Integrating Multiple Electrode Reaction Pathways within a Single Square-Wave Voltammetric Framework-MATHCAD working file

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TWO STEP DIFFUSIONAL ECrevEC'cat Mechanism in SWV

$$E_1:\ \text{Red} \rightleftarrows \text{Int1} + e^- \quad (k_{s,1;}\alpha_1) \tag{a}$$

$$C_{rev}:\ \text{Int1} \rightleftarrows \text{Int2} \quad \left(k_f, k_b;\ K_{eq} = \frac{k_f}{k_b};\ k_{chem} = k_f + k_b\right) \tag{b}$$

$$E_2:\ \text{Int2} \rightleftarrows \text{Ox} + e^- \quad (k_{s,2}, \alpha_2) \tag{c}$$

$$C'(\text{regenerative}):\ \text{Ox} + \text{Y} \rightarrow \text{Int2} \quad (k_c) \tag{d}$$

$EsI := -0.4$ $\Delta E := 1$ $dE := 0.01$ $Esw := 0.05$ $f := 10$ $EsII := -0.7$ $kc := 5$

$n := 1$ $F := 96500$ $R := 8.314$ $T := 298.15$ $\alpha 1 := 0.5$ $kf := 1$

$ks1 := 0.1$ $kb := 2$

$ks2 := 0.1$ $\alpha 2 := 0.5$

$j := 1 .. \frac{\Delta E}{dE} \cdot 50$ $D := 0.000005$

$$Keq := \frac{kf}{kb}$$

$$Kchem := \left(\frac{kf + kb}{f}\right)$$

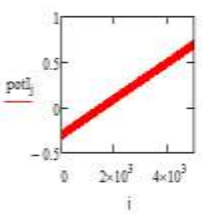
$$Kcat := \frac{kc}{f}$$

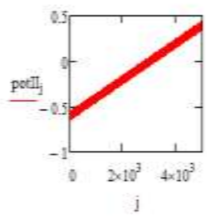
$$KI := \frac{ks1}{(D \cdot f)^{0.5}}$$

$$KII := \frac{ks2}{(D \cdot f)^{0.5}}$$

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

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





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

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

$$S_j := \sqrt{j} - \sqrt{j-1}$$

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

$$\Psi I_1 := \frac{KI \cdot e^{\alpha 1 \cdot \Phi I_1}}{1 - KI \cdot e^{\alpha 1 \cdot \Phi I_1} \cdot \left[\frac{-2}{\sqrt{50\pi}} \cdot \left(\left(1 + \frac{e^{-\Phi I_1}}{1 + Keq}\right)\right) - \frac{KI \cdot e^{-\Phi I_1} \cdot A_1}{\sqrt{Kchem} \cdot (Keq + 1)}\right]}$$

$$\Psi II_1 := \frac{KII \cdot \frac{1}{\sqrt{Kchem}} \cdot e^{\alpha 2 \cdot \Phi II_1}}{1 + \frac{1 \cdot B_1}{(\sqrt{Kcat})} \cdot KII \cdot e^{\Phi II_1 \cdot \alpha 2} + \frac{1 \cdot B_1}{(\sqrt{Kcat})} \cdot KII \cdot e^{-\Phi II_1 \cdot (1 - \alpha 2)}}$$

$$\Psi I_1 = 7.521 \times 10^{-7} \qquad \Psi II_1 = 1.176 \times 10^{-10}$$

$$\Psi I_j := \frac{KI \cdot e^{\alpha 1 \cdot \Phi I_j} \cdot \left[1 - \frac{2}{\sqrt{50\pi}} \cdot \left(1 + \frac{e^{-\Phi I_j}}{1 + Keq}\right) \cdot \sum_{i=1}^{j-1} \left(\Psi I_i \cdot S_{j-i+1}\right) - \frac{KI \cdot e^{-\Phi I_j}}{(1 + Keq) \cdot \sqrt{Kchem}} \cdot \sum_{i=1}^{j-1} \left(\Psi I_i \cdot A_{j-i+1}\right)\right]}{1 - KI \cdot e^{\alpha 1 \cdot \Phi I_j} \cdot \left[\frac{-2}{\sqrt{50\pi}} \cdot \left(\left(1 + \frac{e^{-\Phi I_j}}{1 + Keq}\right)\right) - \frac{KI \cdot e^{-\Phi I_j} \cdot A_1}{\sqrt{Kchem} \cdot (Keq + 1)}\right]}$$

Meaning of the symbols of defined parameters:

-**kf and kb** are rate constants of the forward and backward chemical steos, respectively

-**kc** is rate constant of regenerative step

-**ks1 and ks2** are standard rate constants rekated to the first and second electron transfer step, respectively

-D is diffusion coefficient (equal for all redox species)

-**Kchem** is dimensionless chemical parameter

-**Keq** is equilibrium constant of intermediate chemical reaction

-**KI and KII** are dimensionless rate parameters related to the first and second electron transfer step, respectively

-**Kcat** is dimensionless catalytic parameter

-**ΦI and ΦII** are dimensionless potentials

-j is serial number of time increments

A_j B_j S_j are numerical integration parameters

-n is number of electrons exchanged
-dE is potential step
-Esw is square-wave amplitude
-f is SW frequency

-**EsI and EsII** are stadard potential of first and second electron trasfer step respectively
-**α1 and α2** are electron transfer coefficients related to the first and cesond electron transfer step, respectively
-**F, R and T** are faraday constant, Gas constant and temperautre, respectively

-**potI and potII** are potential modulations related to the first (E1) and second (E2) electron transfer step, respectively

$$\Psi I_j := \frac{KI \cdot e^{\alpha 1 \cdot \Phi I_j} \cdot \left[1 - \frac{2}{\sqrt{50\pi}} \cdot \left(1 + \frac{e^{-\Phi I_j}}{1 + Keq} \right) \cdot \sum_{i=1}^{j-1} \left(\Psi I_i \cdot S_{j-i+1} \right) - \frac{KI \cdot e^{-\Phi I_j}}{(1 + Keq) \cdot \sqrt{Kchem}} \cdot \sum_{i=1}^{j-1} \left(\Psi I_i \cdot A_{j-i+1} \right) \right]}{1 - KI \cdot e^{\alpha 1 \cdot \Phi I_j} \cdot \left[\frac{-2}{\sqrt{50\pi}} \cdot \left(\left(1 + \frac{e^{-\Phi I_j}}{1 + Keq} \right) \right) - \frac{KI \cdot e^{-\Phi I_j} \cdot A_1}{\sqrt{Kchem} \cdot (Keq + 1)} \right]}$$

$$\Psi II_j := \frac{\frac{2KII}{\sqrt{50 \cdot \pi}} \cdot 1 \cdot e^{\alpha 2 \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_i \cdot S_{j-i+1} \right) - \frac{KII}{\left[(1 + Keq) \cdot \sqrt{Kchem} \right]} \cdot e^{\alpha 2 \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_i \cdot A_{j-i+1} \right) - \frac{1}{\left(\sqrt{Kcat} \right)} KII \cdot e^{\Phi II_j \cdot \alpha 2} \cdot \sum_{i=1}^{j-1} \left(\Psi II_i \cdot B_{j-i+1} \right) - \frac{1}{\left(\sqrt{Kcat} \right)} KII \cdot e^{-\Phi II_j \cdot (1 - \alpha 2)} \cdot \sum_{i=1}^{j-1} \left(\Psi II_i \cdot B_{j-i+1} \right)}{1 + \frac{1 \cdot B_1}{\left(\sqrt{Kcat} \right)} KII \cdot e^{\Phi II_j \cdot \alpha 2} + \frac{1 \cdot B_1}{\left(\sqrt{Kcat} \right)} KII \cdot e^{-\Phi II_j \cdot (1 - \alpha 2)}}$$

$$\Psi_j := \Psi I_j + \Psi II_j$$

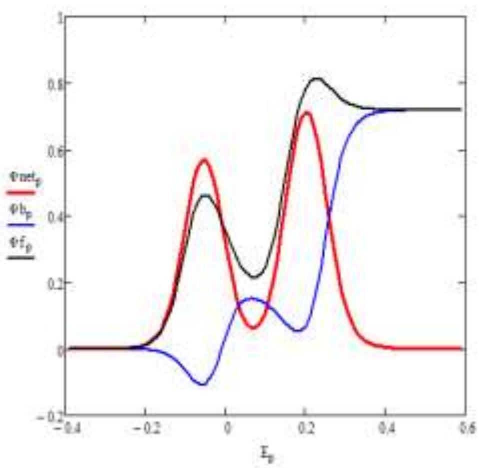
$$p := 1 .. \left(\frac{\Delta E}{dE} \right) - 1$$

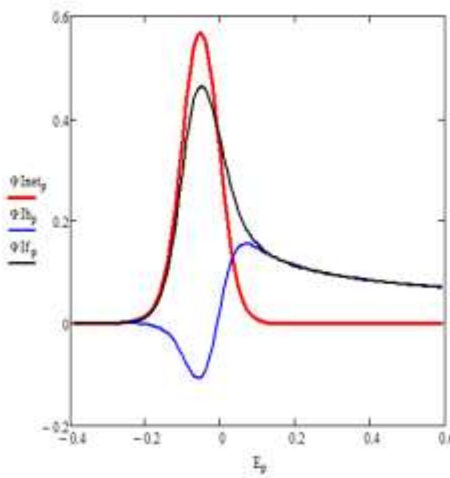
$$\Psi If_p := \Psi I_{(p+1) \cdot 50} \qquad \Psi Ib_p := \Psi I_{50 \cdot p + 25} \qquad \Psi Inet_p := \Psi If_p - \Psi Ib_p$$

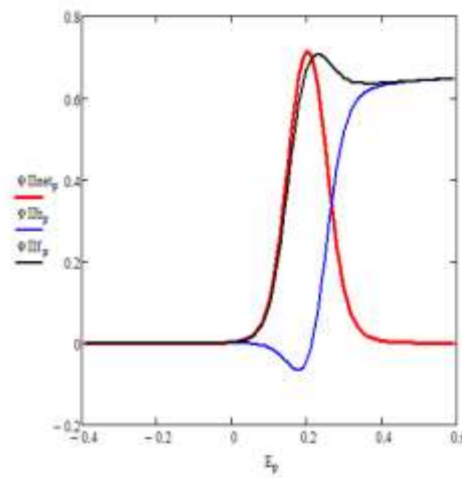
$$\Psi IIb_p := \Psi II_{50 \cdot p + 25} \qquad \Psi IIf_p := \Psi II_{(p+1) \cdot 50} \qquad \Psi IInet_p := \Psi IIf_p - \Psi IIb_p$$

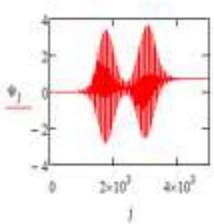
$$E_p := EsI + p \cdot dE$$

$$\Psi b_p := \Psi_{50 \cdot p + 25} \qquad \Psi f_p := \Psi_{(p+1) \cdot 50} \qquad \Psi net_p := \Psi f_p - \Psi b_p$$









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