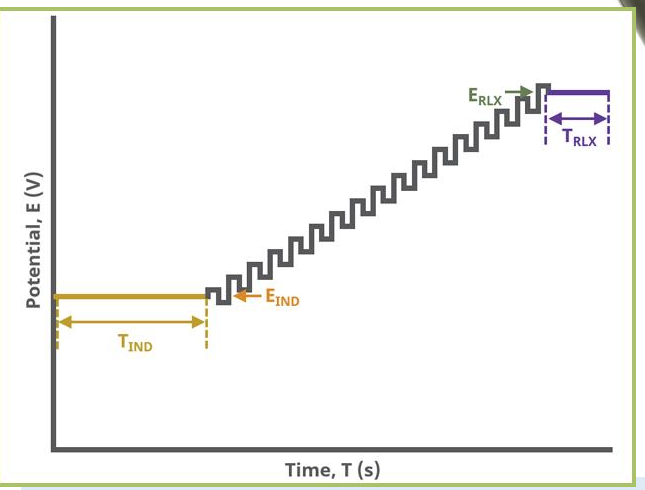
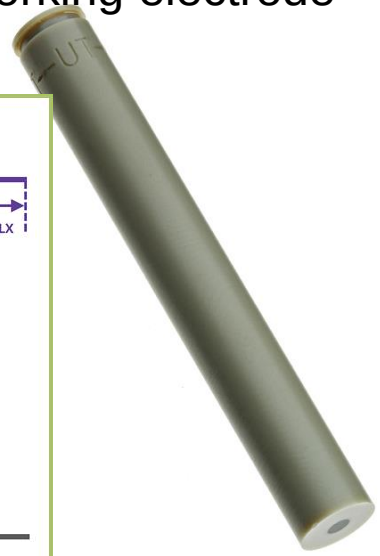
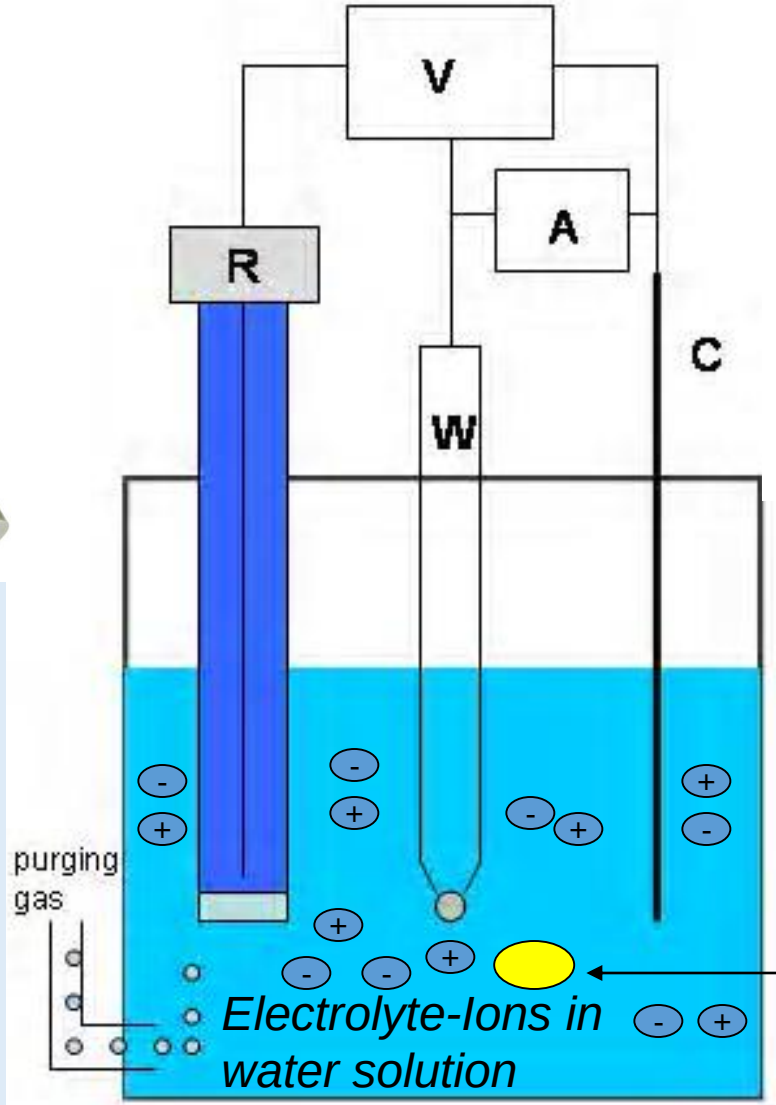
W-working electrode

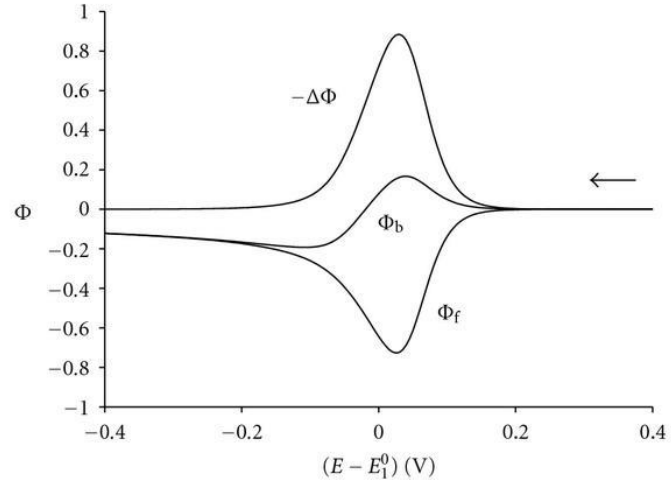


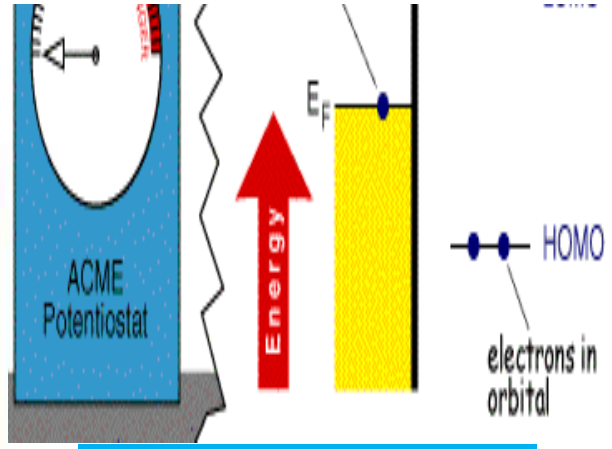


SQUARE-WAVE VOLTAMMETRY

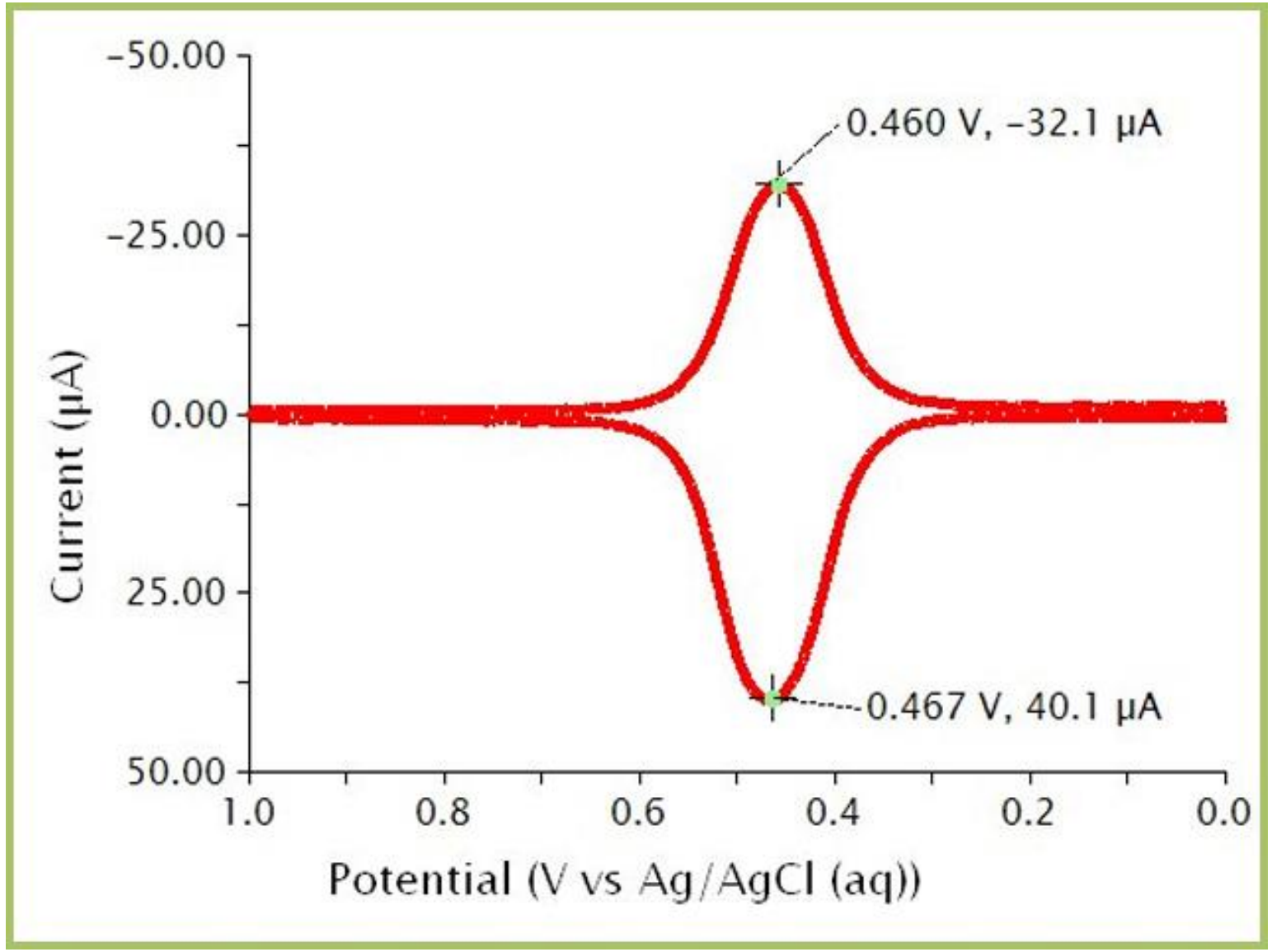
Valentin Mirceski
Rubin Gulaboski
Faculty of Medical Sciences
Goce Delcev University Stip
MACEDONIA





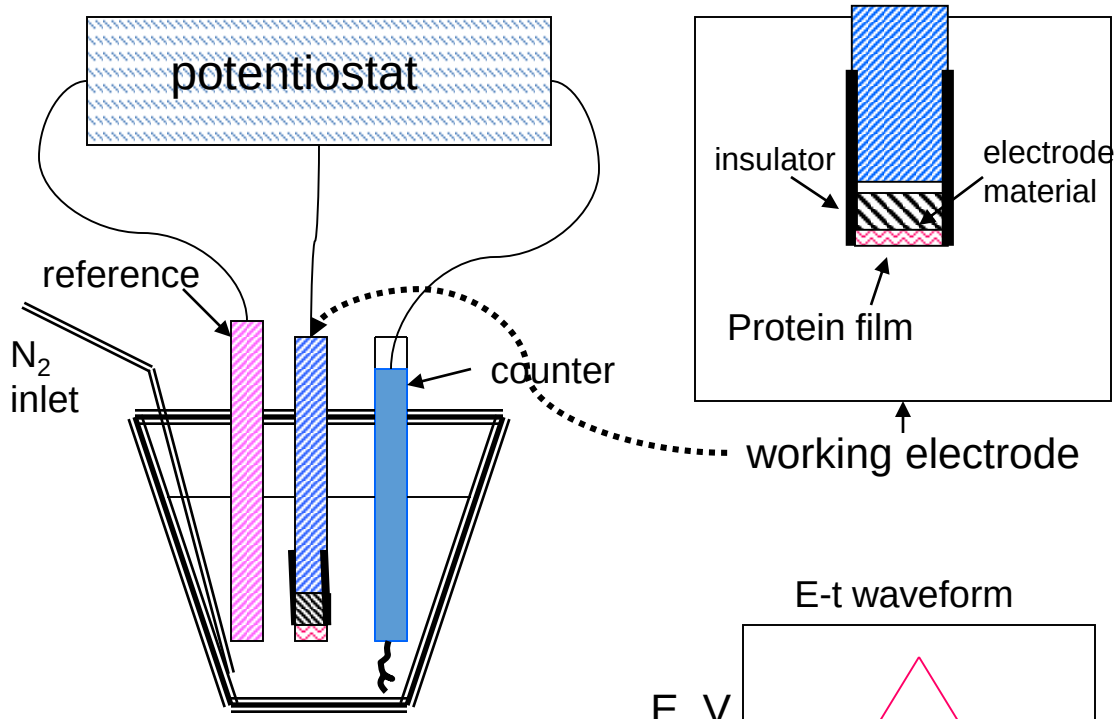


Analyte present in Electrolyte Solution

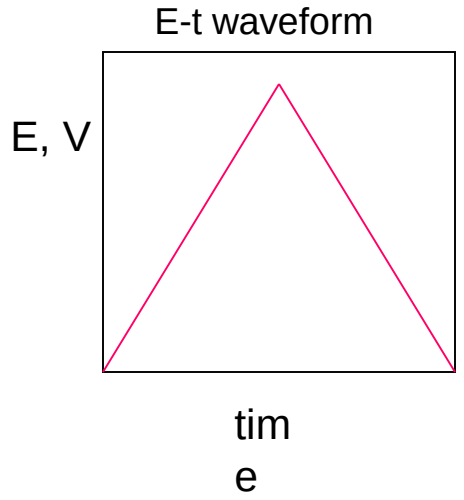


Forward and Backward currents of square-wave voltammogram

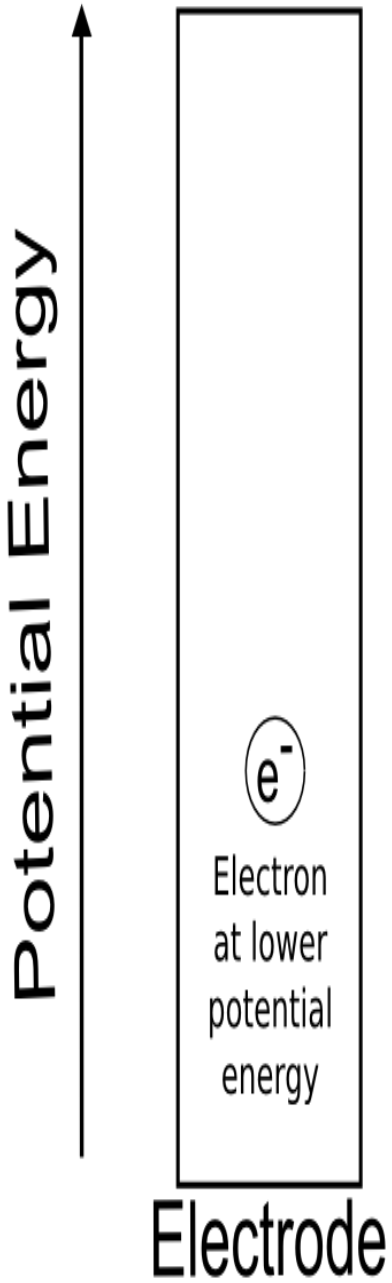
Schematic representation of Instrumentation used in Voltammetry



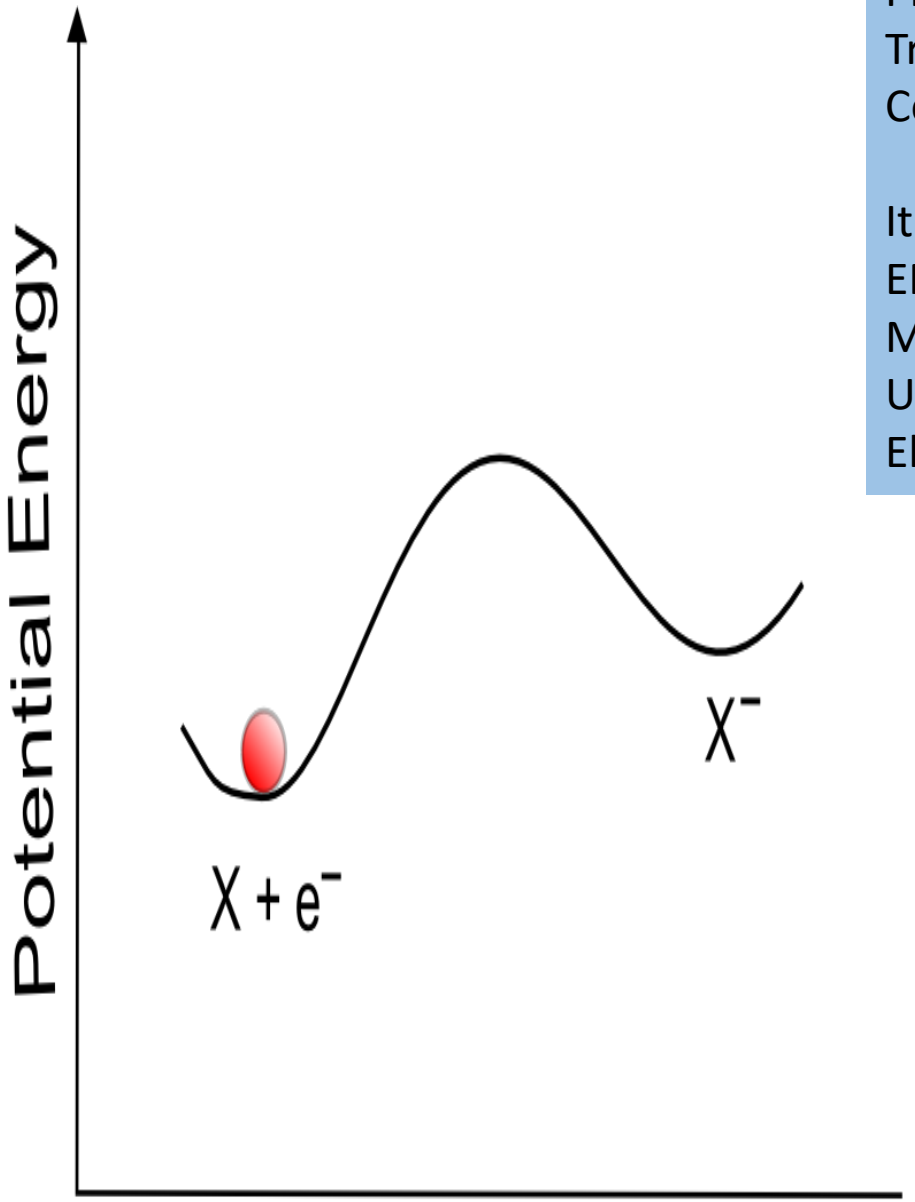
Електрохемиска келија



Cyclic voltammetry



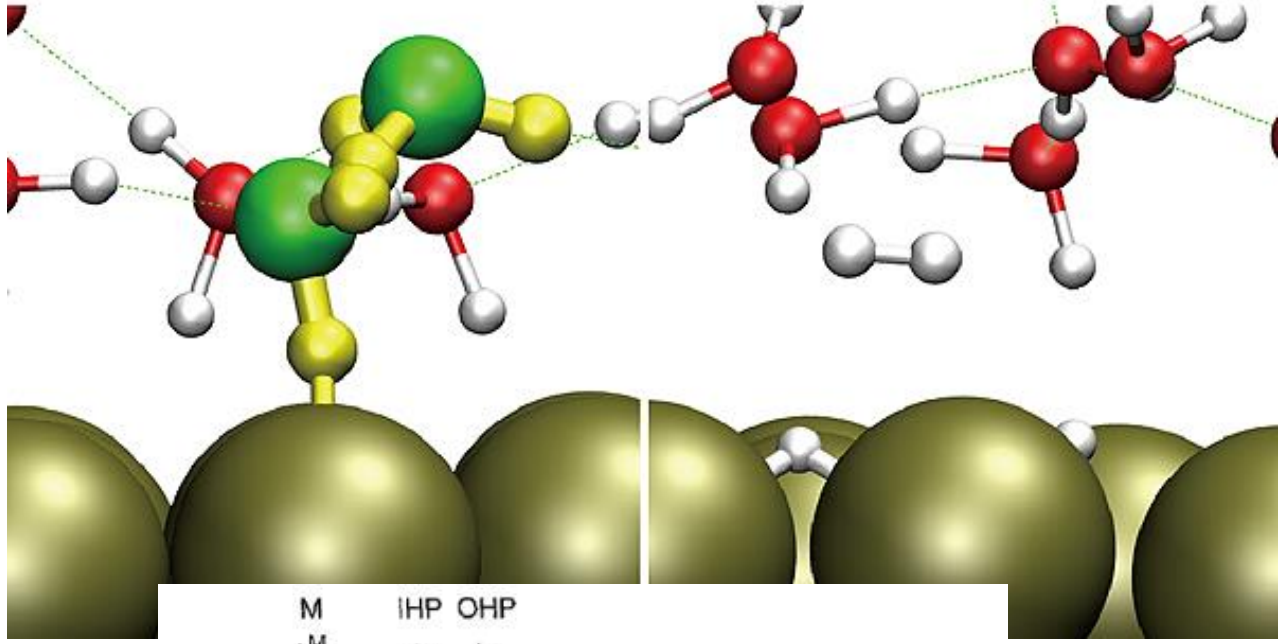
Analyte
Molecular
Orbital

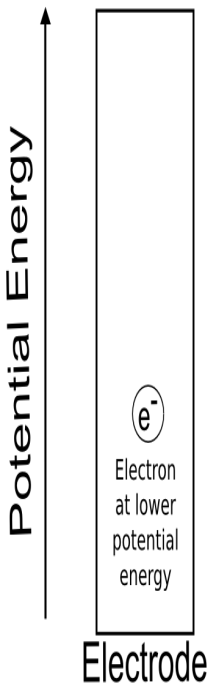


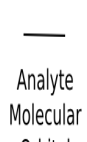
Electrochemistry considers chemical Processes that can contribute to Transfer of charge between two Conjoined systems

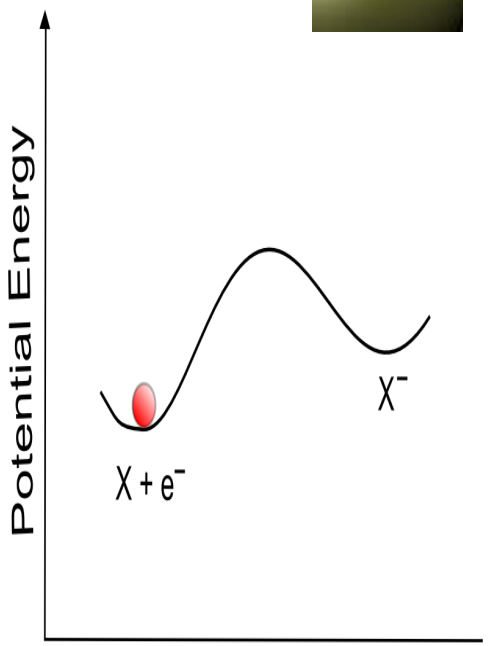
It I important to get knowledge about ENERGY of ELECTRONS and the MASS TRANSPORT in order to Understand some aspects in Electrochemistry

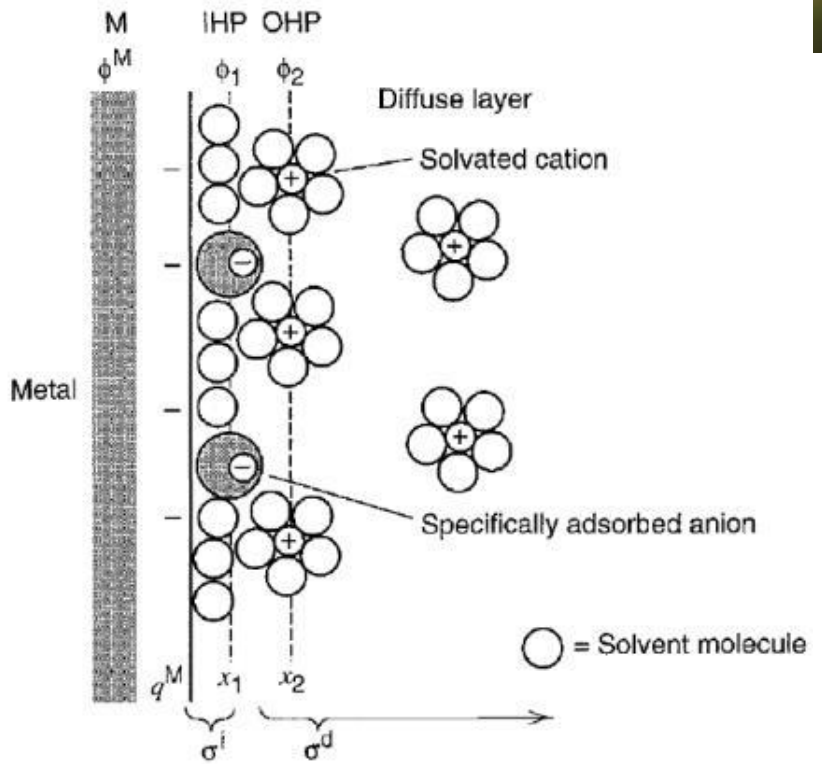
Chemical reactions at a platinum/water interface



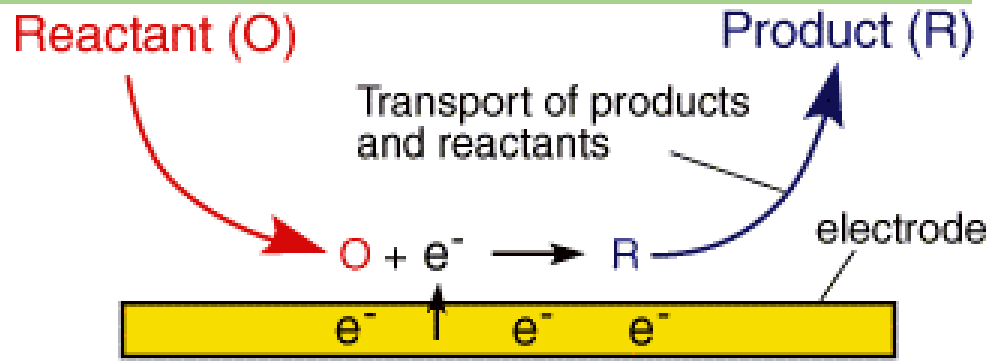


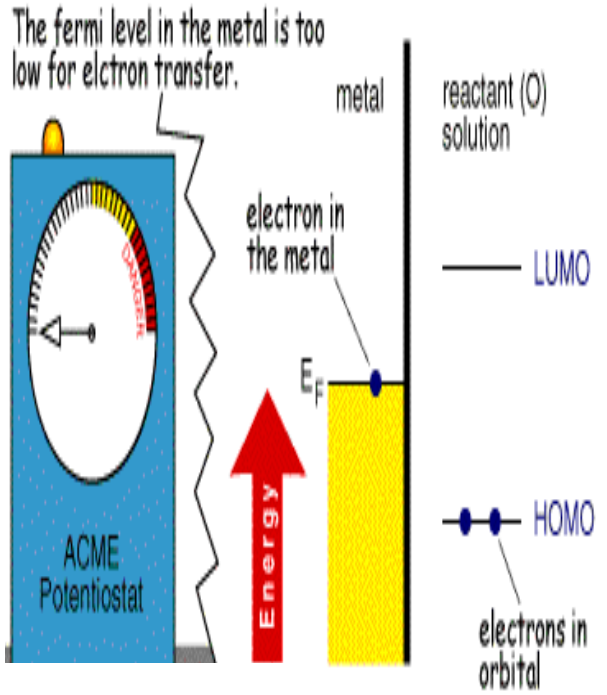


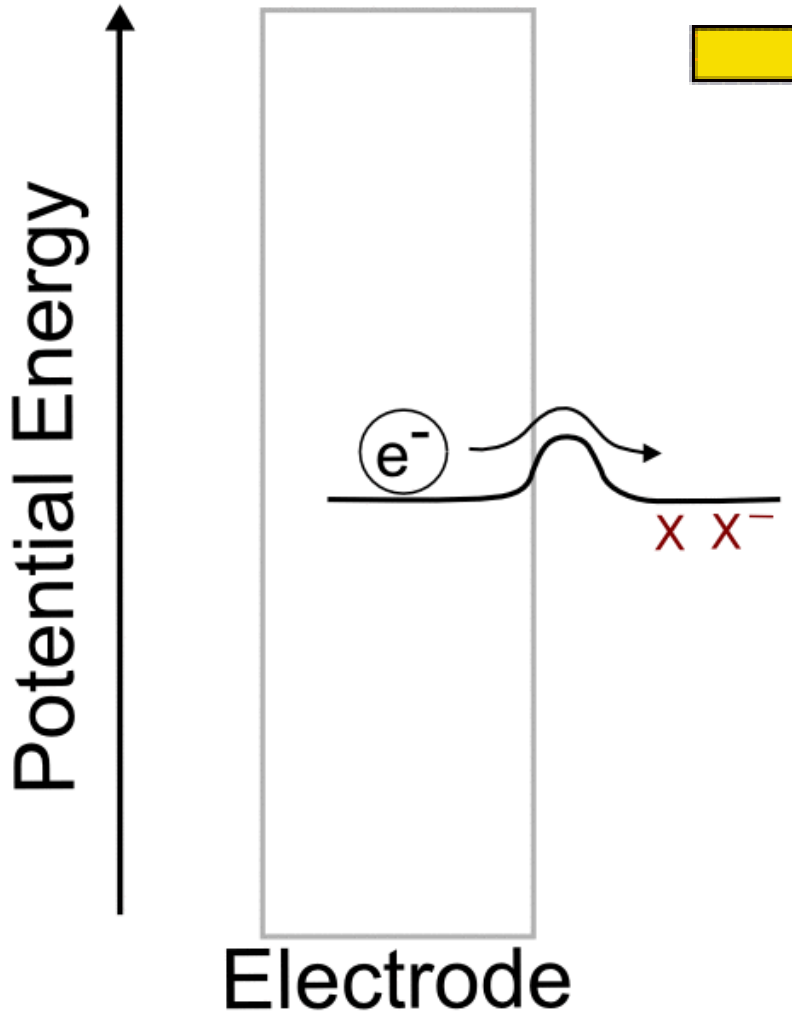


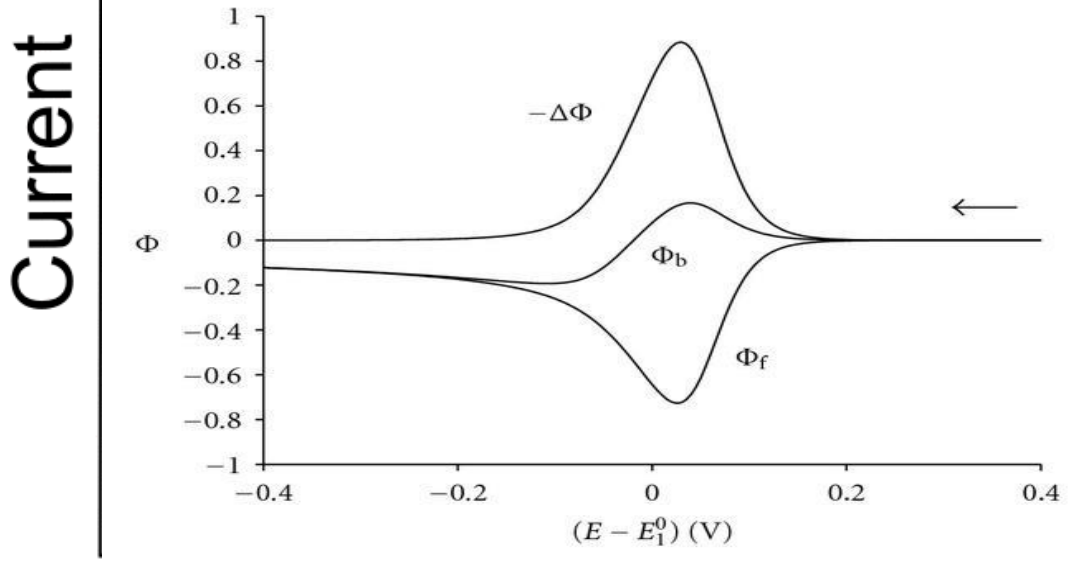


Reactant (O) dissolved in solution at the beginning

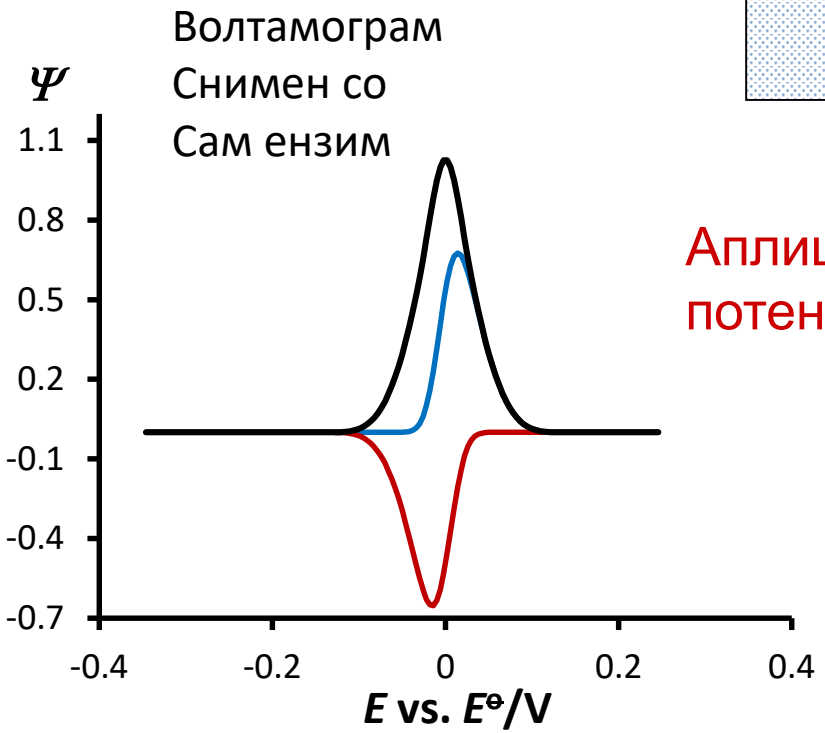


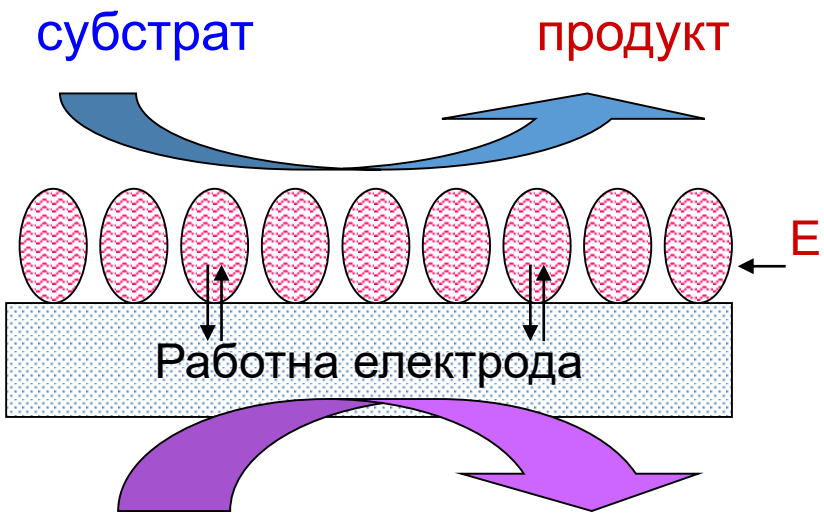






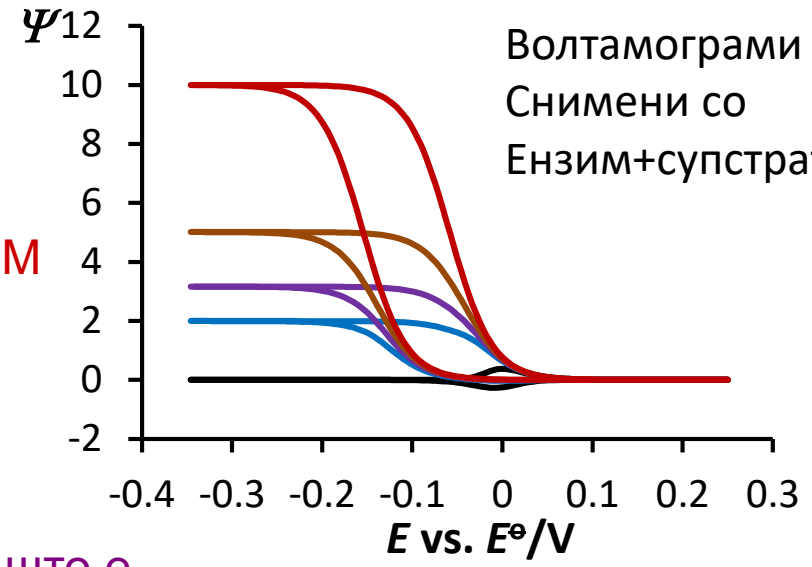
Square-wave voltammetry-Principles



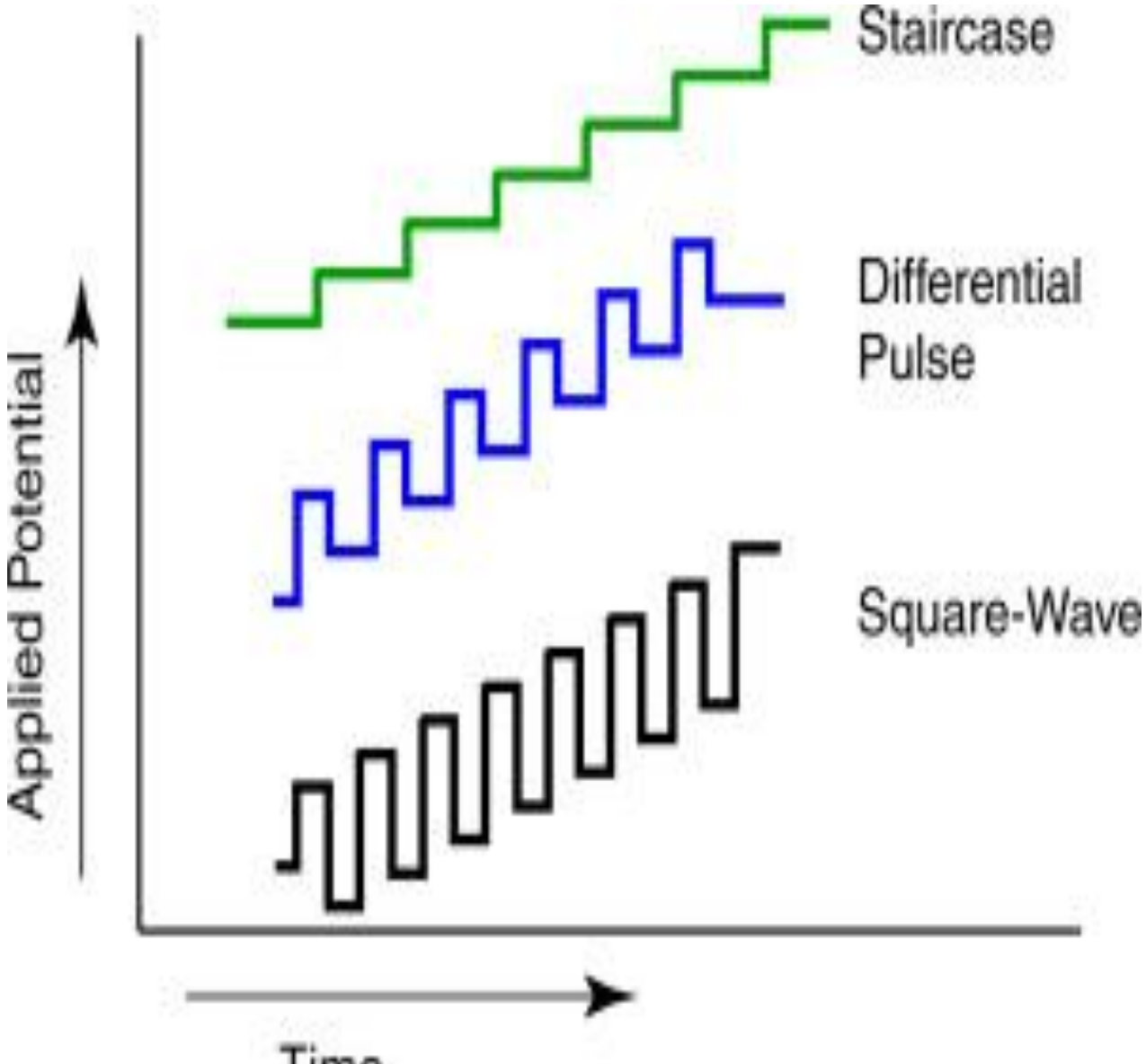


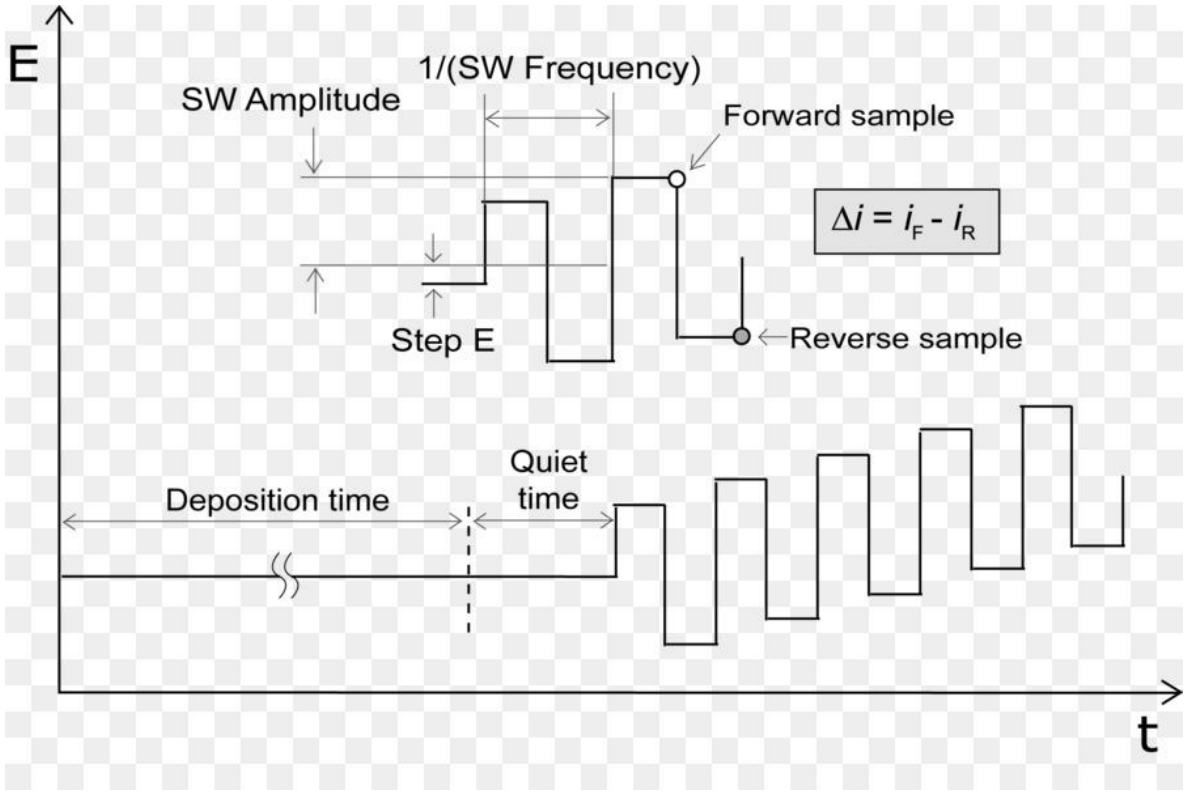
Аплицирај потенцијал

Измери струја што е Пропорционална на Концентрацијата на субстратот

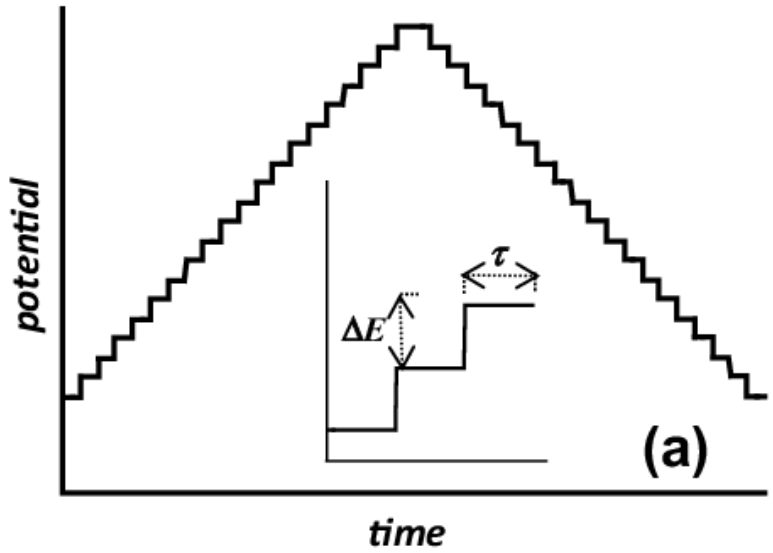


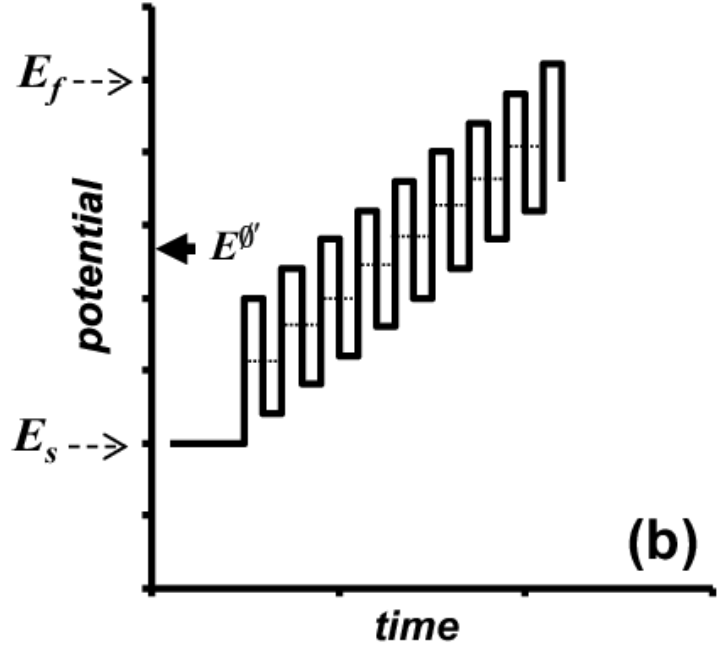
Common forms of potential pulses in Voltammetry

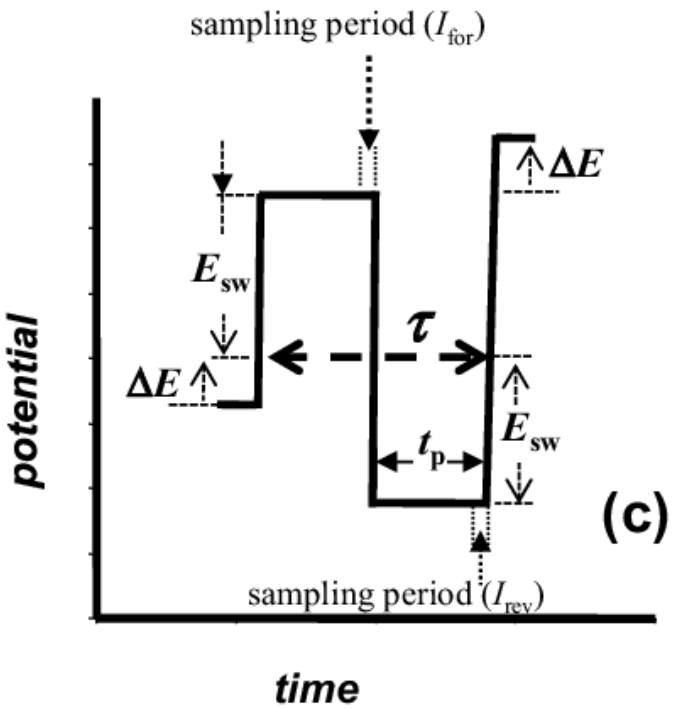


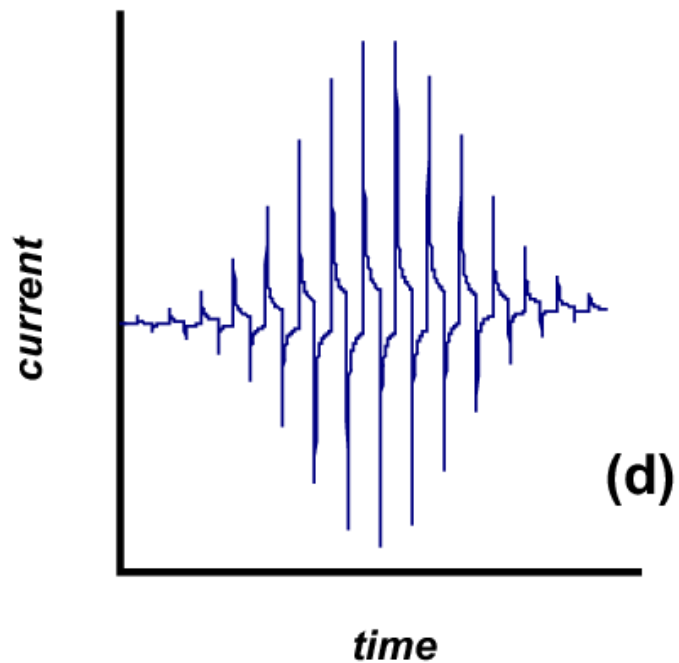


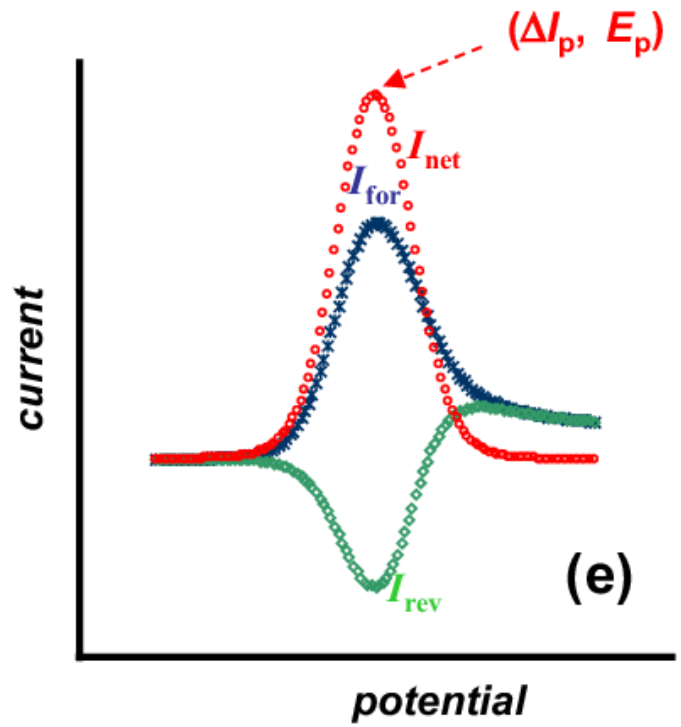
Features of the potential pulse in SWV


potential
ΔE
τ
(a)
time

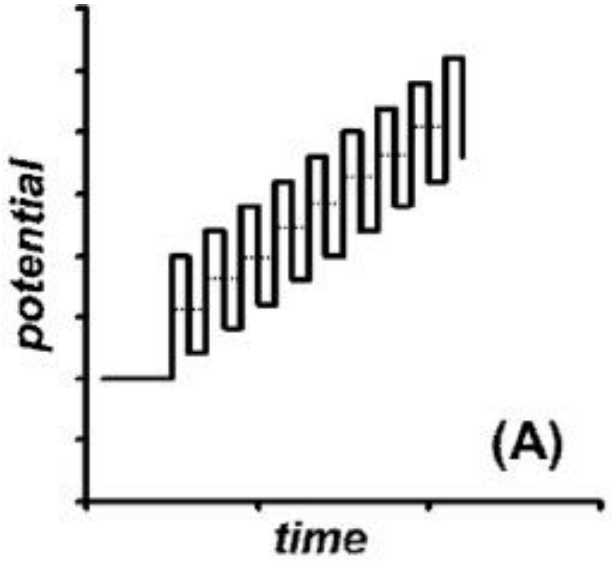

E_f
potential
$E^{\emptyset\prime}$
E_s
(b)
time

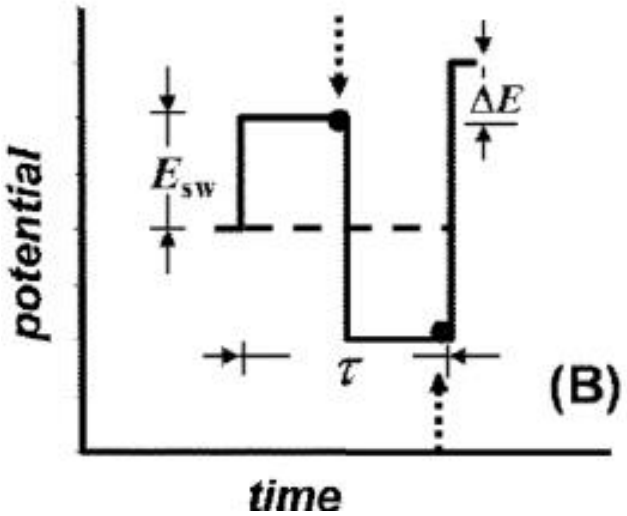

sampling period (I_{for})
ΔE
E_{sw}
τ
ΔE
t_p
E_{sw}
(c)
sampling period (I_{rev})
potential
time

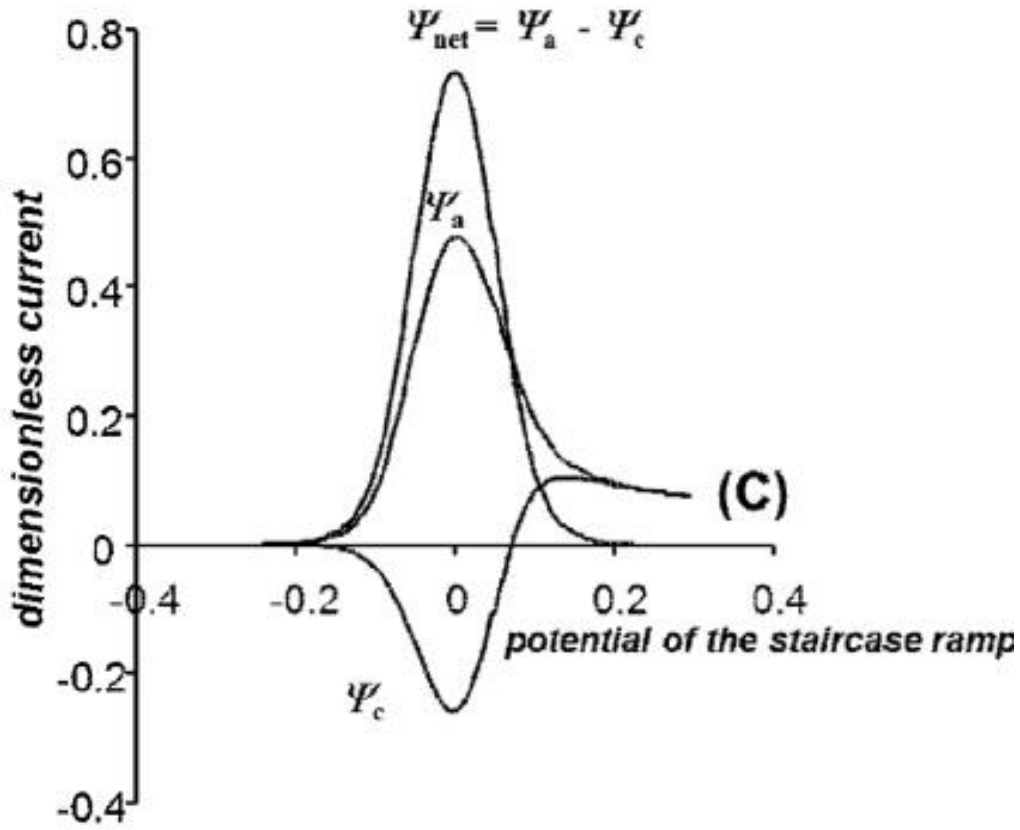

current
(d)
time


(ΔI_p, E_p)
I_{net}
I_{for}
I_{rev}
current
(e)
potential

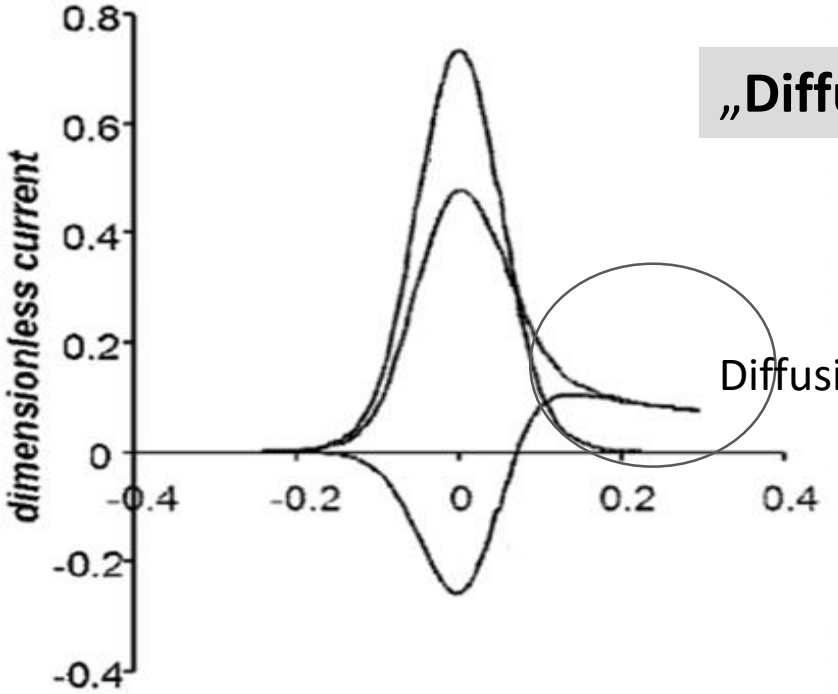
Square-wave voltammetry-potential form of driving force And shape of the instrumental output (SW voltammogram)



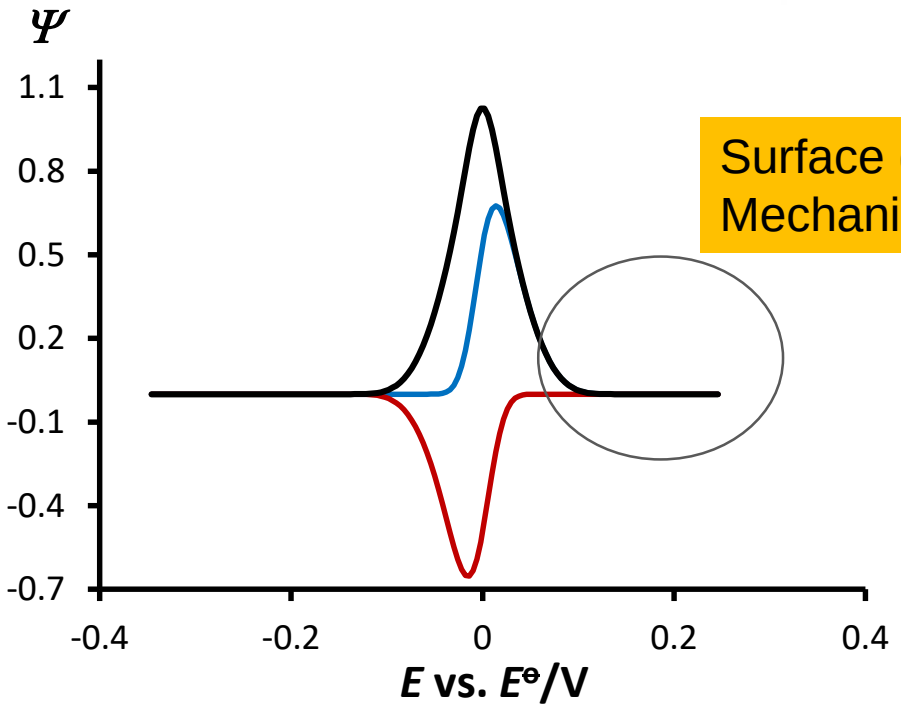




„Diffusion controlled reaction in SWV

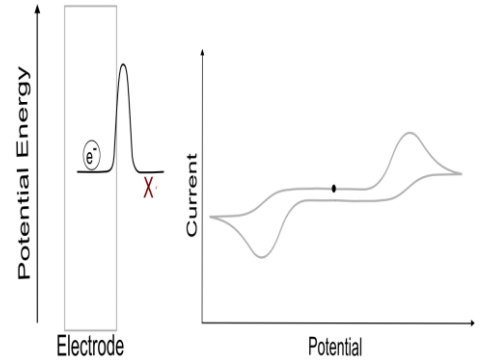


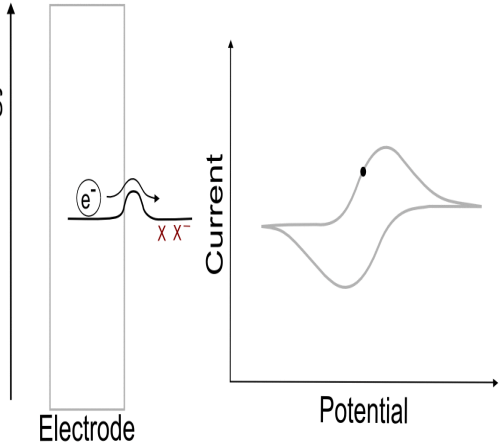
Diffusional tail

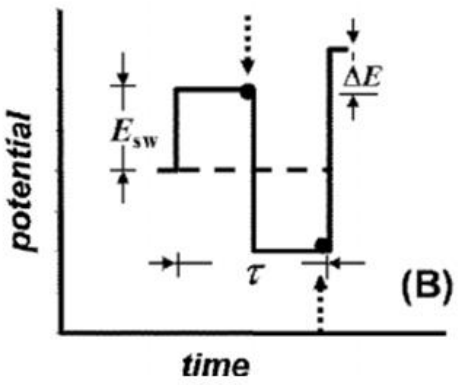


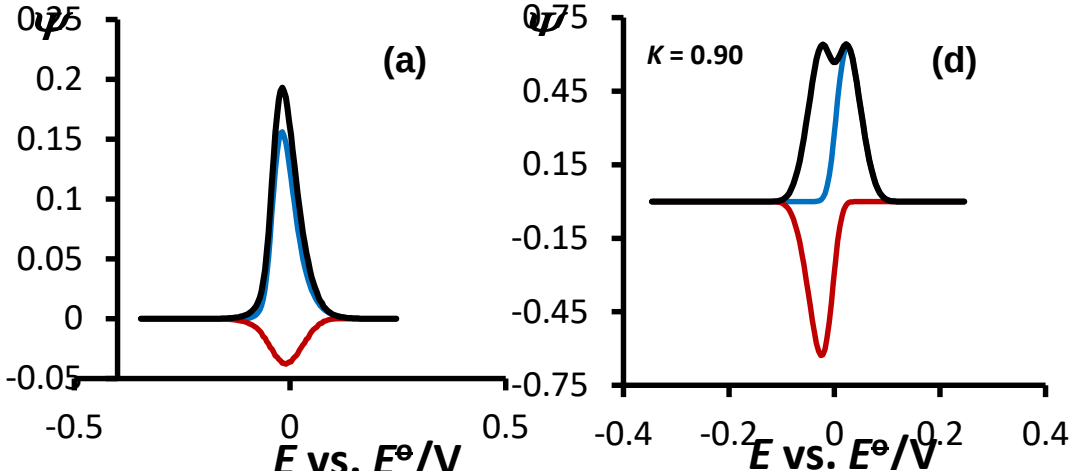
Surface (adsorbed) electrode
Mechanism in SWV

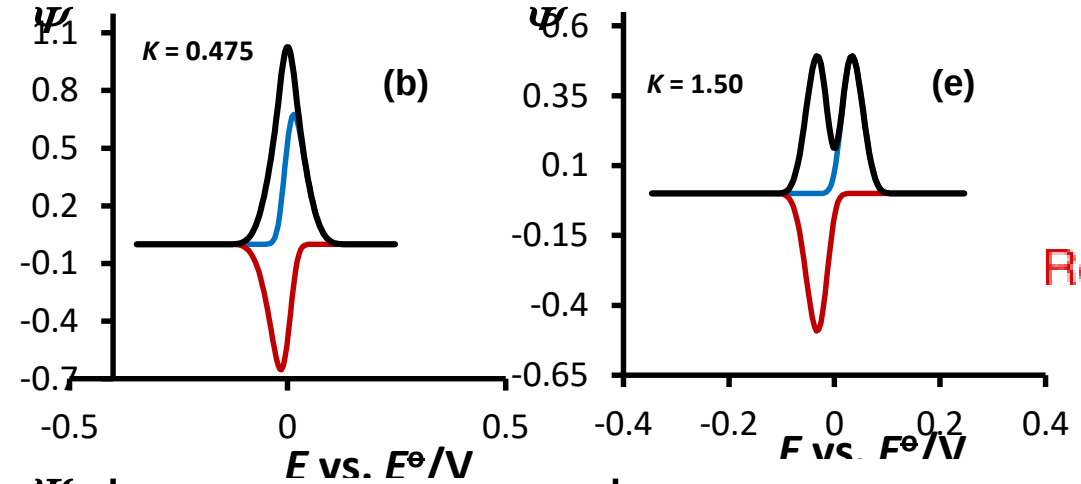
Simple surface mechanism in SWV
Influence of the
KINETICS of
ELECTRON TRANSFER

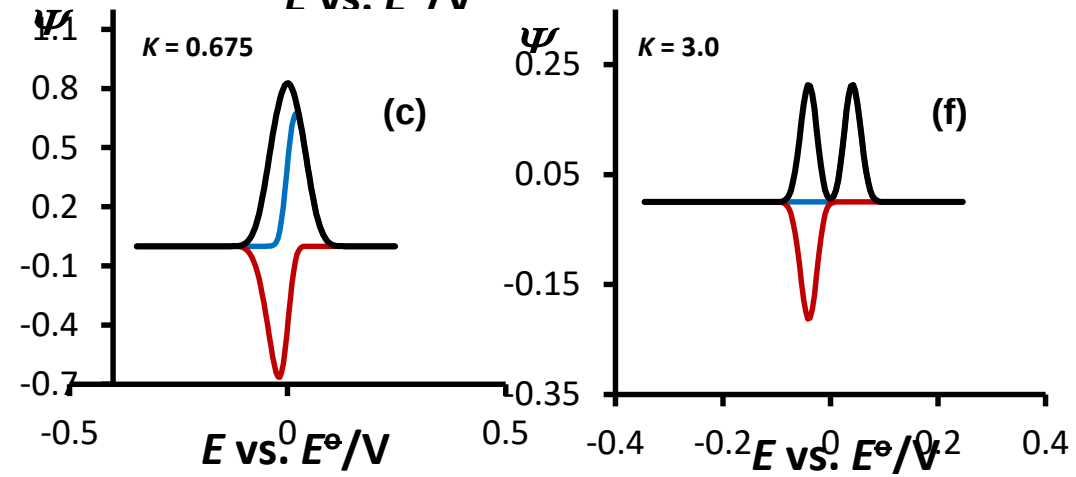


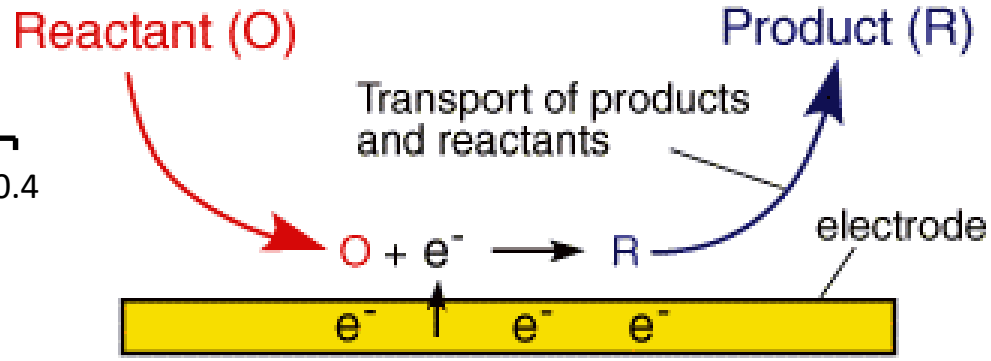


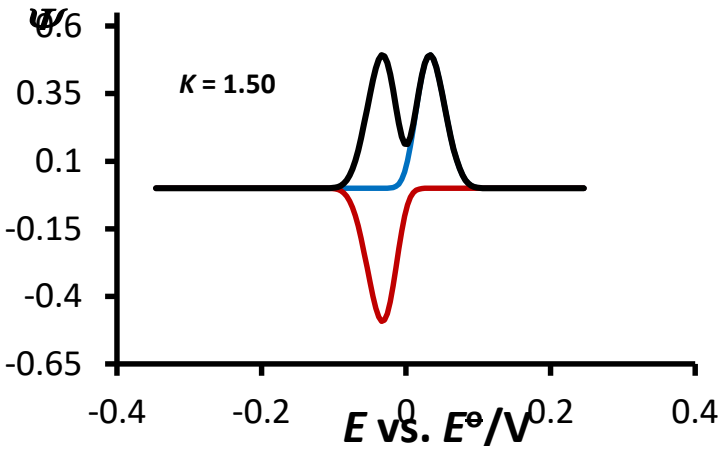


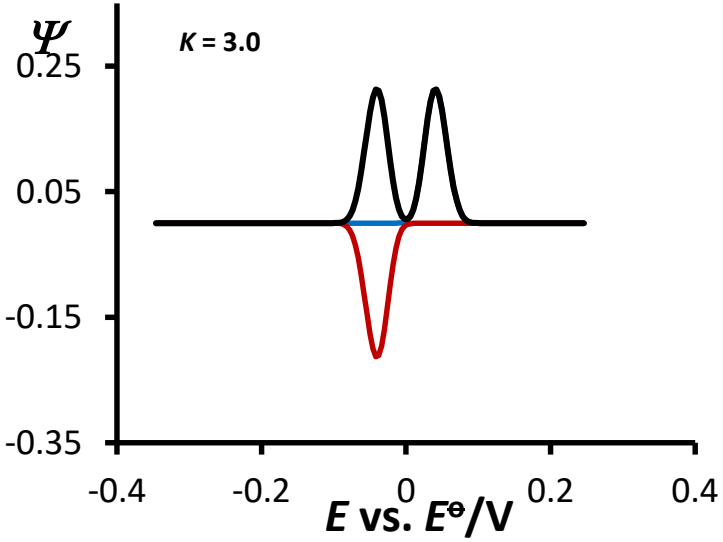


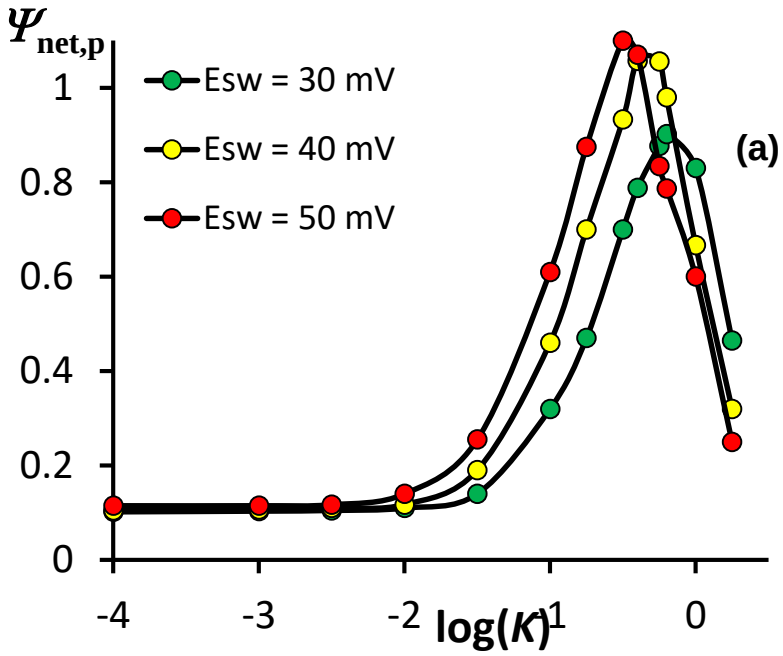


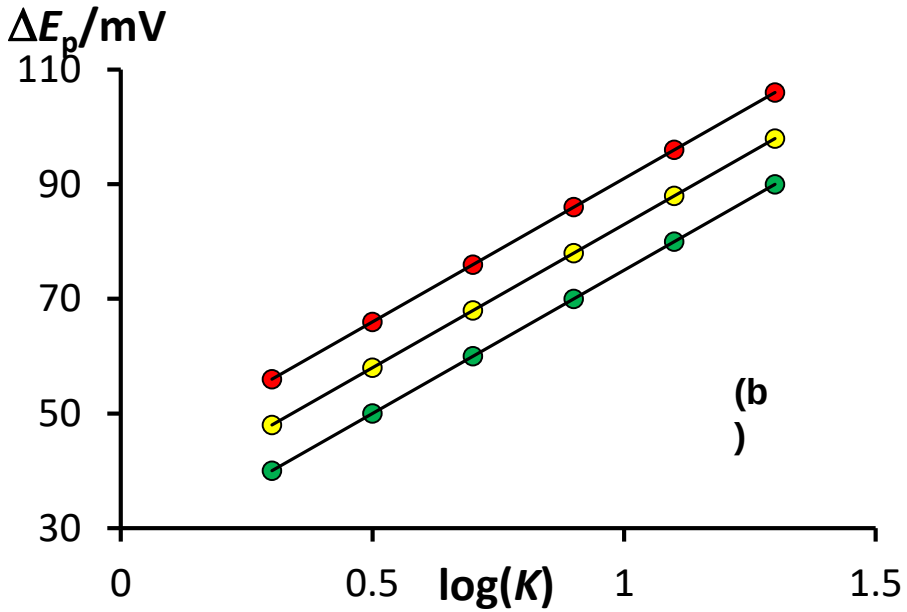








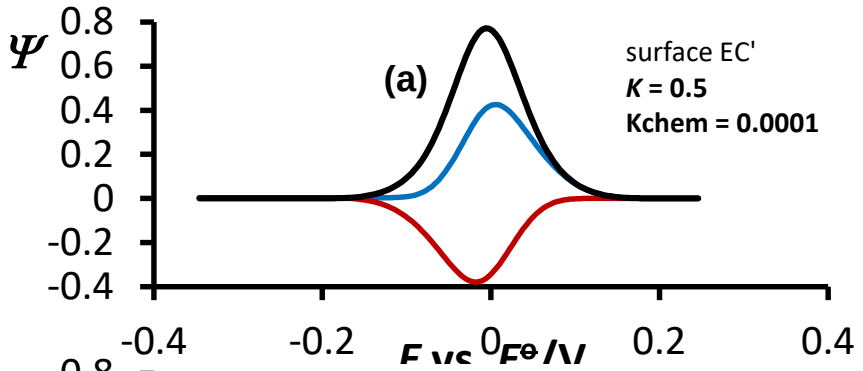


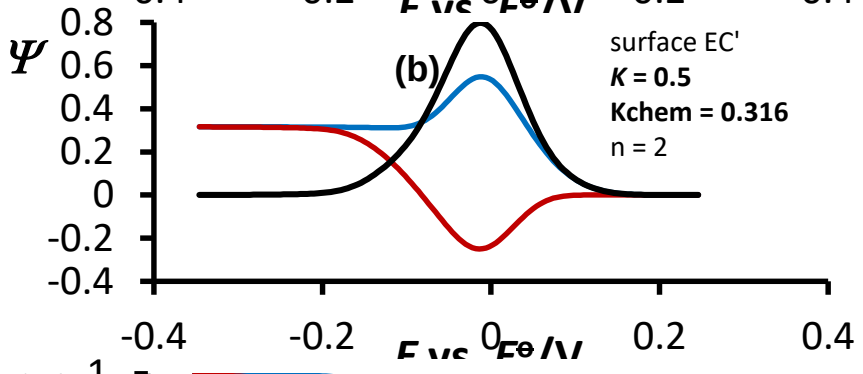


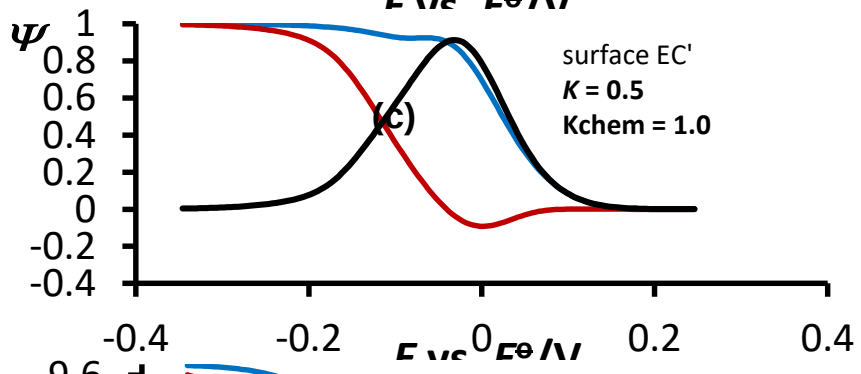
Quasireversible maximum
Parabolic dependenc of peak currents in SWV
As a function of
Kinetic of
Electron transfer

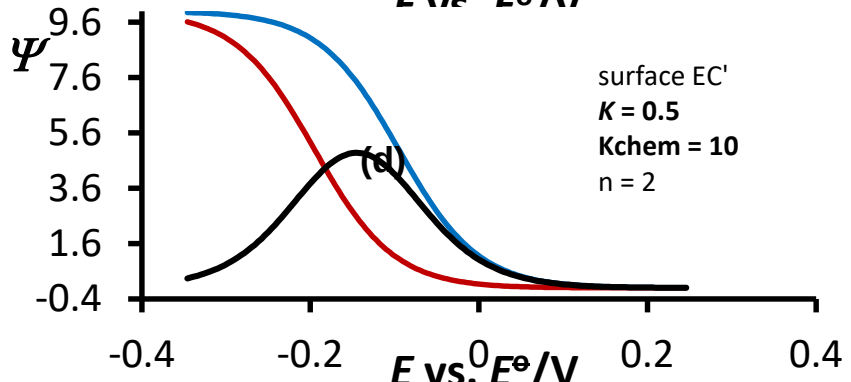
„Splitting of net SWV
Voltammogram
Typical feature of FAST
Electron transfer mechanisms

Surface REGENERATIVE Mechanism in SWV





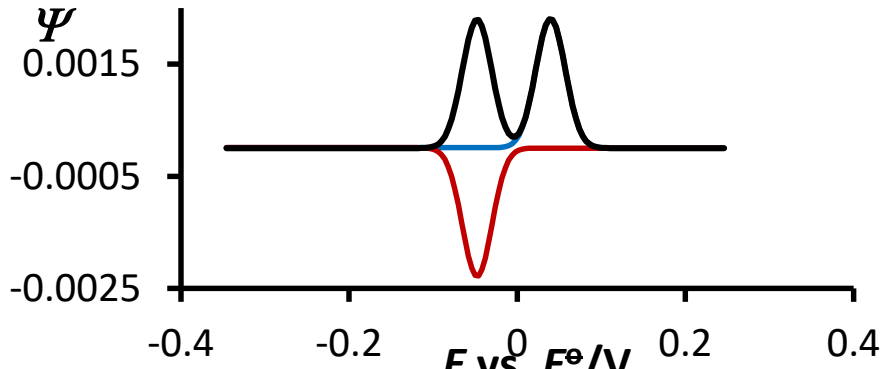


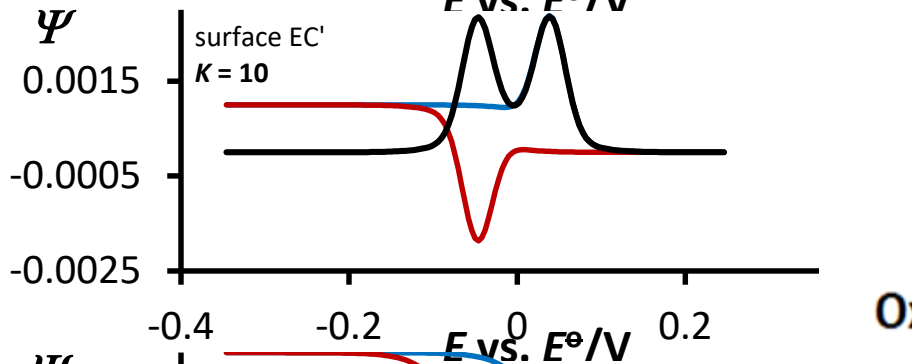


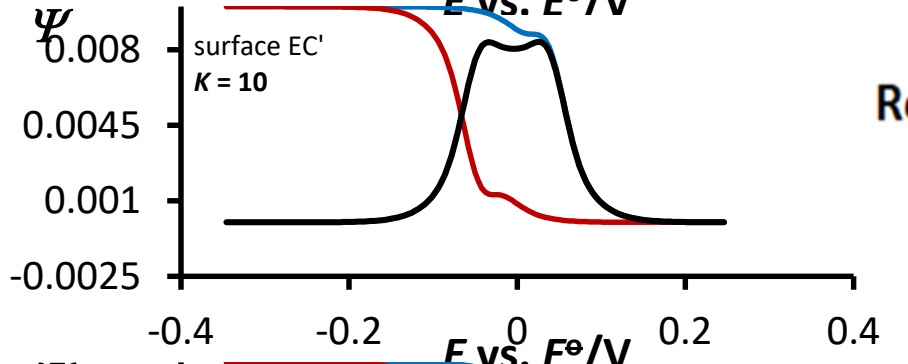
$$Ox_{(ads)} + ne- \underset{}{\overset{k_s^o}{\rightleftharpoons}} Red_{(ads)}$$

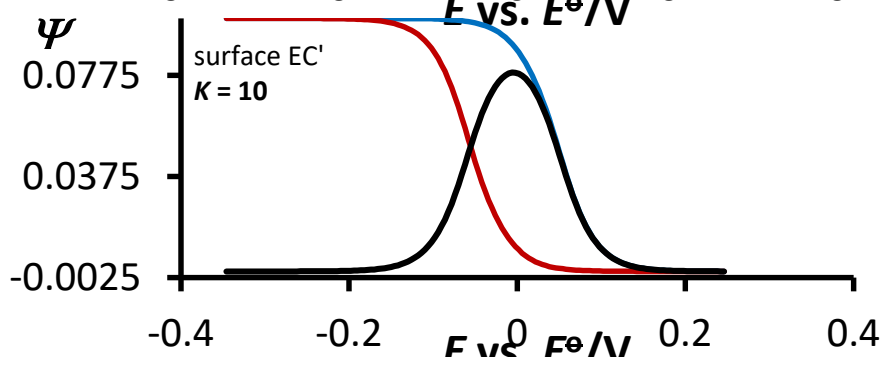
$$Red_{(ads)} + Y \xrightarrow{k_c} Ox_{(ads)}$$

Fast SURFACE REGENERATIVE MECHANISM in SWV



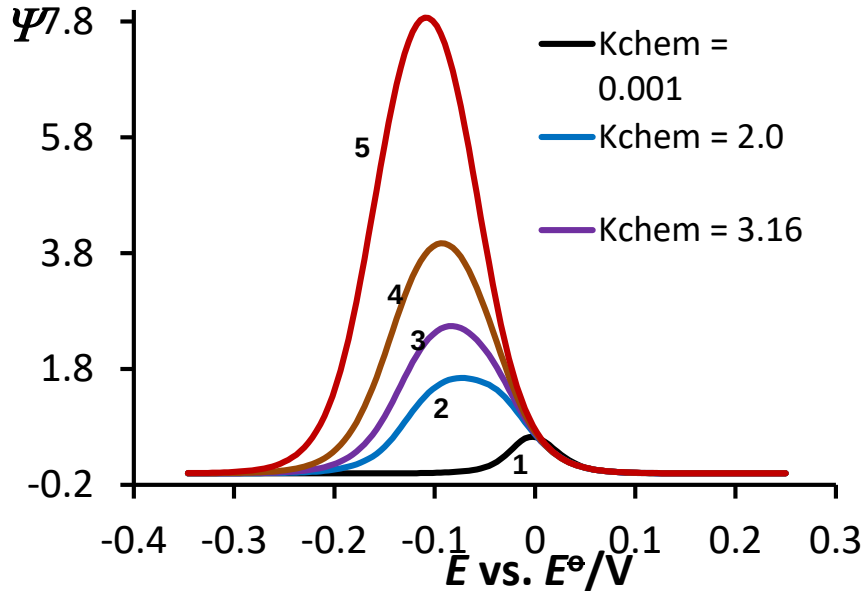


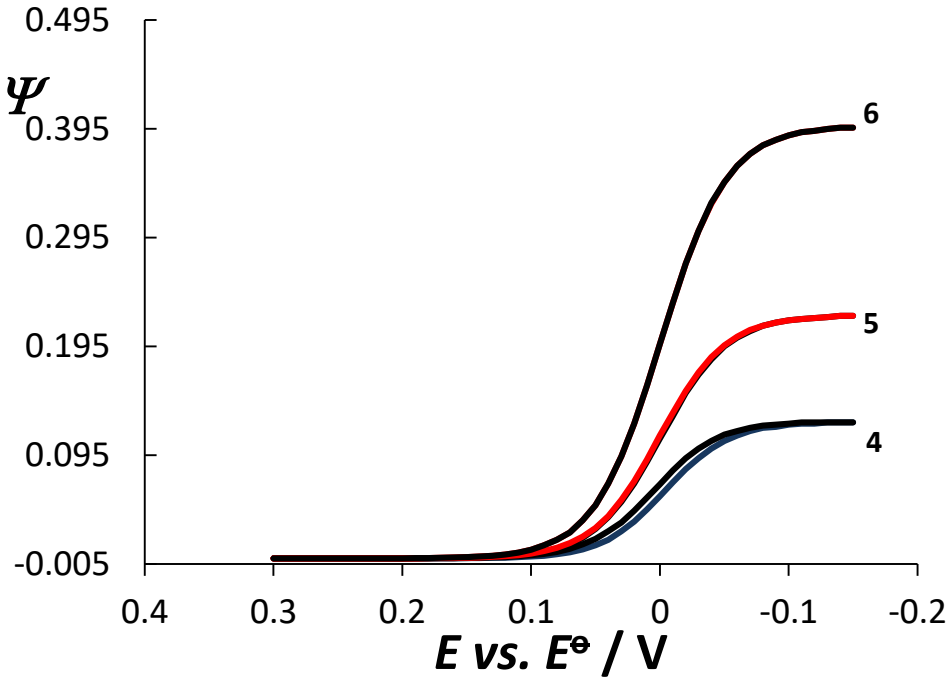


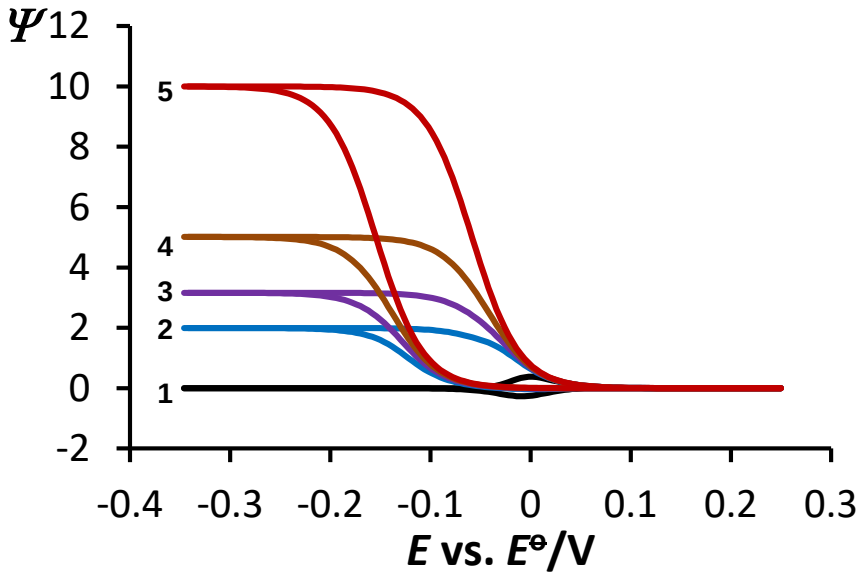


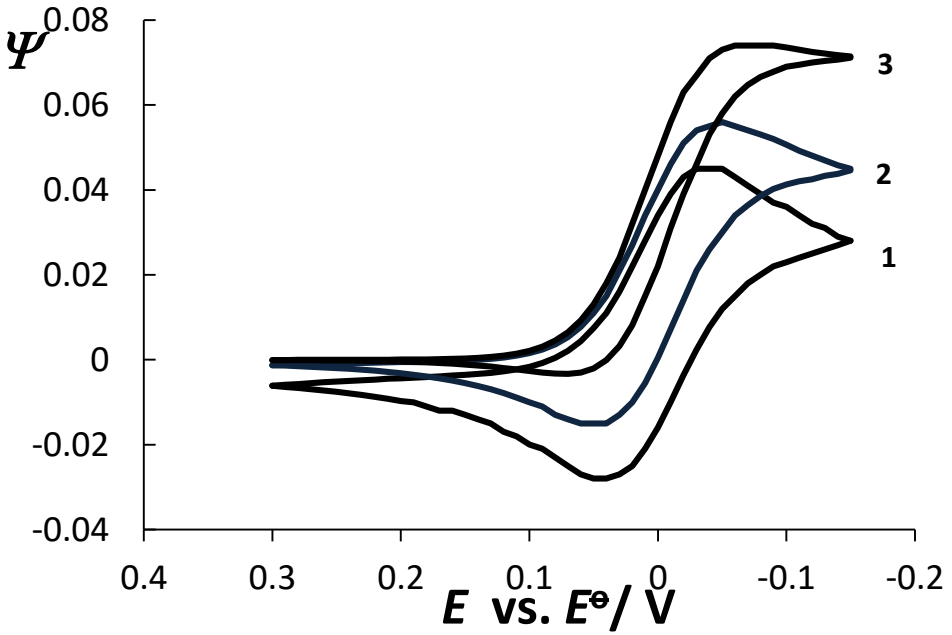
$$Ox_{(ads)} + ne^- \underset{}{\overset{k_s^o}{\rightleftharpoons}} Red_{(ads)}$$

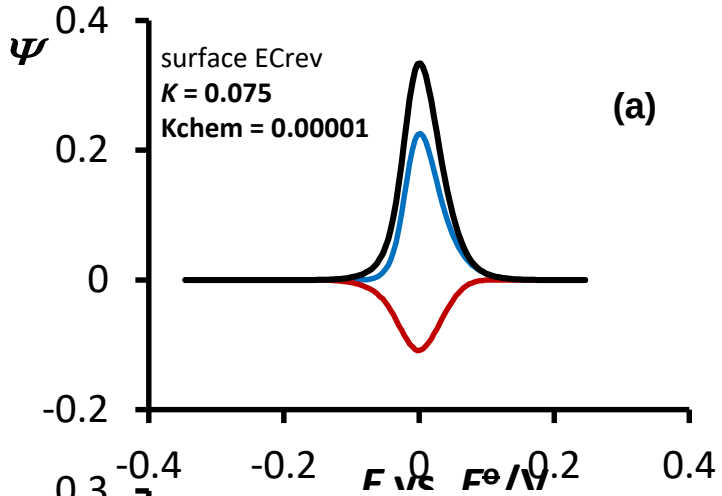
$$Red_{(ads)} + Y \xrightarrow{k_c} Ox_{(ads)}$$

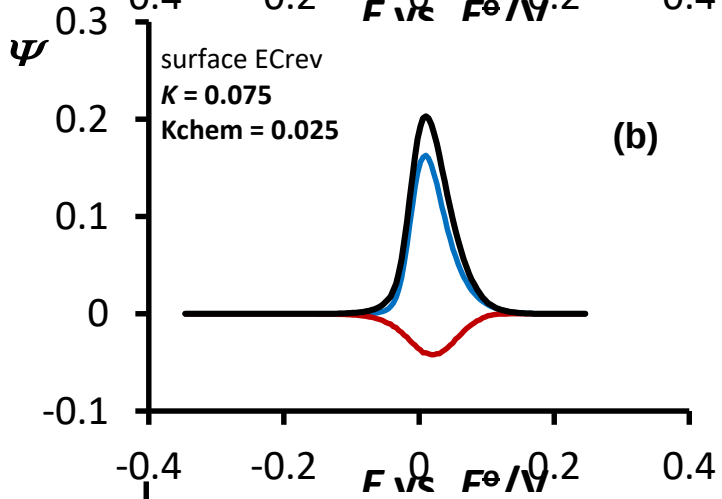

Ψ
7.8
5.8
3.8
1.8
-0.2
Kchem = 0.001
Kchem = 2.0
Kchem = 3.16
5
4
3
2
1
-0.4 -0.3 -0.2 -0.1 0 0.1 0.2 0.3
E vs. E⁰/V

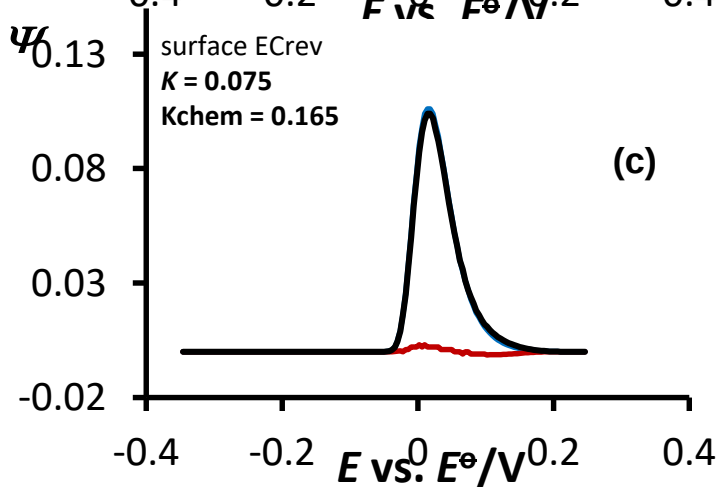

Ψ
0.495
0.395
0.295
0.195
0.095
-0.005
6
5
4
0.4 0.3 0.2 0.1 0 -0.1 -0.2
E vs. E⁰ / V


Ψ
12
10
8
6
4
2
0
-2
5
4
3
2
1
-0.4 -0.3 -0.2 -0.1 0 0.1 0.2 0.3
E vs. E⁰/V


Ψ
0.08
0.06
0.04
0.02
0
-0.02
-0.04
3
2
1
0.4 0.3 0.2 0.1 0 -0.1 -0.2
E vs. E⁰/ V







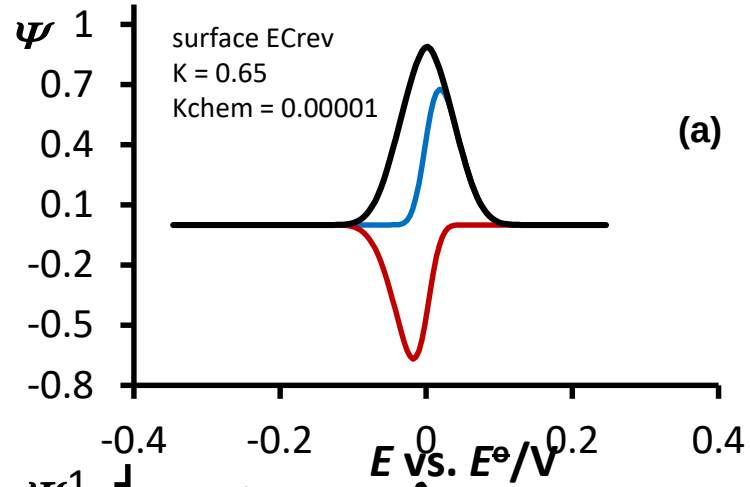
Surface ECrev

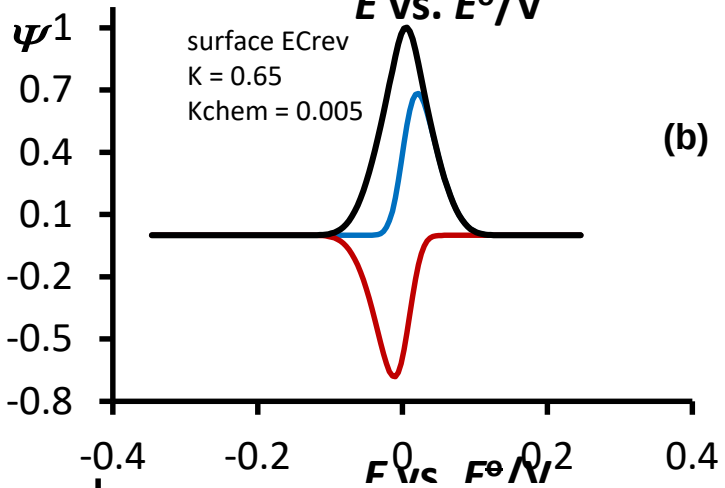
Surface Mechanism coupled with follow up Chemical reversible reaction)

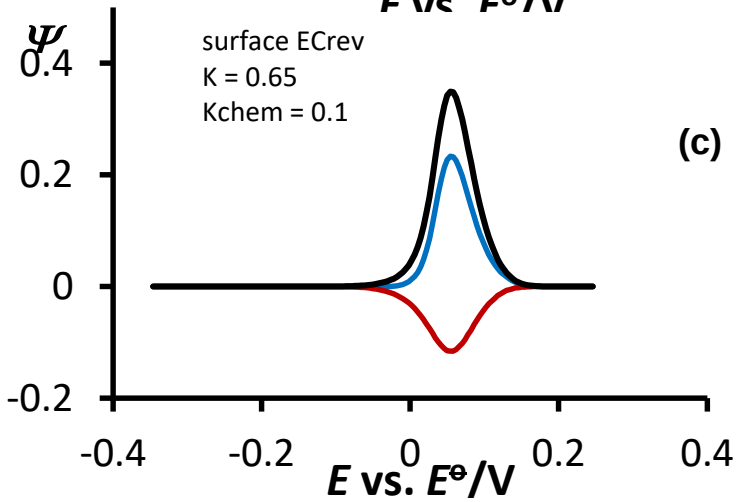
$$Ox_{(ads)} + ne^- \underset{}{\overset{k_s^\ominus}{\rightleftharpoons}} Red_{(ads)}$$

$$Red_{(ads)} + Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} S_{(ads)}$$

Surface Ecrev mechanism With fast Electron Transfer

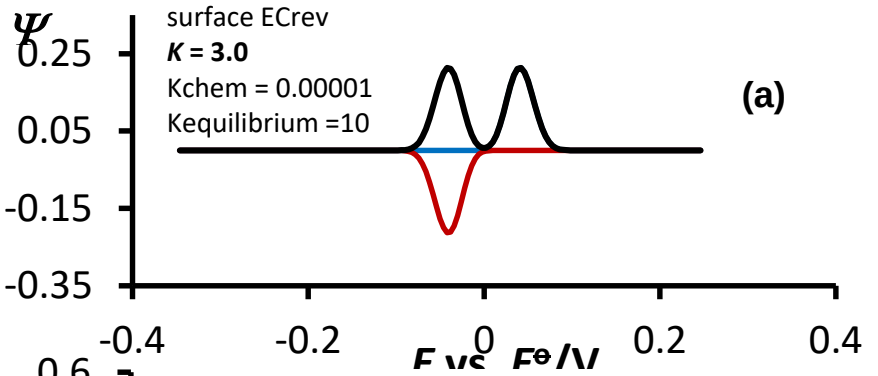


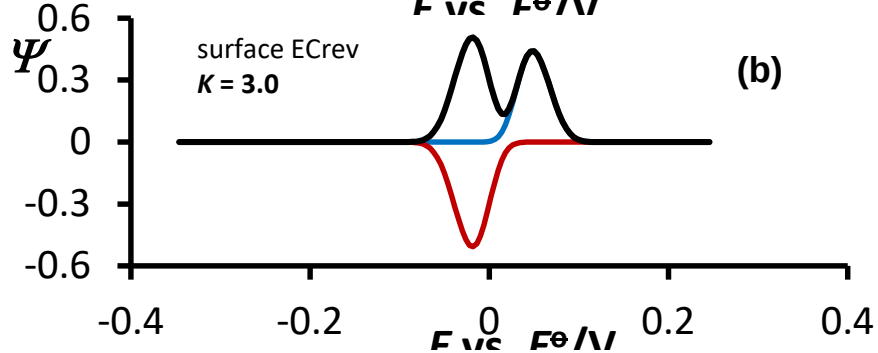


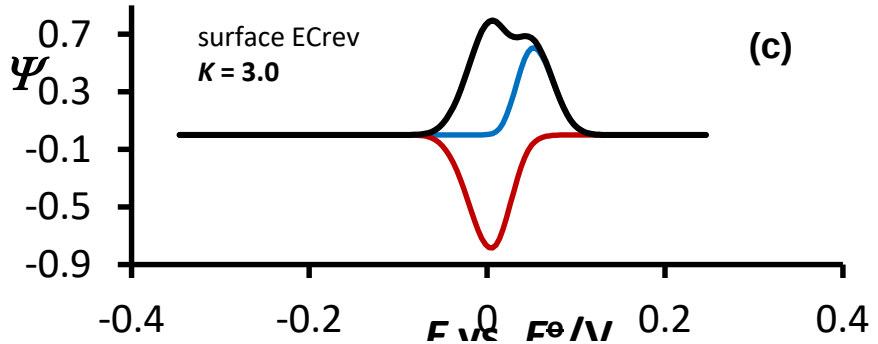


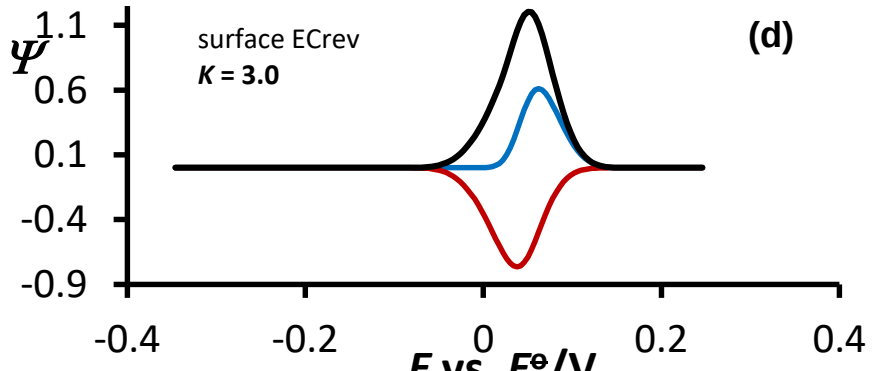
$$Ox_{(ads)} + ne^- \underset{}{\overset{k_s^0}{\rightleftharpoons}} Red_{(ads)}$$

$$Red_{(ads)} + Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} S_{(ads)}$$





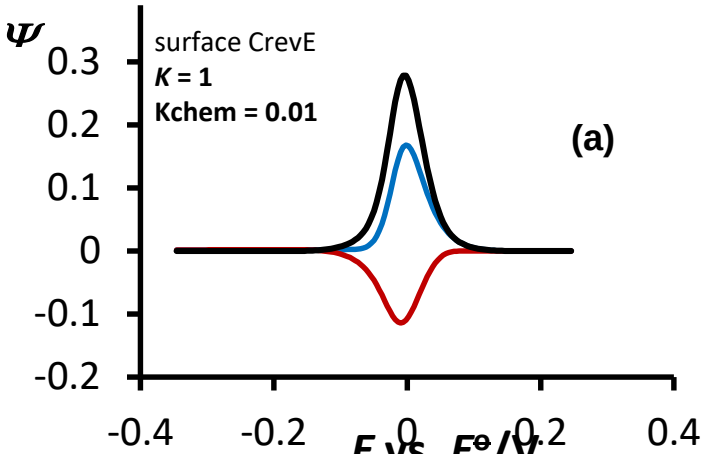


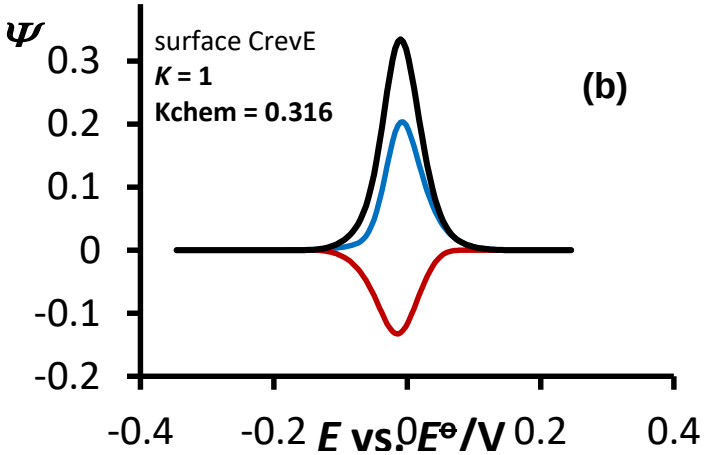


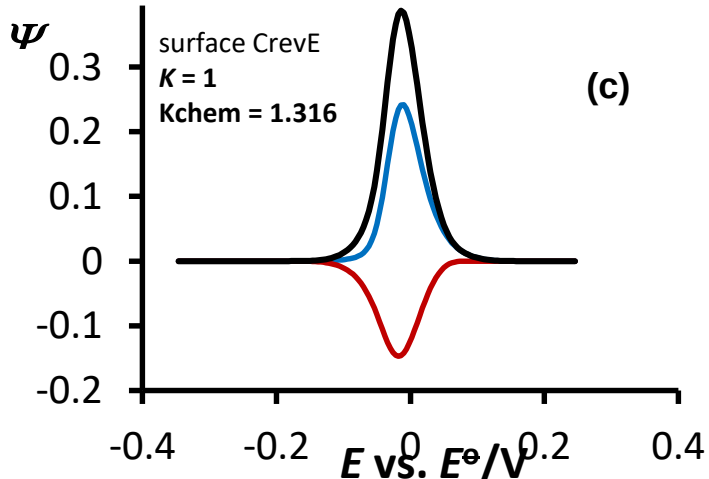
Surface Ecrev with VERY FAST electron transfer step

$$Ox_{(ads)} + ne- \underset{}{\overset{k_s^e}{\rightleftharpoons}} Red_{(ads)}$$

$$Red_{(ads)} + Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} S_{(ads)}$$







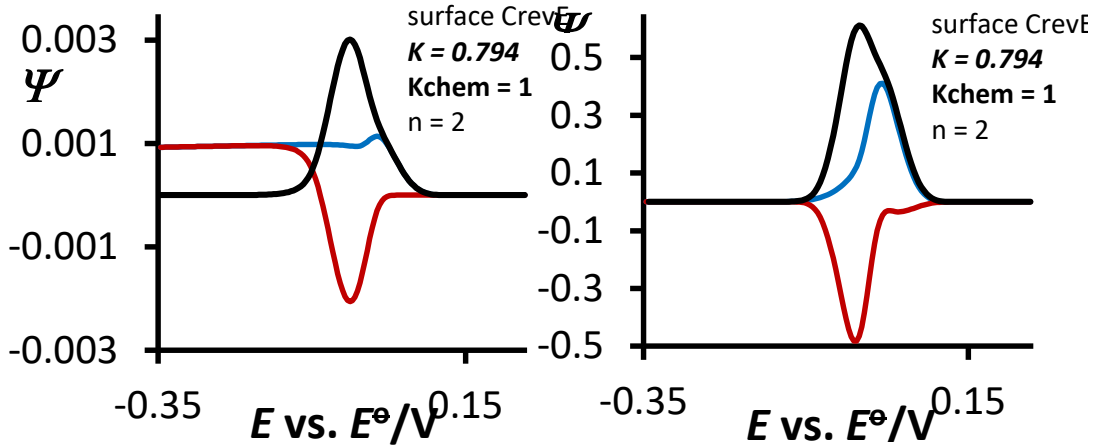
Surface CrevE

Mechanism

Electron transfer coupled with PRECEDING CHEMICAL REACTION

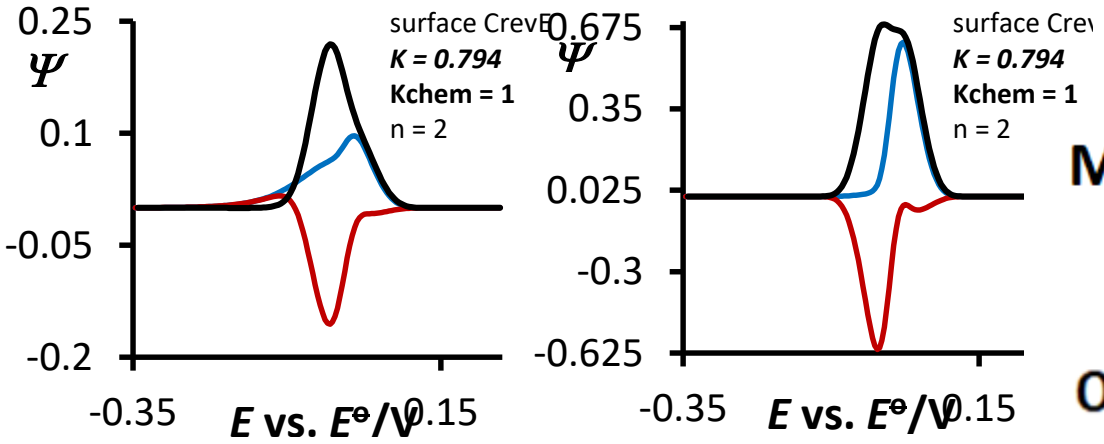
$$M_{(ads)} + Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ox_{(ads)}$$

$$Ox_{(ads)} + ne^- \overset{k_s^e}{\rightleftharpoons} Red_{(ads)}$$



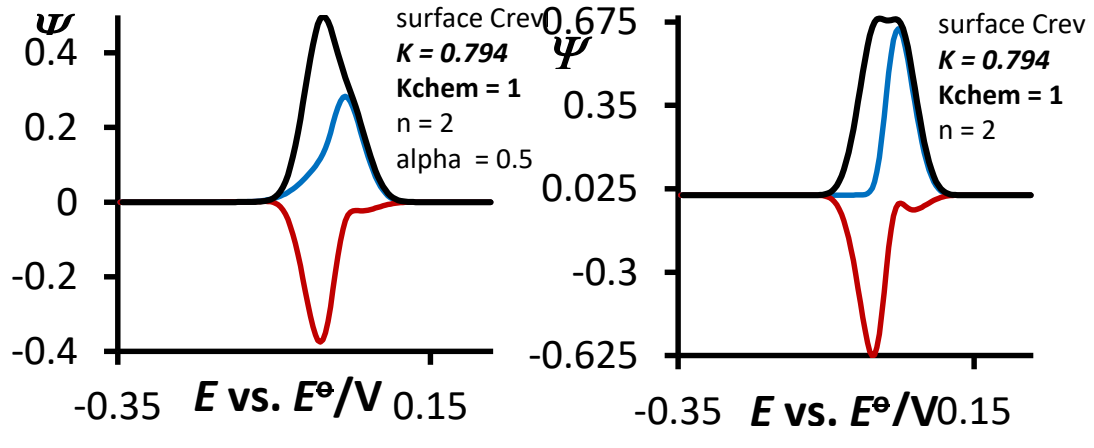
EFFECT OF Kchem

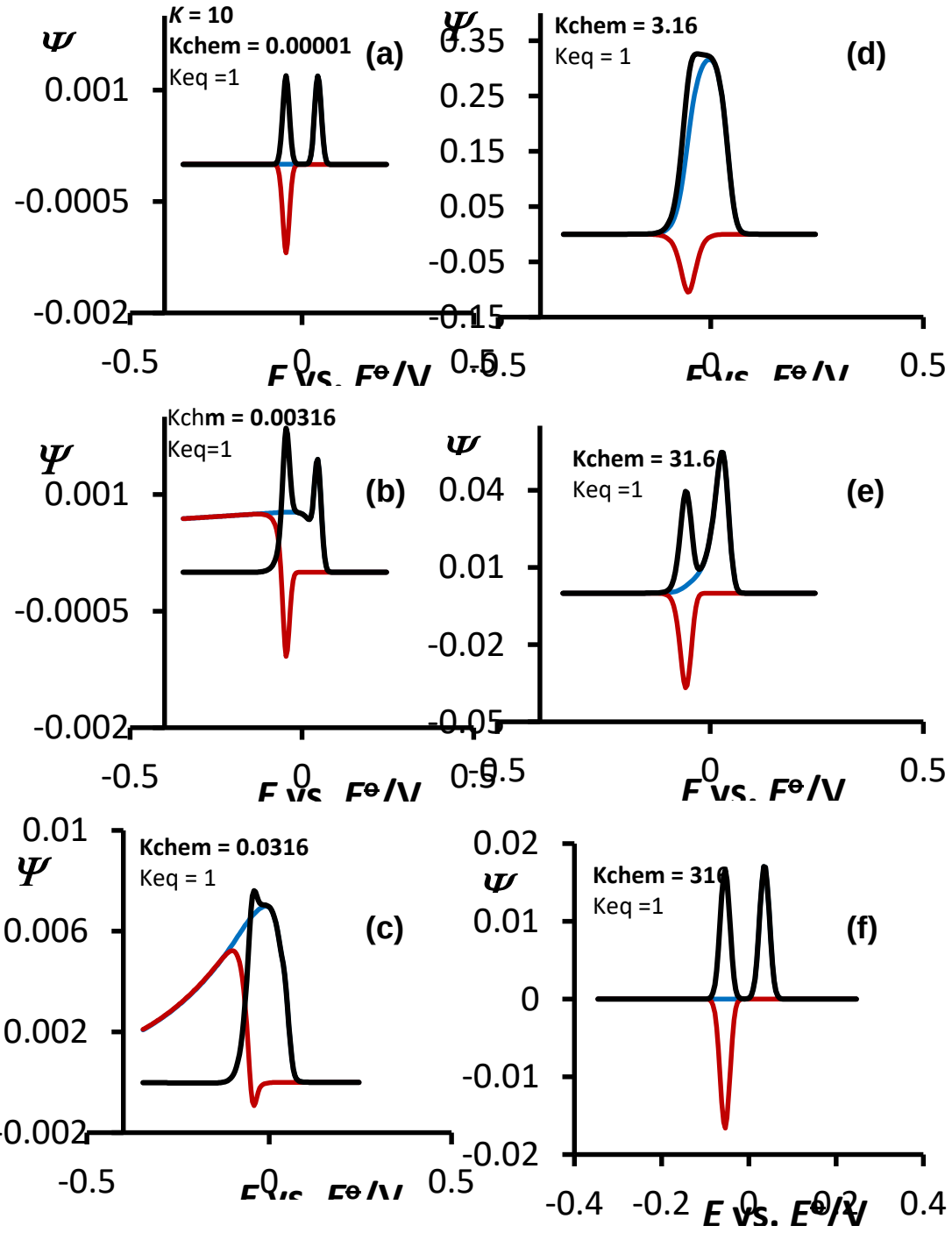
at Keq of 0.001



$$M_{(ads)} + Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ox_{(ads)}$$

$$Ox_{(ads)} + ne^- \overset{k_s^0}{\rightleftharpoons} Red_{(ads)}$$





Површинска CrevE

електродна Реакција—спрегната Со ПРЕТХОДНА Хемиска РЕАКЦИЈА

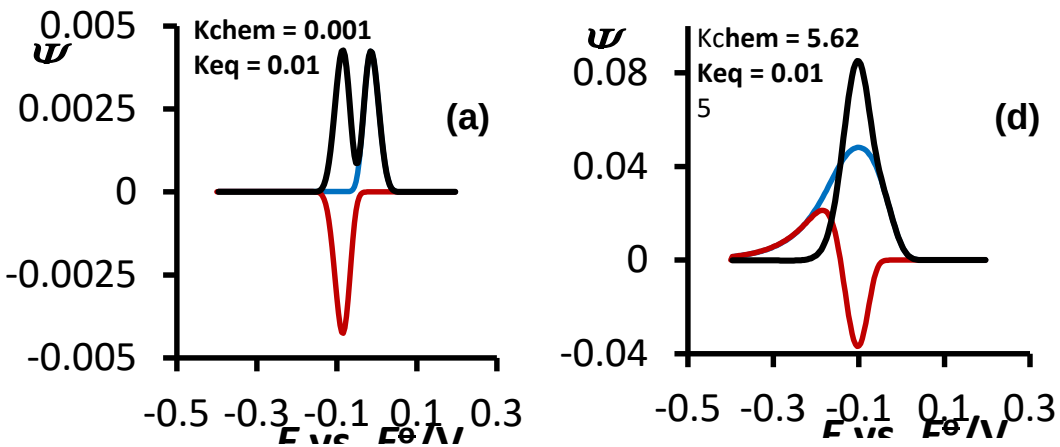
МНОГУ БРЗА Електродна реакција

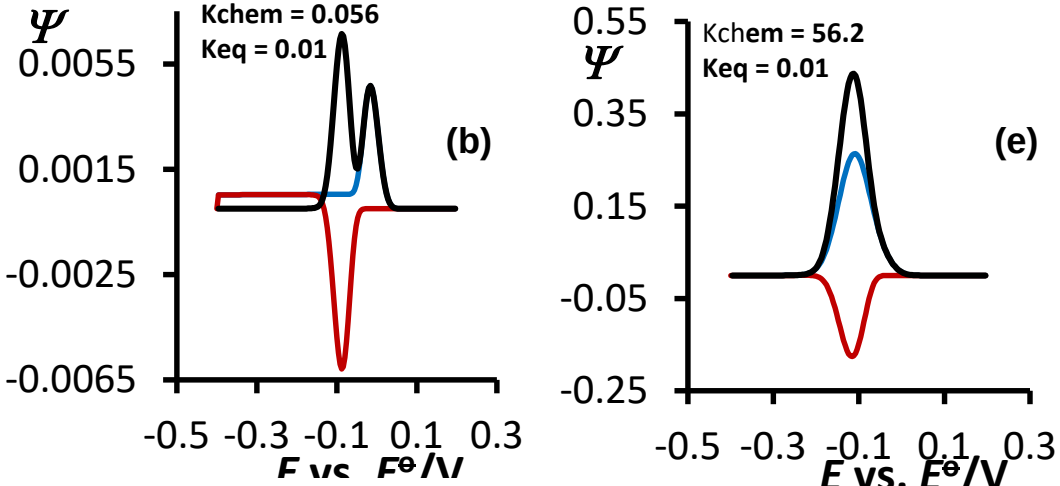
EFFECT OF Kchem

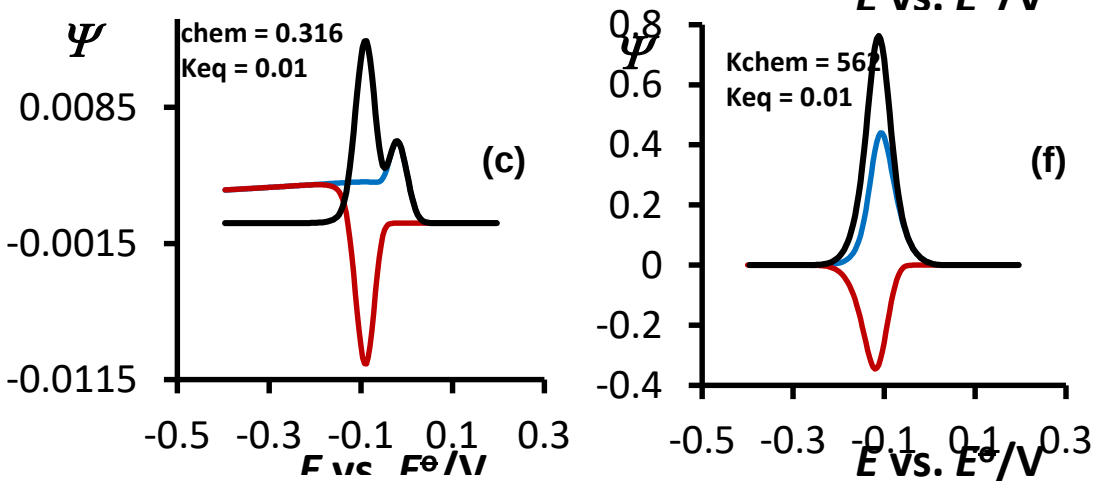
at Keq of 1.0

$$M_{(ads)} + Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ox_{(ads)}$$

$$Ox_{(ads)} + ne- \overset{k_s^{\ominus}}{\rightleftharpoons} Red_{(ads)}$$







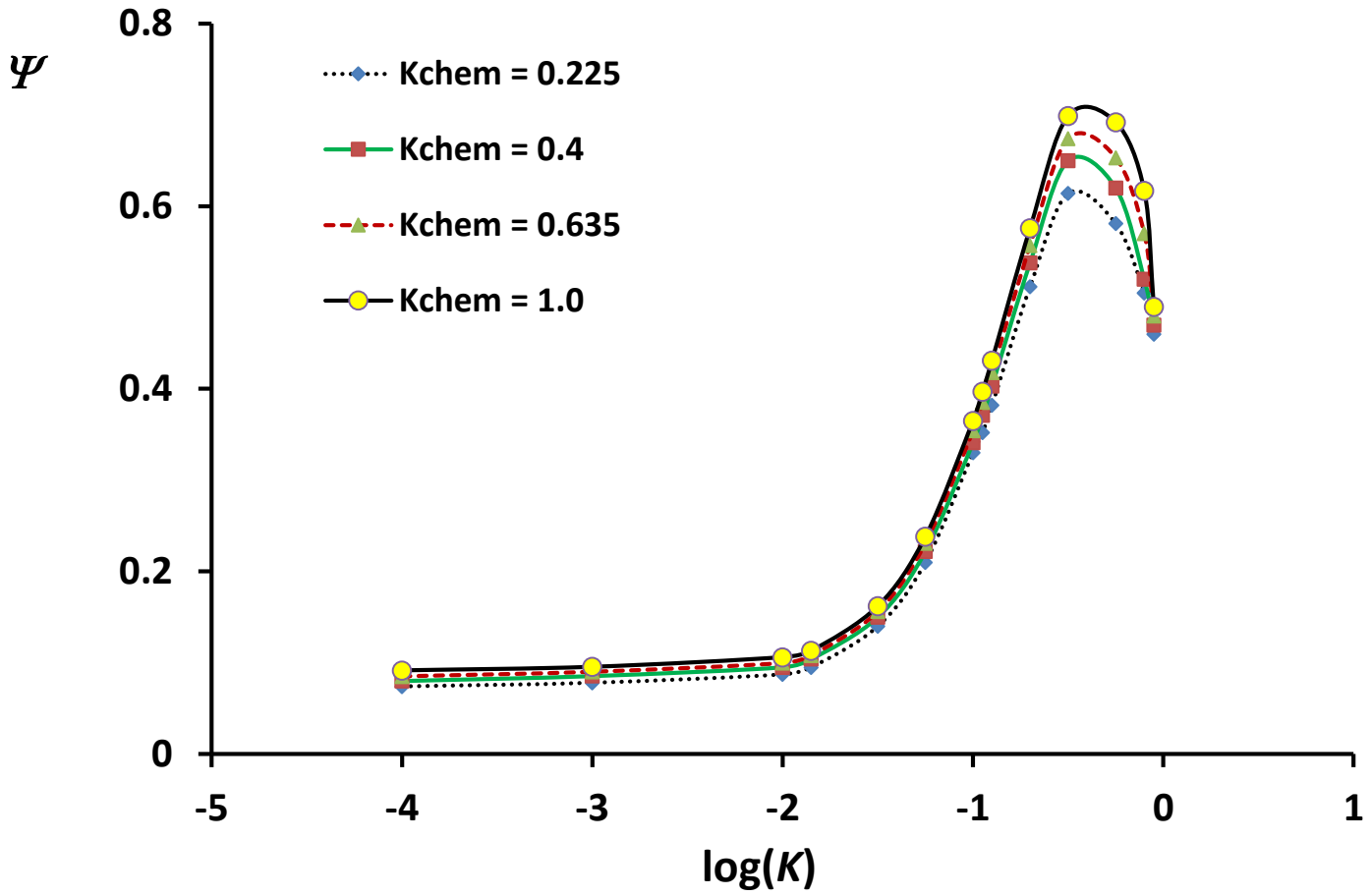
EFFECT на Kchem
t.e. На кинетика на
Претходна хемиска реакција
НО....
при Keq of 0.01

$$M_{(ads)} + Y \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Ox_{(ads)}$$

$$Ox_{(ads)} + ne^- \overset{k_s^{\ominus}}{\rightleftharpoons} Red_{(ads)}$$

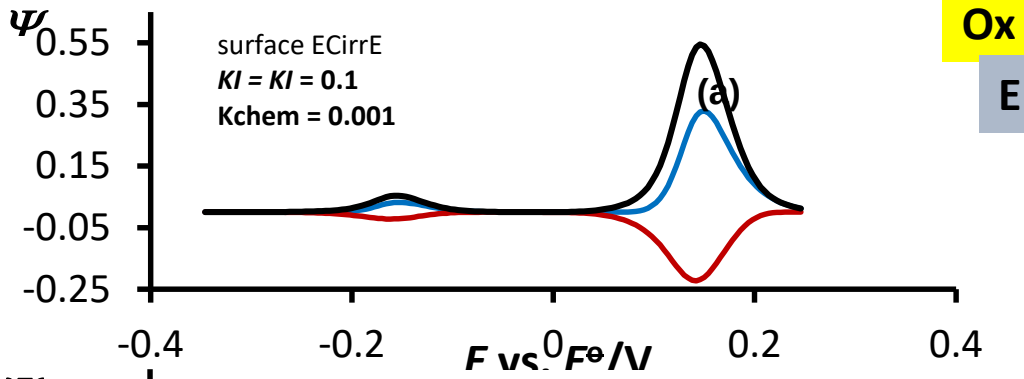
Surface CrevE

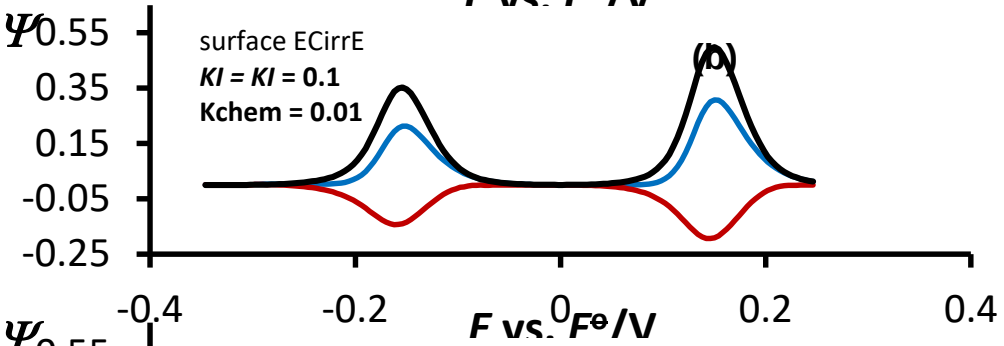
Keq = 1; n = 2.

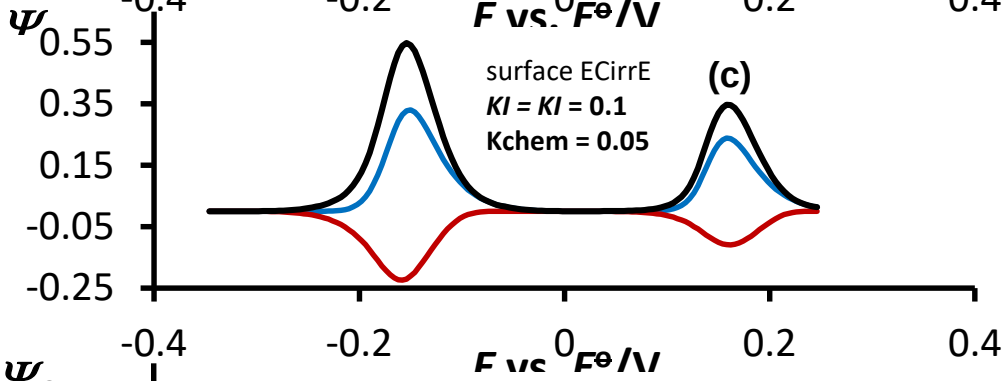


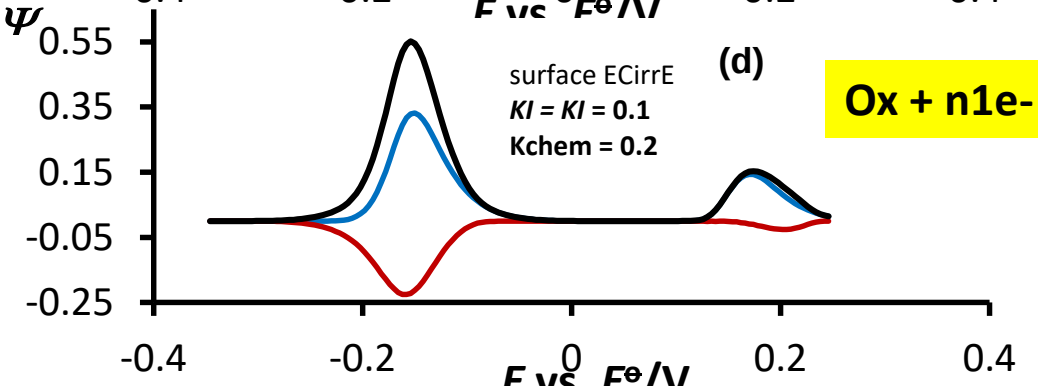
Квадратно-бранова Волтаметрија На ДВОСТЕПЕНИ ПОВРШИНСКИ ЕЛЕКТРОДНИ РЕАКЦИИ----

Кај ензими со кинонски активен дел или некои роливалентни Метални катјони на Mo, Mn, V









Ox + n1e- ⇄ Red1 + n2e- ⇄ Red2

E1-прва ел.реак **E2-втора ел реак**

Површинска ECirrE

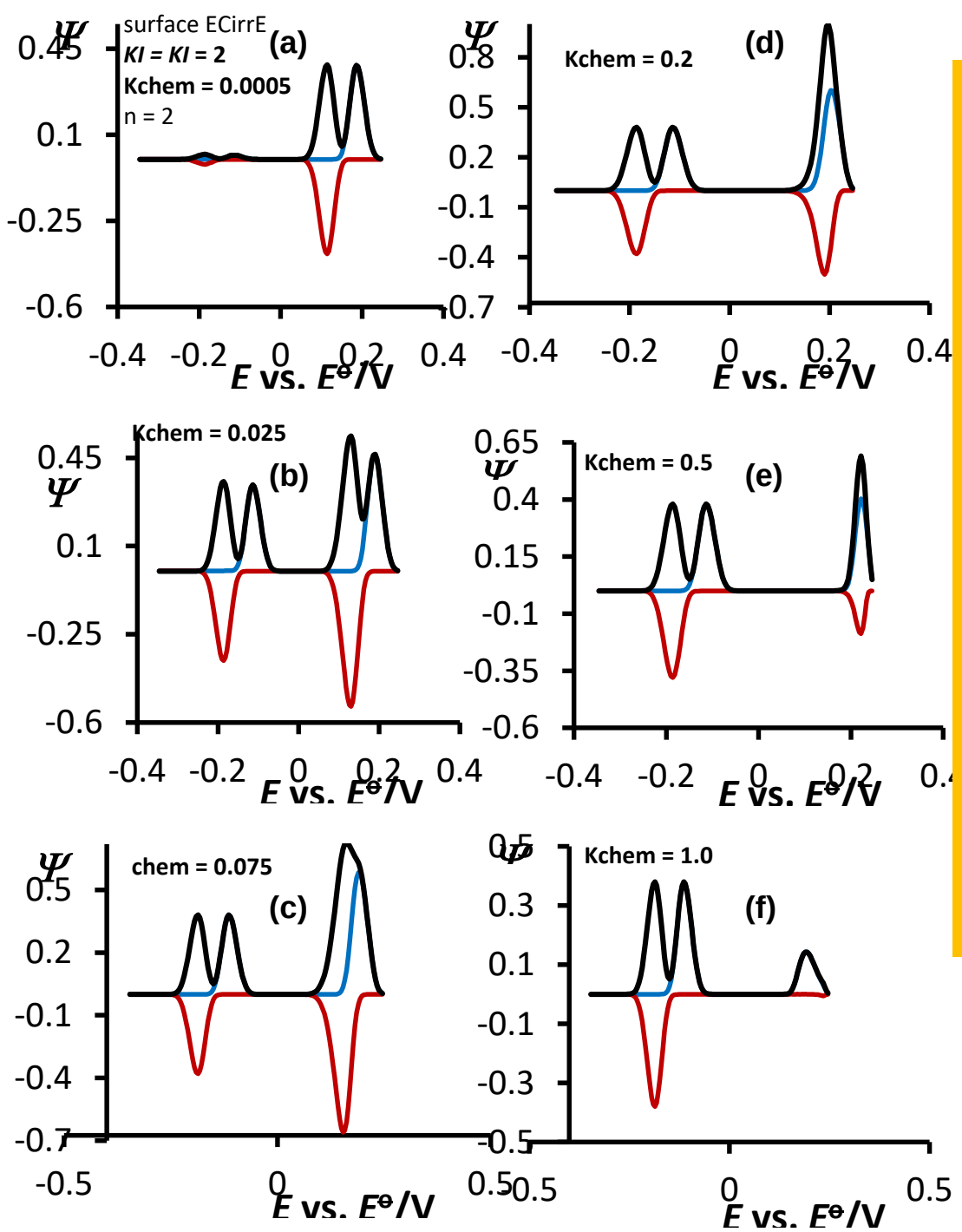
Двостепена електродна Реакција—спрегната Со ИНТЕРЕДИЕРНА Хемиска РЕАКЦИЈА

Сите до Атсорбирана состојба

Ox + n1e- ⇄ Red1+ Y-→Z(ads) n2e- ⇄ Red

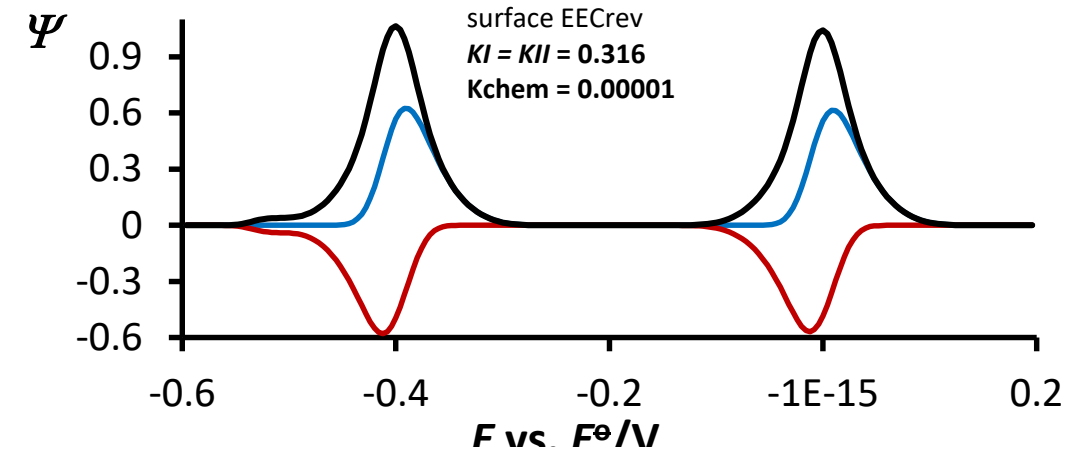
ECE MECHANISM

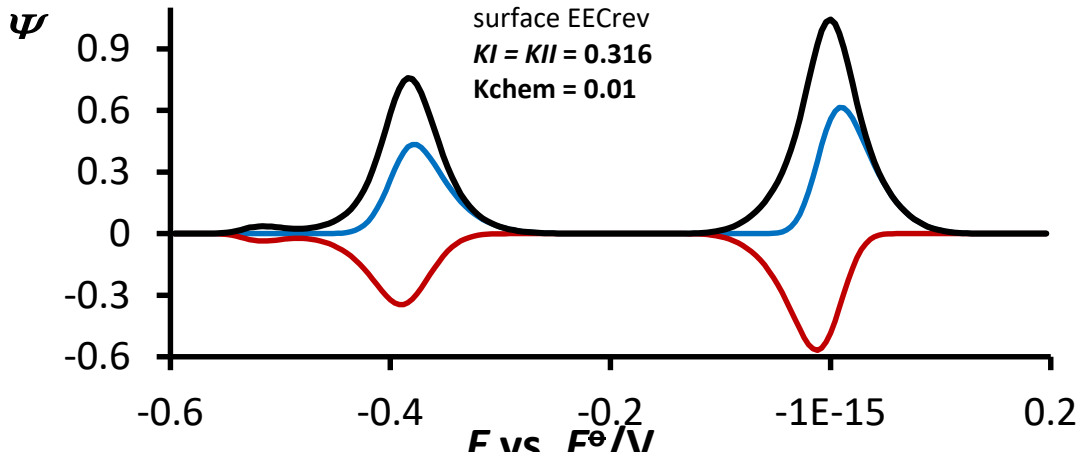
$Q + e \rightleftharpoons Q^{\cdot-}$	E_1	(1)
$Q^{\cdot-} + DH \rightleftharpoons QH^{\cdot} + D^-$	$1/K_2'$	(13')
$QH^{\cdot} + e \rightleftharpoons QH^-$	E_4	(23)
$Q + 2e + DH \rightleftharpoons QH^- + D^-$		(22)

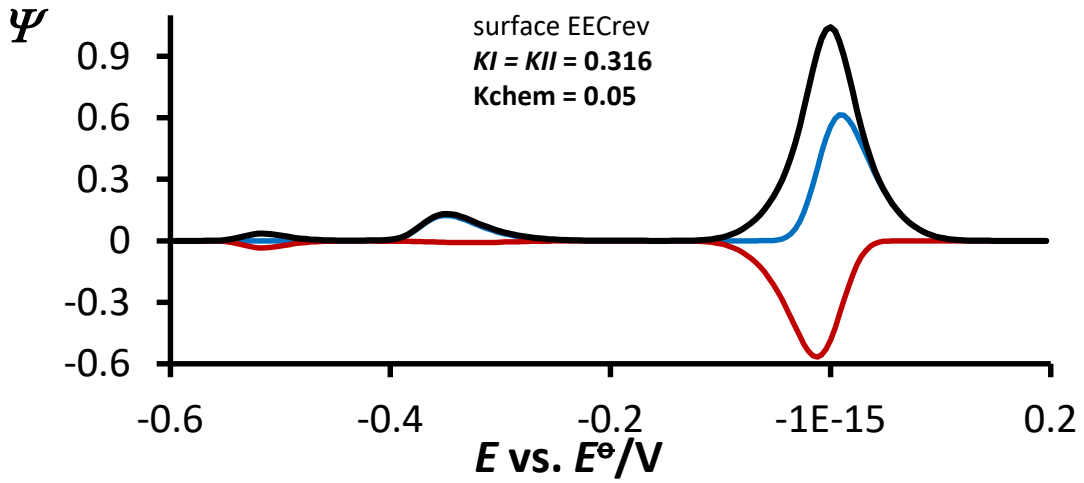


Површинска ECirrE

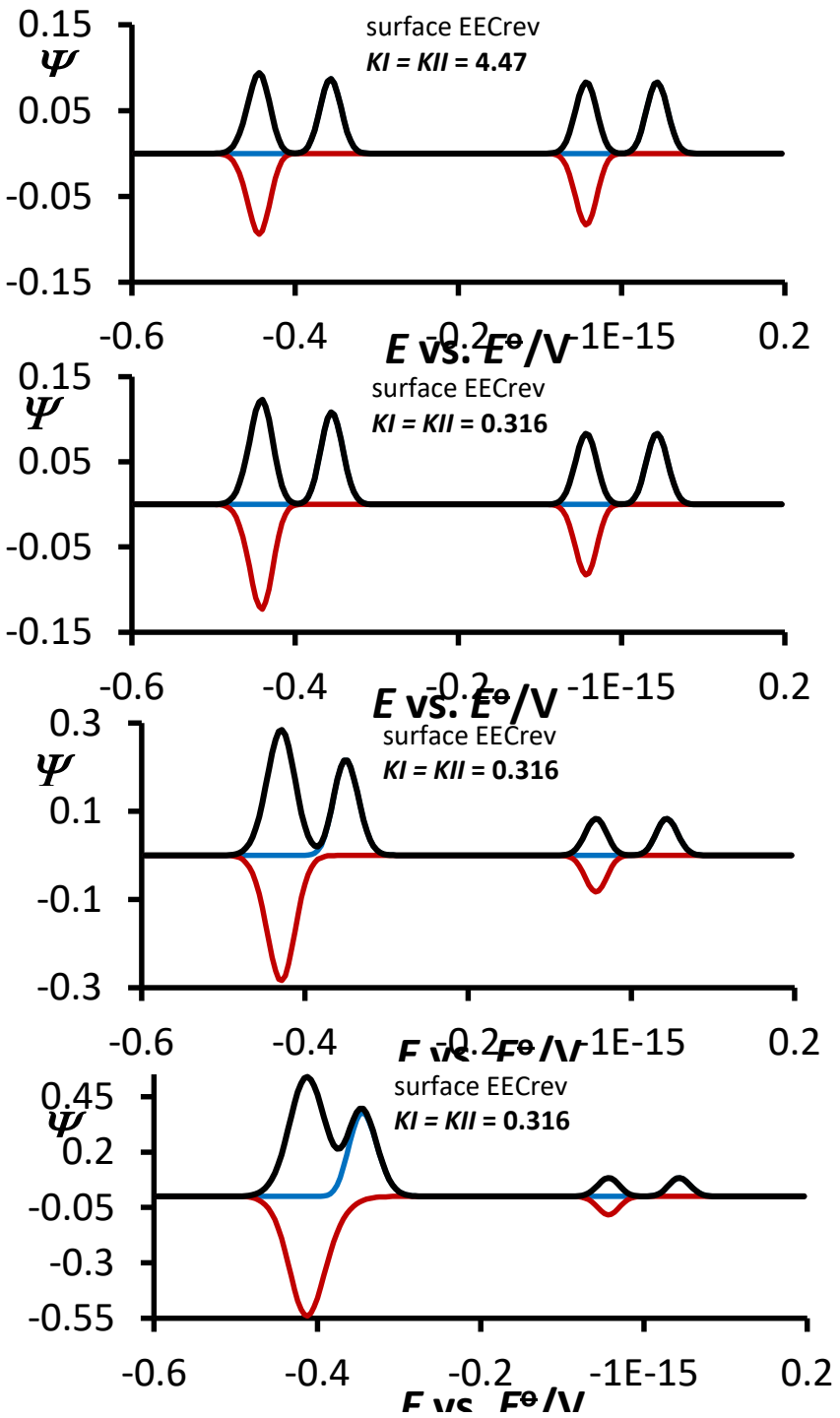
Двостепена електродна Реакција—спрегната Со ИНТЕР-МЕДИЕРНА Хемиска РЕАКЦИЈА **ЕФЕКТ НА БРЗИНАТА НА ХЕМИСКАТА РЕАКЦИЈА** кај **МНОГУ БРЗИ Електродни реакции**





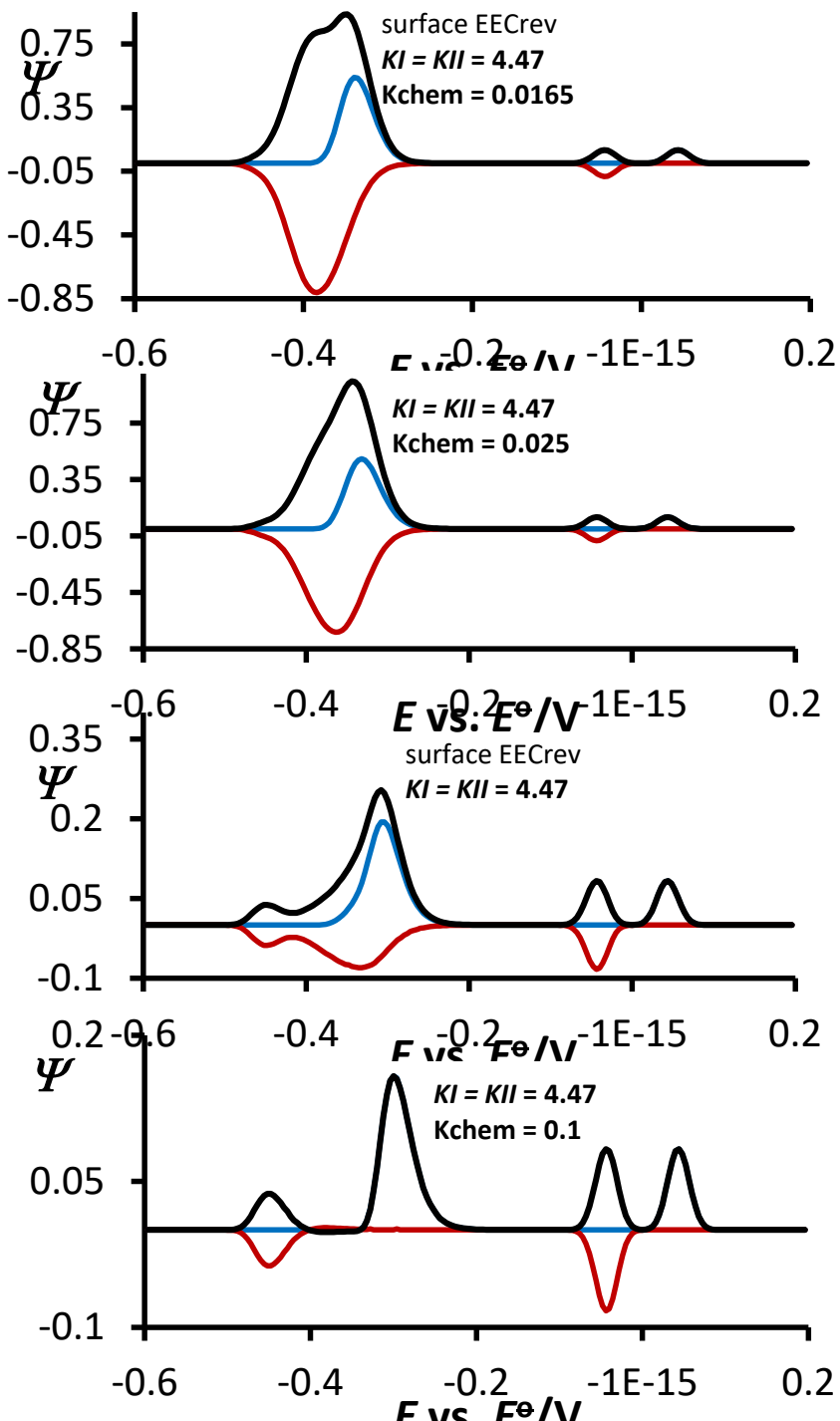


Површинска EECrev
Двостепена електродна Реакција—спрегната Со ПОСЛЕДОВАТЕЛНА Хемиска РЕАКЦИЈА **ЕФЕКТ НА БРЗИНАТА НА ХЕМИСКАТА РЕАКЦИЈА** кај **УМЕРЕНО БРЗА Електродна реакција**



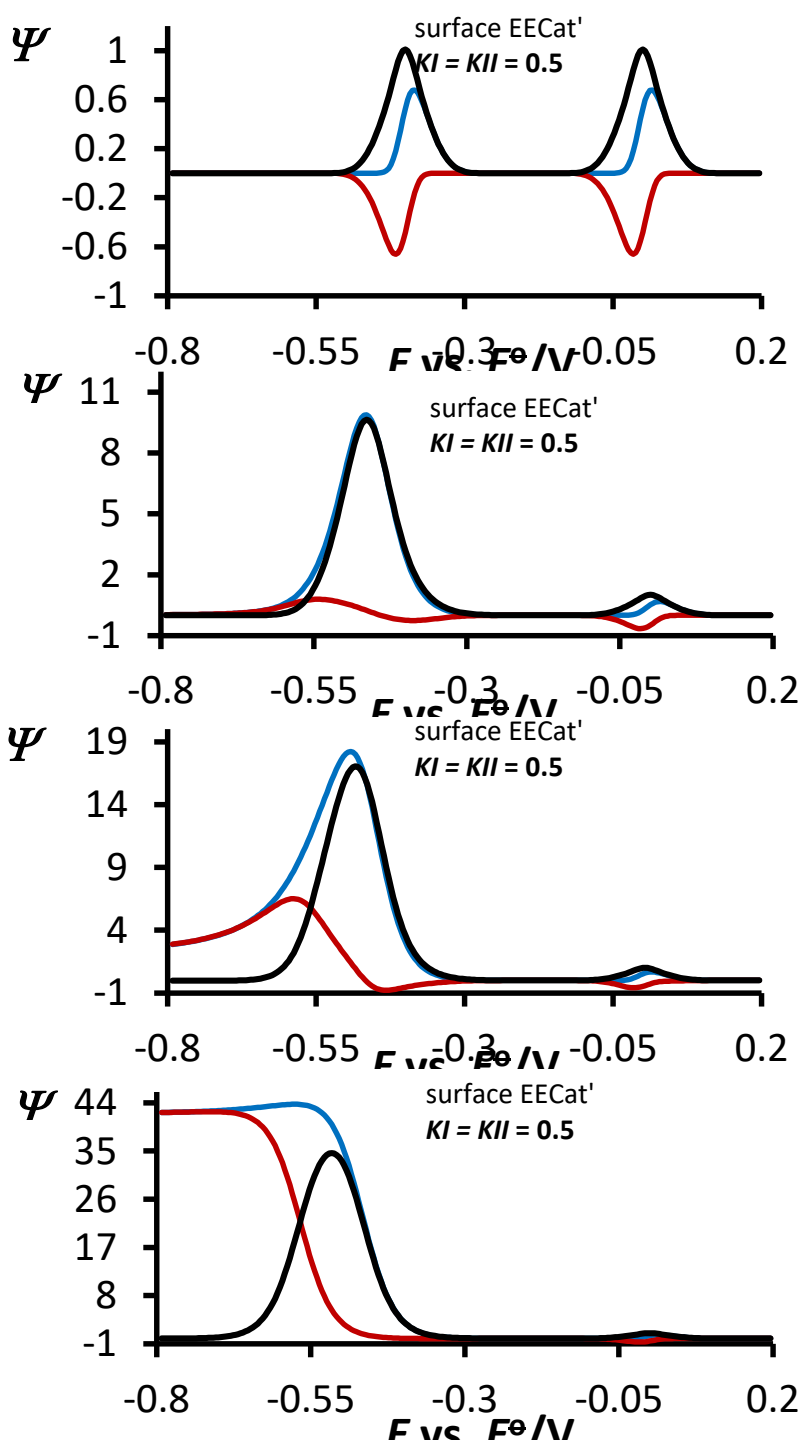
Површинска EECrev

Двостепена електродна Реакција—спрегната Со ПОСЛЕДОВАТЕЛНА Хемиска РЕАКЦИЈА **ЕФЕКТ НА БРЗИНАТА НА ХЕМИСКАТА РЕАКЦИЈА** кај **МНОГУ БРЗА Електродна реакција**



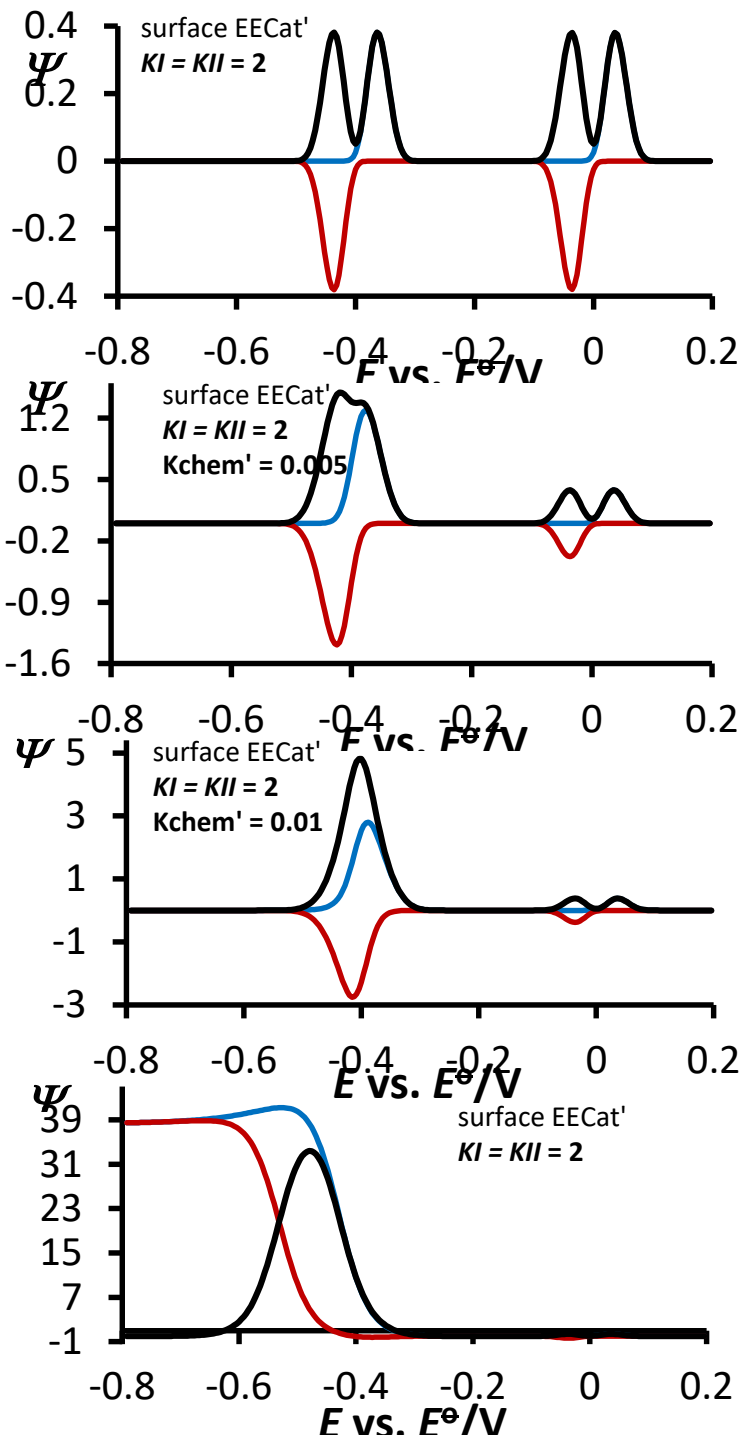
Површинска EECrev

Двостепена електродна Реакција—спрегната Со ПОСЛЕДОВАТЕЛНА Хемиска РЕАКЦИЈА **ЕФЕКТ НА БРЗИНАТА НА ХЕМИСКАТА РЕАКЦИЈА** кај **МНОГУ БРЗА Електродна реакција**



Површинска EECcatalytic

Двостепена електродна Реакција—спрегната Со ПОСЛЕДОВАТЕЛНА РЕГЕНЕРАТИВНА Хемиска РЕАКЦИЈА **ЕФЕКТ НА БРЗИНАТА НА РЕГЕНЕРАТИВНАТА РЕАКЦИЈА** кај **УМЕРЕНО БРЗИ Електродни реакции**



Површинска EECcatalytic

Двостепена електродна Реакција—спрегната Со ПОСЛЕДОВАТЕЛНА РЕГЕНЕРАТИВНА Хемиска РЕАКЦИЈА **ЕФЕКТ НА БРЗИНАТА НА РЕГЕНЕРАТИВНАТА РЕАКЦИЈА** кај **МНОГУ БРЗИ Електродни реакции**

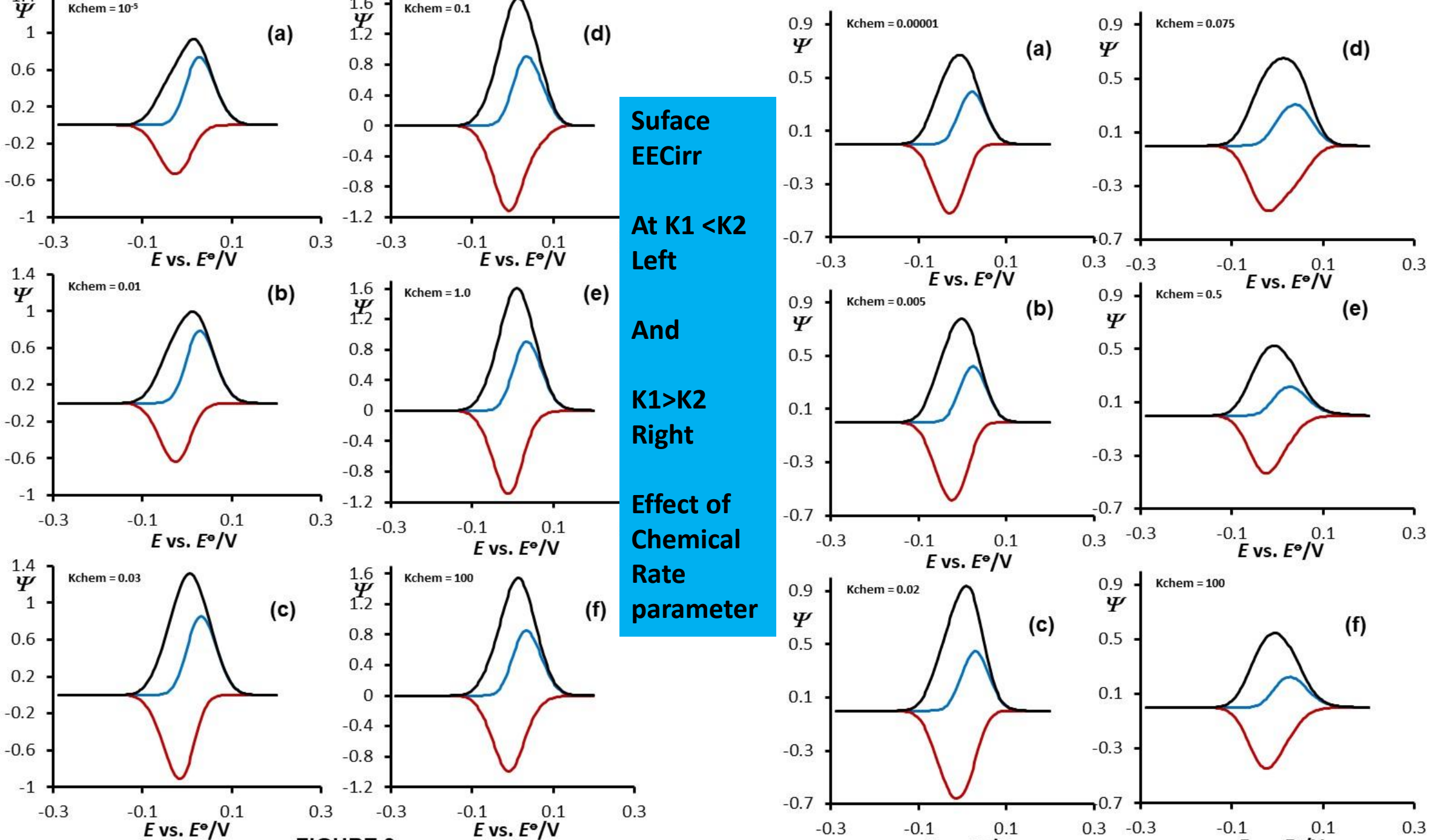


FIGURE 8

Suface EECirr

At K1 <K2 Left

And

K1>K2 Right

Effect of Chemical Rate parameter

FIGURE 9

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