Voltammetric Response of a Two-Step EC’EC’ Double Regenerative Mechanism: First MATHCAD Protocol for Square-Wave Voltammetric Analysis

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Abstract

A two-step electrode mechanism in which **each electron-transfer step is followed by an irreversible regenerative chemical reaction (EC′EC′)** is theoretically analyzed under conditions of square-wave voltammetry (SWV). For the first time, a **complete MATHCAD simulation protocol** is developed and presented in open free format, which is related to theoretical modeling the voltammetric behavior of such a doubly catalytic system, enabling systematic variation of all kinetic, thermodynamic, and instrumental parameters. The model accounts for semi-infinite planar diffusion and electron transfer governed by Butler–Volmer kinetics, while the rates of both irreversible chemical regenerations are expressed through dimensionless catalytic parameters. Simulated voltammograms reveal the characteristic catalytic peak enhancement, potential shifts, and dependence of net peak currents on the kinetic strength of both regenerative steps. This mechanism is electrochemically important because it describes systems such as enzyme-mediated redox cascades, catalytic metal complex recycling, two-step reduction of polyphenols (resveratrol, quercetin, for example), electrocatalytic sensing interfaces, and other biochemically important multi-electron transformations. The provided MATHCAD file enables open, reproducible, and fully interactive exploration of this mechanistic class.

TWO STEP DIFFUSIONAL EC'EC'cat Mechanism in SWV--Oxidation Version 11 11 2025

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

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

$KI_r := 10^{.75 \cdot r}$

$KII := 10^{.75}$

$f := 10$

$kc1 := 100$

$kc2 := 200$

A - 1e = B
B+Y-->A
B - 1e = C
C+Z -->B

λ i z se definirani kako r
na Kc1/f i kc2/f

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

$\alpha 2 := 0.5$

$\alpha 1 := 0.5 \qquad \log(KI_r) =$

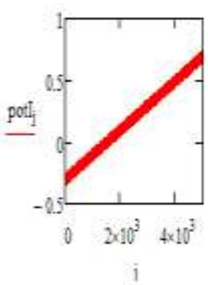
$\lambda := .40612400001$

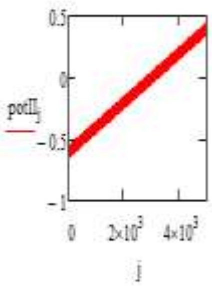
$$potI_j := (EsI + Esw) + \left[\left(ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right) \cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25} \cdot \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]$$

$KI_1 = 5.623$

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

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





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

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

$z := .5001$

z e kataliticki parametar vo ovoj model povrzan so vtor cekor

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

$x := 0.001$

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

$\alpha \cdot \Phi_1$

$$\Psi II_{1,r} := \frac{\lambda^{-.5} KII \cdot e^{\alpha 2 \cdot \Phi II_1}}{1 + \frac{KII \cdot A_1 \cdot 2}{\sqrt{\pi \cdot 50}} \cdot e^{\alpha 2 \cdot \Phi II_1} \cdot \left(1 + e^{-\Phi II_1}\right)} \cdot \Psi I_{1,r} \cdot A_1$$

$$\Psi I_{1,1} = 7.59 \times 10^{-6}$$

$$\Psi II_{1,1} = 0$$

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

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

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

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

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

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

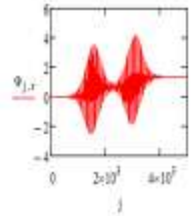
$E_p := EsI + p \cdot dE$

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

$\Phi_{j,r} := \Phi I_{j,r} + \Phi II_{j,r}$

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

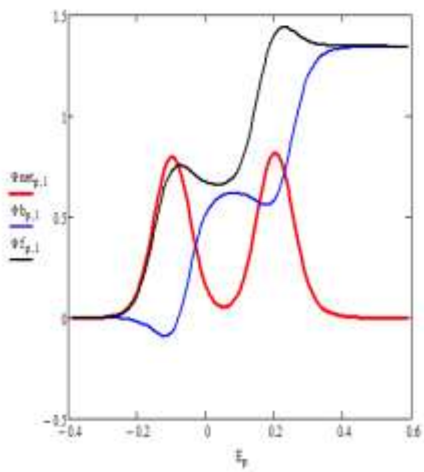
$\Phi If_{p,r} := \Phi I_{(p+1) \cdot 50,r}$ $\Phi Ib_{p,r} := \Phi I_{50 \cdot p+25,r}$ $\Phi Inet_{p,r} := \Phi If_{p,r} - \Phi Ib_{p,r}$

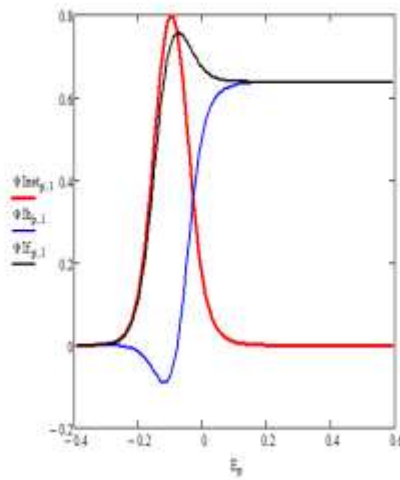


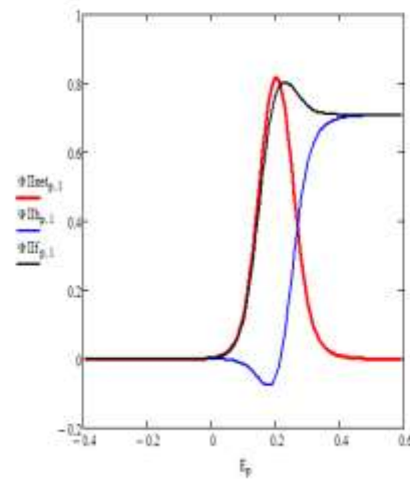
$\Phi IIb_{p,r} := \Phi II_{50 \cdot p+25,r}$ $\Phi IIf_{p,r} := \Phi II_{(p+1) \cdot 50,r}$ $\Phi IInet_{p,r} := \Phi IIf_{p,r} - \Phi IIb_{p,r}$

$E_p := EsI + p \cdot dE$

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







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