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SUPPLEMENTARY MATERIAL

DECODING THE FEATURES OF BIOCHEMICAL MULTISTEP ELECTRON-TRANSFER PATHWAYS WITH THE TWO-STEP DOUBLE-REGENERATIVE ELECTROCHEMICAL MECHANISM IN SQUARE-WAVE VOLTAMMETRY

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Two-step Double-regenerative EC'EC" Mechanism in SWV

$EsI := -0.4 \quad \Delta E := 1 \quad dE := 0.01 \quad Esw := 0.05 \quad f := 10 \quad EsII := -0.7 \quad r := 1..1$

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

$ks1 := 0.1 \quad \alpha 2 := 0.5$

$j := 1..\frac{\Delta E}{dE} \cdot 50 \quad ks2 := 0.1$

$D := 0.000005$

$f := 10$

$kc1 := 100$

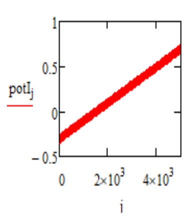
$kc2 := 200$

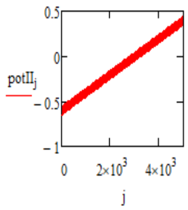
$$potI_j := (EsI + Esw) + \left[\left(ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$$

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

$$K1 := \frac{ks1}{(D\cdot f)^{0.5}} \qquad K2 := \frac{ks2}{(D\cdot f)^{0.5}}$$

$$Kchem1 := \frac{kc1}{f} \qquad Kchem2 := \frac{kc2}{f}$$





$$A_j := \left(1 - erfc\left(\sqrt{\frac{Kchem1}{50\times 1}\cdot j}\right)\right) - \left[1 - erfc\left[\sqrt{\frac{Kchem1}{50\times 1}\cdot(j-1)}\right]\right]$$

$$B_j := \left(1 - erfc\left(\sqrt{\frac{Kchem2}{50\times 1}\cdot j}\right)\right) - \left[1 - erfc\left[\sqrt{\frac{Kchem2}{50\times 1}\cdot(j-1)}\right]\right]$$

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

$$\Psi I_1 := \frac{K1\cdot e^{\alpha 1\cdot\Phi I_1}}{1 + K1\cdot Kchem1^{-.5}\cdot A_1\cdot e^{\alpha 1\cdot\Phi I_1}\cdot\left(1 + e^{-\Phi I_1}\right)}$$

$$\Psi II_1 := \frac{Kchem1^{-.5}K2\cdot e^{\alpha 2\cdot\Phi II_1}}{1 + K2\cdot A_1\cdot e^{\alpha 2\cdot\Phi II_1}\cdot\left(1 + e^{-\Phi II_1}\right)}\cdot\Psi I_1\cdot A_1$$

$\Psi I_1 = 8.082\times 10^{-6} \qquad \Psi II_1 = 0$

R - 1e- ⇄ Ox1	(first electron transfer step; $(k_{s,1}, \alpha_1)$)	(a)
Ox1 + Y → R	(EC' regeneration, $k_{c,1}$)	(b)
Ox1 - 1e- ⇄ Ox2	(second electron transfer step; $(k_{s,2}, \alpha_2)$)	(c)
Ox2 + Y → Ox1	(EC" regeneration, $k_{c,2}$)	(d)

Meaning of the symbols of defined parameters:

-**kc,1 and kc2 are the** rate constants of first and second regenerative step, respectively

-**Kchem1 and Kchem2 are** dimensionless chemical (regenerative) parameters related to the first and second regenerative step, respectively

-**K1 and K2** are dimensionless rate parameters related to the first and second electron transfer step, respectively

-**ks1 and ks2** are standard rate constants of first and second electron transfer steps, respectively

-**ΦI and ΦII** are dimensionless potentials

-**D** is symbol for the diffusion coefficient (assumed to be identical for all redox active species involved in the mechanism

-**j** is serial number of time increments

A_j B_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 trafer 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 and second electron transfer step, respectively

-**Ψ** is symbol for the dimensionless current

Entire simulation protocol for calculating square-wave voltammograms in Mathcad is available for free in:

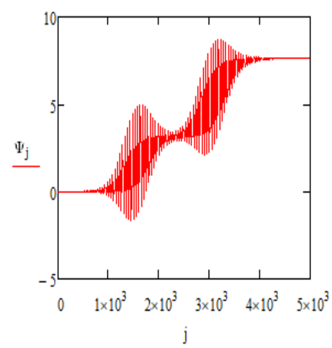
Gulaboski, R.; Mirceski, V. J. Solid State Electrochem. Square-Wave Voltammetry of Two-Step Diffusional Electrode Mechanism Coupled with a Reversible Follow-Up Chemical Reaction. *J. Solid State Electrochem.* **2021**, *25*, 2893-2901. https://doi.org/10.1007/s10008-021-05027-4

30 days free trial version of Mathcad available at:
https://support.ptc.com/products/mathcad/mathcad-15-0/free-trial?refid=cadventure

$$\Psi I_j := \frac{K1 \cdot e^{\alpha 1 \cdot \Phi I_j} \cdot \left[1 - \frac{1 + e^{-\Phi I_j}}{\sqrt{Kchem1}} \cdot \sum_{i=1}^{j-1} \left(\Psi I_i \cdot A_{j-i+1} \right) \right]}{1 + K1 \cdot \frac{1}{\sqrt{Kchem1}} \cdot A_1 \cdot e^{\alpha 1 \cdot \Phi I_j} \cdot \left(1 + e^{-\Phi I_j} \right)}$$

$$\Psi II_j := \frac{K2 \frac{1}{\sqrt{Kchem1}} \cdot e^{\alpha 2 \cdot \Phi II_j} \cdot \sum_{i=1}^{j} \left(\Psi I_i \cdot A_{j-i+1} \right) - \frac{1}{\left(\sqrt{Kchem2}\right)} K2 \cdot e^{\Phi II_j \cdot \alpha 2} \cdot \sum_{i=1}^{j-1} \left(\Psi II_i \cdot B_{j-i+1} \right) - \frac{1}{\left(\sqrt{Kchem2}\right)} K2 \cdot e^{-\Phi II_j \cdot (1-\alpha 2)} \cdot \sum_{i=1}^{j-1} \left(\Psi II_i \cdot B_{j-i+1} \right)}{1 + \frac{1 \cdot B_1}{\left(\sqrt{Kchem2}\right)} K2 \cdot e^{\Phi II_j \cdot \alpha 2} + \frac{1 \cdot B_1}{\left(\sqrt{Kchem2}\right)} K2 \cdot e^{-\Phi II_j \cdot (1-\alpha 2)}}$$

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



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

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

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

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

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