Resolving Double Regenerative Catalytic Pathways in Redox Protein Films via Cyclic Voltammetry

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Abstract

Redox protein films immobilized on electrode surfaces often exhibit complex catalytic behavior arising from coupled electron-transfer and chemical regeneration steps. In this work, we present a comprehensive theoretical model describing double regenerative catalytic pathways in surface-confined redox protein systems, resolved for the first time through numerical simulations implemented in *Mathcad*. The model is based on a sequential EC′EC″-type mechanism, in which an initial interfacial electron transfer is followed by two kinetically coupled chemical regeneration steps that sustain catalytic turnover.

The system of governing differential equations, incorporating surface confinement, finite electron-transfer kinetics, and regenerative chemical reactions, was solved under cyclic voltammetric conditions. Systematic simulations were performed to evaluate the influence of key dimensionless parameters, including kinetic rate constants, on the shape, position, and magnitude of voltammetric responses.

The results reveal distinct voltammetric signatures characteristic of double regenerative catalysis, including amplified peak currents, asymmetric peak profiles, and the emergence of quasi-steady-state regimes at high catalytic efficiencies. Importantly, the analysis identifies critical parameter domains in which the two catalytic pathways interact synergistically or competitively, thereby governing the overall electrochemical response. A generalized scaling relationship between peak current and the composite kinetic parameter is proposed, providing a unified framework for interpreting complex protein-film voltammetry.

This study establishes a robust theoretical platform for understanding multi-step catalytic mechanisms in redox protein films and demonstrates the power of Mathcad-based modeling in resolving intricate electrochemical systems. The findings are expected to facilitate the rational design and interpretation of bioelectrochemical experiments involving enzymatic and protein-modified electrodes.

TWO STEP SURFACE PROTEIN-FILM VOLTAMMETRY of Double Regenerative EC'EC'cat Mechanism in CYCLIC VOLTAMMETRY---towards Oxidation Version date: 23 03 2026

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

(all A BC adsorbed)no diffusion

$kc1 := 100$

$kc2 := 200$

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

$EfI := 0.6$ $EfII := 0.3$ $\tau := 0.05$

$EsI := -0.4$ $\Delta E := 1$ $dE := 0.005$ $EsII := -0.7$ $r := 1..1$

$n := 1$ $F := 96500$ $R := 8.314$ $T := 298.15$ $\Delta EI := EfI - EsI$ $KI := 10^{-0.2}$

$M := 25$ $\Delta EII := EfII - EsII$ $KII := 10^{-0.2}$

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

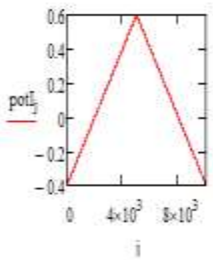
$\alpha 2 := 0.5$ $\alpha 1 := 0.5$

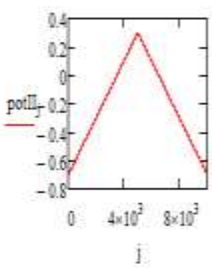
$$potI_j := if\left[j \le \frac{\Delta E}{dE}\cdot 25, EsI + \left(ceil\left(\frac{j}{25}\right)\cdot dE - dE\right), EfI - \left[ceil\left[\frac{j - \left(\frac{\Delta E}{dE}\cdot 25\right)}{25}\right]\cdot dE - dE\right]\right]$$

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

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

$KII = 0.631$





$\lambda := 0.035$

$z := .085001$

z e kataliticki parametar vo ovoj model povrzan so vtor cekor

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

$$A_j := e^{-\lambda\cdot\frac{j}{25}} - e^{-\lambda\cdot\frac{j+1}{25}}$$

$$B_j := e^{-z\cdot\frac{j}{25}} - e^{-z\cdot\frac{j+1}{25}}$$

$x := 0.001$

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

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

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

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

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

serial number of potential steps

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

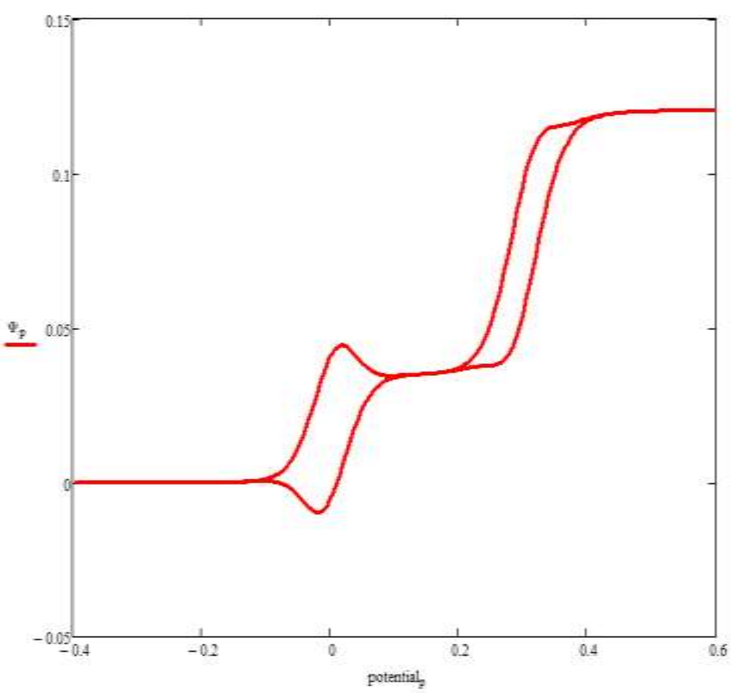
$$\Psi II_p := \Psi II_{\left(\frac{\tau}{d \cdot 25} + p\right) \cdot 25}$$

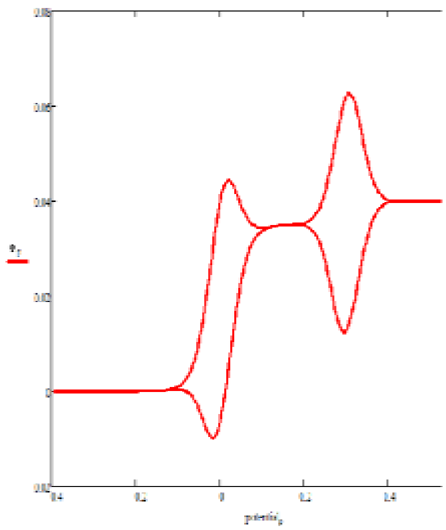
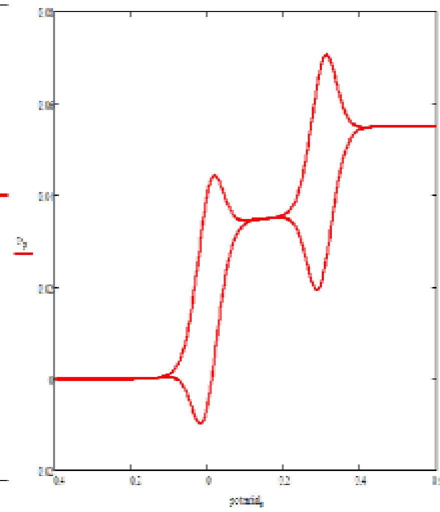
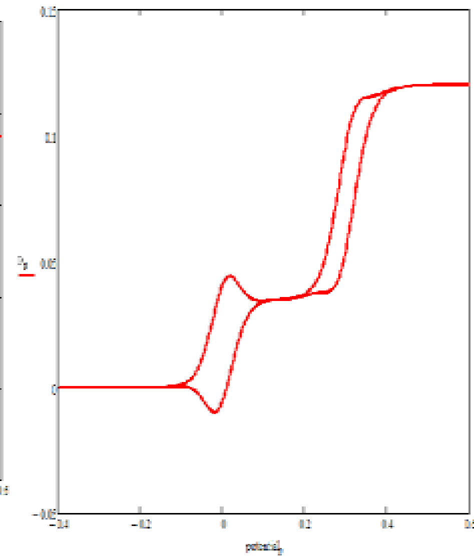
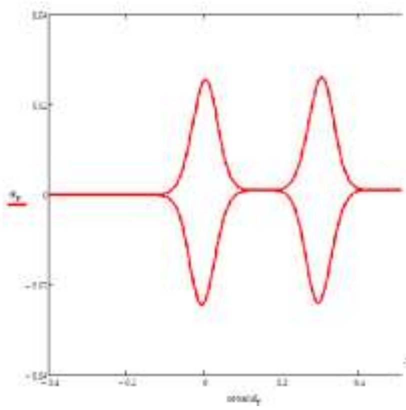
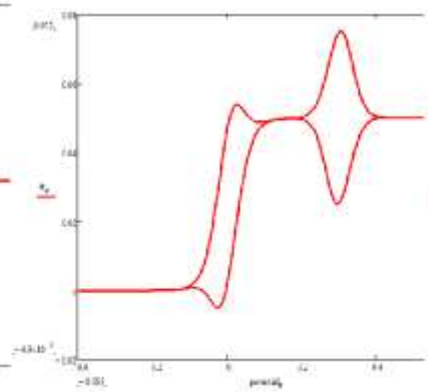
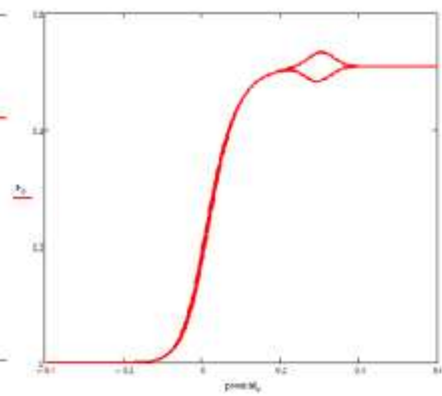
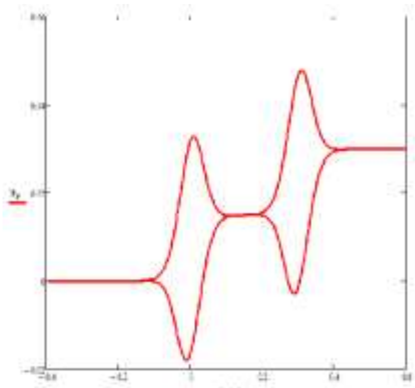
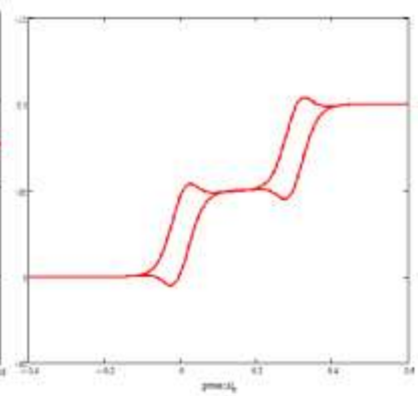
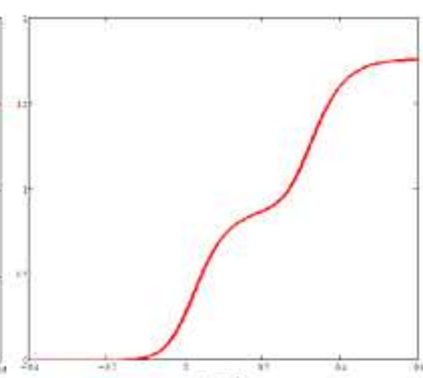
$$\Psi_p := \Psi I_p + \Psi II_p$$

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

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

potential value of each potential step in V



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