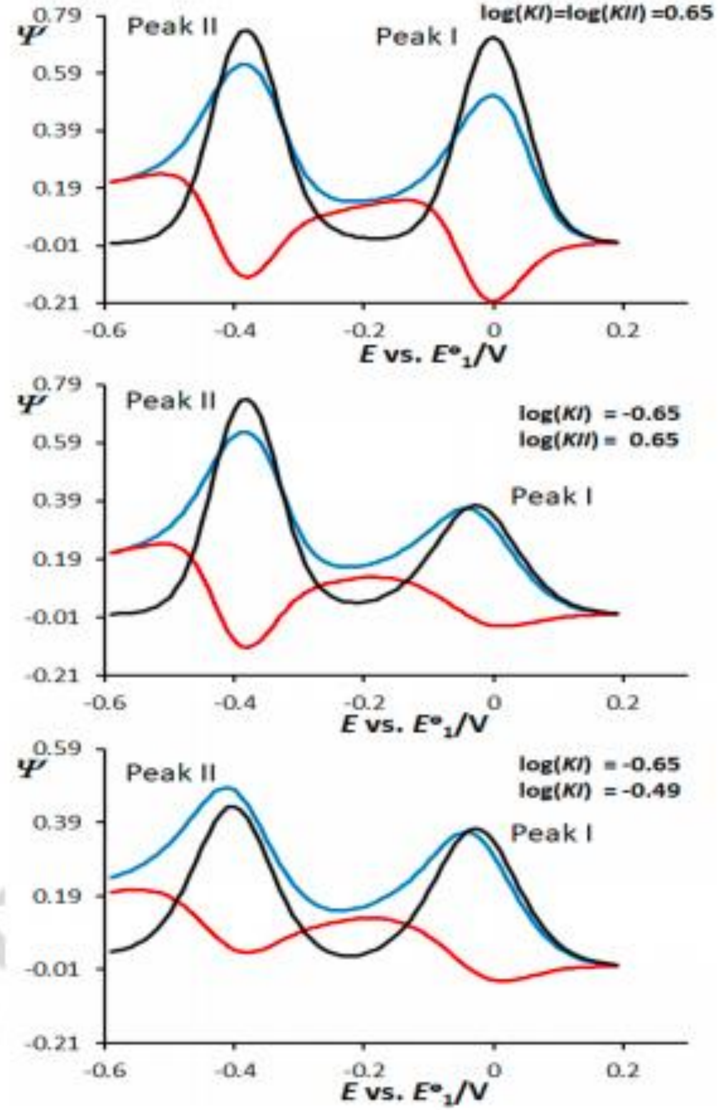


Fig. 2 Square-wave voltammograms of the EECr mechanism when the second electrode reaction occurs at 400 mV more negative potentials than the first one. Voltammetric patterns reflect the effect of the rate of electron transfers, characterized with different values of the electrode kinetic parameters, as given in the plot. The parameters of the chemical reaction are $K_{chemical} = 10^{-3}$ and $K_{eq} = 10^{3}$. Other simulation parameters are same as those in Fig. 1

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