Educational Voltammetry, Part VII: Simulation of a diffusional electrochemical reaction coupled with a reversible follow up chemical reaction (the EC mechanism) at stationary planar electrode under conditions of square-wave voltammetry

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Abstract

This study examines the EC mechanism i.e. an electrode reaction coupled with a reversible homogeneous chemical step, under square-wave voltammetry at a stationary planar electrode using Butler–Volmer kinetics. It provides a complete, ready-to-use MATHCAD protocol for simulating square-wave voltammograms and includes detailed explanations of each parameter used. This resource is designed to help students and experienced researchers alike become familiar with the theoretical calculation of square-wave voltammograms and supports interpretation of experimental results. It is first of such format to be given freely available to anyone.

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

Red = Ox + e⁻ $\quad (k_s, \alpha) \quad$ **(1)**

Ox = Y $\quad (k_f, k_b, K_{eq}) \quad$ **(2)**

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

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

$\Delta E := 1$ potential window

$f := 10$ frequency in Hz

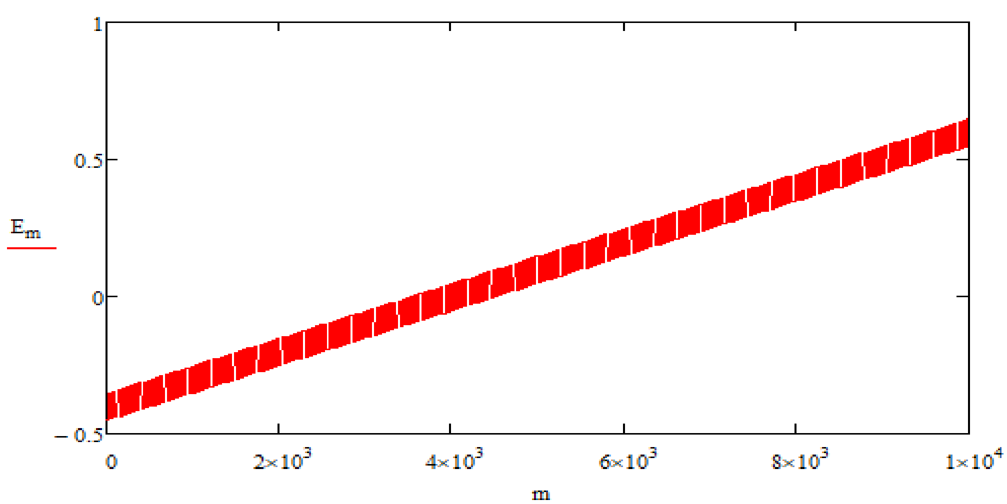
$Esw := 0.05$ amplitude in V

$m := 1 .. \frac{\Delta E}{dE} \cdot 50$ serial number of time inceremnts

$$relativenpot_m := \left(\operatorname{ceil}\left(\frac{m}{25} \cdot \frac{1}{2}\right) \cdot dE + \operatorname{if}\left(\frac{\operatorname{ceil}\left(\frac{m}{25}\right)}{2} = \operatorname{ceil}\left(\frac{m}{25} \cdot \frac{1}{2}\right), 1, -1 \right) \cdot Esw + Esw \right) - dE \qquad \textbf{(3)}$$

$$E_m := (Es + Esw) + relativenpot_m$$

potential



$F := 96485$ Farady constant

$T := 298.15$ theromodynamic 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 cm²/s

$ks := 0.05$ electrochemical standard rate constant in cm/s

$\alpha := 0.5$ electron transfer coefficient

$kf := 00001.10$ forward rate constant of the chemical recation in s^{-1}

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

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

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

$Kchem := \frac{(kf + kb)}{f}$ dimensioless chemical kinetic parameter

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

$M_m := \mathrm{erf}\left(\sqrt{Kchem \cdot \frac{m}{50}}\right) - \mathrm{erf}\left[\sqrt{Kchem \cdot \frac{(m-1)}{50}}\right]$ numerical integration parameter **(6)**

$$\Psi_1 := \frac{K \cdot e^{\alpha \cdot \Phi_1}}{1 - K \cdot e^{\alpha \cdot \Phi_1} \cdot \left[\frac{-2}{\sqrt{50\pi}} \cdot \left(\left(1 + \frac{e^{-\Phi_1}}{1 + Keq}\right)\right) - \frac{K \cdot e^{-\Phi_1} \cdot M_1}{\sqrt{Kchem} \cdot (Keq + 1)}\right]} \quad (7)$$

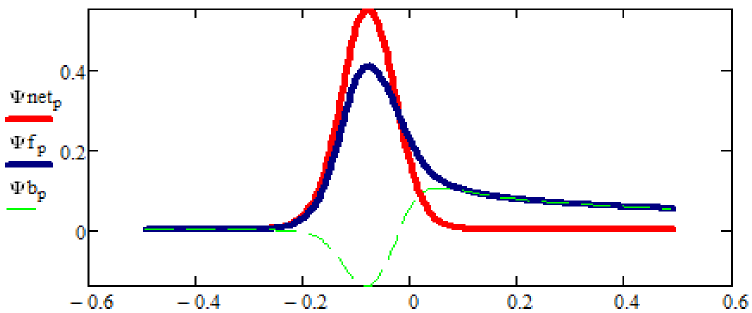
Recurent formulas for calculating the dimensioless current

$$\Psi_m := \frac{K \cdot e^{\alpha \cdot \Phi_m} \cdot \left[1 - \frac{2}{\sqrt{50\pi}} \cdot \left(1 + \frac{e^{-\Phi_m}}{1 + Keq}\right) \cdot \sum_{j=1}^{m-1} \left(\Psi_j \cdot S_{m-j+1}\right) - \frac{K \cdot e^{-\Phi_m}}{(1 + Keq) \cdot \sqrt{Kchem}} \cdot \sum_{j=1}^{m-1} \left(\Psi_j \cdot M_{m-j+1}\right)\right]}{1 - K \cdot e^{\alpha \cdot \Phi_m} \cdot \left[\frac{-2}{\sqrt{50\pi}} \cdot \left(\left(1 + \frac{e^{-\Phi_m}}{1 + Keq}\right)\right) - \frac{K \cdot e^{-\Phi_m} \cdot M_1}{\sqrt{Kchem} \cdot (Keq + 1)}\right]} \quad (8)$$

The following equation is recurrent formula to calculate current in *the EC*{rev} mechanism:

$$\Psi_m := \frac{Ke^{\alpha\Phi m}\left[1 - \frac{2}{\sqrt{50\pi}}\left(\frac{1+e^{-\Phi m}}{1+K_{eq}}\right)\sum_{j=1}^{m-1}(\psi_j \cdot S_{m-j+1}) - \frac{Ke^{-\Phi m}}{(1+K_{eq})\sqrt{K_{chem}}}\sum_{j=1}^{m-1}(\psi_j \cdot M_{m-j+1})\right]}{1 - Ke^{\alpha\Phi m}\left[-\frac{2}{\sqrt{50\pi}}\left(\frac{1+e^{-\Phi m}}{1+K_{eq}}\right) - \frac{Ke^{-\Phi m}M_1}{\sqrt{K_{chem}}(K_{eq}+1)}\right]}$$

$p := 1..\frac{\Delta E}{dE} - 2$	serial number of potential pulses	**(9)**
$\Psi f_p := \Psi_{(p+1)\cdot 50}$	dimesinoless current at the end of forward potential pulses	**(10)**
$\Psi b_p := \Psi_{50\cdot p+25}$	dimesinoless current at the end of backward potential pulses	**(11)**
$\Psi net_p := \Psi f_p - \Psi b_p$	dimesinoless "net" current	**(12)**
$pot_p := Es + (p)\cdot dE$	potential value of each potential pulse in V	**(13)**



dimensionless SW voltammogram

$S := 0.05$ electrode surface area in cm²

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

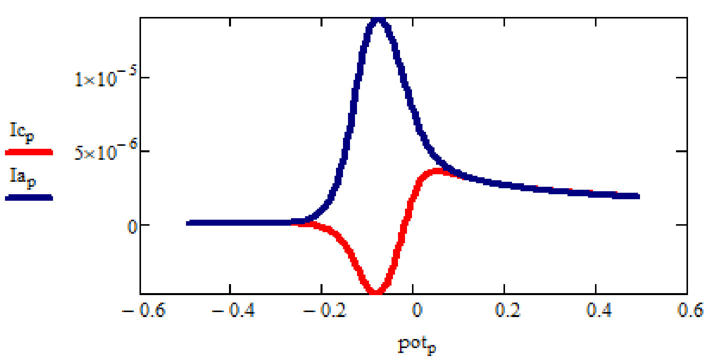
$A := n\cdot F\cdot S\cdot c\cdot\left(\sqrt{D\cdot f}\right)$ amperometric contsant

$I_p := \Psi_p A$ real current in A

$Ia_p := \Psi f_p\cdot A$

$Ic_p := \Psi b_p\cdot A$

$Inet_p := Ia_p - Ic_p$



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