Unifying Common Protein-Film Square-Wave Voltammetric Mechanisms within a Single Theoretical Framework: Simulation Protocol in Mathcad

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Abstract

Protein-film square-wave voltammetry (SWV) provides a powerful approach for probing electron-transfer reactions and coupled chemical processes of surface-confined redox systems. However, individual reaction mechanisms are commonly treated using separate theoretical models, making systematic comparison between related pathways difficult. In this work, we present a unified theoretical framework that integrates several common mechanisms encountered in protein-film voltammetry within a single computational model. By appropriate adjustment of kinetic and thermodynamic parameters, the model reproduces characteristic voltammetric behavior associated with simple electron transfer, coupled preceding irreversible and intermediate reversible chemical reactions, sequential electron-transfer steps, and catalytic transformations associated to the second electron transfer step. Particular attention is given to the relationships between kinetic parameters and experimentally accessible SWV features, including peak potentials, peak currents, forward and backward components, and peak morphology. The framework therefore provides a systematic basis for recognizing mechanistic transitions and distinguishing between related reaction pathways. Beyond its theoretical significance, the proposed approach offers a practical tool for mechanistic interpretation and kinetic analysis of complex surface-confined redox processes by square-wave voltammetry. The Mathcad simulation protocol provided in this work enables straightforward generation and systematic exploration of different mechanistic scenarios by varying the relevant kinetic and thermodynamic parameters. It therefore provides a practical computational tool for testing reaction pathways, identifying characteristic voltammetric signatures, and supporting mechanistic discrimination and kinetic analysis. The proposed framework connects apparently different protein-film voltammetric mechanisms within a common theoretical and computational basis.

Theoretical Protocol to simulate surface CirrE1CrevE2C' mechanism in MATHCAD under conditions of Square-wave voltammetry

$Eff := 0.8 \quad Effl := .5 \quad \tau := 0.05 \quad Esw := 0.05$

$Esl := -0.4 \quad \Delta E := 1.2 \quad dE := 0.01 \quad EslI := -0.7$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15 \quad \Delta El := Eff - Esl \quad Kl := 10^{-0}$

$\Delta Ell := Effl - Eslf \quad Kll := 10^{-0}$

$\alpha l := 0.5 \quad \alpha 2 := 0.5$

$f := 10$

$kc1 := 100$

$kc := 2.5$

$Cirr :=$ Cirr. A--->Red (kc1)

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

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

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

C'(regenerative): Ox + Y $\rightarrow$ Int2 (k_c) (d)

$j := 1 .. \frac{\Delta E}{dE} \cdot 50$

$$potI_j := (Esl + Esw) + \left[\left(ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$$

$$potII_j := (Esll + Esw) + \left[\left(ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$$

u, λ and z are defined as
u = kc1/f
λ = kchem/f and
z = kc /f

Kll = 1

u := 01.50

u is Kchem,1

λ := .02000000000000500

λ is Kchem,2

Keq := 2.51000

z := .4174532

z is Kcat

α1 and α2 are electron transfer coefficients

τ is duration of potential step

dE is potential step

Surface CirrE1CrevE2C' in Square-Wace Voltammetry-meaning of symbols

Kchem1 is chemical rate parameter of preceding irreversible chemical step

Keq is equilibrium constant of reversible chemical step

Kchem2 is chemical rate parameter of reversible chemical step

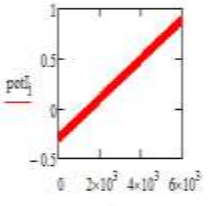
Kcat is chemical rate parameter of renegenerative reaction C'

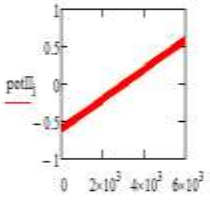
Kl is parameter related to the rate of first electron transfer

Kll is parameter reletaed to the rate of second electron transfer

MODEL ASSUMES ALL ADSORBED redox species

PROTEIN-FILM SW VOLTAMMETRY





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

ΦI and ΦII are dimensionless potentials of first and second electrode reaction, correspondingly

$$L_j := e^{-u\cdot\frac{j}{50}} - e^{-u\cdot\frac{j+1}{50}} \quad A_j := e^{-\lambda\cdot\frac{j}{50}} - e^{-\lambda\cdot\frac{j+1}{50}} \quad B_j := e^{-z\cdot\frac{j}{50}} - e^{-z\cdot\frac{j+1}{50}}$$

$$\Psi I_1 := \frac{Kl\cdot e^{\alpha l\cdot\Phi I_1}}{1 - Kl\cdot e^{\alpha l\cdot\Phi I_1}\left[\frac{-L_1}{u} + \frac{-1}{50}\left(\left(1 + \frac{e^{-\Phi I_1}}{1 + Keq}\right)\right) - \frac{1\cdot e^{-\Phi I_1}\cdot A_1}{\lambda\cdot(Keq + 1)}\right]}$$

$$\Psi II_1 := \frac{Kll\cdot\frac{1}{50}\cdot e^{\alpha 2\cdot\Phi II_1}}{1 + \frac{1\cdot B_1}{(z)}Kll\cdot e^{\Phi II_1\cdot\alpha 2} + \frac{1\cdot B_1}{(z)}Kll\cdot e^{-\Phi II_1\cdot(1-\alpha 2)}}$$

$$\left\lfloor u \quad 50 \right\rfloor \left\lfloor 1 + Keq \right\rfloor \left\lfloor \lambda\cdot(Keq + 1) \right\rfloor$$

$$\Psi II_j := \frac{\frac{Kll\cdot e^{-\Phi II_j\cdot(1-\alpha 2)}}{(1 + Keq)\cdot\lambda}\cdot\left[\sum_{i=1}^{j}\left(\Psi I_i\cdot A_{j-i+1}\right)\right] - Kll\cdot e^{\alpha 2\cdot\Phi II_j}\cdot\left[-1 + \frac{1 + e^{-\Phi II_j}}{z}\cdot\sum_{i=1}^{j-1}\left(\Psi II_i\cdot B_{j-i+1}\right)\right]}{1 + \frac{Kll\cdot e^{-\Phi II_j\cdot(1-\alpha 2)}\cdot A_1}{(1 + Keq)\cdot\lambda} + \frac{Kll\cdot e^{\alpha 2\cdot\Phi II_j}\cdot B_1}{z}\left(1 + e^{-\Phi II_j}\right) + Kll\cdot e^{\alpha 2\cdot\Phi II_j}\cdot B_1} = \ldots$$

$\Psi_j := \Psi I_j + \Psi II_j$

$p := 1 .. \left(\frac{\Delta E}{dE}\right) - 1$

$\Psi If_p := \Psi I_{(p+1)\cdot 50}$ $\Psi Ib_p := \Psi I_{50\cdot p+25}$ $\Psi Inet_p := \Psi If_p - \Psi Ib_p$

$\Psi IIb_p := \Psi II_{50\cdot p+25}$ $\Psi IIf_p := \Psi II_{(p+1)\cdot 50}$ $\Psi IInet_p := \Psi IIf_p - \Psi IIb_p$

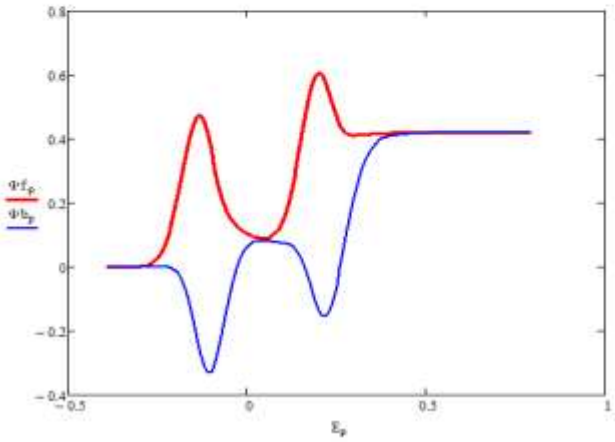
$E_p := Esl + p \cdot dE$

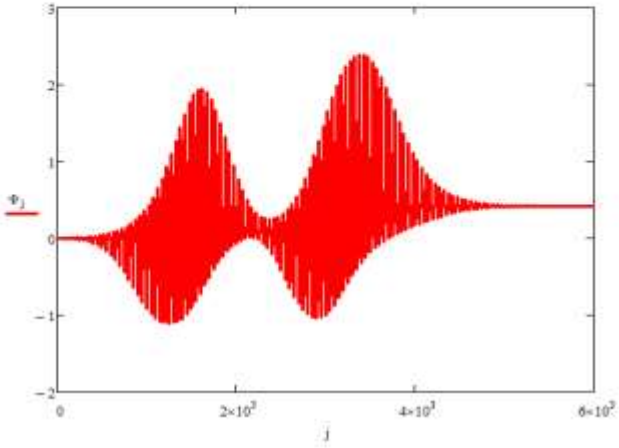
$\Psi b_p := \Psi_{50\cdot p+25}$ $\Psi f_p := \Psi_{(p+1)\cdot 50}$ $\Psi net_p := \Psi f_p - \Psi b_p$

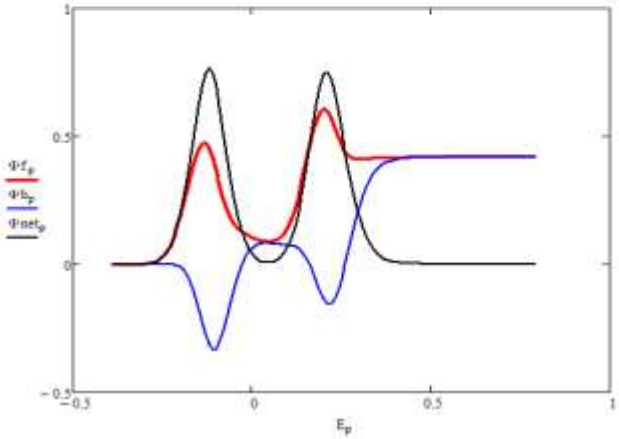
p is serial number of potential steps

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 value of each potential step in V







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