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Education

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

$$\mathbf{Red = Ox + e^-} \qquad (k_s, \alpha) \qquad \mathbf{(1)}$$

$$\mathbf{Ox = C} \qquad (k_f, k_b, K_{eq}) \qquad \mathbf{(2)}$$

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

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

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

$\Delta E := Ef - Es$ potential window

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

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

$\tau = 0.05$

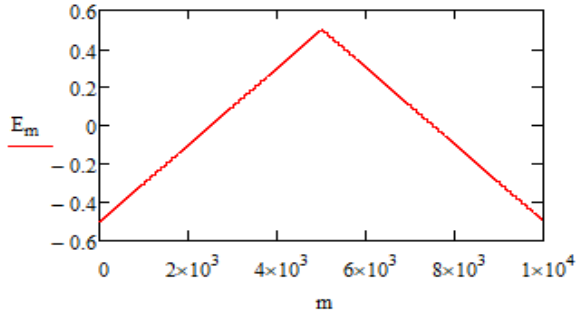
$M := 25$ numer of time increments in a single potential step

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

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

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

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



$F := 96485$ Faraday constant

$T := 298.15$ thermodynamic temperature

$R := 8.314$ Gass constant

$n := 1$ stoichiometric number of electrons

$\Phi_m := n \cdot \frac{F}{R \cdot T} \cdot E_m$ dimensionless potential **(4)**

$D := 5 \cdot 10^{-6}$ common diffusion coefficient in cm^2/s

$ks := 0.005$ electrochemical standard rate constant in cm/s

$\alpha := 0.5$ electron transfer coeffcient

$kf := 3$ forward rate constant of the chemical recation in s^{-1}

$kb := 10$ backward rate constant of the chemical reaction in s^{-1}

$Keq := \frac{kf}{kb}$ equilibrium constant of the follow-up chemical reaction

$K := \frac{ks \cdot \sqrt{\tau}}{\sqrt{D}}$ dimensionless electrode kinetic parameter

$Kchem := (kf + kb) \cdot \tau$ dimensionless chemical kinetic parameter

$S_m := \sqrt{m} - \sqrt{m-1}$ numerical integration parameter **(5)**

$M_m := \operatorname{erf}\left(\sqrt{Kchem \cdot \frac{m}{25}}\right) - \operatorname{erf}\left[\sqrt{Kchem \cdot \frac{(m-1)}{25}}\right]$ numerical integration parameter **(6)**

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

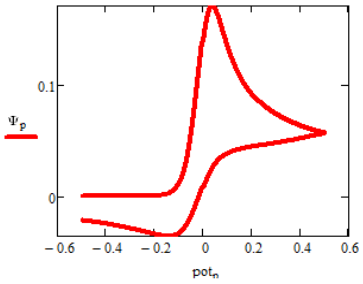
Recurrent formulas for calculating the dimensionless current

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

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

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

$pot_p := if\left[p \le \frac{\Delta E}{dE}, Es + p \cdot dE, Ef - \left(p - \frac{\Delta E}{dE}\right) \cdot dE\right]$ potential value of each potential step in V **(11)**



dimensionless cyclic staircase voltammogram

$S := 0.05$ electrode surface area in cm²

$c := 1 \cdot 10^{-6}$ bulk concentration of the electroactive reactant in mol/cm³

$A := n \cdot F \cdot S \cdot c \cdot \left(\sqrt{\frac{D}{\tau}}\right)$ amperometric constant

$I_p := 10^6 \cdot \Psi_p \cdot A$ real current in μA