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Supplementary Materials

Multistep Surface Electrode Mechanism Coupled with Preceding Chemical Reaction-Theoretical Analysis in Square-Wave Voltammetry

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MATHCAD working file for simulation of theoretical voltammograms of a Surface CEE Mechanism

Meaning of the symbols:

$potI_j$ and $potII_j$ are symbols for time-dependent potential in SWV

j and k- are symbols of the magnitude of potential steps applied

r - is a counter parameter

R - is universal gas constant

x - is symbol for initiation of calculation of the complex equation for current estimation

ΔE – is the potential width of simulation

S_k – is numerical integration parameter

$\alpha 1$ and $\alpha 2$ – are symbols for the electron transfer coefficients of the first and second electron transfer step, respectively

Meaning of other symbols is given in the working file

TWO STEP SURFACE CEE MECHANISM
MATHEMATICAL MODEL **IN**
SQUARE WAVE VOLTAMMETRY

KI and KII are kinetic parameters related to the first and second electron transfer step
alpha is the electron transfer coefficient
EsI and EsII are potentials related to the first and the second electron transfer step
n is number of electron exchanged
F is Faraday constant
Esw is SWV amplitude
T is temperature
dE is potential step
Φ is dimensionless potential
Ψ is dimensionless current
K is equilibrium constant -Keq
z is dimensionless chemical parameter-Kchemical = ε/f

$EsI := 0.2 \quad \Delta E := 0.8 \quad dE := 0.01 \quad Esw := 0.05 \quad EsII := 0.6 \quad r := 1..1$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad KI_r := 10^{0\cdot r}$

$KII := 10^{0}$

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

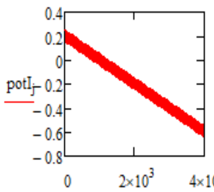
$\alpha 2 := 0.5 \quad \alpha 1 := 0.5 \quad \log(KI_r) = \boxed{0}$

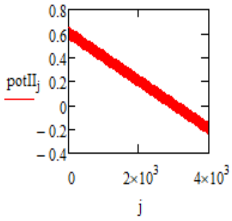
$$potI_j := EsI + Esw - \left[\left(ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right),1,-1\right)\cdot Esw + Esw\right) - dE\right]$$

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

$K := 0.1$

$z := 2$





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

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

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

$x := 0.001$

$$\Psi I_{1,r} := root\left[\left[\frac{\frac{KI_r\cdot e^{-\alpha 1\cdot\Phi I_1}\cdot K}{1+K}\cdot\left(1-\frac{1}{50}\cdot 0\right)-(z)^{-1}\cdot KI_r\cdot\left(\frac{1}{1+K}\right)\cdot(-1)\cdot e^{-\alpha 1\cdot\Phi I_1}\cdot 0-\frac{KI_r}{50}\cdot e^{\Phi I_1\cdot(1-\alpha 1)}\cdot 0}{\frac{KI_r\cdot e^{-\alpha 1\cdot\Phi I_1}\cdot K}{1+K}\cdot\frac{1}{50}+1+(z)^{-1}\cdot KI_r\cdot(-1)\cdot\left(\frac{1}{1+K}\right)\cdot S_1\cdot e^{-\alpha 1\cdot\Phi I_1}+\frac{KI_r}{50}\cdot e^{\Phi I_1\cdot(1-\alpha 1)}}\cdot(1+0)\right]\cdot x-\frac{KI_r}{50}\cdot e^{(1-\alpha 1)\cdot\Phi I_1}\cdot\left[\frac{x\cdot\frac{KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{50}}{1+\frac{KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{50}\cdot\left(1+e^{\Phi II_1}\right)}\right]-KI_r\cdot e^{-\alpha 2\cdot\Phi I_1},x\right]$$

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

$$\Psi I_{j,r} := \mathrm{root}\left[x - KI_r\cdot e^{-\alpha 1\cdot\Phi I_j}\cdot 1\cdot\left[\frac{\frac{1\cdot K}{1+K}\cdot\left[1-\frac{1}{50}\cdot\left(x+\sum_{i=1}^{j-1}\Psi I_{i,r}\right)\right]-(z)^{-1}\cdot 1\cdot\left(\frac{1}{1+K}\right)\cdot(-1)\cdot e^{0}\cdot\left[x+\sum_{i=1}^{j-1}\left(\Psi I_{i,r}\cdot S_{j-i+1}\right)\right]-0}{\frac{1\cdot K}{1+K}\cdot\frac{KI_r\cdot e^{-\alpha 1\cdot\Phi I_j}}{50}+1+(z)^{-1}\cdot KI_r\cdot(-1)\cdot\left(\frac{1}{1+K}\right)\cdot S_1\cdot e^{-\alpha 1\cdot\Phi I_j}+KI_r\cdot e^{(1-\alpha 1)\cdot\Phi I_j}}+\frac{e^{\Phi I_j}}{0.02\cdot\left[\frac{1\cdot K}{1+K}\cdot\frac{KI_r\cdot e^{-\alpha 1\cdot\Phi I_j}}{1}+1+(z)^{-1}\cdot\frac{KI_r}{50}\cdot(-1)\cdot\left(\frac{1}{1+K}\right)\cdot S_1\cdot e^{-\alpha 1\cdot\Phi I_j}+KI_r\cdot e^{(1-\alpha 1)\cdot\Phi I_j}\right]}\cdot\left[\frac{1}{1+e^{\Phi II_j}}\cdot\left(x+\sum_{i=1}^{j-1}\Psi I_{i,r}\right)-\frac{50}{KII\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot\left(1+e^{\Phi II_j}\right)}\cdot\left[KII\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot\left[\frac{1}{50}\cdot\left(x+\sum_{i=1}^{j-1}\Psi I_{i,r}\right)-\frac{1}{50}\cdot\left(1+e^{\Phi II_j}\right)\cdot\left[\frac{50\cdot x}{KI_r\cdot e^{(1-\alpha 1)\cdot\Phi I_j}}-50\cdot e^{-\Phi I_j}\cdot\left[1-\frac{1}{50}\cdot\left(1+e^{\Phi I_j}\right)\cdot\left(x+\sum_{i=1}^{j-1}\Psi I_{i,r}\right)\right]\right]\right]\right]\right]\right], x\right]$$

$$\Psi II_{j,r} := \frac{KII\cdot e^{-\alpha 2\cdot\Phi II_j}}{50+KII\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot\left(1+e^{\Phi II_j}\right)}\cdot\sum_{i=1}^{j}\Psi I_{i,r}-\frac{KII\cdot e^{(-\alpha 2)\cdot\Phi II_j}\cdot\left(1+e^{\Phi II_j}\right)}{50+KII\cdot e^{-\alpha 2\cdot\Phi II_j}\cdot\left(1+e^{\Phi II_j}\right)}\cdot\sum_{i=1}^{j-1}\Psi II_{i,r}$$

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

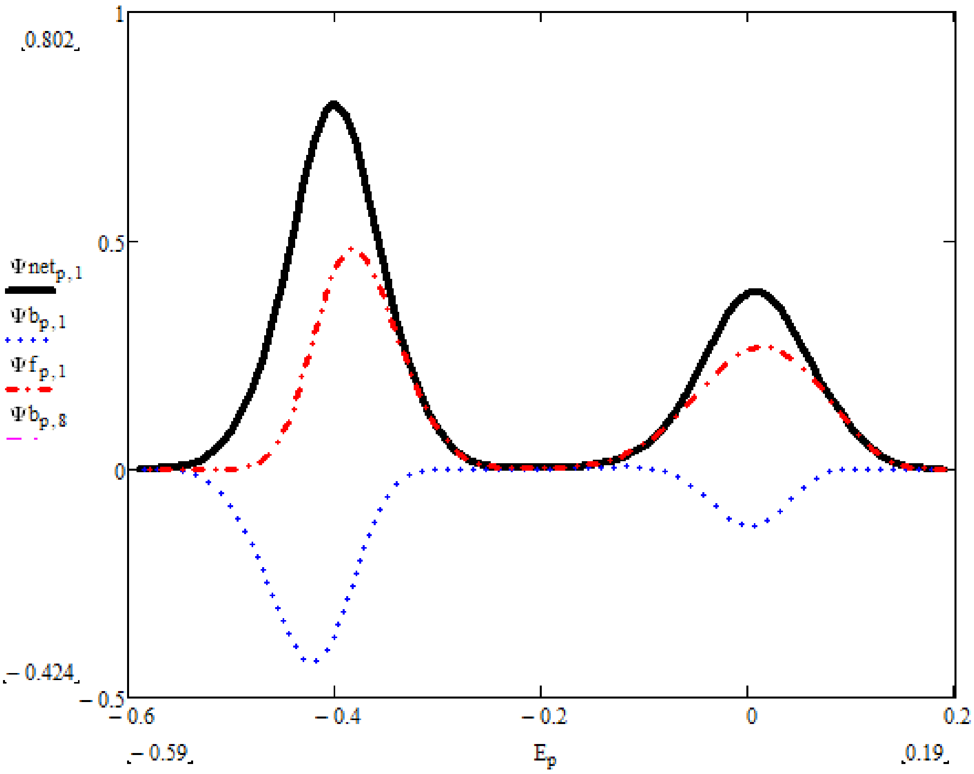
$$p := 1..\left(\frac{\Delta E}{dE}\right)-1$$

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

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

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

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



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