

Supplementary Material

PDF version of File 2. MATHCAD simulation protocol of ECrev mechanism

FROM THEORY TO SIMULATION: OPEN INTERACTIVE MATHCAD SIMULATION PROTOCOLS FOR EXPLORING COMMON ELECTRODE MECHANISMS IN CYCLIC VOLTAMMETRY

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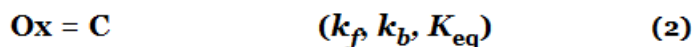
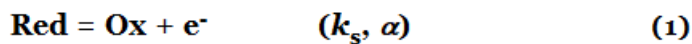
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EC_{rev} electrode mechanism at a planar electrode of a dissolved redox couple in Cyclic Staircase Voltammetry



$E_s := -0.5$ starting potential (in V vs. the formal potential)

$E_f := 0.5$ switching potential (in V vs. the formal potential)

$dE := 0.005$ potential step increment (in V)

$\Delta E := E_f - E_s$ potential window

$v := 0.1$ potential scan rate in V/s

$\tau := \frac{dE}{v}$ duration of a single step (in s)

$\tau = 0.05$

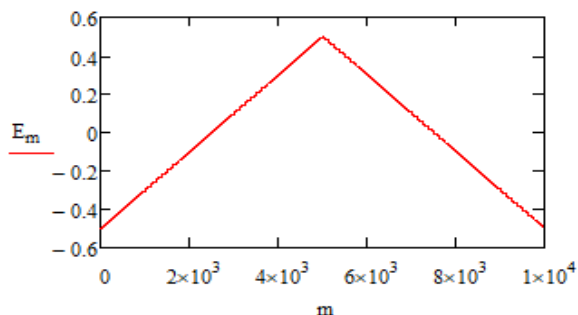
$M := 25$ number of time increments in a single potential step

$d := \frac{\tau}{M}$ time increment (in s)

$2 \cdot \frac{\Delta E}{dE} = 400$ total number of potential steps

$\frac{m}{25} := 1..2 \cdot \frac{\Delta E}{dE} \cdot 25$ serial number of time increments

$$E_m := \text{if} \left[m \leq \frac{\Delta E}{dE} \cdot 25, E_s + \left(\text{ceil} \left(\frac{m}{25} \right) \cdot dE - dE \right), E_f - \left[\text{ceil} \left[\frac{m - \left(\frac{\Delta E}{dE} \cdot 25 \right)}{25} \right] \cdot dE - dE \right] \right] \quad \text{potential ramp} \quad (3)$$



$$F := 96485$$

Faraday constant

$$T := 298.15$$

thermodynamic temperature

$$R := 8.314$$

Gass constant

$$n := 1$$

stoichiometric number of electrons

$$\Phi_{em} := n \cdot \frac{F}{R \cdot T} \cdot E_m$$

dimensionless potential **(4)**

$$D := 5 \cdot 10^{-6}$$

common diffusion coefficient in cm²/s

$$k_s := 0.005$$

electrochemical standard rate constant in cm/s

$$\alpha := 0.5$$

electron transfer coefficient

$$k_f := 3$$

forward rate constant of the chemical reaction in s⁻¹

$$k_b := 10$$

backward rate constant of the chemical reaction in s⁻¹

$$K_{eq} := \frac{k_f}{k_b}$$

equilibrium constant of the follow-up chemical reaction

$$K := \frac{k_s \cdot \sqrt{\tau}}{\sqrt{D}}$$

dimensionless electrode kinetic parameter

$$K_{chem} := (k_f + k_b) \cdot \tau$$

dimensionless chemical kinetic parameter

$$S_{\infty m} := \sqrt{m} - \sqrt{m-1} \quad \text{numerical integration parameter} \quad (5)$$

$$M_{\infty m} := \operatorname{erf}\left(\sqrt{\frac{K_{\text{chem}}}{25} m}\right) - \operatorname{erf}\left[\sqrt{\frac{K_{\text{chem}}}{25} (m-1)}\right] \quad \text{numerical integration parameter} \quad (6)$$

$$\Psi_m := \frac{K \cdot e^{\alpha \cdot \Phi_1}}{1 - K \cdot e^{\alpha \cdot \Phi_1} \left[\frac{-2}{\sqrt{25\pi}} \left(1 + \frac{e^{-\Phi_1}}{1 + K_{\text{eq}}} \right) - \frac{K_{\text{eq}} e^{-\Phi_1} \cdot M_1}{(1 + K_{\text{eq}}) \cdot \sqrt{K_{\text{chem}}}} \right]} \quad (7)$$

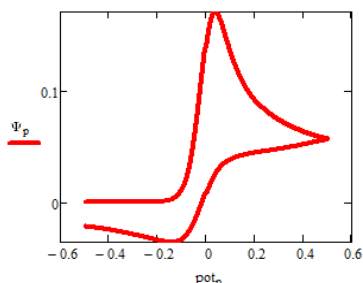
Recurrent formulas for calculating the dimensionless current

$$\Psi_m := \frac{K \cdot e^{\alpha \cdot \Phi_m} \left[1 - \frac{2}{\sqrt{25\pi}} \left(1 + \frac{e^{-\Phi_m}}{1 + K_{\text{eq}}} \right) \cdot \sum_{j=1}^{m-1} (\Psi_j \cdot S_{m-j+1}) - \frac{K_{\text{eq}} e^{-\Phi_m}}{(1 + K_{\text{eq}}) \cdot \sqrt{K_{\text{chem}}}} \cdot \sum_{j=1}^{m-1} (\Psi_j \cdot M_{m-j+1}) \right]}{1 - K \cdot e^{\alpha \cdot \Phi_m} \left[\frac{-2}{\sqrt{25\pi}} \left(1 + \frac{e^{-\Phi_m}}{1 + K_{\text{eq}}} \right) - \frac{K_{\text{eq}} e^{-\Phi_m} \cdot M_1}{(1 + K_{\text{eq}}) \cdot \sqrt{K_{\text{chem}}}} \right]} \quad (8)$$

$$p := 1..2 \cdot \frac{\Delta E}{dE} - 1 \quad \text{serial number of potential steps} \quad (9)$$

$$\Psi_p := \Psi\left(\frac{\tau}{d \cdot 25} + p\right) \quad \text{dimensionless current at the end of each potential step} \quad (10)$$

$$\text{pot}_p := \text{if} \left[p \leq \frac{\Delta E}{dE} \cdot E_s + p \cdot dE, E_f - \left(p - \frac{\Delta E}{dE} \right) \cdot dE \right] \quad \text{potential value of each potential step in V} \quad (11)$$



dimensionless cyclic staircase voltammogram

$$S = 0.05 \quad \text{electrode surface area in cm}^2$$

$$c_{\infty} := 1 \cdot 10^{-6} \quad \text{bulk concentration of the electroactive reactant in mol/cm}^3$$

$$A_{\infty} := n \cdot F \cdot S \cdot c_{\infty} \cdot \left(\sqrt{\frac{D}{\tau}} \right) \quad \text{amperometric constant}$$

$$I_p := 10^6 \cdot \Psi_p \cdot A \quad \text{real current in } \mu\text{A}$$

