

Cyclic Voltammetry Makes Clear Distinction between Decomposition of Enzymatic Adsorbed Film and the Chemical Inactivation of Initial Redox Enzymatic Form in Protein-Film Voltammetry

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$$\begin{aligned}
 m &:= \frac{tac}{d} + 1.. \frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} & n &:= \frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} + 1.. \left(\frac{\Delta E}{dE} \cdot 25 \cdot 2 + \frac{tac}{d} \right) & k_s &:= 10^{1.6995} \\
 E_m &:= Es + \left(\text{ceil} \left(\frac{m - \frac{tac}{d}}{25} \right) \cdot dE - dE \right) & \alpha &:= 0.5 & K_{et} &:= \frac{k_s \cdot \tau}{1} \\
 E_n &:= Ef - \left[\text{ceil} \left[\frac{n - \left(\frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} \right)}{25} \right] \cdot dE - dE \right] & s &:= 1.. \frac{tac}{d} & K_{et} &:= 1.001 \\
 el &:= 1 & k &:= 1.. 2 \cdot \left(\frac{\Delta E}{dE} \cdot 25 + \frac{tac}{d} \right) & \frac{dE}{\tau} &:= 0.2 \\
 F &:= 96500 & T &:= 298 & K_{chem} &:= \frac{k_c \cdot \tau}{1} \\
 R &:= 8.314 & & & K_{chem} &:= 3 \\
 \Phi_m &:= el \cdot \frac{F}{R \cdot T} \cdot (E_m) & b_n &:= el \cdot \frac{F}{R \cdot T} \cdot (E_n) & S_k &:= e^{\frac{K_{chem}}{25} \cdot (-k)} - e^{\frac{K_{chem}}{25} \cdot (-k+1)} \\
 \Psi_1 &:= \frac{K_{et} \cdot e^{-\alpha \cdot \Phi_1} - \left[K_{et} \cdot e^{-\alpha \cdot \Phi_1} \cdot \frac{\left(1 + e^{-\Phi_1} \right)}{25} \cdot 0 + \frac{K_{chem}^1 \cdot e^{-\alpha \cdot \Phi_1} \cdot 1 \cdot S_1}{1+0} \right]}{1 + \frac{K_{et} \cdot e^{-\alpha \cdot \Phi_1} \cdot \left(1 + e^{-\Phi_1} \right)}{25} - \frac{K_{chem}^1 \cdot e^{-\alpha \cdot \Phi_1} \cdot 1 \cdot S_1}{1+0}} \\
 \Psi_s &:= \frac{K_{et} \cdot e^{-\alpha \cdot \Phi_{ac}} + \frac{K_{chem}^1 \cdot e^{-\alpha \cdot \Phi_{ac}} \cdot 1}{1} \cdot \sum_{j=1}^{s-1} (\Psi_1_j \cdot S_{s-j+1}) - K_{et} \cdot e^{-\alpha \cdot \Phi_{ac}} \cdot \frac{\left(1 + e^{-\Phi_{ac}} \right)}{25} \cdot \sum_{j=1}^{s-1} \Psi_1_j}{1 + \frac{K_{et} \cdot e^{-\alpha \cdot \Phi_{ac}} \cdot \left(1 + e^{-\Phi_{ac}} \right)}{25} - \frac{K_{chem}^1 \cdot e^{-\alpha \cdot \Phi_{ac}} \cdot 1 \cdot S_1}{1+0}}
 \end{aligned}$$

Coupled to Initial Redox Form in Protein-Film Cyclic Voltammetry

Definitions and Meanings of the Symbols

- τ is the duration of potential steps
- k_s is standard rate constant of electron transfer
- α is electron transfer coefficient
- el is number of exchanged electrons
- dE is potential step
- E_m is potential of reduction ramp
- E_n is potential of oxidation ramp
- T is thermodynamic temperature
- R is universal gas constant
- k_c is rate constant of irreversible chemical reaction
- K_{et} is dimensionless kinetic electrode parameter
- K_{chem} is dimensionless kinetic chemical parameter
- S_k is numerical integration factor
- Es is starting potential
- Φ is dimensionless potentials
- F is the Faraday constant
- Ψ is dimensionless current
- Φ_m is cathodic potential ramp
- b_n is anodic potential ramp

$$\Psi_{1m} := \frac{\text{Ket} \cdot e^{-\alpha \cdot \Phi_m} + \frac{\text{Kchem}^1 \cdot e^{-\alpha \cdot \Phi_m}}{1+0} \cdot \sum_{j=1}^{m-1} (\Psi_{1j} \cdot S_{m-j+1}) - \text{Ket} \cdot e^{-\alpha \cdot \Phi_m} \cdot \frac{(1+e^{\Phi_m})}{25} \cdot \sum_{j=1}^{m-1} \Psi_{1j}}{1 + \frac{\text{Ket} \cdot e^{-\alpha \cdot \Phi_m} \cdot (1+e^{\Phi_m})}{25} - \frac{\text{Kchem}^1 \cdot e^{-\alpha \cdot \Phi_m} \cdot 1 \cdot S_1}{1+0}}$$

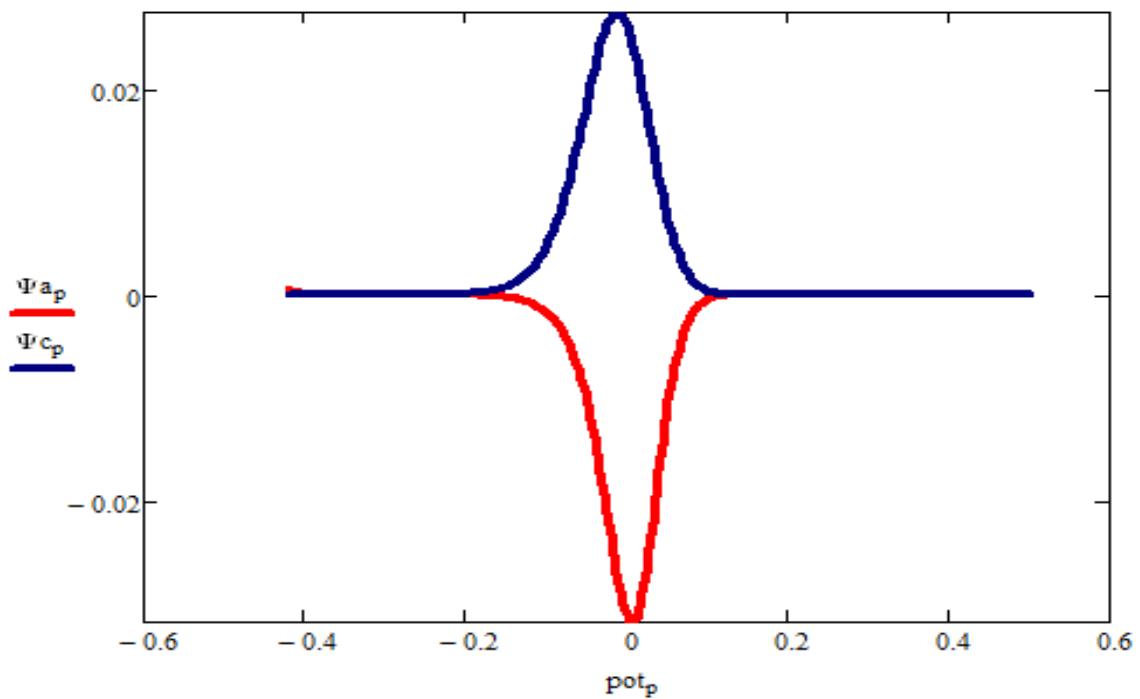
$$\Psi_{1n} := \frac{\text{Ket} \cdot e^{-\alpha \cdot b_n} + \frac{\text{Kchem}^1 \cdot e^{-\alpha \cdot b_n} \cdot 1}{1} \cdot \sum_{j=1}^{n-1} (\Psi_{1j} \cdot S_{n-j+1}) - \text{Ket} \cdot e^{-\alpha \cdot b_n} \cdot \frac{(1+e^{b_n})}{25} \cdot \sum_{j=1}^{n-1} \Psi_{1j}}{1 + \frac{\text{Ket} \cdot e^{-\alpha \cdot b_n} \cdot (1+e^{b_n})}{25} - \frac{\text{Kchem}^1 \cdot e^{-\alpha \cdot b_n} \cdot 1 \cdot S_1}{1}}$$

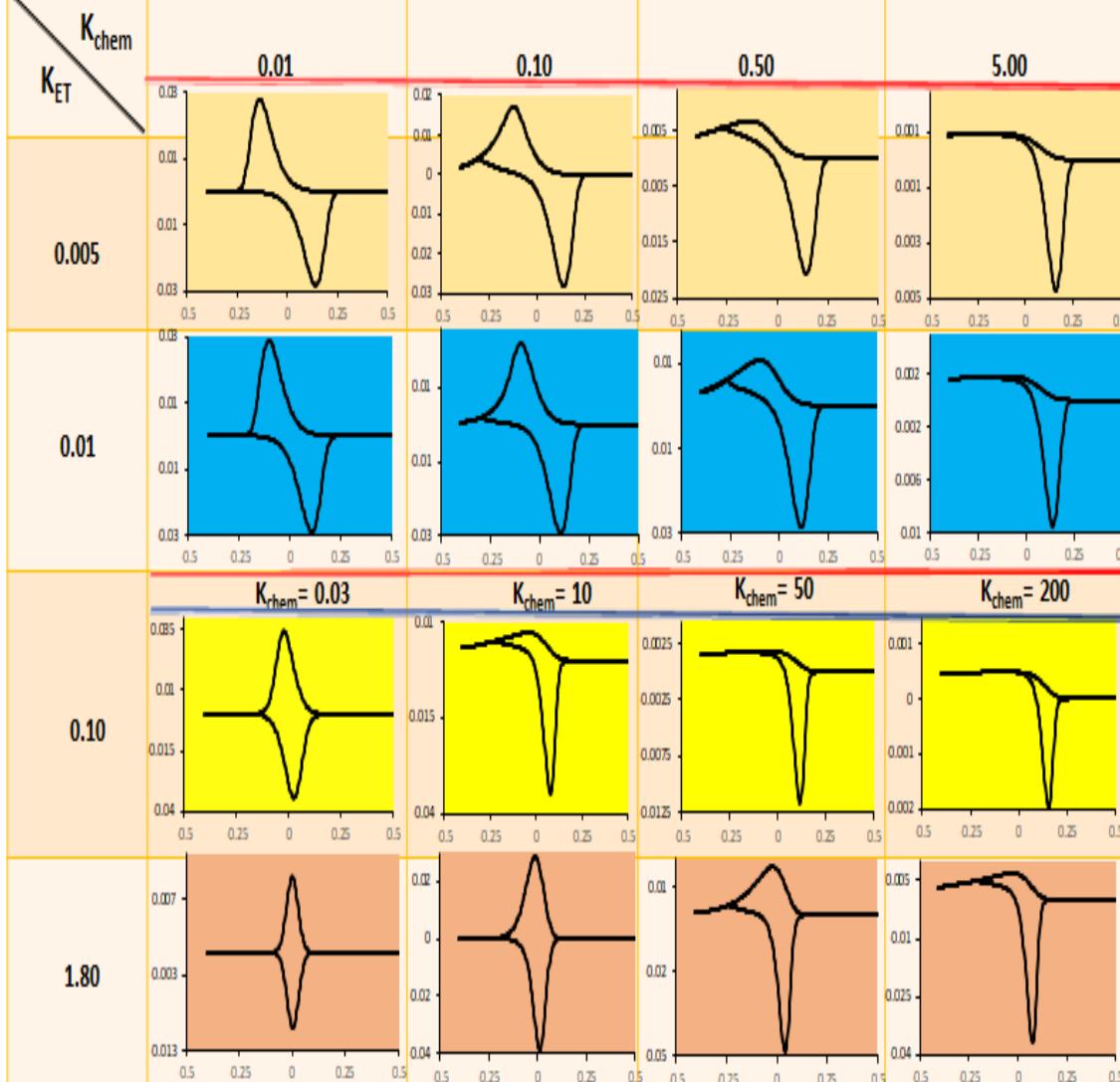
$$p := 20 \cdot \frac{\Delta E}{dE}$$

$$\Psi_{ap} := (\Psi_1) \left(\frac{\tau}{d \cdot 25} + p \right) \cdot 25$$

$$\Psi_{cp} := (\Psi_1) \left[\left[\frac{\Delta E}{dE} \cdot 2 + \left(\frac{\tau}{25 \cdot d} \right) \right] - p \right] \cdot 25$$

$$pot_p := Es + p \cdot dE$$





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