Interactive Mathcad Simulations for Common Electrode Mechanisms in Cyclic Voltammetry

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Abstract

Cyclic voltammetry is a cornerstone of electrochemical analysis, used to interrogate mechanistic pathways as well as the kinetics and thermodynamics of redox processes. Many biochemical transformations comprise electron-transfer steps coupled to homogeneous reactions that precede, follow, or regenerate the electroactive species, classically denoted CE, EC, and EC′ mechanisms. Robust simulation of these pathways is essential for sound interpretation of experimental data, yet freely accessible tools remain limited. Here we present a set of ready-to-use Mathcad files for simulating cyclic staircase voltammograms of diffusional CE, EC, and EC′ mechanisms within the Butler–Volmer framework. The protocols specify all relevant physical constants and waveform parameters, and define the dimensionless kinetic and thermodynamic variables required to build recurrent relations for current calculation. The implementation explicitly resolves anodic and cathodic current components, enabling reconstruction of complete voltammograms and extraction of standard descriptors (e.g., peak currents, peak potentials, peak-to-peak separations, and mid-peak potentials). We further illustrate how these features can be used diagnostically to distinguish mechanisms and delineate kinetic regimes. By making the simulation files freely available, the platform provides students and practitioners with an interactive, transparent environment for learning and method development, while offering experienced researchers a practical computational aid for experiment design and data analysis. This work thus helps bridge theoretical electrochemistry and laboratory practice, facilitating deeper mechanistic understanding of complex electrode processes.

DIFFUSIONAL CE MECHANISM
in CYCLIC VOLTAMMETRY 2024

$tac := 0.01$

$Es := -1 \qquad Ef := 1 \qquad \Delta E := Ef - Es \qquad dE := 0.01 \qquad \tau := 0.01 \qquad d := \frac{\tau}{25}$

$i := 1 .. \frac{tac}{d}$

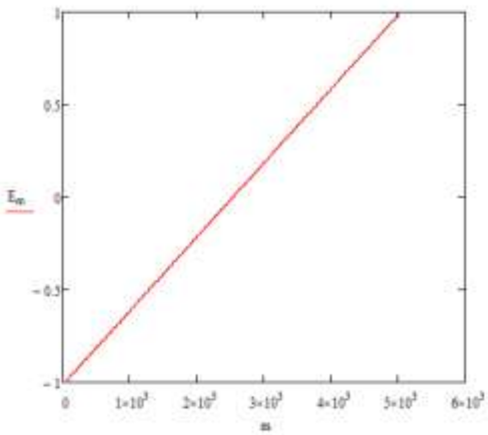
$m := \frac{tac}{d} + 1 .. \frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} \qquad n := \frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} + 1 .. \left(\frac{\Delta E}{dE} \cdot 25 \cdot 2 + \frac{tac}{d}\right)$

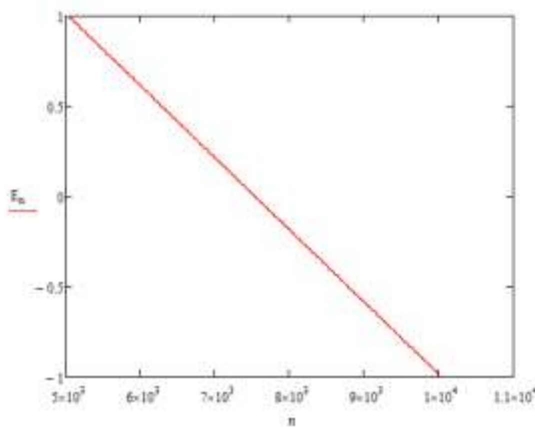
$\frac{\Delta E}{dE} = 200$

$$E_m := Es + \left(\mathrm{ceil}\left(\frac{m - \frac{tac}{d}}{25}\right) \cdot dE - dE\right)$$

$$E_n := Ef - \left[\mathrm{ceil}\left[\frac{n - \left(\frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d}\right)}{25}\right] \cdot dE - dE\right]$$

$\frac{dE}{\tau} = 1 \qquad \frac{dE}{\tau} = 1$





$ks := 0.05 \qquad D := 5 \cdot 10^{-6}$

$K := \frac{ks \cdot \sqrt{\tau}}{\sqrt{D}} \qquad \alpha := 0.5$

$kf := 100.003$

$kb := 100.5$

$\varepsilon := kf + kb \qquad Keq := \frac{kf}{kb}$

$Kchem := \varepsilon \cdot \tau$

$F := 96500 \qquad el := 1 \qquad R := 8.314 \qquad T := 298.15 \qquad Kchem := 10.4 \qquad Keq := 0.05$

$\Phi_m := el \cdot \frac{F}{R \cdot T} \cdot (E_m) \qquad \Phi_n := el \cdot \frac{F}{R \cdot T} \cdot (E_n) \qquad \Phi ac := el \cdot \frac{F}{R \cdot T} \cdot Es \qquad k := 1 .. 2 \cdot \left(\frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d}\right)$

$$S1_k := \sqrt{k} - \sqrt{k - 1}$$

$$S_k := \mathrm{erfc}\left[\left(Kchem \cdot \frac{k}{25}\right)^{0.5}\right] - \mathrm{erfc}\left[\left[Kchem \cdot \frac{(k-1)}{25}\right]^{0.5}\right]$$

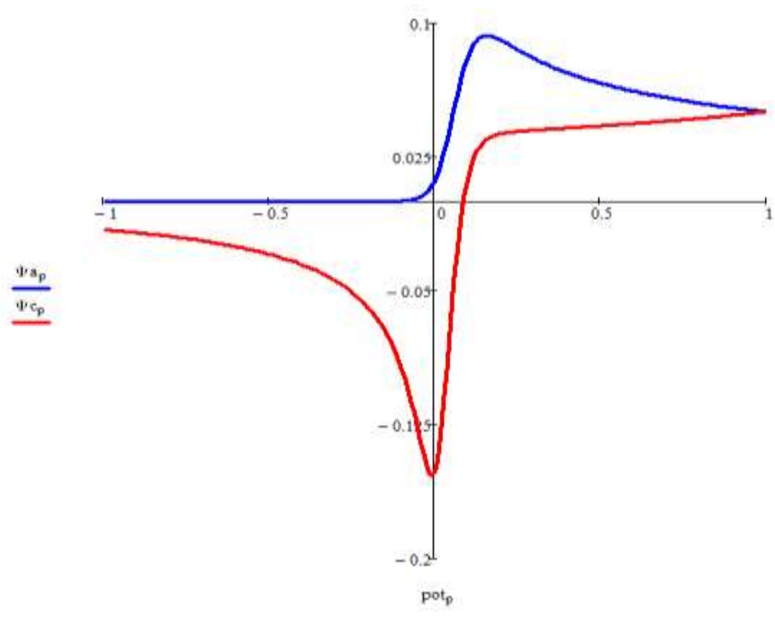
$$\Psi_1 := \frac{K \cdot e^{\alpha \cdot \Phi_1}\left[\frac{Keq}{1+Keq} - \frac{2 \cdot e^{-\alpha \cdot \Phi_1}}{\sqrt{25 \cdot \pi}} \cdot 0 - 1 \cdot \left(\frac{Keq}{1+Keq}\right) \cdot \left[\frac{2}{(25 \cdot \pi)^{0.5}}\right] \cdot 0 - 1 \cdot \frac{1}{\sqrt{Kchem}} \cdot \frac{1}{(Keq+1)} \cdot 0\right]}{1 - K \cdot e^{\alpha \cdot \Phi_1}\left[\left(\frac{Keq}{1+Keq}\right) \cdot 1 - 0 - 0\right]}$$

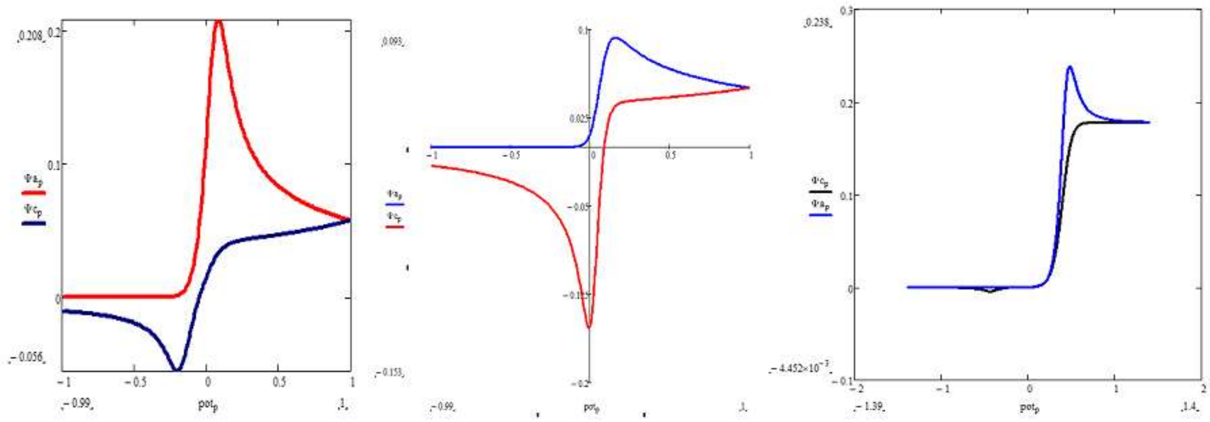
$$\Psi_s := \frac{K \cdot e^{\alpha \cdot \Phi ac}\left[\frac{Keq}{1+Keq} \cdot \left[1 - \frac{2}{(25 \cdot \pi)^{0.5}} \cdot \sum_{j=1}^{s-1} \left(\Psi_j \cdot S1_{s-j+1}\right)\right] - 1 \cdot \frac{-1}{\left(\sqrt{Kchem}\right)} \cdot \frac{1}{(Keq+1)} \cdot \sum_{j=1}^{s-1} \left(\Psi_j \cdot S_{s-j+1}\right) - \frac{2 \cdot e^{-\Phi ac}}{(25 \cdot \pi)^{0.5}} \cdot \sum_{j=1}^{s-1} \left(\Psi_j \cdot S1_{s-j+1}\right)\right]}{1 - K \cdot e^{\alpha \cdot \Phi ac}\left[\frac{-2 \cdot Keq \cdot S1_1}{(25 \cdot \pi)^{0.5} \cdot (1+Keq)} - \frac{-S_1}{\sqrt{Kchem} \cdot (1+Keq)} - \frac{2 \cdot e^{-\Phi ac} \cdot S1_1}{(25 \cdot \pi)^{0.5}}\right]}$$

$$\Psi_m := \frac{K \cdot e^{\alpha \cdot \Phi_m}\left[\frac{Keq}{1+Keq} \cdot \left[1 - \frac{2}{(25 \cdot \pi)^{0.5}} \cdot \sum_{j=1}^{m-1} \left(\Psi_j \cdot S1_{m-j+1}\right)\right] - 1 \cdot \frac{-1}{\left(\sqrt{Kchem}\right)} \cdot \frac{1}{(Keq+1)} \cdot \sum_{j=1}^{m-1} \left(\Psi_j \cdot S_{m-j+1}\right) - \frac{2 \cdot e^{-\Phi_m}}{(25 \cdot \pi)^{0.5}} \cdot \sum_{j=1}^{m-1} \left(\Psi_j \cdot S1_{m-j+1}\right)\right]}{1 - K \cdot e^{\alpha \cdot \Phi_m}\left[\frac{-2 \cdot Keq \cdot S1_1}{(25 \cdot \pi)^{0.5} \cdot (1+Keq)} - \frac{-S_1}{\sqrt{Kchem} \cdot (1+Keq)} - \frac{2 \cdot e^{-\Phi_m} \cdot S1_1}{(25 \cdot \pi)^{0.5}}\right]}$$

$$\Psi_n := \frac{K \cdot e^{\alpha \cdot \Phi_n}\left[\frac{Keq}{1+Keq} \cdot \left[1 - \frac{2}{(25 \cdot \pi)^{0.5}} \cdot \sum_{j=1}^{n-1} \left(\Psi_j \cdot S1_{n-j+1}\right)\right] - 1 \cdot \frac{-1}{\left(\sqrt{Kchem}\right)} \cdot \frac{1}{(Keq+1)} \cdot \sum_{j=1}^{n-1} \left(\Psi_j \cdot S_{n-j+1}\right) - \frac{2 \cdot e^{-\Phi_n}}{(25 \cdot \pi)^{0.5}} \cdot \sum_{j=1}^{n-1} \left(\Psi_j \cdot S1_{n-j+1}\right)\right]}{1 - K \cdot e^{\alpha \cdot \Phi_n}\left[\frac{-2 \cdot Keq \cdot S1_1}{(25 \cdot \pi)^{0.5} \cdot (1+Keq)} - \frac{-S_1}{\sqrt{Kchem} \cdot (1+Keq)} - \frac{2 \cdot e^{-1 \cdot \Phi_n} \cdot S1_1}{(25 \cdot \pi)^{0.5}}\right]}$$

$p := 1 .. \frac{\Delta E}{dE}$ $\quad \Psi a_p := (\Psi)_{\left(\frac{\tau}{d \cdot 25}+p\right) \cdot 25}$ $\quad \Psi c_p := (\Psi)_{\left[\left[\frac{\Delta E}{dE} \cdot 2+\left(\frac{\tau}{25 \cdot d}\right)\right]-p\right] \cdot 25}$ $\quad pot_p := Es + p \cdot dE$





Original profiles of cyclic voltammograms simulated in MATHCAD platform for an EC mechanism featuring reversible follow up chemical reaction (left)m CE mechanism with reversible preceding chemical reaction (middle) and EC' catalytic mechanism (right)

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