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Education

Supplementary Material

PDF version of File 3. MATHCAD simulation protocol of EC′ mechanism

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

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EC' electrode mechanism at a planar electrode of a dissolved redox couple in Cyclic Staircase Voltammetry

Red = Ox + e⁻ (k_s, α) **(1)**

Ox + Y --> Red (k_c) **(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)

$\tau = 0.05$

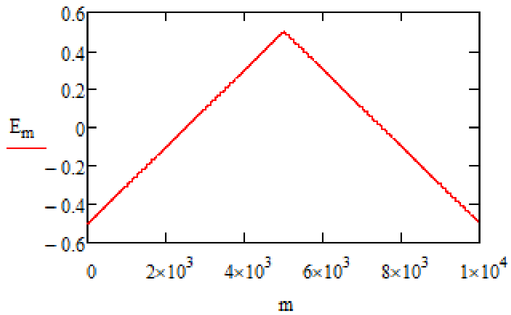
$M := 25$ number of time increments in a single potential step

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

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

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

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



$F := 96485$	Faraday constant in C/mol
$T := 298.15$	thermodynamic temperature in K
$R := 8.314$	Gass constant in J/(mol K)
$n := 1$	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 cm²/s
$ks := 0.005$	electrochemical standard rate constant in cm/s
$\alpha := 0.5$	electron transfer coeffcient
$kc := 0.6$	rate constant of the chemical regenerative recation in s^{-1}
$K := \frac{ks \cdot \sqrt{\tau}}{\sqrt{D}}$	dimensionless electrode kinetic parameter
$Kchem := kc \cdot \tau$	dimensionless chemical kinetic parameter

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

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

$$\Psi_1 := \frac{K \cdot e^{\alpha \cdot \Phi_1}}{1 + \frac{K \cdot e^{\alpha \cdot \Phi_1} \cdot M_1}{\sqrt{Kchem}} \left(1 + e^{-\Phi_1}\right)} \quad (7)$$

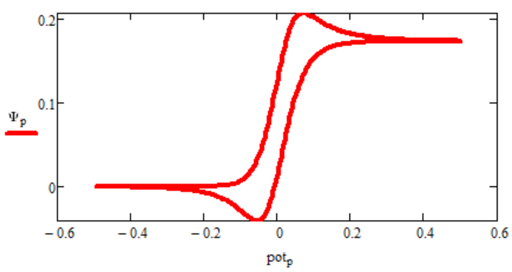
Recurrent formulas for calculating the dimensionless current

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

$p := 1 .. 2 \cdot \frac{\Delta E}{dE} - 1$ 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)**

$pot_p := \mathrm{if}\left[p \le \frac{\Delta E}{dE}, Es + p \cdot dE, Ef - \left(p - \frac{\Delta E}{dE}\right) \cdot dE\right]$ 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