A Single Mechanistic Platform that Unifies all Common Electrochemical Mechanism via the ECrevEC′ Reaction Scheme in Cyclic Voltammetry

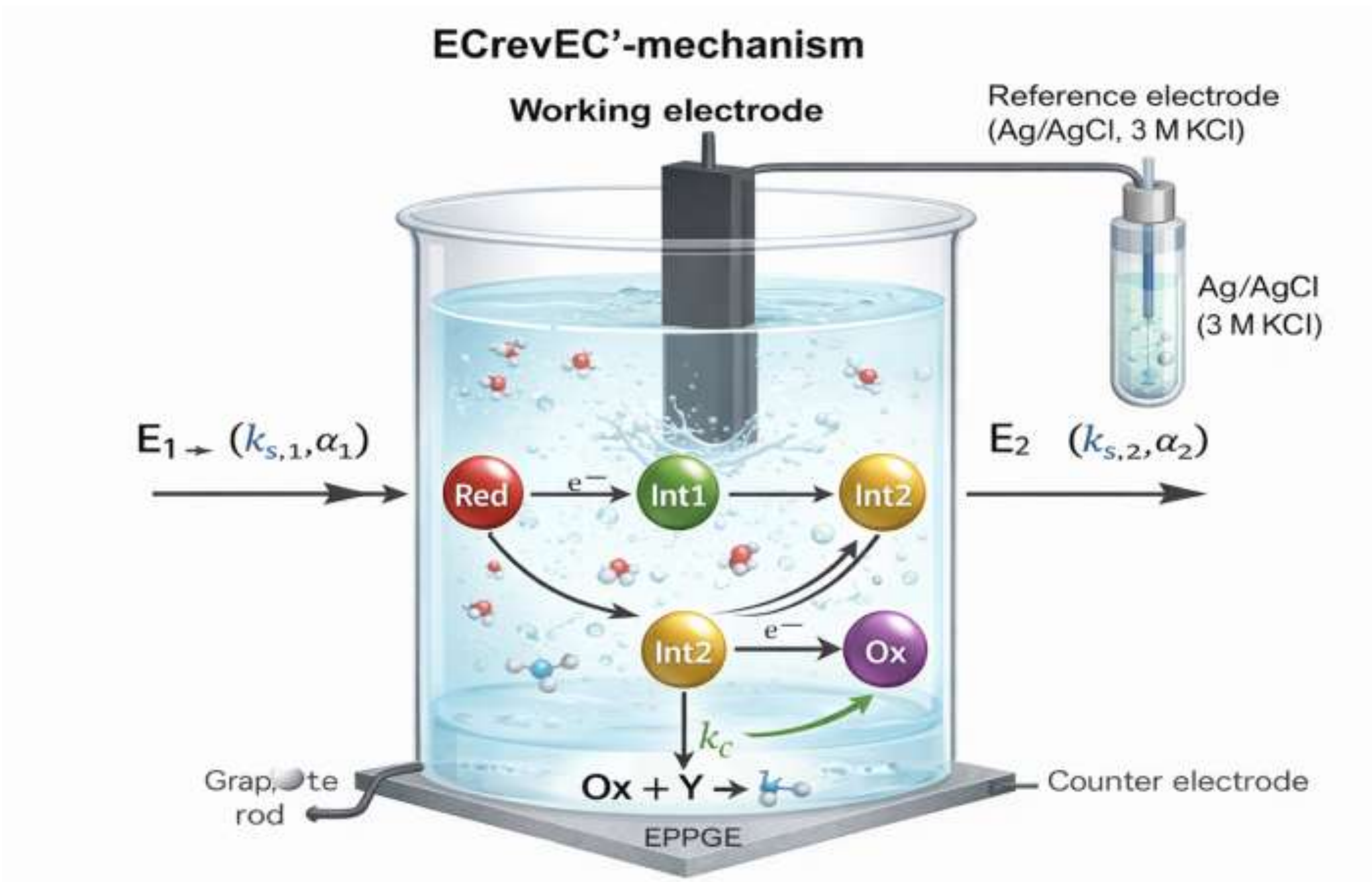
Milkica Janeva, Pavlinka Kokoskarova, Sanja Lazarova, Rubin Gulaboski

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

Abstract

A unified theoretical framework capable of describing diverse electrochemical mechanisms is of fundamental importance for the interpretation of voltammetric data. In this work, we present a single mechanistic platform based on the ECrevEC′ reaction scheme in cyclic voltammetry, which integrates a wide range of commonly encountered electrode processes within one generalized model. The proposed mechanism comprises two sequential electron-transfer steps separated by a reversible chemical transformation, coupled with a regenerative catalytic pathway. Through systematic theoretical analysis, it is demonstrated that, under specific limiting conditions, the ECrevEC′ scheme converges to several fundamental mechanisms, including E, EE, EC, EC′, ECE, EEC’, CEC’ and related variants. This intrinsic flexibility establishes the model as a universal framework for studying complex electrochemical systems involving coupled chemical and catalytic processes. The influence of kinetic parameters, equilibrium constants, and signal parameters on voltammetric responses is examined, revealing characteristic features that enable mechanistic discrimination and kinetic evaluation.

The results highlight the potential of the ECrevEC′ platform to serve as a powerful tool for interpreting cyclic voltammetric behavior of redox-active systems, including biological, catalytic, and surface-confined processes. This unified approach provides a consistent basis for bridging theoretical analysis and experimental voltammetry, thereby facilitating deeper insight into multistep electrochemical mechanisms. Entire MATHCAD simulation file of this important mechanism adapted for cyclic voltammetry is given the readers for free.


ECrevEC'-mechanism
Working electrode
Reference electrode (Ag/AgCl, 3 M KCl)
Ag/AgCl (3 M KCl)
E_1 $(k_{s,1}, \alpha_1)$
E_2 $(k_{s,2}, \alpha_2)$
Red
e^-
Int1
Int2
Int2
e^-
Ox
k_c
Ox + Y →
Graphite rod
Counter electrode
EPPGE

MATHCAD FILE of ECrevEC’ Mechanism in Cyclic Voltammetry

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

$EsI := -0.3 \quad \Delta E := 1 \quad dE := 0.005 \quad EsII := -0.65 \quad t := 1..1$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad \Delta EI := EfI - EsI \quad KI := 10^{2} \quad kc1 := 100$

$M := 25 \quad \Delta EII := EfII - EsII \quad KII := 10^{2} \quad kc2 := 200$

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

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

$$E_1:\ \mathrm{Red} \rightleftarrows \mathrm{Int1} + e^- \quad (k_{s,1}, \alpha_1) \qquad (a)$$

$$C_{rev}:\ \mathrm{Int1} \rightleftarrows \mathrm{Int2} \quad \left(k_f, k_b;\ K_{eq} = \frac{k_f}{k_b};\ k_{chem} = k_f + k_b\right) \qquad (b)$$

$$E_2:\ \mathrm{Int2} \rightleftarrows \mathrm{Ox} + e^- \quad (k_{s,2}, \alpha_2) \qquad (c)$$

$$C'(\mathrm{regenerative}):\ \mathrm{Ox} + Y \rightarrow \mathrm{Int2} \quad (k_c) \qquad (d)$$

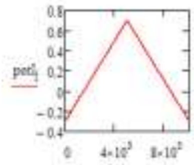
$$potI_j := \mathrm{if}\left[j \le \frac{\Delta E}{dE}\cdot 25, EsI + \left(\mathrm{ceil}\left(\frac{j}{25}\right)\cdot dE - dE\right), EfI - \left[\mathrm{ceil}\left[\frac{j - \left(\frac{\Delta E}{dE}\cdot 25\right)}{25}\right]\cdot dE - dE\right]\right]$$

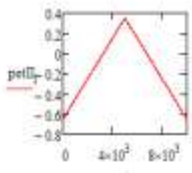
λ e kineticki parametar na reverzibilna hemiska reakcija (follow up) povrzana so prv elektroden cekor

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

$KII = 100$

$Keq := 0.100006051000$





$\lambda := 000.0100000$

$z := .150000581001049035$

z e kataliticki parametar vo ovoj model povrzan so vtor cekor

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

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

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

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

$$\Psi I_1 := \frac{KI\cdot e^{\alpha 1\cdot \Phi I_1}}{1 - KI\cdot e^{\alpha 1\cdot \Phi I_1}\left[\frac{-2}{\sqrt{50\pi}}\cdot\left(\left(1 + \frac{e^{-\Phi I_1}}{1 + Keq}\right)\right) - \frac{KI\cdot e^{-\Phi I_1}\cdot A_1}{\sqrt{\lambda}\cdot(Keq + 1)}\right]}$$

$$\Psi II_1 := \frac{KII\cdot\frac{1}{\sqrt{\lambda}}\cdot e^{\alpha 2\cdot \Phi II_1}}{1 + \frac{1\cdot B_1}{(\sqrt{z})}KII\cdot e^{\Phi II_1\cdot \alpha 2} + \frac{1\cdot B_1}{(\sqrt{z})}KII\cdot e^{-\Phi II_1\cdot(1-\alpha 2)}}$$

$\Psi II_1 = 4.548\times 10^{-10}$

$\Psi I_1 = 4.1\times 10^{-7}$

$$\Psi I_j := \frac{KI\cdot e^{\alpha 1\cdot \Phi I_j}\left[1 - \frac{2}{\sqrt{50\pi}}\cdot\left(1 + \frac{e^{-\Phi I_j}}{1 + Keq}\right)\cdot\sum_{i=1}^{j-1}\left(\Psi I_i\cdot S_{j-i+1}\right) - \frac{KI\cdot e^{-\Phi I_j}}{(1 + Keq)\cdot\sqrt{\lambda}}\cdot\sum_{i=1}^{j-1}\left(\Psi I_i\cdot A_{j-i+1}\right)\right]}{1 - KI\cdot e^{\alpha 1\cdot \Phi I_j}\left[\frac{-2}{\sqrt{50\pi}}\cdot\left(\left(1 + \frac{e^{-\Phi I_j}}{1 + Keq}\right)\right) - \frac{KI\cdot e^{-\Phi I_j}\cdot A_1}{\sqrt{\lambda}\cdot(Keq + 1)}\right]}$$

$$\Psi II_j := \frac{\frac{1KII}{\sqrt{50\cdot\pi}}\cdot 1\cdot e^{\alpha 2\cdot\Phi II_j}\cdot\sum_{i=1}^{j}\left(\Psi I_i\cdot S_{j-i+1}\right) - \frac{-2KII}{((1 + Keq))\cdot\sqrt{50\pi}}\cdot e^{\alpha 2\cdot\Phi II_j}\cdot\sum_{i=1}^{j}\left(\Psi I_i\cdot S_{j-i+1}\right) - \frac{KII\cdot e^{-\Phi I_j}}{(1 + Keq)\cdot\sqrt{\lambda}}\cdot\sum_{i=1}^{j-1}\left(\Psi I_i\cdot A_{j-i+1}\right) - \frac{1}{(\sqrt{z})}KII\cdot e^{\Phi II_j\cdot\alpha 2}\cdot\sum_{i=1}^{j-1}\left(\Psi II_i\cdot B_{j-i+1}\right) - \frac{1}{(\sqrt{z})}KII\cdot e^{-\Phi II_j\cdot(1-\alpha 2)}\cdot\sum_{i=1}^{j-1}\left(\Psi II_i\cdot B_{j-i+1}\right)}{1 + \frac{1\cdot B_1}{(\sqrt{z})}KII\cdot e^{\Phi II_j\cdot\alpha 2} + \frac{1\cdot B_1}{(\sqrt{z})}KII\cdot e^{-\Phi II_j\cdot(1-\alpha 2)}}$$

$p := 1 .. 2\cdot\frac{\Delta EI}{dE} - 1$ — serial number of potential steps

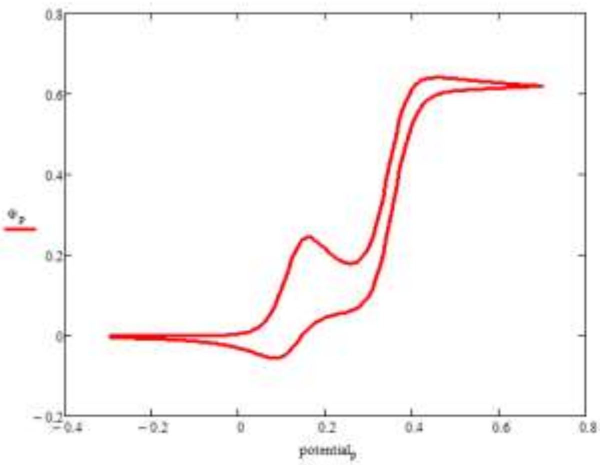
$\Psi I_p := \Psi I_{\left(\frac{\tau}{d\cdot 25}+p\right)\cdot 25}$

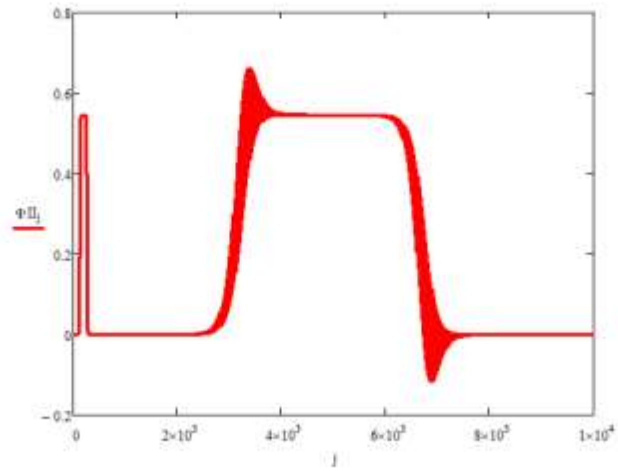
$\Psi II_p := \Psi II_{\left(\frac{\tau}{d\cdot 25}+p\right)\cdot 25}$

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

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

$\text{potential}_p := \text{if}\left[p \le \frac{\Delta EI}{dE}, EsI + p\cdot dE, EfI - \left(p - \frac{\Delta EI}{dE}\right)\cdot dE\right]$ — potential value of each potential step in V





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

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