Edicational Voltammetry, Part IV: EC'(reversible) Mechanism in Cyclic Voltammetry

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EC'$_{(reversible\ catalytic)}$ electrode mechanism at a planar electrode of a dissolved redox couple in Cyclic Staircse Voltammetry

Red = Ox + e$^-$ (k_s, D, α) **(1)**

Ox + Y = Red (k_f, k_b, K_{eq}) **(2)**

$Es := -0.8$ startiung potential (in V vs. the formal potential)

$Ef := 0.8$ 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)

$\tau = 0.05$

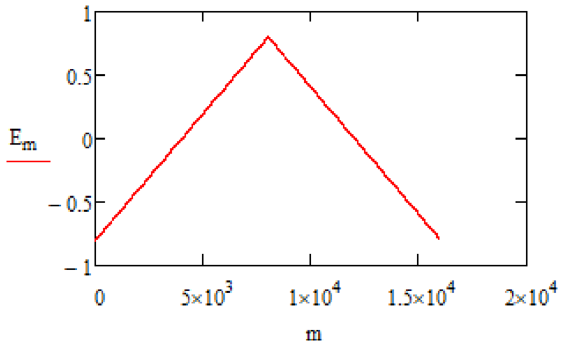
$M := 25$ numer of time increments in a single potential step

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

$2 \cdot \frac{\Delta E}{dE} = 640$ total number of potential steps

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

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



$F := 96485$	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 cm^2/s
$ks := 0.05$	electrochemical standard rate constant in cm/s
$\alpha := 0.5$	electron transfer coeffcient
$kf := 0.010$	forward rate constant of the chemical recation in s^{-1}
$kb := .5$	backward rate constant of the chemical reaction in s^{-1}
$Keq := \frac{kf}{kb}$	equilibrium contant of the follow up chemical reaction
$K := \frac{ks \cdot \sqrt{\tau}}{\sqrt{D}}$	dimensionless electrode kinetic parameter
$Kchem := (kf + kb) \cdot \tau$	dimensioless chemical (catalytic) kinetic parameter

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

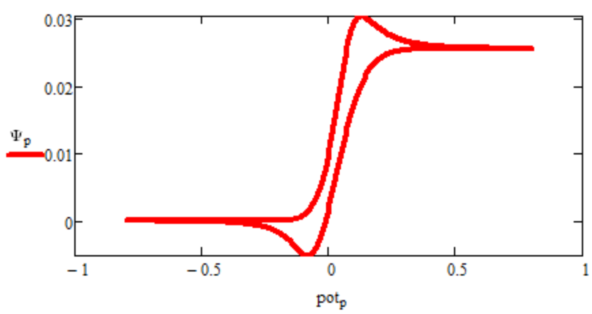
Recurent formulas for calculating the dimensioless current

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

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

$\Psi_p := \Psi_{\left(\frac{\tau}{d\cdot 25}+p\right)\cdot 25}$ — dimesnioless 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)**



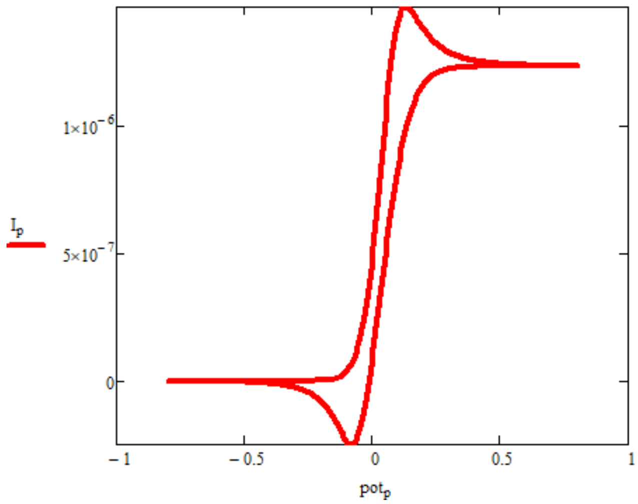
dimensionless cyclic staircase voltammogram

$S := 0.05$ electrode surface area in cm²

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

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

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



Graph of real current-potential curve (current in A)

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