Theory of two-step electrode transformations coupled with chemical equilibria relevant to electrochemistry of lipophilic redox enzymes studied under conditions of square-wave voltammetry

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Abstract

Protein-film voltammetry is recognized as a simple but useful technique that can provide access to the electrochemical features of various lipophilic redox enzymes. The so-called "two-step electrode mechanisms" pare related to the redox chemistry of relevant enzymatic systems whose redox transformation occurs in two consecutive steps. In our recent works we published several theories of two-step electrode mechanisms, in which the electron transfer steps were associated with preceding, follow up or regenerative chemical step. In this work, we present some of the major achievements of the protein-film voltammetry of two-step electrode mechanisms coupled with various chemical equilibria. We also provide the readers several hints on how to use methodologies for the determination of thermodynamic and kinetic parameters relevant to two-step protein-film mechanisms. The considered mechanisms are applicable to many lipophilic redox proteins and enzymes that undergo electrochemical transformations in more than one successive electron steps. Such examples exist by proteins containing quinone moiety and some polyvalent ions of transition metals as redox active sites.

ECCE

$$\begin{aligned} P + e^- &\rightleftharpoons Q \\ Q + A &\xrightarrow{k_1} B \\ B + Z &\xrightarrow{k_2} Q'' \\ Q'' + e^- &\rightleftharpoons C + P \end{aligned}$$

ECEC

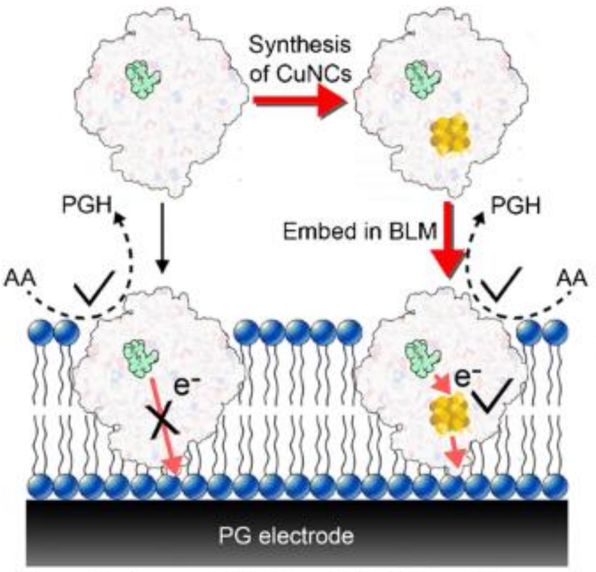
$$\begin{aligned} P + e^- &\rightleftharpoons Q \\ Q + A &\xrightarrow{k_1} Q' \\ Q' + e^- &\rightleftharpoons B \\ B + Z &\xrightarrow{k_2} C + P \end{aligned}$$

ECCE′

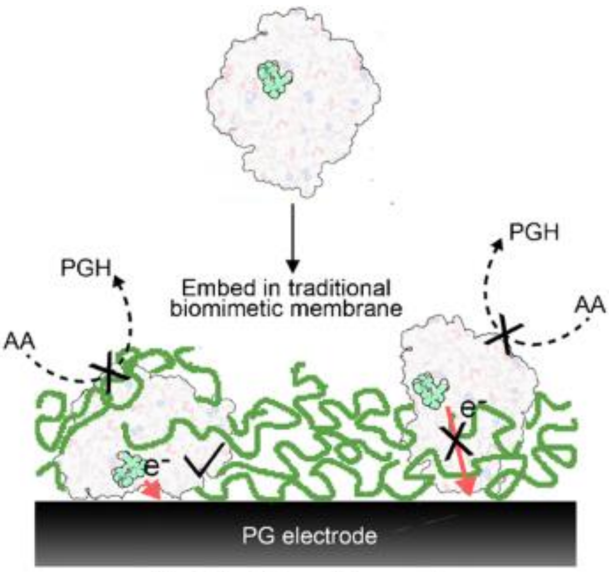
$$\begin{aligned} P + e^- &\rightleftharpoons Q \\ Q + A &\xrightarrow{k_1} B \\ B + Z &\xrightarrow{k_2} Q'' \\ Q'' + Q &\rightleftharpoons C + 2P \end{aligned}$$

ECE′C

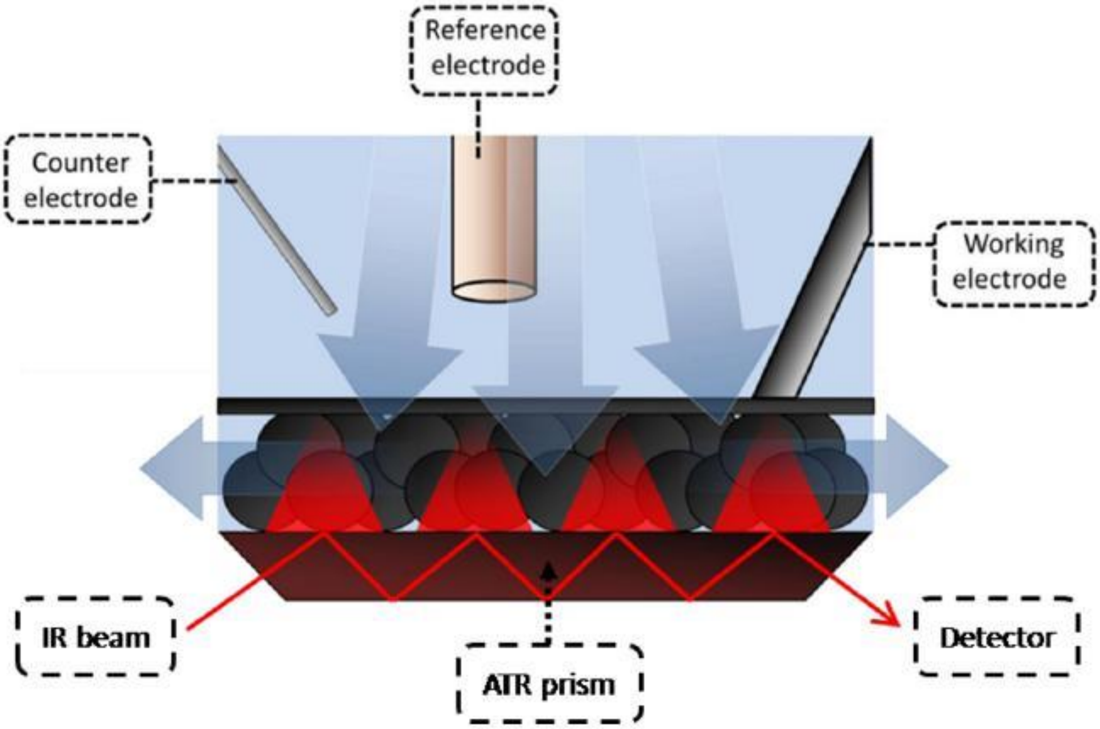
$$\begin{aligned} P + e^- &\rightleftharpoons Q \\ Q + A &\xrightarrow{k_1} Q' \\ Q' + Q &\rightleftharpoons B + P \\ B + Z &\xrightarrow{k_2} C + P \end{aligned}$$

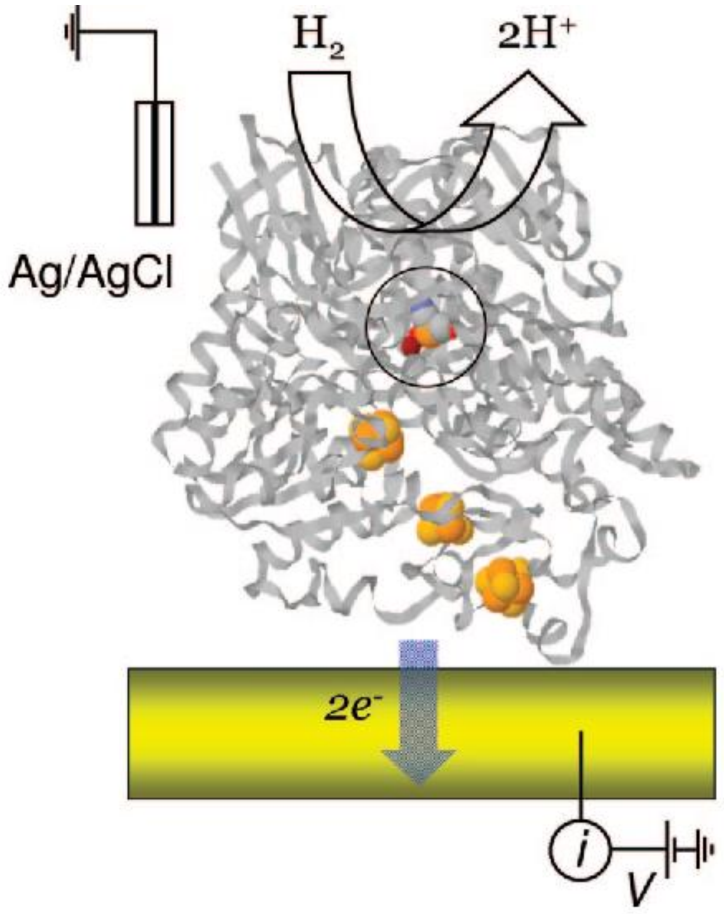


Nanocluster-assisted protein-film voltammetry

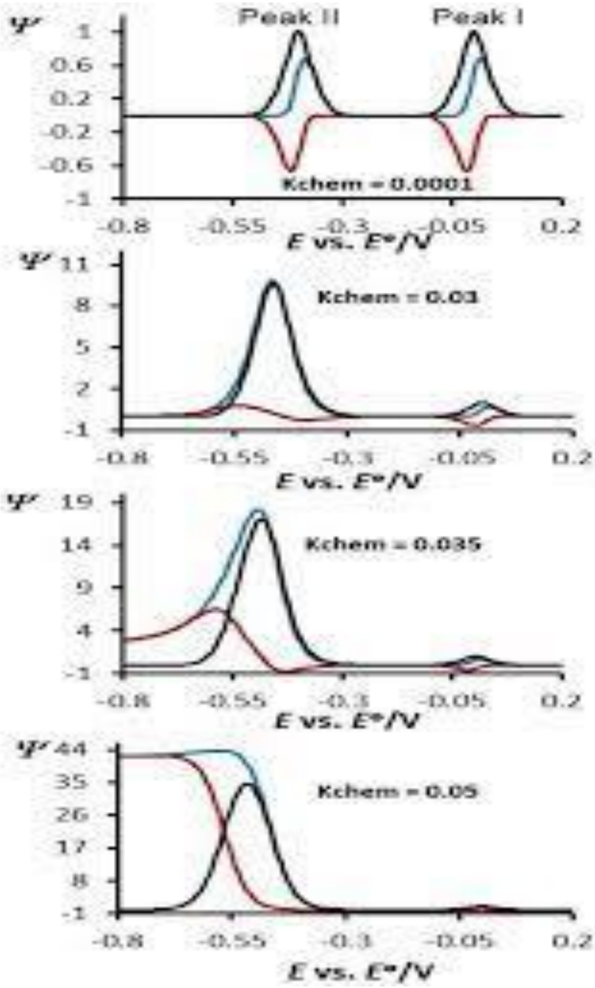


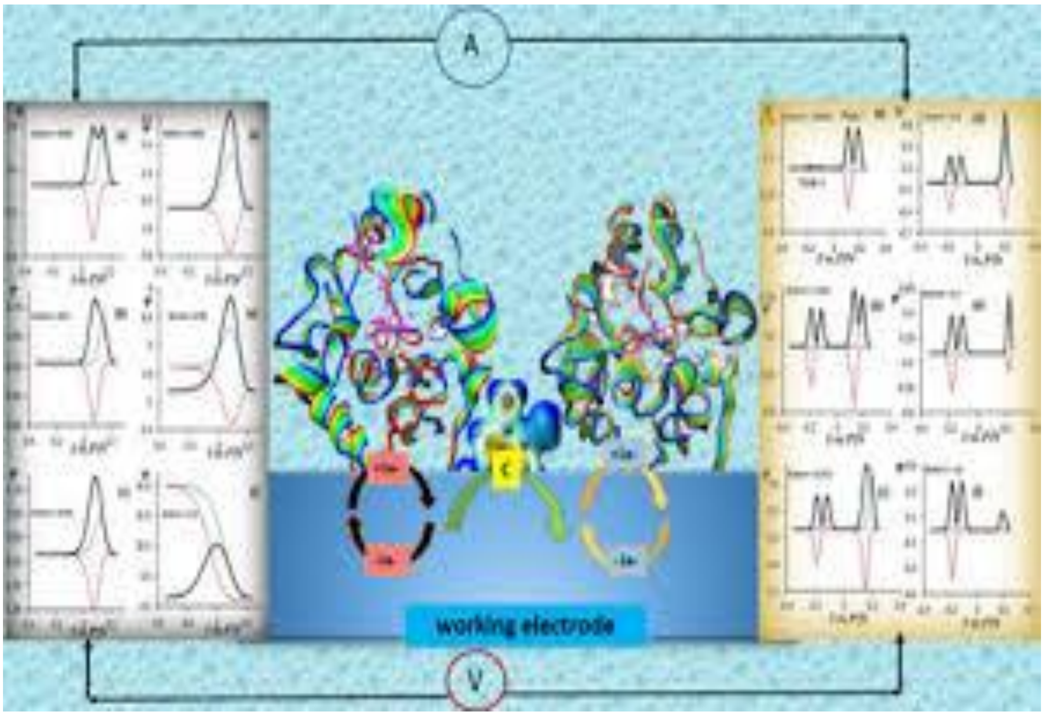
Protein-film voltammetry

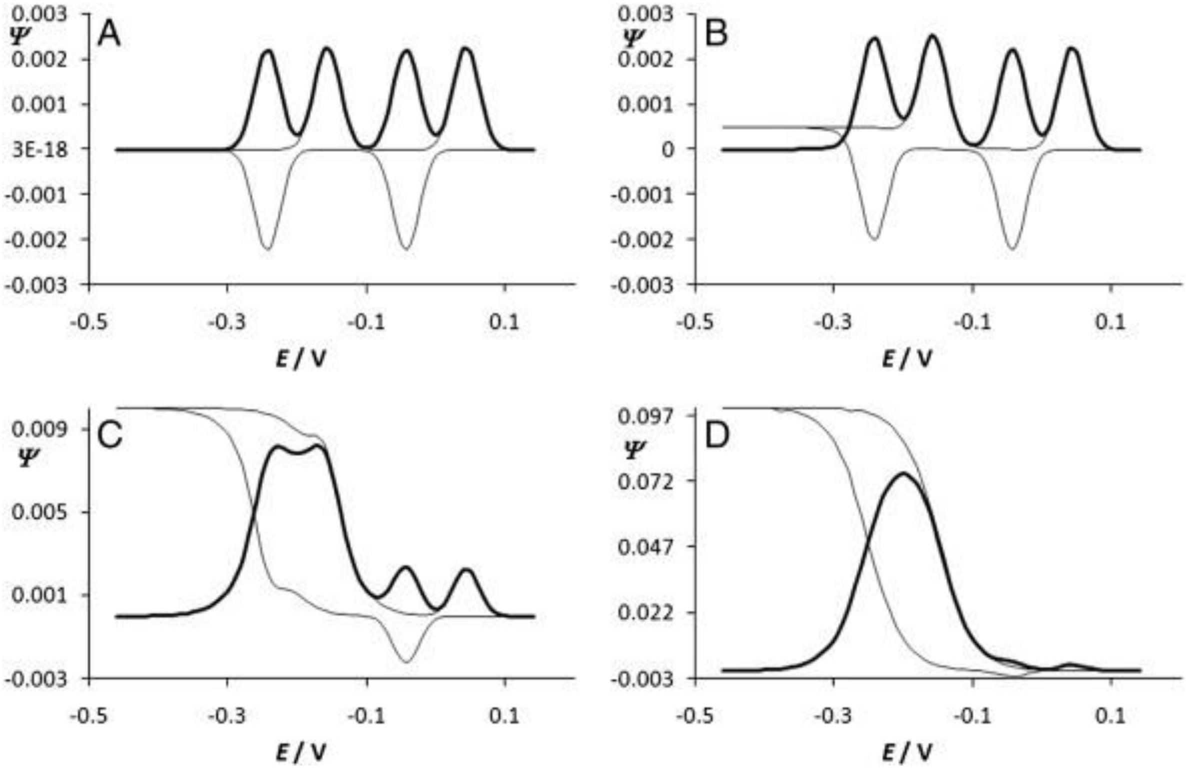


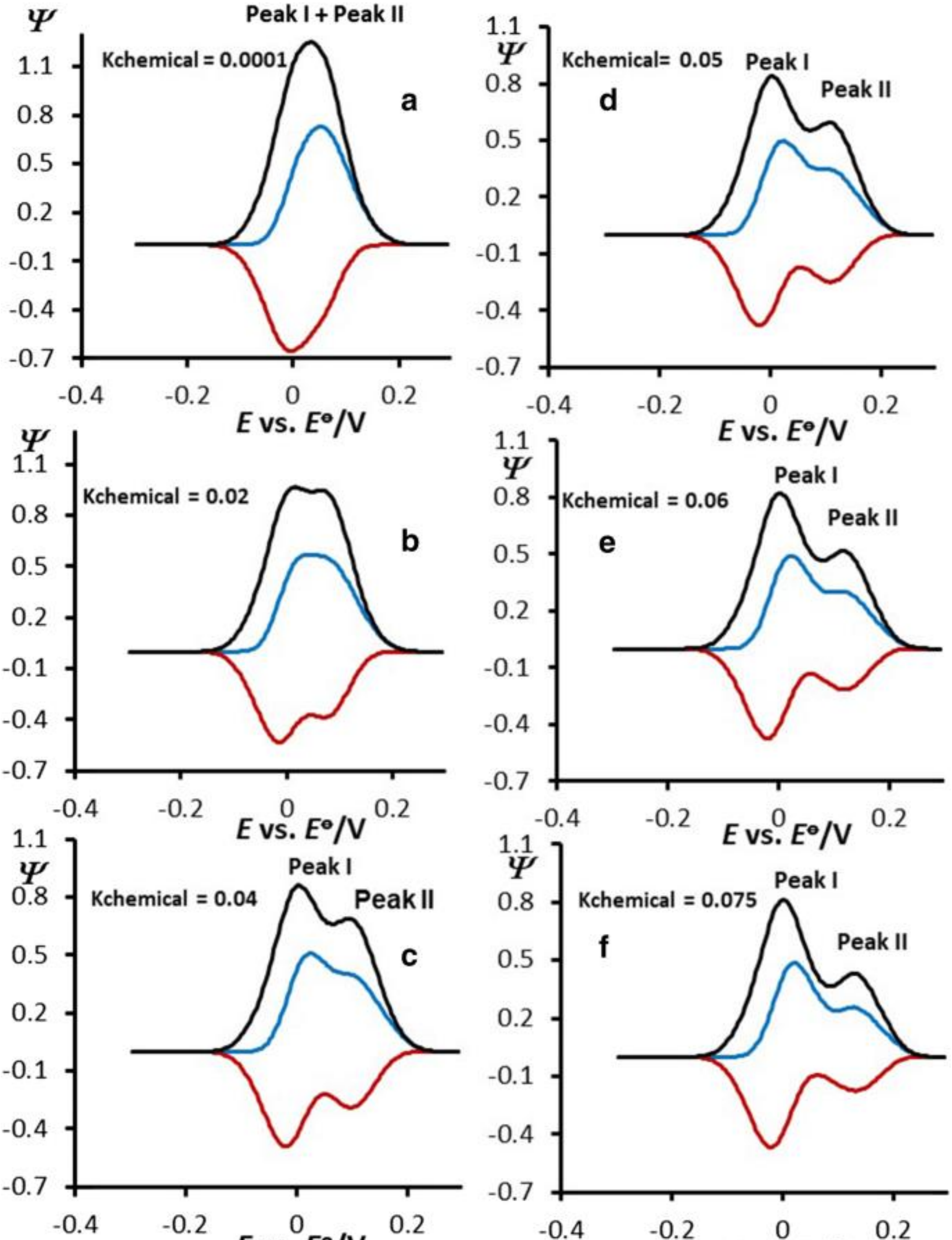


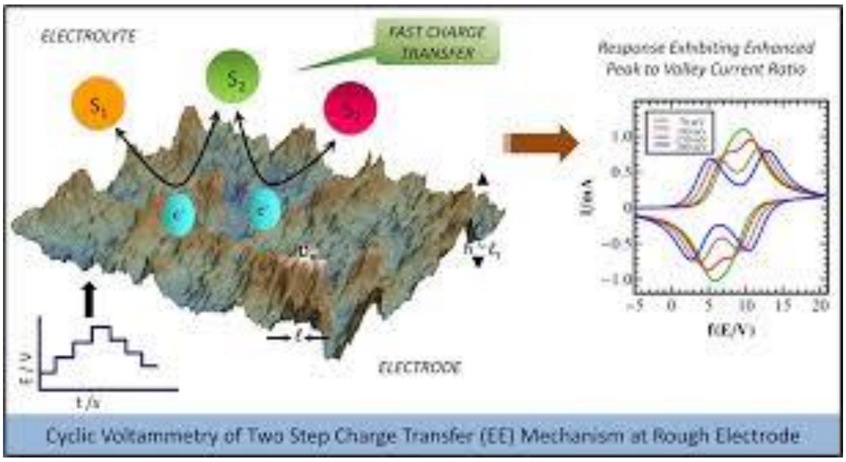
re 1. Schematic illustration depicting a single redox

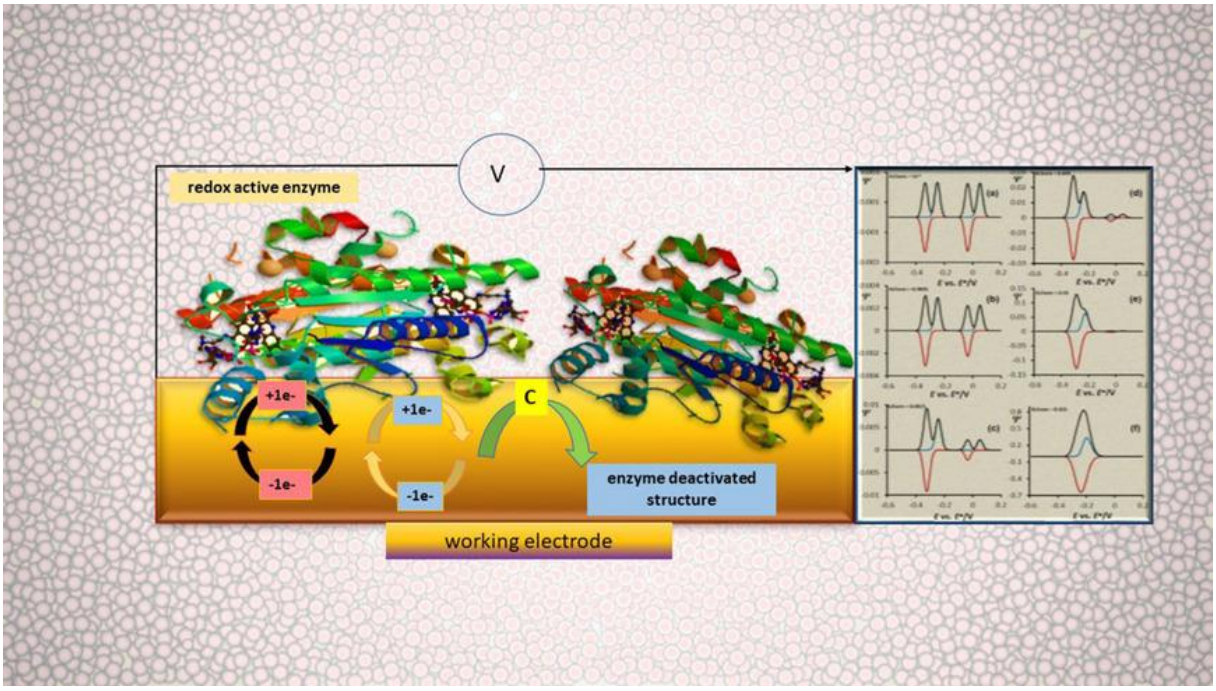

Ψ'
Peak II
Peak I
1
0.6
0.2
-0.2
-0.6
-1
Kchem = 0.0001
-0.8
-0.55
-0.3
-0.05
0.2
E vs. E°/V
Ψ' 11
8
5
2
-1
Kchem = 0.03
-0.8
-0.55
-0.3
-0.05
0.2
E vs. E°/V
Ψ' 19
14
9
4
-1
Kchem = 0.035
-0.8
-0.55
-0.3
-0.05
0.2
E vs. E°/V
Ψ' 44
35
26
17
8
-1
Kchem = 0.05
-0.8
-0.55
-0.3
-0.05
0.2
E vs. E°/V

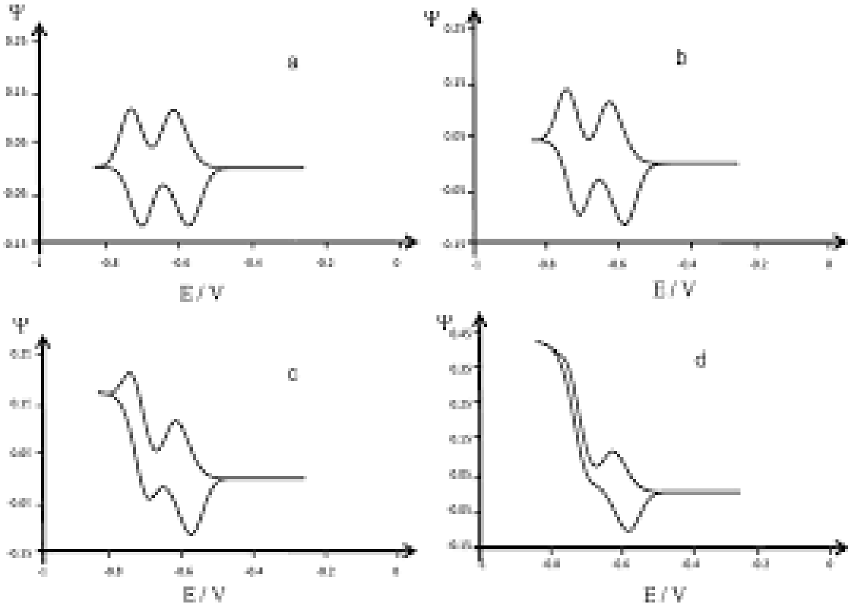

A
C
working electrode
V


A
B
C
D
Ψ
0.003
0.002
0.001
3E-18
0
-0.001
-0.002
-0.003
0.009
0.005
0.001
0.097
0.072
0.047
0.022
-0.5
-0.3
-0.1
0.1
E / V

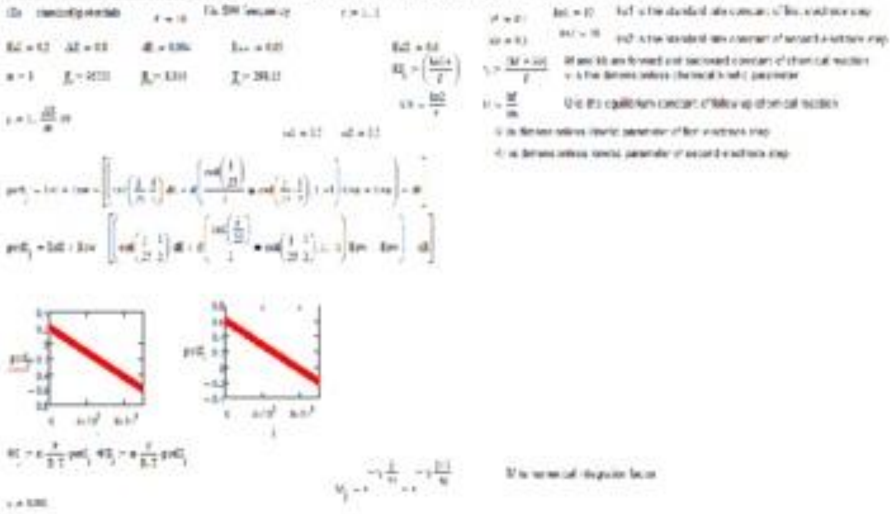

Ψ
Peak I + Peak II
Kchemical = 0.0001
a
1.1
0.8
0.5
0.2
-0.1
-0.4
-0.7
-0.4
-0.2
0
0.2
E vs. E⁰/V
Kchemical= 0.05
Peak I
Peak II
d
Kchemical = 0.02
b
Kchemical = 0.06
e
Kchemical = 0.04
c
Kchemical = 0.075
f


ELECTROLYTE
FAST CHARGE TRANSFER
S_1
S_2
S_3
Response Exhibiting Enhanced Peak to Valley Current Ratio
ℓ
ELECTRODE
E / V
t / s
I(E/V)
Cyclic Voltammetry of Two Step Charge Transfer (EE) Mechanism at Rough Electrode


V
redox active enzyme
+1e-
-1e-
+1e-
-1e-
C
enzyme deactivated structure
working electrode
(a)
(b)
(c)
(d)
(e)
(f)



SUPPLEMENTARY MATERIAL: MATHCAD FILE for TWO-STEP SURFACE EECrev MECHANSIM



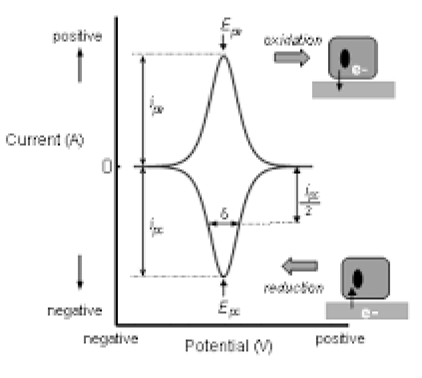


Figure 2. Cyclic voltammetric response from a film of adsorbed protein containing a single redox active centre undergoing reversible electron transfer.

TWO STEP SURFACE CEE MECHANISM
MATHEMATICAL MODEL IN
SQUARE WAVE VOLTAMMETRY

KI and KII are kinetic parameters related to the first and second electron transfer step
alpha is the electron transfer coefficient
EsI and EsII are potentials related to the first and the second electron transfer step
n is number of electron exchanged
F is Faraday constant
Esw is SWV amplitude
T is temperature
dE is potential step
Φ is dimensionless potential
Ψ is dimensionless current
K is equilibrium constant -Keq
z is dimensionless chemical parameter-Kchemical = ε/f

$EsI := 0.2 \quad \Delta E := 0.8 \quad dE := 0.01 \quad Esw := 0.05$

$n := 1 \quad F := 96500 \quad R := 8.314 \quad T := 298.15$

$EsII := 0.6$

$KI_r := 10^{0-r}$

$KII := 10^{0}$

$r := 1..1$

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

$\alpha 2 := 0.5$

$\alpha 1 := 0.5$

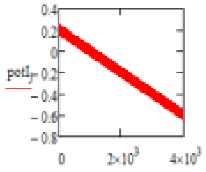
$\log(KI_r) = \boxed{0}$

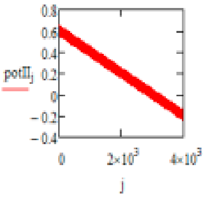
$$potI_j := EsI + Esw - \left[\left(ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right)\cdot dE + if\left(\frac{ceil\left(\frac{j}{25}\right)}{2} = ceil\left(\frac{j}{25}\cdot\frac{1}{2}\right), 1, -1\right)\cdot Esw + Esw\right) - dE\right]$$

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

$K := 0.1$

$z := 2$





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

$$S_k := e^{\frac{z}{50}\cdot(-k)} - e^{\frac{z}{50}\cdot(-k+1)}$$

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

$x := 0.001$

$$\Psi I_{1,r} := root\left[\left[\frac{\frac{KI_r\cdot e^{-\alpha 1\cdot\Phi I_1}\cdot K}{1+K}\cdot\left(1-\frac{1}{50}\cdot 0\right) - (z)^{-1}\cdot KI_r\cdot\left(\frac{1}{1+K}\right)\cdot(-1)\cdot e^{-\alpha 1\cdot\Phi I_1}\cdot 0 - \frac{KI_r}{50}\cdot e^{\Phi I_1\cdot(1-\alpha 1)}\cdot 0}{\frac{KI_r\cdot e^{-\alpha 1\cdot\Phi I_1}\cdot K}{1+K}\cdot\frac{1}{50} + 1 + (z)^{-1}\cdot KI_r\cdot(-1)\cdot\left(\frac{1}{1+K}\right)\cdot S_1\cdot e^{-\alpha 1\cdot\Phi I_1} + \frac{KI_r}{50}\cdot e^{\Phi I_1\cdot(1-\alpha 1)}}\cdot(1+0)\right]\cdot x - \frac{KI_r}{50}\cdot e^{(1-\alpha 1)\cdot\Phi I_1}\cdot\left[\frac{x\cdot\frac{KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{50}}{1+\frac{KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{50}\cdot\left(1+e^{\Phi II_1}\right)}\right] - KI_r\cdot e^{-\alpha 2\cdot\Phi I_1}, x\right]$$

$$\Psi II_{1,r} := \frac{\Psi I_{1,r}\cdot\frac{KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{50}}{1+\frac{KII\cdot e^{-\alpha 2\cdot\Phi II_1}}{50}\cdot\left(1+e^{\Phi II_1}\right)}$$

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