# SUPPLEMENTARY MATERIAL-MATHCAD working file

# Electrochemistry of Lipophilic Redox Enzymes Associated with a Reversible Follow-up Chemical Reaction-Theoretical Consideration in Cyclic Staircase Voltammetry

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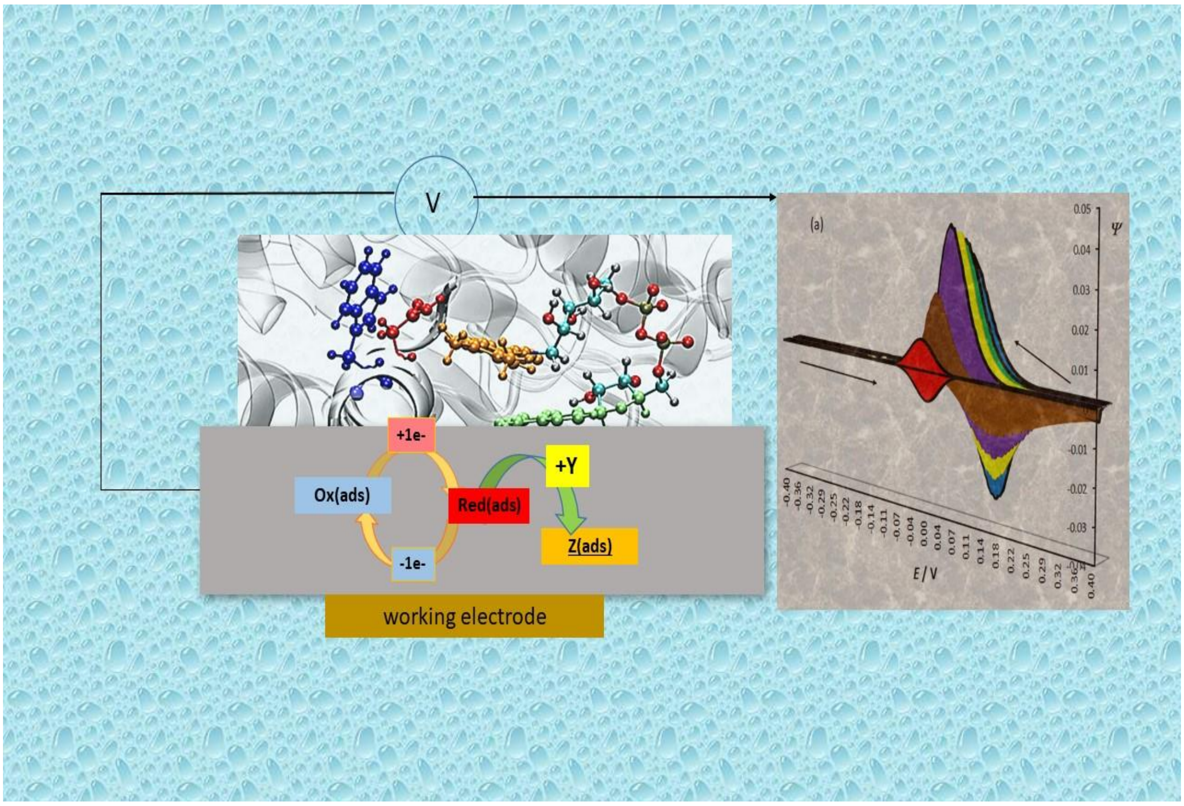



This supporting material provides entire MATHCAD File that contains all formulas for simulation of cyclic staircase voltammograms of protein-film voltammetric electrode mechanism that is associated with reversible chemical reaction to the final product of the enzymatic transformation. It can be used for free from anyone interested in simulating this electrochemical mechanism.

## Surface ECrev Mechanism
## in Cyclic Staircase Voltammetry
-meaning of the symbols in working MATHCAD file-

$tac := 0.01$

$Es := -0.4 \quad Ef := 0.4 \quad \Delta E := Ef - Es \quad dE := 0.004 \quad \tau := 0.01 \quad d := \frac{\tau}{25}$

$s := 1 .. \frac{tac}{d}$

$m := \frac{\tau}{d} + 1 .. \frac{\Delta E}{dE} \cdot 25 + \frac{\tau}{d} \qquad n := \frac{\Delta E}{dE} \cdot 25 + \frac{\tau}{d} + 1 .. \left(\frac{\Delta E}{dE} \cdot 25 \cdot 2 + \frac{\tau}{d}\right)$

$\frac{\Delta E}{dE} = 200$

$el := 1 \quad \alpha := 0.5$

$E_m := Es + \left(\mathrm{ceil}\left(\frac{m - \frac{\tau}{d}}{25}\right) \cdot dE - dE\right) \qquad E_n := Ef - \left[\mathrm{ceil}\left[\frac{n - \left(\frac{\Delta E}{dE} \cdot 25 + \frac{\tau}{d}\right)}{25}\right] \cdot dE - dE\right]$

$F := 96500 \quad R := 8.314 \quad T := 298.15$

$Keq := 10.00$

$k := 1 .. 2 \cdot \left(\frac{\Delta E}{dE} \cdot 25 + \frac{\tau}{d}\right)$

$ks := 5.0$

$\varepsilon := 2500.00$

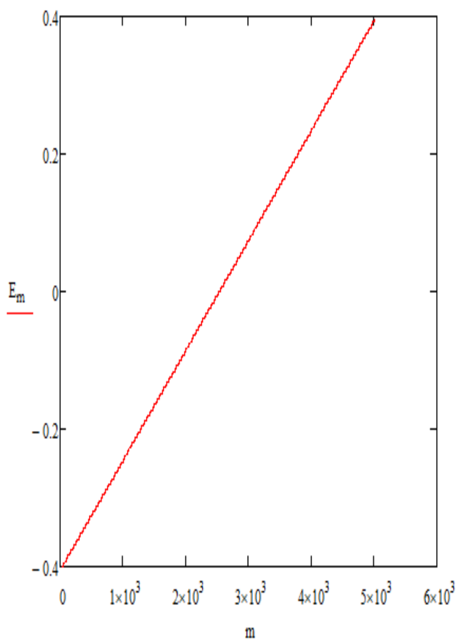
$\Phi_m := \frac{el \cdot F}{R \cdot T} \cdot E_m \quad \Phi_n := \frac{el \cdot F}{R \cdot T} \cdot E_n \quad \Phi ac := \frac{el \cdot F}{R \cdot T} \cdot Es$

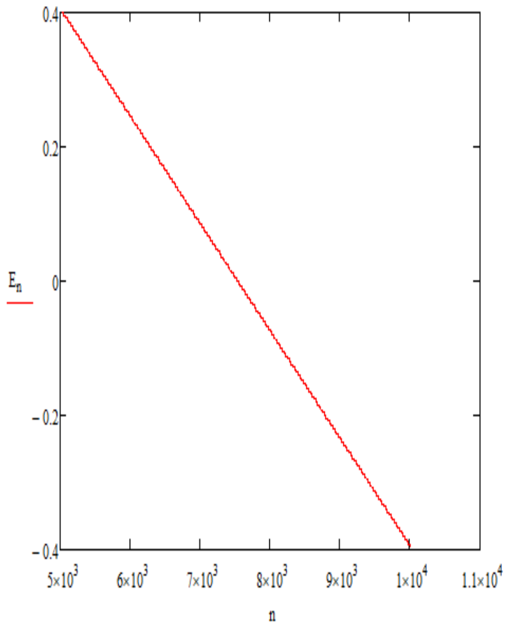
$K := ks \cdot \tau$

$K = 0.05 \qquad Kchem := \frac{\varepsilon \cdot \tau}{1} \qquad Kchem = 25$

$M_k := e^{-Kchem \cdot \frac{(k)}{25}} - e^{-Kchem \cdot \frac{(k+1)}{25}}$

K is dimensionless kinetic parameter related to electrode reaction
ks-is rate constant of electron transfer
Kchem - is dimensionless rate parameter related to follow up chemical reaction
Keq is equilibrium constant of follow up chemical reaction
α is electron transfer coefficient
M is numerical integration factor
τ is duration of potential steps
Es is starting potential
Ef is final potential
dE is height of potential step
Ψ is symbol for dimensionless current
Em is cathodic potential ramp in cyclic voltammetry
En is anodic potential ramp
Mk is integration factor
el = n-is number of electrons
R - is universal gas constant
T-is thermodynamic temperature
F - is Faraday constant
Φ-is symbol of the dimensionless potential



$$\Psi_s := \frac{K\cdot e^{-\alpha\cdot\Phi ac}}{1+\frac{K}{25}\cdot e^{-\alpha\cdot\Phi ac}+\frac{K\cdot Keq}{25\cdot(1+Keq)}\cdot e^{(1-\alpha)\cdot\Phi ac}+\frac{1}{(1+Keq)}Kchem^{1}\cdot e^{\Phi ac\cdot(1-\alpha)}\cdot M_1}$$

$$\Psi_m := \frac{K\cdot e^{-\alpha\cdot\Phi_m}-\frac{K}{25}\cdot e^{-\alpha\cdot\Phi_m}\cdot\sum_{j=1}^{m-1}\Psi_j-\frac{K\cdot Keq}{25\cdot(1+Keq)}\cdot e^{(1-\alpha)\cdot\Phi_m}\cdot\sum_{j=1}^{m-1}\left(\Psi_j\right)-\frac{Kchem}{1\cdot(1+Keq)}\cdot e^{\Phi_m\cdot(1-\alpha)}\cdot\sum_{j=1}^{m-1}\left(\Psi_j\cdot M_{m-j+1}\right)}{1+\frac{K}{25}\cdot e^{-\alpha\cdot\Phi_m}+\frac{K\cdot Keq}{25\cdot(1+Keq)}\cdot e^{(1-\alpha)\cdot\Phi_m}+\frac{Kchem}{1\cdot(1+Keq)}\cdot e^{\Phi_m\cdot(1-\alpha)}\cdot M_1}$$

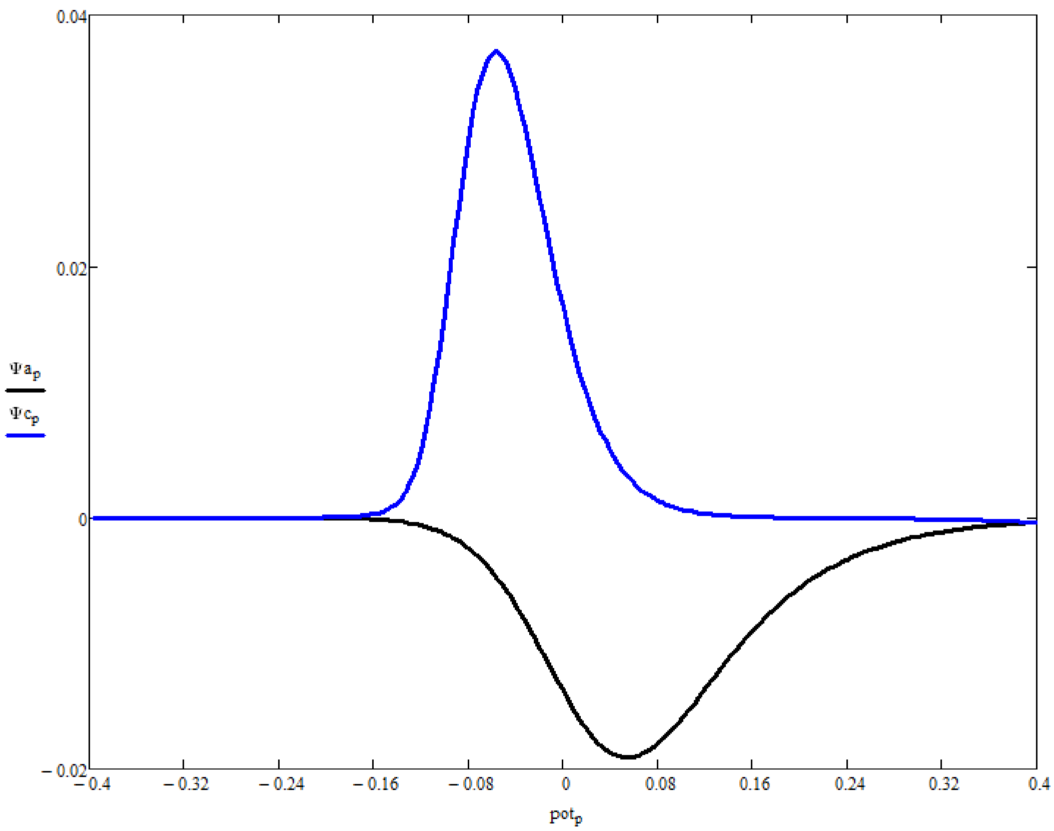
$$\Psi_n := \frac{K\cdot e^{-\alpha\cdot\Phi_n}-\frac{K}{25}\cdot e^{-\alpha\cdot\Phi_n}\cdot\sum_{j=1}^{n-1}\Psi_j-\frac{K\cdot Keq}{25\cdot(1+Keq)}\cdot e^{(1-\alpha)\cdot\Phi_n}\cdot\sum_{j=1}^{n-1}\left(\Psi_j\right)-\frac{1}{(1+Keq)}Kchem^{1}\cdot e^{\Phi_n\cdot(1-\alpha)}\cdot\sum_{j=1}^{n-1}\left(\Psi_j\cdot M_{n-j+1}\right)}{1+\frac{K}{25}\cdot e^{-\alpha\cdot\Phi_n}+\frac{K\cdot Keq}{25\cdot(1+Keq)}\cdot e^{(1-\alpha)\cdot\Phi_n}+\frac{1}{(1+Keq)}Kchem^{1}\cdot e^{\Phi_n\cdot(1-\alpha)}\cdot M_1}$$

$$p := 1 .. \frac{\Delta E}{dE}$$

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

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

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



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