Solving the EC′E Diffusional Mechanism – Mathematical Model

Pavlinka Kokoskarova, Milkica Janeva, Rubin Gulaboski

Faculty of Medical Sciences, Goce Delcev University, Stip, Macedonia

Abstract

The EC′E mechanism, involving two consecutive electron-transfer steps coupled with a homogeneous catalytic regeneration of the intermediate, represents a fundamental yet complex class of electrochemical reactions frequently encountered in redox-active systems. In this work, a comprehensive mathematical model of the fully diffusional EC′E mechanism is developed under conditions of semi-infinite planar diffusion. The model is based on coupled reaction–diffusion equations incorporating Butler–Volmer kinetics for both electrode processes and second-order chemical kinetics for the catalytic step. Numerical solutions presented in MATHCAD reveal the interplay between electron-transfer rates and catalytic regeneration, highlighting their combined influence on voltammetric response. The analysis demonstrates how variations in kinetic parameters govern the transition between limiting mechanistic regimes and identifies characteristic features in the current–potential profiles that can be used for mechanistic discrimination. Under specific conditions, the model converges to simpler mechanisms, including E, EC′, and EE systems, providing a unified theoretical framework for their interpretation. This study offers a robust platform for understanding complex catalytic electrochemical processes and supports the quantitative analysis of EC′E-type systems in modern voltammetry.

Scheme of Electrochemical Mechanism:

$A \rightleftharpoons B$ (electron transfer)

$B + Y \rightarrow A + Z$ (catalytic step)

$B \rightleftharpoons C$ (electron transfer)

Model is represented by following Partial Differential Equations (Fick's Second Law + Reaction Terms):

Partial Differential Equations

$$\frac{\partial c_A}{\partial t} = \frac{D_A \partial^2 c_A}{\partial x^2} + k_c c_B c_Y$$

$$\frac{\partial c_B}{\partial t} = \frac{D_B \partial^2 c_B}{\partial x^2} - k_c c_B c_Y$$

$$\frac{\partial c_C}{\partial t} = \frac{D_C \partial^2 c_C}{\partial x^2}$$

Initial Conditions

$$c_{A(x,0)} = c_A *$$

$$c_{B(x,0)} = 0$$

$$c_{C(x,0)} = 0$$

$$c_{Y(x,0)} = c_Y *$$

$$c_{Z(x,0)} = 0$$

Boundary Conditions

$$c_{A(\infty,t)} = c_A *$$

$$c_{B(\infty,t)} = 0$$

$$c_{C(\infty,t)} = 0$$

$$c_{Y(\infty,t)} = c_Y *$$

$$c_{Z(\infty,t)} = 0$$

Butler–Volmer Kinetics at x=0

$$v_1 = k_{\{s1\}} e^{\left\{\frac{\alpha_1 F(E-E_1{}^{\circ})}{RT}\right\}} c_A - k_{\{s1\}} e^{\left\{-\frac{(1-\alpha_1) F(E-E_1{}^{\circ})}{RT}\right\}} c_B$$

$$v_2 = k_{\{s2\}} e^{\left\{\frac{\alpha_2 F(E-E_2{}^{\circ})}{RT}\right\}} c_B - k_{\{s2\}} e^{\left\{-\frac{(1-\alpha_2) F(E-E_2{}^{\circ})}{RT}\right\}} c_C$$

Current Expression

$$I(t) = n\, F\, A\, (v_1 + v_2)$$

MATHCAD WORKING PROTOCOL

TWO STEP DIFFUSIONAL Double Regenerative
EC'EC'cat Mechanism in CYCLIC
VOLTAMMETRY--towards Oxidation Version date: 03
04 2026

A - 1e = B
B+Y-->A
B - 1e = C
C+Z -->B

(all A BC) only diffusion

$kc1 := 100$

$kc2 := 200$

λ i z se definirani kako odnos
na Kc1x τ i kc2xτ

note: If z is small, then entire mechanism converts to EC'E mechanism

λ e kineticki parametar na ireverzibilna hemiska
reak75cija na regeneracija
povrzana so prv elektroden cekor

$EfI := 0.7 \qquad EfII := 0.35 \qquad \tau := 0.05$

$EsI := -0.3 \qquad \Delta E := 1 \qquad dE := 0.005 \qquad EsII := -0.65 \qquad r := 1..1$

$n := 1 \qquad F := 96500 \qquad R := 8.314 \qquad T := 298.15 \qquad \Delta EI := EfI - EsI \qquad KI := 10^{-5}$

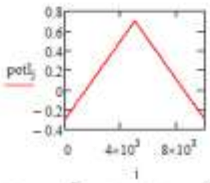
$M := 25 \qquad \Delta EII := EfII - EsII \qquad KII := 10^{0.5}$

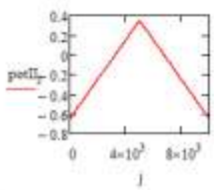
$j := 1..2\frac{\Delta E}{dE}\cdot 25 \qquad d := \frac{\tau}{M} \qquad \alpha 2 := 0.5 \qquad \alpha 1 := 0.5$

$$potI_j := if\left[j \le \frac{\Delta E}{dE}\cdot 25, EsI + \left(ceil\left(\frac{j}{25}\right)\cdot dE - dE\right), EfI - \left[ceil\left[\frac{j - \left(\frac{\Delta E}{dE}\cdot 25\right)}{25}\right]\cdot dE - dE\right]\right]$$

$KII = 3.162$

$$potII_j := if\left[j \le \frac{\Delta E}{dE}\cdot 25, EsII + \left(ceil\left(\frac{j}{25}\right)\cdot dE - dE\right), EfII - \left[ceil\left[\frac{j - \left(\frac{\Delta E}{dE}\cdot 25\right)}{25}\right]\cdot dE - dE\right]\right]$$





$\lambda := .65$

$z := .0000581001049035$

z e kataliticki parametar vo ovoj
model povrzan so vtor cekor

$$A_j := \left(1 - erfc\left(\sqrt{\frac{\lambda}{25}\cdot j}\right)\right) - \left[1 - erfc\left[\sqrt{\frac{\lambda}{25}\cdot(j-1)}\right]\right]$$

$$B_j := \left(1 - erfc\left(\sqrt{\frac{z}{25}\cdot j}\right)\right) - \left[1 - erfc\left[\sqrt{\frac{z}{25}\cdot(j-1)}\right]\right]$$

$\Phi I_j := n\cdot\frac{F}{R\cdot T}\cdot potI_j \qquad \Phi II_j := n\cdot\frac{F}{R\cdot T}\cdot potII_j$

$x := 0.001$

$$\Phi I_1 := \frac{KI\cdot e^{\alpha 1\cdot \Phi I_1}}{1 + KI\cdot\lambda^{-0.5}\cdot A_1\cdot e^{\alpha 1\cdot\Phi I_1}\cdot\left(1 + e^{-\Phi I_1}\right)}$$

$$\Phi II_1 := \frac{\lambda^{-0.5}\cdot KII\cdot e^{\alpha 2\cdot\Phi II_1}}{1 + \frac{KII\cdot A_1}{z^{0.5}}\cdot e^{\alpha 2\cdot\Phi II_1}\cdot\left(1 + e^{-\Phi II_1}\right)}\cdot\Phi I_1\cdot A_1$$

$\Phi I_1 = 3.77\times10^{-5}$

$\Phi II_1 = 0$

$$\Phi I_j := \frac{KI\cdot e^{\alpha 1\cdot\Phi I_j}\cdot\left[1 - \frac{1 + e^{-\Phi I_j}}{\lambda^{0.5}}\cdot\sum_{i=1}^{j-1}\left(\Phi I_i\cdot A_{j-i+1}\right)\right]}{1 + KI\cdot\frac{1}{\lambda^{0.5}}\cdot A_1\cdot e^{\alpha 1\cdot\Phi I_j}\cdot\left(1 + e^{-\Phi I_j}\right)}$$

$$\Phi II_j := \frac{KII\cdot\frac{1}{\lambda^{0.5}}\cdot e^{\alpha 2\cdot\Phi II_j}\cdot\sum_{i=1}^{j}\left(\Phi I_i\cdot A_{j-i+1}\right) - \frac{1}{\left(z^{0.5}\right)}KII\cdot e^{\Phi II_j\cdot\alpha 2}\cdot\sum_{i=1}^{j-1}\left(\Phi II_i\cdot B_{j-i+1}\right) - \frac{1}{\left(z^{0.5}\right)}KII\cdot e^{-\Phi II_j\cdot(1-\alpha 2)}\cdot\sum_{i=1}^{j-1}\left(\Phi II_i\cdot B_{j-i+1}\right)}{1 + \frac{1\cdot B_1}{\left(z^{0.5}\right)}KII\cdot e^{\Phi II_j\cdot\alpha 2} + 0 + \frac{1\cdot B_1}{\left(z^{0.5}\right)}KII\cdot e^{-\Phi II_j\cdot(1-\alpha 2)}}$$

$n := 1..2\cdot\frac{\Delta EI}{dE} - 1$ serial number of potential st

$$p := 1 .. 2\cdot\frac{\Delta EI}{dE} - 1$$

serial number of potential steps

$$\Psi I_p := \Psi I_{\left(\frac{\tau}{d\cdot 25}+p\right)\cdot 25}$$

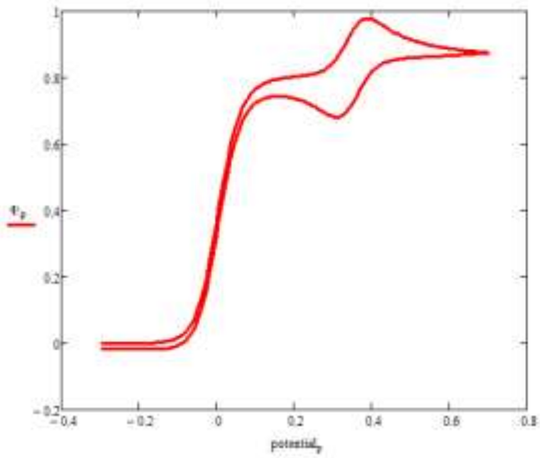
$$\Psi II_p := \Psi II_{\left(\frac{\tau}{d\cdot 25}+p\right)\cdot 25}$$

$$\Psi_p := \Psi I_p + \Psi II_p$$

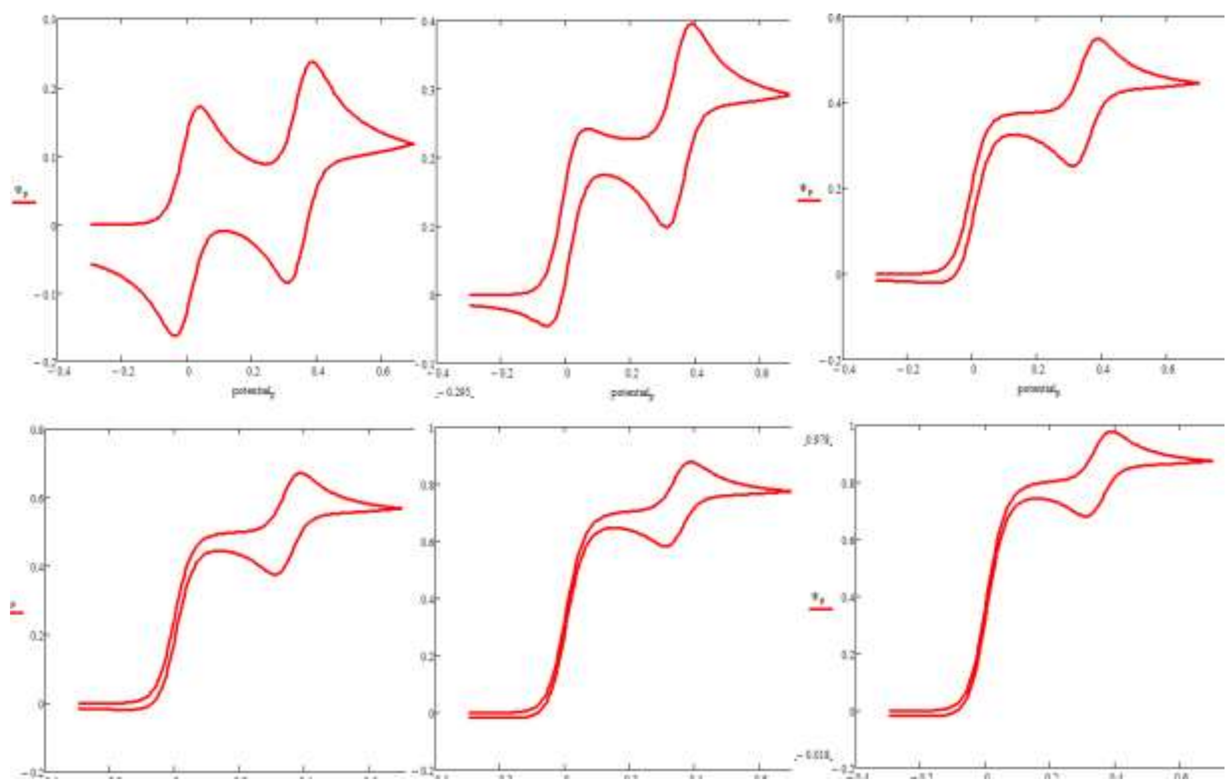
dimesnioless current at the end of each potential step of first electrode reaction ΨI and of second selectrode reaction ΨII Ψp is symbol the cumulative current measured as final output

$$potential_p := if\left[p \le \frac{\Delta EI}{dE}, Esl + p\cdot dE, Efl - \left(p - \frac{\Delta EI}{dE}\right)\cdot dE\right]$$

potential value of each potential step in V



Figures showing the effect of catalytic rate constant to the features of simulated cyclic voltammograms at EC'E diffusional mechanism in cyclic voltammetry



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