CYCLIC SQUARE WAVE VOLTAMMETRY
-MODEL FOR A SURFACE CE MECHANISM-

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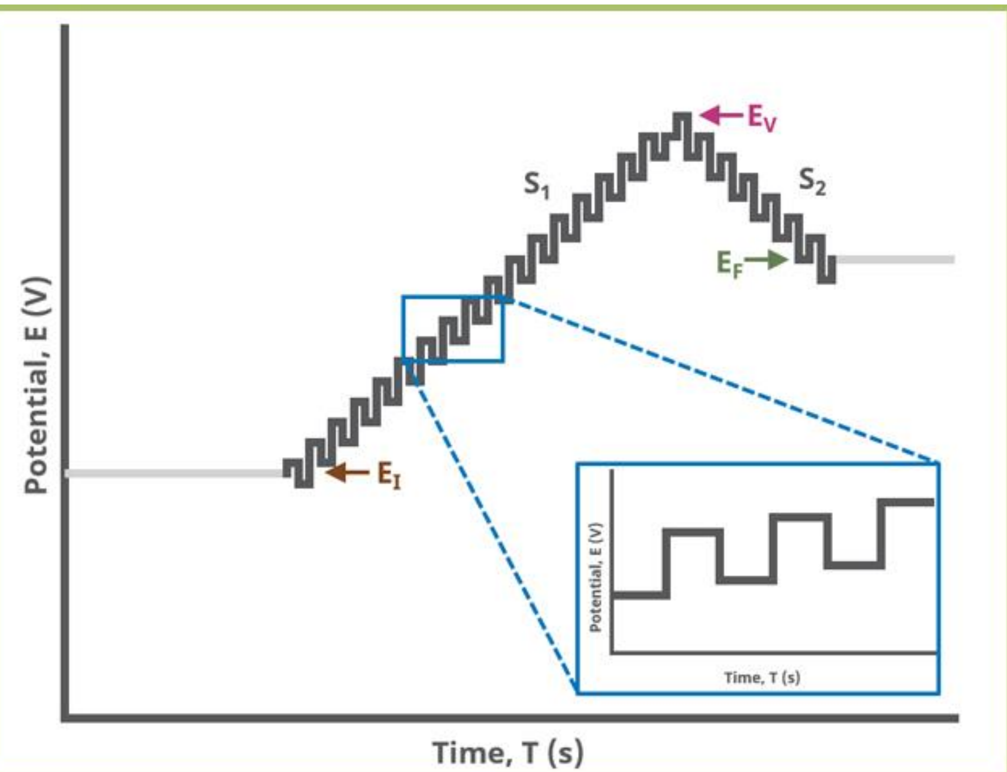
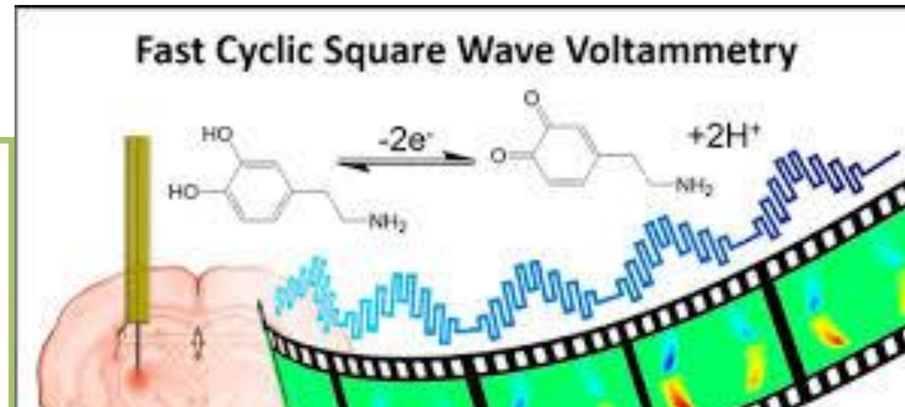
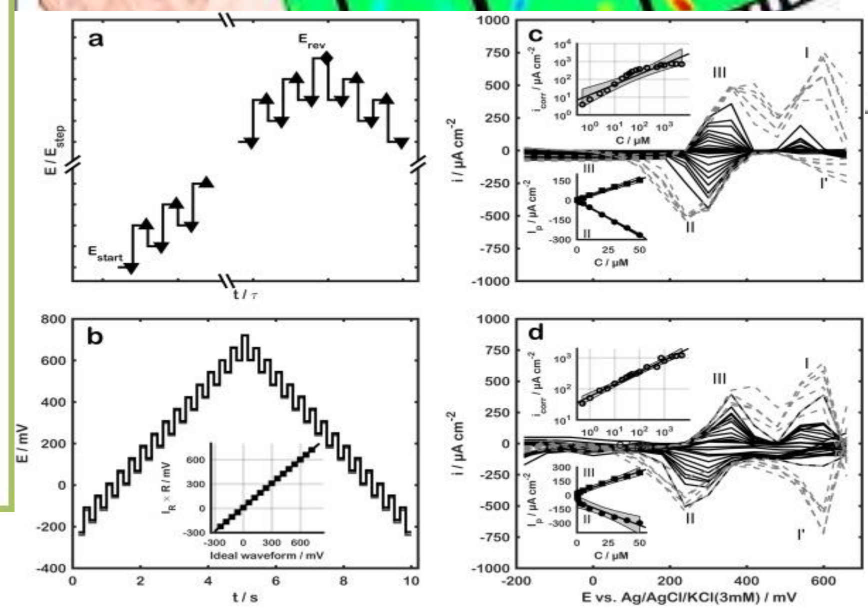






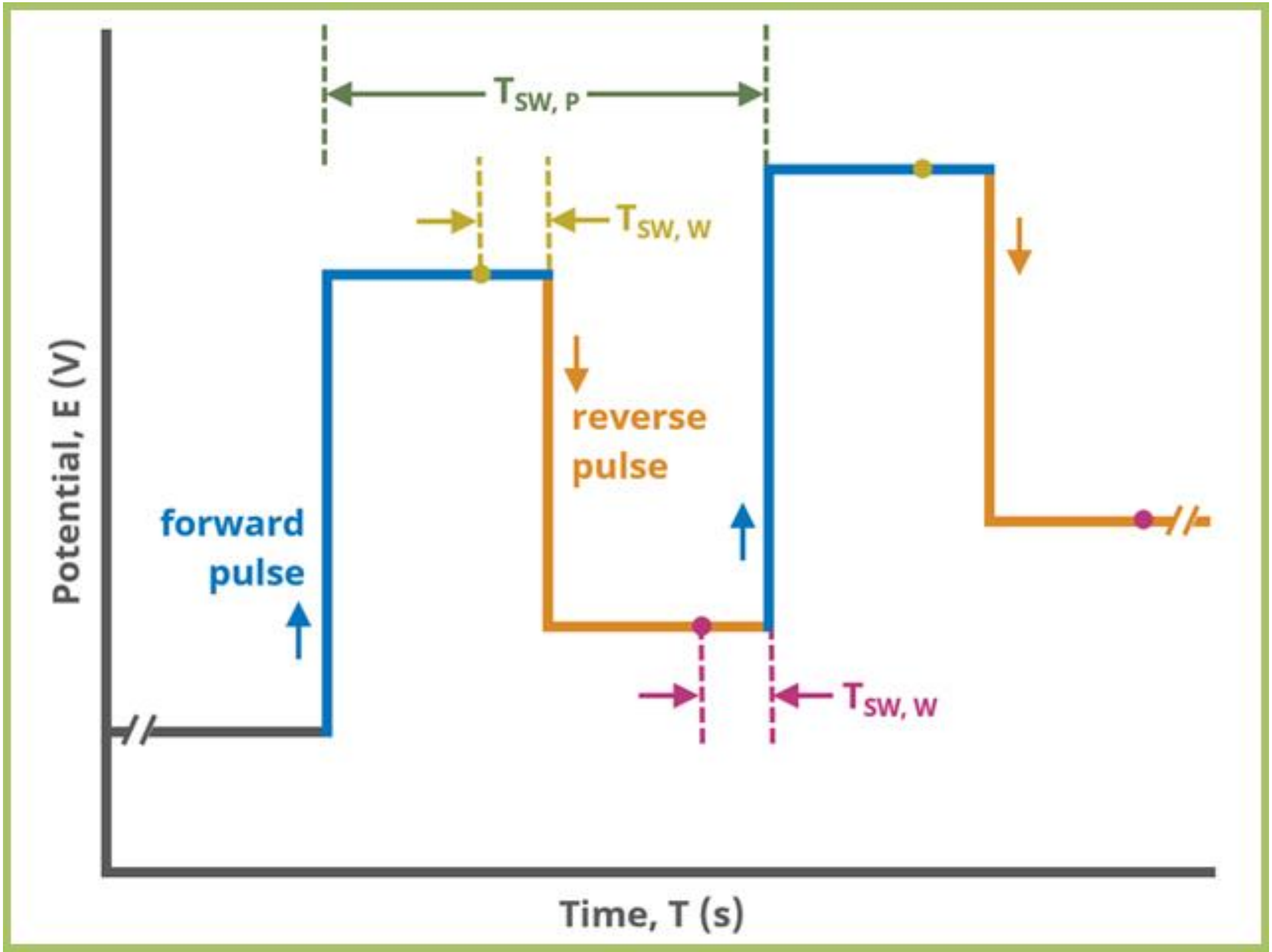
ABSTRACT

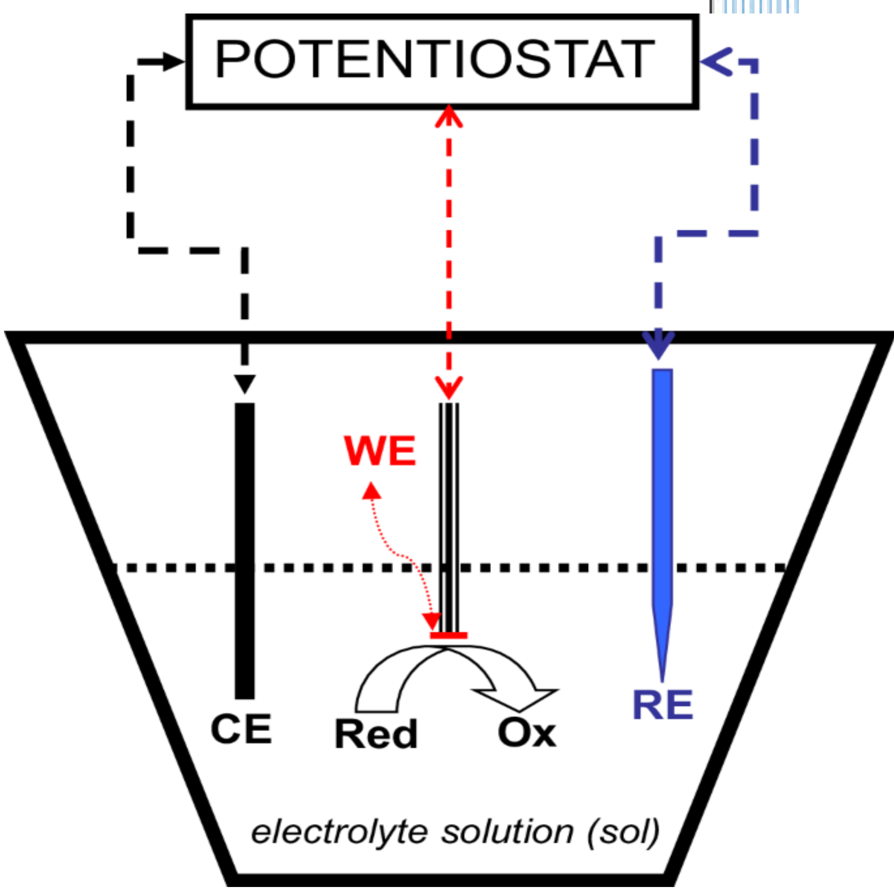
Although the potential ramp of cyclic square wave voltammetry is defined more than 30 years ago, it has been 5 years ago to explore this technique for charactering the so-called surface-confined electrode reactions (M. Mann, L. Bottomley, Cyclic Square Wave Voltammetry of Surface-Confined Quasireversible Electron Transfer Reactions, Langmuir 31 (2015) 9511-9520**). Since this technique unifies the features of both cyclic and square-wave voltammetry, it has been a real challenge to apply this technique for experimental verification of the redox features of many lipophilic enzymes and drugs that can be strongly adsorbed at the surface of working electrode. We present in this work a set of theoretical voltammograms calculated for a Surface CE mechanism of**

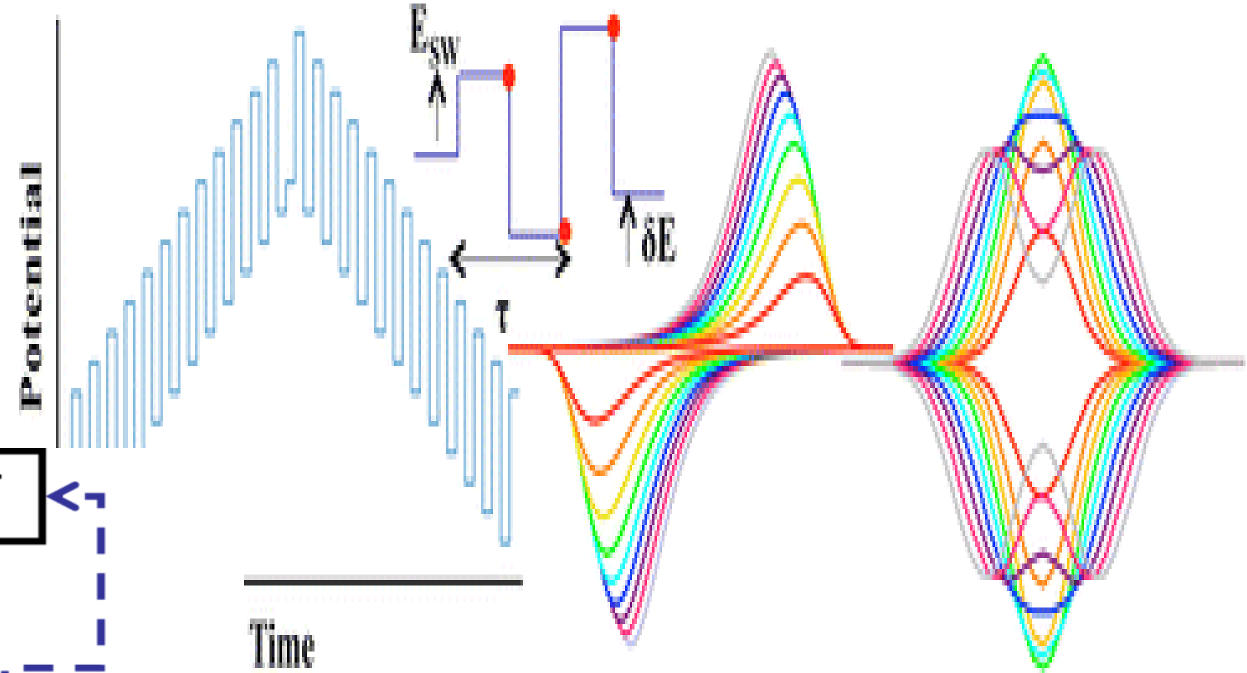
We present the readers entire MATHCAD Simulation working file to simulate voltammograms of this mechanism under conditions of Cyclic Square-Wave Voltammetry.

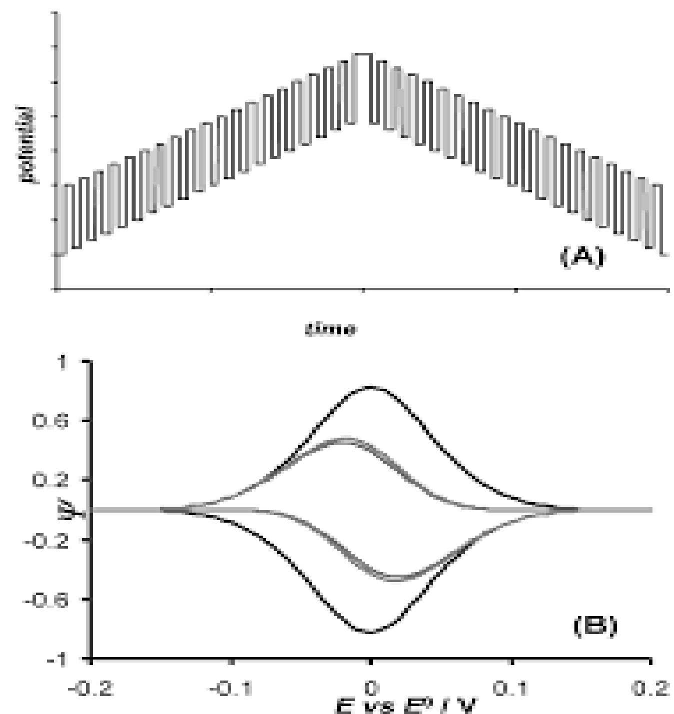
The simulated voltammograms, together with the criteria given will enable experimentalists to assign the electrode reaction mechanism and accurately measure electrode reaction kinetics.

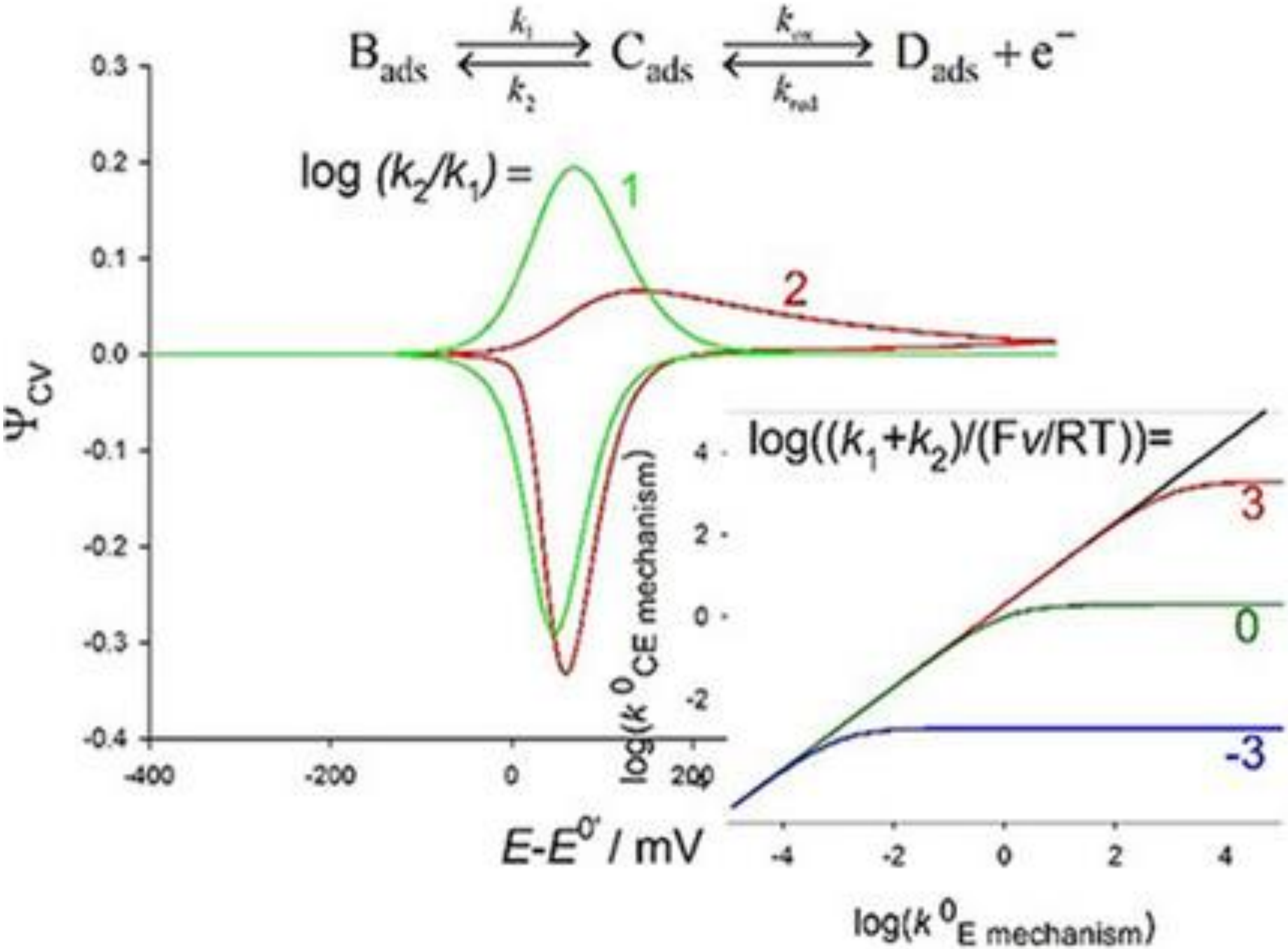
FEATURES OF A SINGLE SWV PULSE




POTENTIOSTAT
WE
CE
Red
Ox
RE
electrolyte solution (sol)


Potential
Time
E_{sw}
δE
τ


potential
time
(A)
1
0.6
0.2
-0.2
-0.6
-1
-0.2
-0.1
0
0.1
0.2
(B)



$B_{ads} \underset{k_2}{\overset{k_1}{\rightleftarrows}} C_{ads} \underset{k_{red}}{\overset{k_{ox}}{\rightleftarrows}} D_{ads} + e^-$
log (k_2/k_1) =
1
2
Ψ_{CV}
E-$E^{0'}$ / mV
log((k_1+k_2)/(Fv/RT))=
3
0
-3
log(k^0 CE mechanism)
log(k^0 E mechanism)

MATHCAD Working File of CYCLIC SWV of a SURFACE CE Mechanism

CYCLIC SWV MODEL
for SURFACE CE MECHANISM

$Es := 0.4$ $\quad Ef := -0.4$ $\quad r := 1..1$

$\Delta E := Es - Ef - Ef + Es$ $\quad dE := 0.01$ $\quad Esw := 0.05$

$n := 2$ $\quad F := 96500$ $\quad R := 8.314$ $\quad T := 298.15$ $\quad \Delta E = 1.6$

$$j := 1..\frac{\frac{\Delta E}{2}}{dE}\cdot 50$$

$\alpha := 0.5$

$f := 10$ $\quad \varepsilon := kf + kb$

$ks_r := 10^{.65r}$

$kf := 5$

$kb := 5$

$\lambda_r := \frac{ks_r}{f}$ $\quad K := 10^2$ $\quad K = 100$

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

$\varepsilon := 10^{3.4}$

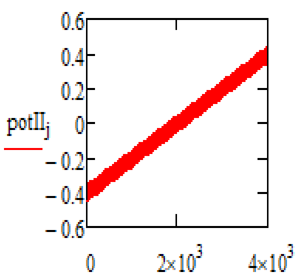
$\lambda_r =$ $\boxed{0.447}$ $\quad \varepsilon = 2.512\times 10^3$

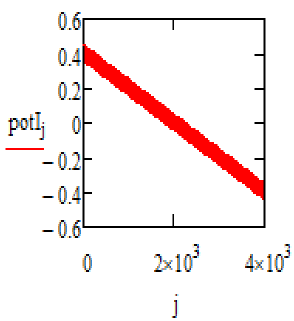
$z := \frac{\varepsilon}{f}$

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

$$k := 1..\frac{\frac{\Delta E}{2}}{dE}\cdot 50$$

$\log\left(\frac{ks}{\varepsilon_r}\cdot K\right) =$ $\quad z = 251.189$ $\quad \log(z_r) =$





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

$\varepsilon = 2.512\times 10^3$

$z = 251.189$

$u := \frac{\Delta E}{dE}\cdot 50..1$ $\quad \log(\lambda_1) = -0.$

$10^{1.2} = 15.849$

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

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

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

$$\Psi I_{1,r} := \lambda_r \cdot e^{-\alpha \cdot \Phi I_1} \cdot \frac{K}{1+K} \cdot \left[1 + \lambda_r \cdot e^{-\alpha \cdot \Phi I_1} \cdot \frac{K}{(1+K)\cdot 50} - \frac{\lambda_r \cdot e^{-\alpha \cdot \Phi I_1} \cdot S_1}{(K+1)\cdot z} \cdot (1) + \frac{\lambda_r \cdot e^{(1-\alpha)\cdot \Phi I_1}}{50}\right]^{-1}$$

$\Psi_{1,r} =$

$$\Psi I_{k,r} := \frac{\frac{\lambda_r \cdot e^{-\alpha \cdot \Phi I_k} \cdot K}{1+K} \cdot \left(1 - \frac{1}{50} \cdot \sum_{j=1}^{k-1} \Psi I_{j,r}\right) - (z)^{-1} \cdot \lambda_r \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{-\alpha \cdot \Phi I_k} \cdot \sum_{j=1}^{k-1} \left(\Psi I_{j,r} \cdot S_{k-j+1}\right) - \frac{\lambda_r}{50} \cdot e^{\Phi I_k \cdot (1-\alpha)} \cdot \sum_{j=1}^{k-1} \Psi I_{j,r}}{\left(\frac{\lambda_r \cdot e^{-\alpha \cdot \Phi I_k} \cdot K}{1+K} \cdot \frac{1}{50}\right) + 1 + (z)^{-1} \cdot \lambda_r \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{-\alpha \cdot \Phi I_k} + \frac{\lambda_r}{50} \cdot e^{\Phi I_k \cdot (1-\alpha)}}$$

$$\Psi II_{1,r} := \lambda_r \cdot e^{-\alpha \cdot \Phi II_1} \cdot \frac{K}{1+K} \cdot \left[1 + \lambda_r \cdot e^{-\alpha \cdot \Phi II_1} \cdot \frac{K}{(1+K)\cdot 50} - \frac{\lambda_r \cdot e^{-\alpha \cdot \Phi II_1} \cdot S_1}{(K+1)\cdot z} \cdot (1) + \frac{\lambda_r \cdot e^{(1-\alpha)\cdot \Phi II_1}}{50}\right]^{-1}$$

$$\Psi II_{k,r} := \frac{\frac{\lambda_r \cdot e^{-\alpha \cdot \Phi II_k} \cdot K}{1+K} \cdot \left(1 - \frac{1}{50} \cdot \sum_{j=1}^{k-1} \Psi II_{j,r}\right) - (z)^{-1} \cdot \lambda_r \cdot \left(\frac{1}{1+K}\right) \cdot (-1) \cdot e^{-\alpha \cdot \Phi II_k} \cdot \sum_{j=1}^{k-1} \left(\Psi II_{j,r} \cdot S_{k-j+1}\right) - \frac{\lambda_r}{50} \cdot e^{\Phi II_k \cdot (1-\alpha)} \cdot \sum_{j=1}^{k-1} \Psi II_{j,r}}{\left(\frac{\lambda_r \cdot e^{-\alpha \cdot \Phi II_k} \cdot K}{1+K} \cdot \frac{1}{50}\right) + 1 + (z)^{-1} \cdot \lambda_r \cdot (-1) \cdot \left(\frac{1}{1+K}\right) \cdot S_1 \cdot e^{-\alpha \cdot \Phi II_k} + \frac{\lambda_r}{50} \cdot e^{\Phi II_k \cdot (1-\alpha)}}$$

$$\Psi T_{k,r} := \Psi I_{k,r} + \Psi II_{k,r}$$

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

$$E_p := Es - p \cdot dE$$

$$\Psi Af_{p,r} := \Psi I_{(p+1)\cdot 50,r} \qquad \Psi Ab_{p,r} := \Psi I_{50\cdot p+25,r}$$

$$\Psi Bb_{p,r} := \Psi II_{50\cdot p+25,r} \qquad \Psi Bf_{p,r} := \Psi II_{(p+1)\cdot 50,r}$$

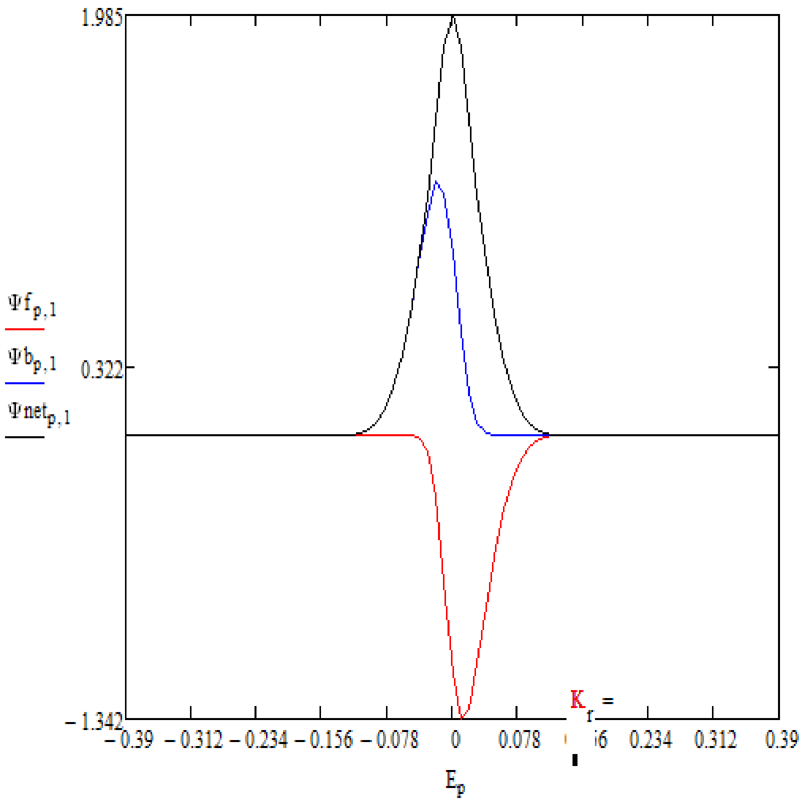
$$\Psi Bnet_{p,r} := \Psi Ab_{p,r} - \Psi Bb_{p,r}$$

$$\Psi b_{p,r} := \Psi Bb_{p,r} - \Psi Ab_{p,r}$$

$$\Psi f_{p,r} := \Psi Bf_{p,r} - \Psi Af_{p,r}$$

$$\Psi Anet_{p,r} := \Psi Af_{p,r} + \Psi Bf_{p,r}$$

$$\Psi net_{p,r} := \Psi b_{p,r} - \Psi f_{p,r}$$



$K_r =$

$E_p =$

0.39
0.38
0.37
0.36
0.35
0.34
0.33
0.32
0.31
0.3
0.29
0.28
0.27
0.26

$\Psi f_{p,1} =$

$\Psi net_{p,1} =$

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