EDUCATIONAL VOLTAMMETRY: PART 3: Open Interactive Protocol to Simulate the electrochemical-regenerative EC' Mechanism in Cyclic Staircase Voltammetry

Rubin Gulaboski, Valentin Mirceski

[1]*Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia*

[2]*Department of Inorganic and Analytical Chemistry, University of Lodz, Pomorska 163/165, 90-236 Lodz, Poland*

[3]*Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss Cyril and Methodius University in Skopje, P.O. Box 162, 1000, Skopje, Macedonia*

[4]*Research Center for Environment and Materials, Macedonian Academy of Sciences and Arts, Bul. Krste Misirkov 2, 1000 Skopje, Macedonia*

Abstract

This is an extension of previous works aiming to provide for the first time an open and freely accessible simulation platform based on MATHCAD is introduced for educational purposes in electrochemistry. This work, *Educational Voltammetry: Part 3*, provides interactive step-by-step protocols that enable students, educators, and researchers to simulate cyclic staircase voltammograms of a diffusional **EC′ (regenerative)** electrode mechanism under a variety of experimental and kinetic conditions. The approach is designed both for learning and for practical training, making it possible to explore the effects of mass transfer, electrode kinetics, and the regenerative chemical step without requiring advanced programming skills. Upon request, the original MATHCAD files can be obtained directly from the authors. In forthcoming contributions to this series, free interactive protocols for additional important electrode mechanisms will be provided, further broadening the educational toolkit for voltammetric analysis. A 30-day free trial version of MATHCAD 15 is available at:

https://support.ptc.com/products/Mathcad/Mathcad-15-0/free-trial?refid=cadventure

This initiative aims to encourage wider adoption of theoretical modeling in electrochemical education and to provide experimentalists with freely available tools for mechanistic understanding.

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)

$\tau = 0.05$

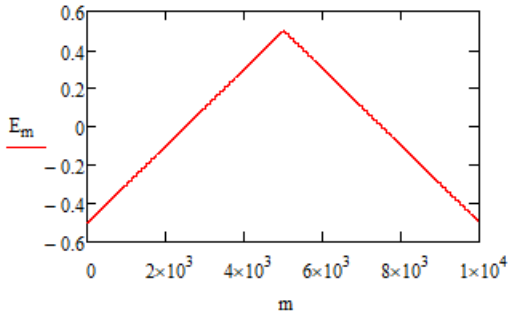
$M := 25$ number of time increments in a single potential step

$d := \frac{\tau}{M}$ 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

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



$F := 96485$ 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 cm^2/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

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$\delta_m := \sqrt{m} - \sqrt{m-1}$ 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)**

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

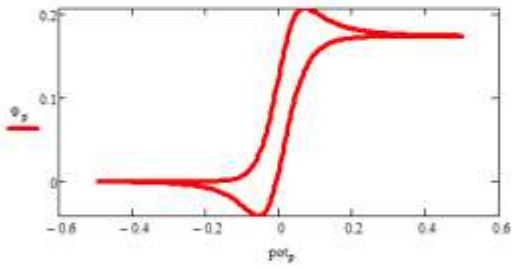
Recurrent formulas for calculating the dimensionless current

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



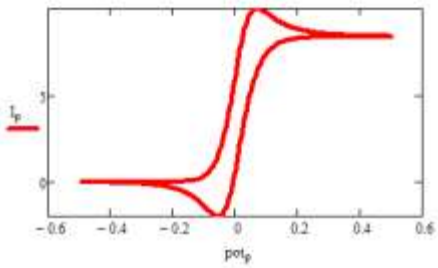
dimensionless cyclic staircase voltammogram

$S := 0.05$ electrode surface area in cm^2

$c := 1 \cdot 10^{-6}$ bulk concentration of the electroactive reactant in mol/cm^3

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

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



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