Calculating of square-wave voltammograms—a practical on-line simulation platform-MATHCAD File

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MATHCAD File for calculating SW voltammograms

MATHCAD SIMULATION FILE
SQUARE-WAVE VOLTAMMETRY OF A QUASI-REVERSIBLE ELCTRODE REACTION OF A DISSOLVED REDOX COUPLE AT MACROSCOPIC PLANAR ELECTRODE

Definition of parameters of the potential modulation

$Es := -0.2$ Starting potential vs. $E^{0'}$ (V) (1)

$Esw := 0.05$ SW amplitude (V) (2)

$dE := 0.01$ Step potential increment (V) (3)

$\Delta E := 0.4$ Length of potential interval studied (V) (4)

Serial number of time increments and potential modulation in SWV

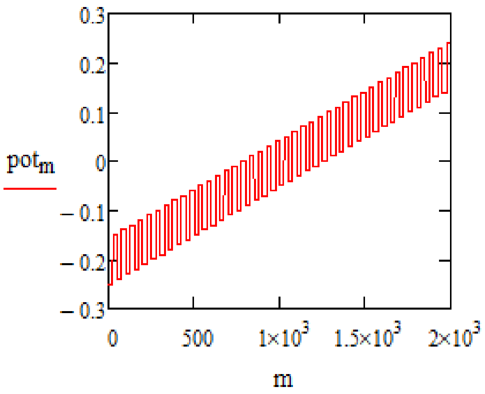
$m := 1 .. \frac{\Delta E}{dE} \cdot 50$ Serial number of time increments (5)

$f := 10$ Frequency of the potential modulation (Hz = 1/s) (6)

$d := \frac{1}{50f}$ Time increment (s) (7)

$$pot_m := Es - Esw + \left[\left(\mathrm{ceil}\left(\frac{m}{25} - \frac{1}{2}\right) \cdot dE + \mathrm{if}\left(\frac{\mathrm{ceil}\left(\frac{m}{25}\right)}{2} = \mathrm{ceil}\left(\frac{m}{25} - \frac{1}{2}\right), 1, -1\right) \cdot Esw + Esw\right) - dE\right]$$

SW potential modulation (8)



Graph (I)

Basic constants and dimensionles potential

$F := 96485$	Faraday constnat (C/mol)	(9)
$T := 298.15$	Theromodynamic temperature (K)	(10)
$R := 8.314$	Universal Gass constant (J mol^{-1} K^{-1})	(11)
$\Phi_m := \frac{F}{R \cdot T} \cdot pot_m$	Dimensioles potential	(12)

Basic constants of the electrode reaction

$D := 5 \cdot 10^{-6}$	Diffusion coefficient (cm^2/s)	(13)
$ks := 0.005$	Standard rate constant of electron transfer (cm/s)	(14)
$\alpha := 0.5$	Electron transfer coeffcient	(15)

Dimensioless parameters

$\kappa := \frac{ks}{D \cdot f}$	Dimensioless electrode kinetic parameter	(16)
$S_m := \sqrt{m} - \sqrt{m-1}$	Numerical intergation parameter	(17)

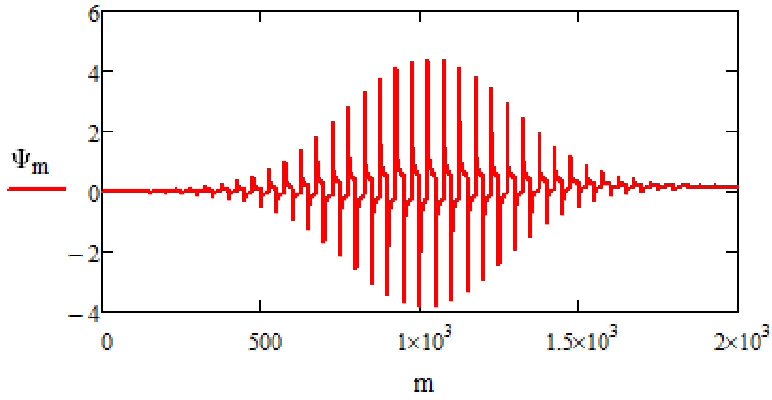
Recurent formula for calculation of the dimensioless current

$$\Psi_1 := \frac{\kappa \cdot e^{\alpha \cdot \Phi_1}}{1 + \frac{2 \cdot \kappa \cdot e^{\alpha \cdot \Phi_1}}{\sqrt{\pi \cdot 50}} \cdot \left(1 + e^{-\Phi_1}\right)} \qquad (18)$$

Dimensioless current of the first time increment

$$\Psi_m := \frac{\kappa \cdot e^{\alpha \cdot \Phi_m} \cdot \left[1 - \frac{2 \cdot \left(1 + e^{-\Phi_m}\right)}{\sqrt{\pi \cdot 50}} \cdot \sum_{j=1}^{m-1} \left(\Psi_j \cdot S_{m-j+1}\right)\right]}{1 + \frac{2 \cdot \kappa \cdot e^{\alpha \cdot \Phi_m}}{\sqrt{\pi \cdot 50}} \cdot \left(1 + e^{-\Phi_m}\right)} \qquad (19)$$

Dimensioless currents



Graph (II)

Serial numeber of potential cycles in SWV and the mid-potential of each potential cycle
(i.e., the potential of underlying staircase ramp)

$p := 0 .. \left(\frac{\Delta E}{dE}\right) - 1$ Serial number of a potential cyle (20)

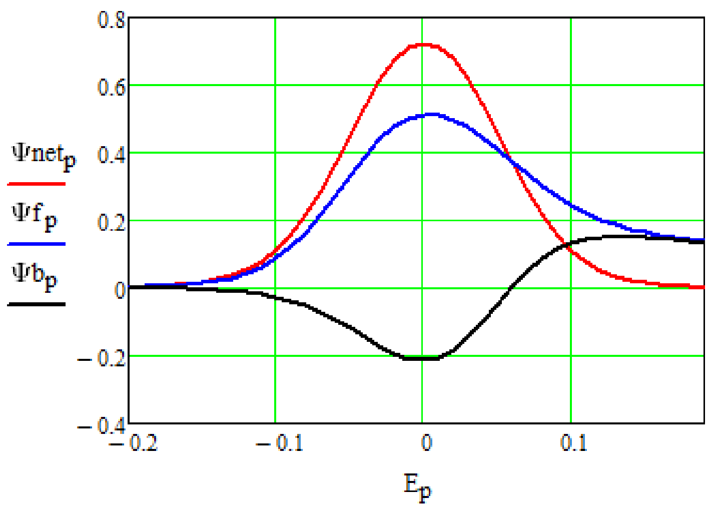
$E_p := Es + p \cdot dE$ Mid-potential of potential cycles vs. $E^{0'}$ (V) (21)

Dimensioless forward, backward (reverse) and the net current components

$\Psi f_p := \Psi_{(p+1)\cdot 50}$ Dimensioless forward currents (22)

$\Psi b_p := \Psi_{(50 \cdot p+25)}$ Dimensioless backward currents (23)

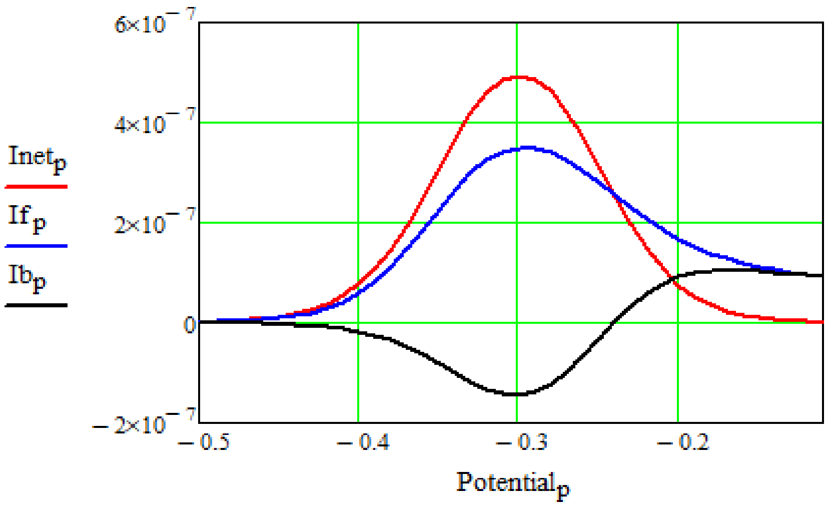
$\Psi net_p := \Psi f_p - \Psi b_p$ Net currents (23)



Graph (III)

Definition of the amperometric constant, real currents and potential

$c := 1\cdot 10^{-7}$	Bulk concnetration of the initial reactant Red (mol/cm³)	(24)
$A := 0.01$	Electrode surface area (cm²)	(25)
$C := F\cdot A\cdot c\cdot\sqrt{D\cdot f}$	Amperometric constant (A)	(26)
$If_p := \Psi f_p\cdot C$	Real forward currents	(27)
$Ib_p := \Psi b_p\cdot C$	Real backward currents (A)	(28)
$Inet_p := \Psi net_p\cdot C$	Real net currents (A)	(29)
$E0 := -0.3$	Formal potential vs. a given reference electrode (V)	(30)
$Potential_p := E0 + E_p$	Real potential vs. a given reference electrode (V)	(31)



Graph (IV)

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