

Beyond Classical Electrochemical Mechanisms-For the First time Resolved the “Father” of all Electrode Mechanisms: The CrevECiEC’ Diffusional Model as All-in-One Electrochemical Framework

**Pavle Apostoloski, Pavlinka Kokoskarova, Sanja Lazarova, Milkica Janeva
Rubin Gulaboski**

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

Abstract

The diffusional CrevECirrEC’ mechanism represents the first comprehensive electrochemical framework capable of unifying virtually all common mechanistic electrode reactions within a single theoretical platform. By integrating reversible chemical pre-equilibrium, sequential electron-transfer steps (Crev), irreversible chemical transformation (Cirr), and catalytic regeneration (C’), this mechanism encompasses numerous classical limiting cases including E, ECirrE, CrevE, CrevECirr, EC’, ECirrE, ECirrEC’, and related multistep systems. For the first time, this work provides a rigorous mathematical solution of the CrevECirrEC’ mechanism under cyclic voltammetry conditions, combining Butler–Volmer kinetics with diffusional mass transport and homogeneous chemical kinetics.

The importance of this approach lies in its unprecedented versatility: rather than developing separate mathematical treatments for individual mechanisms, the CrevECiEC’ framework serves as a universal mechanistic parent model from which simpler systems naturally emerge through parameter adjustments. This establishes the mechanism as a foundational tool for mechanistic interpretation, kinetic evaluation, and simulation of complex electrochemical processes across chemistry, biomedicine, catalysis, and energy sciences.

To maximize accessibility and educational value, the model is also implemented for the first time as a freely available Mathcad simulation protocol, enabling researchers, students, and educators to perform advanced cyclic voltammetric simulations through an open computational platform. This work not only expands theoretical electrochemistry but also provides a practical and highly adaptable simulation environment for future mechanistic exploration.

MATHCAD WORKING FILE to SIMULATE CYCLIC VOLTAMMOGRAMS of CrevECirrEC' mechanism

$$E_{s1} = 0.9 \quad E_{s2} = 5 \quad \tau = 0.05$$

$$E_{s1} = -0.3 \quad \Delta E = 1.2 \quad dE = 0.01 \quad E_{s2} = -0.7 \quad \tau = 1.1$$

$$n = 1 \quad F = 96500 \quad R = 8.314 \quad \bar{A}_1 = 298.15 \quad \Delta E1 = E_{s1} - E_{s2} \quad KI = 10^0 \quad k_{c1} = 100$$

$$M = 25 \quad \Delta E1 = E_{s2} - E_{s1} \quad KII = 10^0 \quad k_{c2} = 200$$

$$j = 1..25 \quad \frac{\Delta E}{dE} = 25 \quad d = \frac{\tau}{M} \quad \alpha_1 = 0.5 \quad \alpha_2 = 0.5$$

CrevE1CirrE2Cat mechanism diffusional May 2026 OK

(a) Crev:
A ⇌ Red (kf, kb, Keq = kf/kb)

(b) E₁Cirr:
Red ⇌ Int1 + e⁻ (ks,1, α₁)

Int1 → Int2 (kc,irr)

(c) E₂:
Int2 ⇌ Ox + e⁻ (ks,2, α₂)

(d) C':
Ox + Y → Int2 (kcatalytic)

Ova e (CrevECirrECat)mehanizam

"k" e kinetiki parametar na ireverzibilna intermediarna hemiska reakcija (follow up) povzana so prv elektroden cekor

"u" e kinetiki hemiski parametar na prv reverzibilna hemiska reakcija

Keq" e konstanta na ramnotaza so preceding chemical step (a)

$$KII = 1$$

$$u = 5$$

$$\lambda = .0034$$

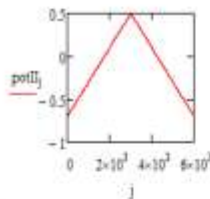
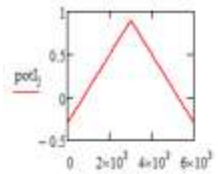
$$Keq = 00.50000010000006051000$$

$$\tau = 00.0000581001049035$$

z e kataliticki parametar vo ovoj model povzan so vtor cekor

$$potI_j = d \left[j \leq \frac{\Delta E}{dE} \cdot 25 \cdot E_{s1} - \left(\text{cel} \left(\frac{j}{25} \right) dE - dE \right) \cdot E_{s1} - \left[\text{cel} \left[\frac{j - \left(\frac{\Delta E}{dE} \cdot 25 \right)}{25} \right] dE - dE \right] \right]$$

$$potII_j = d \left[j \leq \frac{\Delta E}{dE} \cdot 25 \cdot E_{s2} + \left(\text{cel} \left(\frac{j}{25} \right) dE - dE \right) \cdot E_{s2} - \left[\text{cel} \left[\frac{j - \left(\frac{\Delta E}{dE} \cdot 25 \right)}{25} \right] dE - dE \right] \right]$$



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

$$\Phi I_1 = \frac{KI \cdot e^{-\alpha_1 \Phi I_1}}{1 - KI \cdot e^{-\alpha_1 \Phi I_1} \left[\frac{-2 \cdot Keq \cdot S_1}{\sqrt{50\pi} \cdot (1 + Keq)} - \frac{2 \cdot S_1 \cdot e^{-\Phi I_1}}{\sqrt{50\pi}} - \frac{L_1}{(1 + Keq) \cdot \sqrt{u}} - \frac{A_1 \cdot e^{-\Phi I_1}}{\lambda^{0.5}} \right]}$$

$$\Phi II_1 = \frac{\frac{KII}{\sqrt{50\pi}} \cdot e^{-\alpha_2 \Phi II_1}}{1 + \frac{1 \cdot B_1}{\sqrt{z}} \cdot e^{\Phi II_1 \cdot \alpha_2} + \frac{1 \cdot B_1}{\sqrt{z}} \cdot KII \cdot e^{-\Phi II_1 \cdot (1 - \alpha_2)}}$$

$$\Phi II_1 = 5.171 \times 10^{-13}$$

$$\Phi I_1 = 2.182 \times 10^{-3}$$

$$\Phi I_j = \frac{KI \cdot e^{-\alpha_1 \Phi I_j} \left[\frac{Keq}{(1 + Keq)} - \left[\frac{2 \cdot Keq}{\sqrt{50\pi} \cdot (1 + Keq)} - \frac{0 \cdot e^{-\Phi I_j}}{\sqrt{50\pi}} \right] \sum_{i=1}^{j-1} (\Phi I_i \cdot S_{j-i+1}) - \frac{1}{(1 + Keq) \cdot \sqrt{u}} \sum_{i=1}^{j-1} (\Phi I_i \cdot L_{j-i+1}) - \frac{e^{-\Phi I_j}}{\lambda^{0.5}} \sum_{i=1}^{j-1} (\Phi I_i \cdot A_{j-i+1}) \right]}{1 - KI \cdot e^{-\alpha_1 \Phi I_j} \left[\frac{-2 \cdot Keq \cdot S_1}{\sqrt{50\pi} \cdot (1 + Keq)} - \frac{0 \cdot S_1 \cdot e^{-\Phi I_j}}{\sqrt{50\pi}} - \frac{L_1}{(1 + Keq) \cdot \sqrt{u}} - \frac{A_1 \cdot e^{-\Phi I_j}}{\lambda^{0.5}} \right]}$$

$$\Phi II_j = \frac{\frac{2 \cdot KII}{\sqrt{50\pi}} \cdot e^{-\alpha_2 \Phi II_j} \sum_{i=1}^j (\Phi II_i \cdot S_{j-i+1}) - \frac{KII \cdot e^{-(1 - \alpha_2) \Phi II_j}}{(1) \cdot \sqrt{\lambda}} \sum_{i=1}^j (\Phi II_i \cdot A_{j-i+1}) - KII \cdot e^{-\alpha_2 \Phi II_j} \left[-1 + \frac{1 \cdot e^{-\Phi II_j}}{\sqrt{z}} \sum_{i=1}^{j-1} (\Phi II_i \cdot B_{j-i+1}) \right]}{1 + \left(\frac{S_1 \cdot KII}{\sqrt{\lambda}} \cdot e^{\Phi II_j \cdot \alpha_2} \right) + \frac{KII \cdot e^{-(1 - \alpha_2) \Phi II_j} \cdot A_1}{(1) \cdot \sqrt{\lambda}} - \frac{KII \cdot e^{-\alpha_2 \Phi II_j} \cdot B_1}{\sqrt{z}} (1 + e^{-\Phi II_j})}$$

$$A_j = \left(\text{erf} \left(\sqrt{\frac{\lambda}{25}} j \right) \right) - \left[\text{erf} \left(\sqrt{\frac{\lambda}{25}} (j - 1) \right) \right]$$

$$B_j = \left(\text{erf} \left(\sqrt{\frac{z}{25}} j \right) \right) - \left[\text{erf} \left(\sqrt{\frac{z}{25}} (j - 1) \right) \right]$$

$$S_j = \sqrt{j} - \sqrt{j - 1}$$

$$L_j = \left(\text{erf} \left(\sqrt{\frac{u}{25}} j \right) \right) - \left[\text{erf} \left(\sqrt{\frac{u}{25}} (j - 1) \right) \right]$$

$$p = 1, 2 \frac{\Delta E}{dE} - 1$$

serial number of potential steps

$$\Psi_{p,1}^I = \Psi^I \left(\frac{\tau}{\delta \cdot 25} + p \right) \cdot 25$$

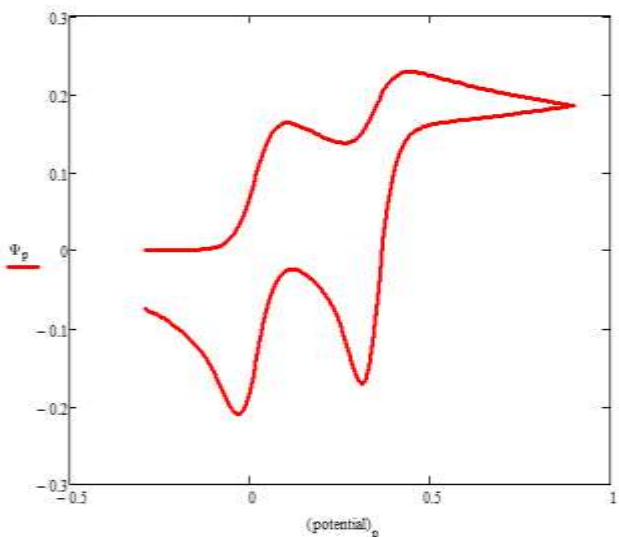
dimensionless current at the end of each potential step of first electrode reaction Ψ^I and of second electrode reaction Ψ^II

$$\Psi_{p,1}^{II} = \Psi^{II} \left(\frac{\tau}{\delta \cdot 25} + p \right) \cdot 25$$

Ψ_p is symbol the cumulative current measured as final output

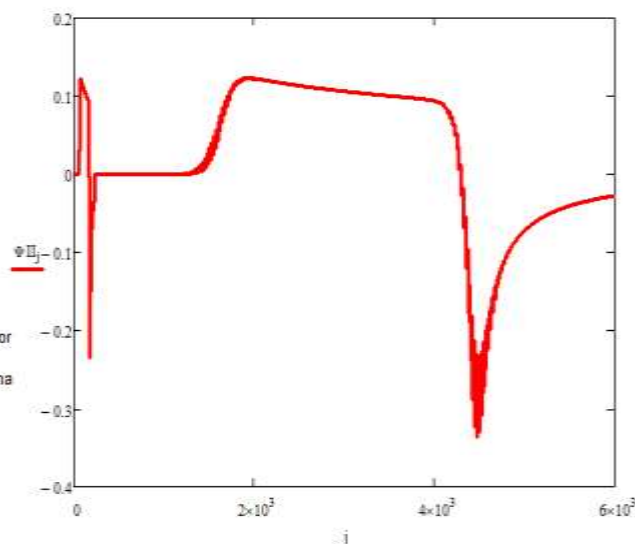
$$\Psi_p = \Psi_{p,1}^{II} + \Psi_{p,1}^I$$

$$\text{potential}_p = \text{if} \left[p \leq \frac{\Delta E}{dE} \cdot E_{s1} + p \cdot dE, E_{s1} - \left(p - \frac{\Delta E}{dE} \right) dE \right] \text{ potential value of each potential step in V}$$



OVOJ E TOCHEN MODEL
CrevECirevEC' difuzionen
vo ciklicna
27 04 2026ta

Koga Keq za prv cekor e golemo
i koga dvata kineticki parametri
u za prv cekor i lambda za vtr cekor
se golemi
togas imame samo E mehanizam na
prv proces, kako i sto treba



ako hemiskiot kineticki parametar se zgolemuva
...pri Keq od 0.1, prvo se namaluva pa potoa raste
povratne pik, a celiot proces se poestuva
ponegativno ([pri oksidacija] ova e OK
0.001; 0.1; 1; 100; 1000; 10000 da e lambda pri
Keq of 0.1

Pri ova lambda i z, da se napravi i vlijanie na Keq
pri ovie isti uslovi

$$\Psi_{p,1}^f = \Psi_{p,1}^f$$

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