Theory of Square-wave Voltammetry of Two-step Surface Electrode Mechanisms Associated with Chemical Equilibria

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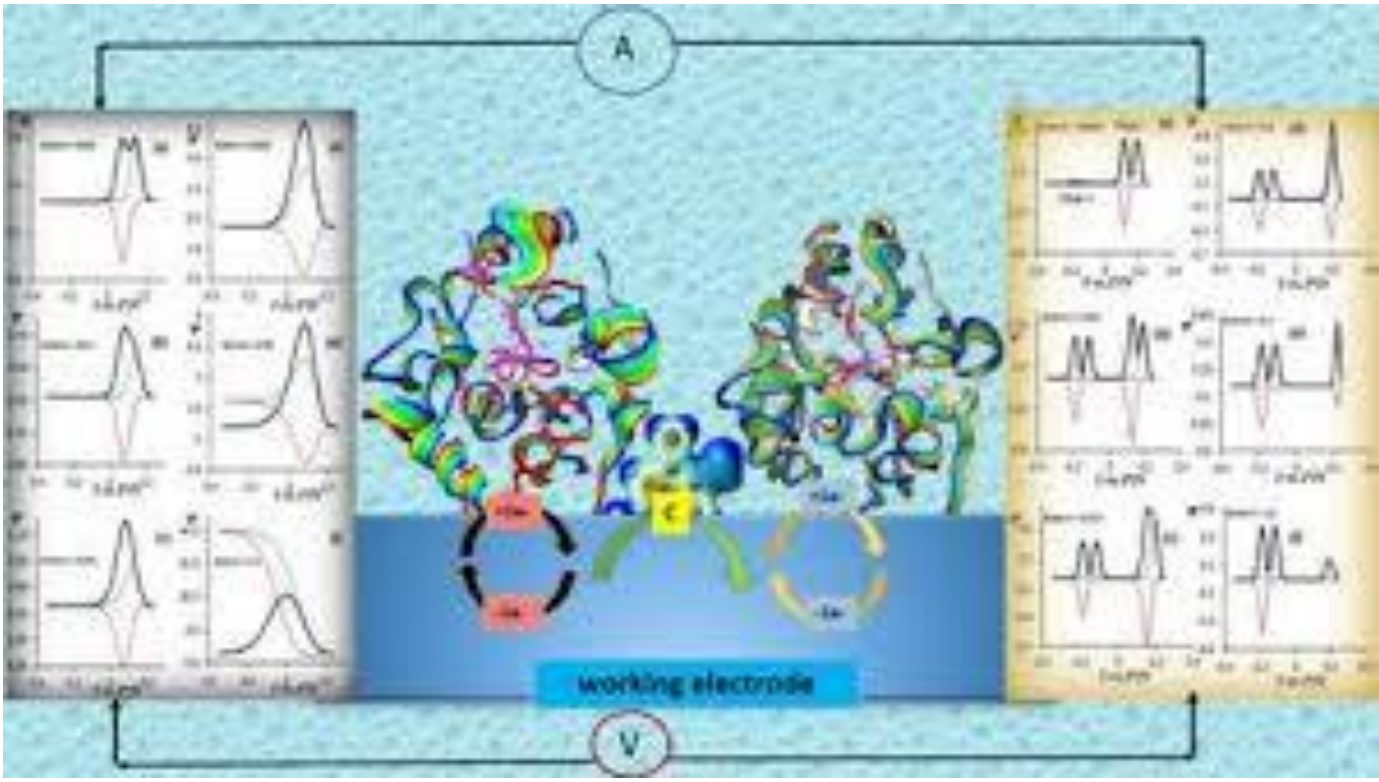
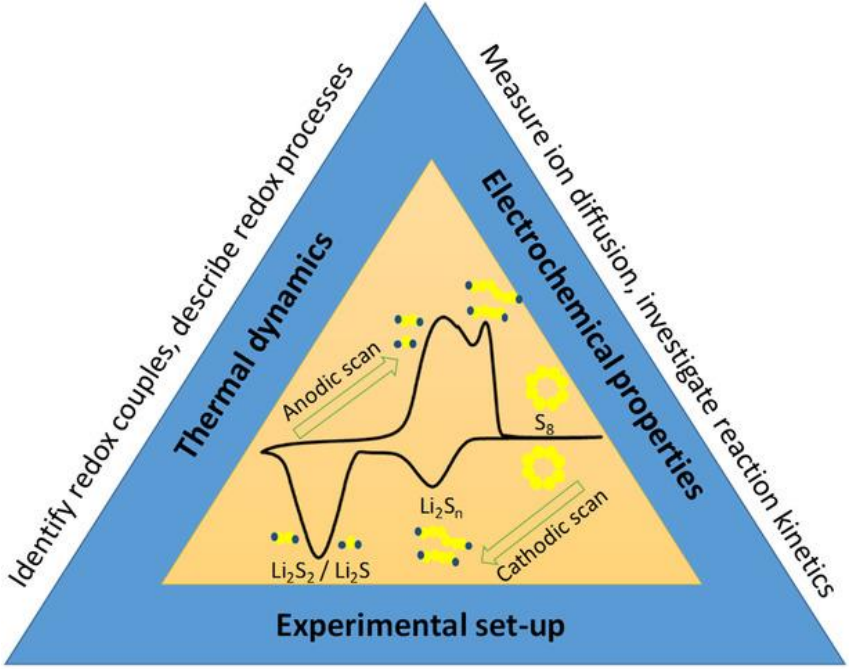




3-electrode, regular 2-electrode and special a/symmetrical cells

ECCE

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

ECEC

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

ECCE´

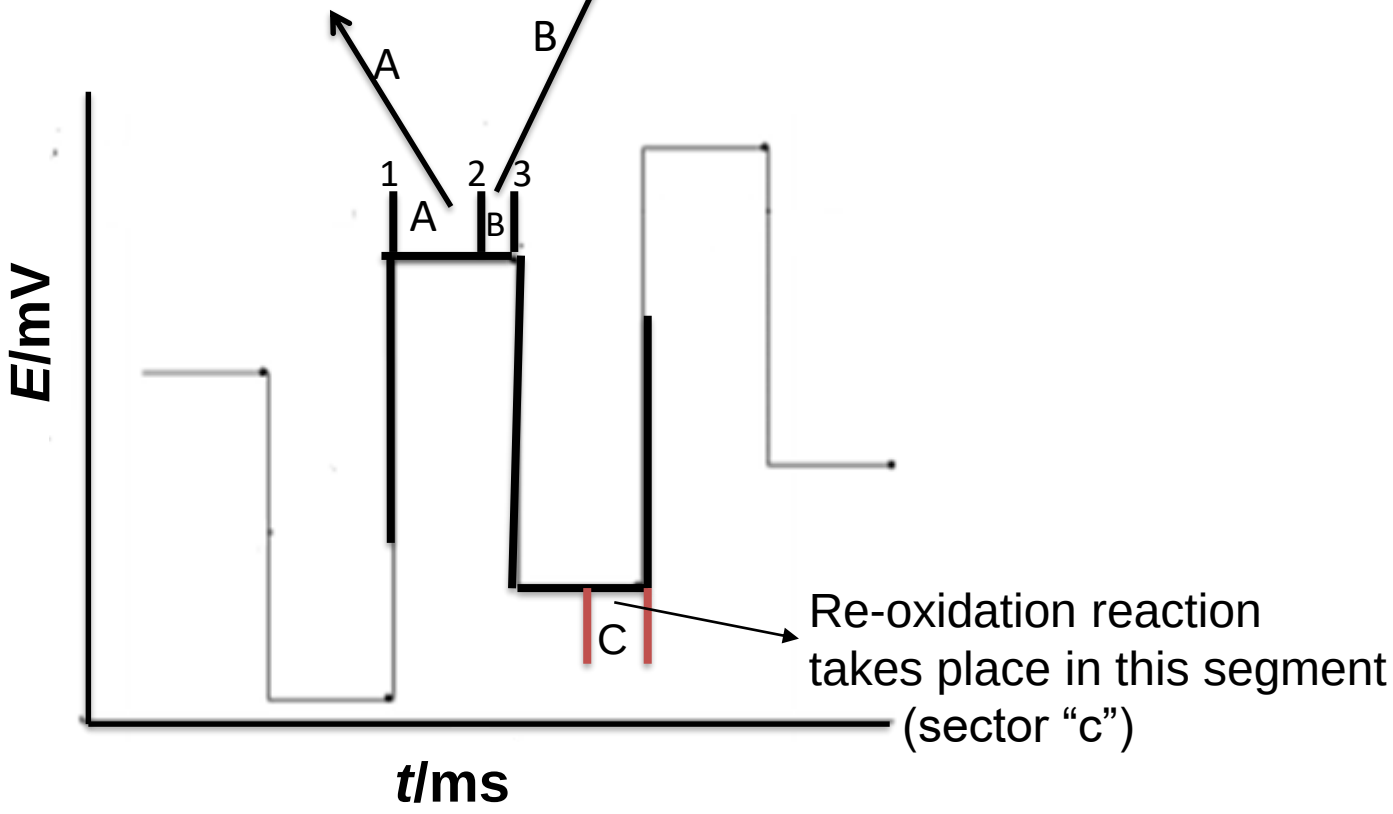
$$P + e^- \rightleftharpoons Q$$
$$Q + A \xrightarrow{k_1} B$$
$$B + Z \xrightarrow{k_2} Q''$$
$$Q'' + Q \rightleftharpoons C + 2P$$

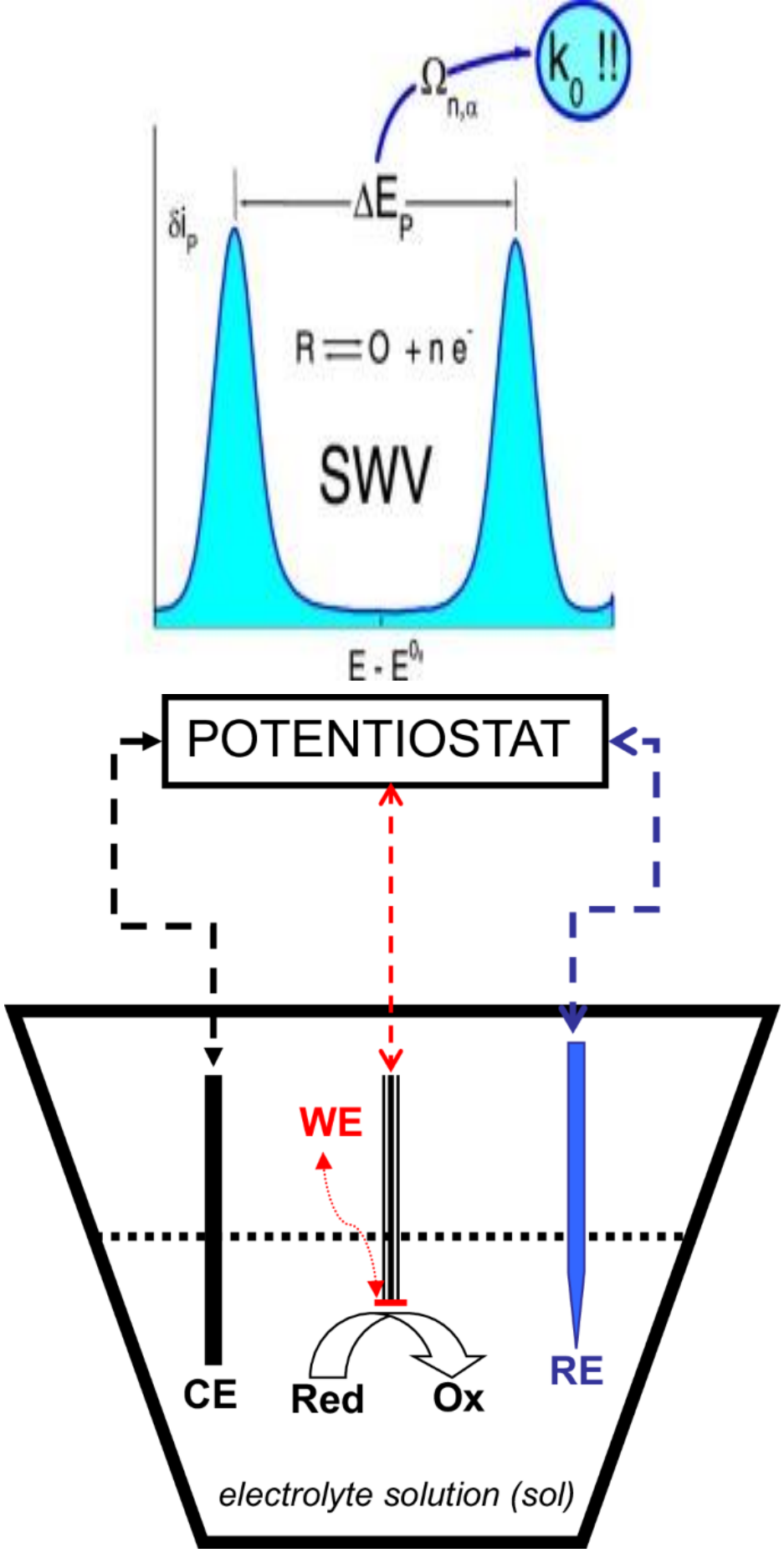
ECE´C

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

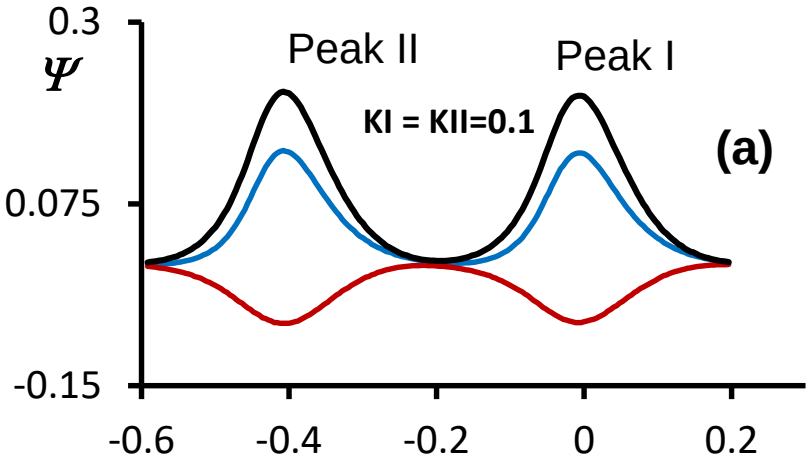
Sector „A“ is a „dead-time“
i.e. the „non-current measuring segment“). In this segment
the folowing reactions mainly occurs
Ox(ads) +ne- → Red(ads)
but gives no current measured

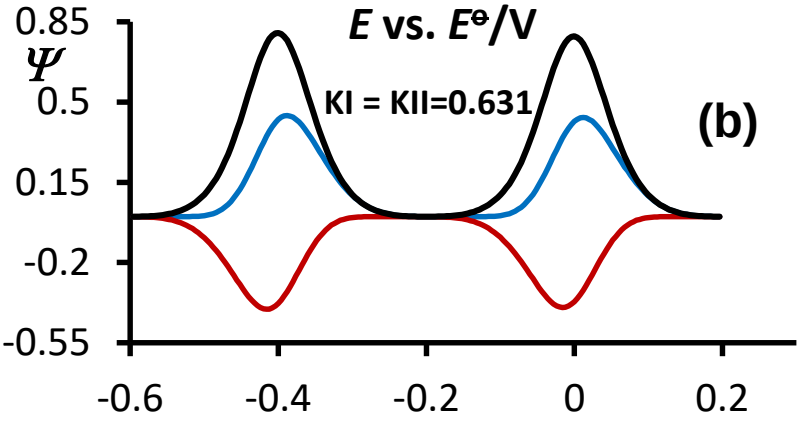
Between points „2“ and „3“ is sector „B“ i.e.
the current-measuring segment of „forward“ currents
in this segment, the current is (mainly) due to reaction
Ox(ads) +ne- → Red(ads)

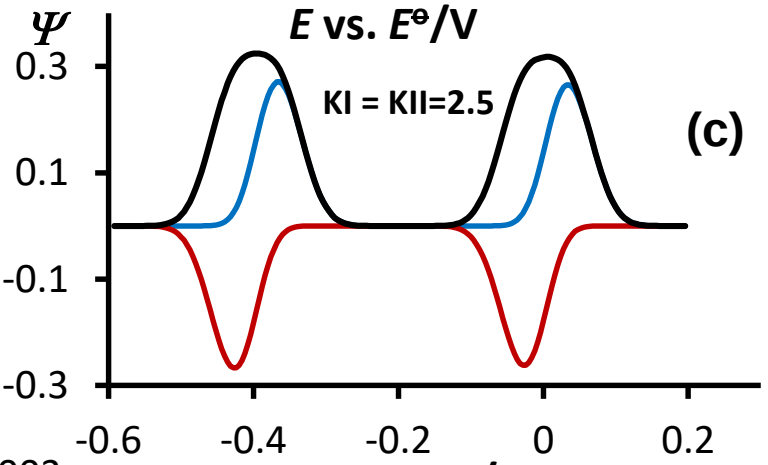


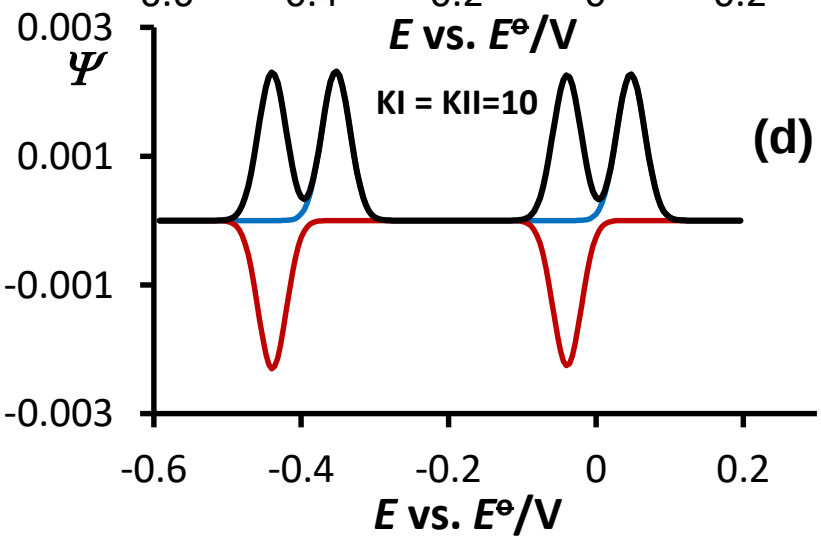

k_0 !!
$\Omega_{n,\alpha}$
ΔE_P
δi_P
R = O + n e⁻
SWV
E - $E^{0'}$
POTENTIOSTAT
WE
CE
Red
Ox
RE
electrolyte solution (sol)

Surface
EE
Mechanism

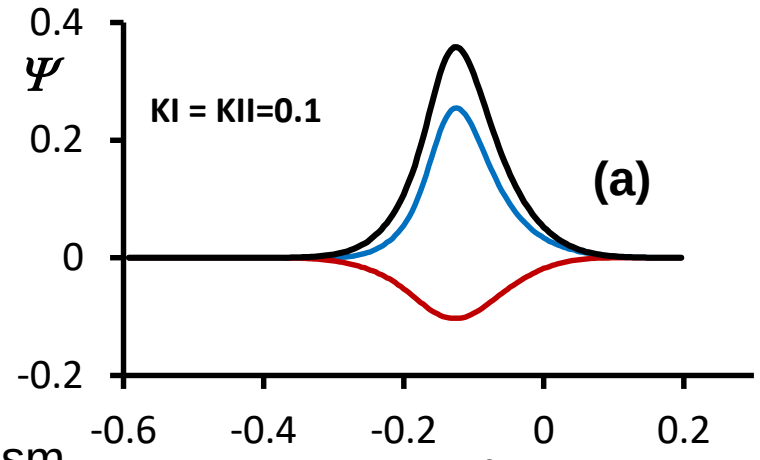


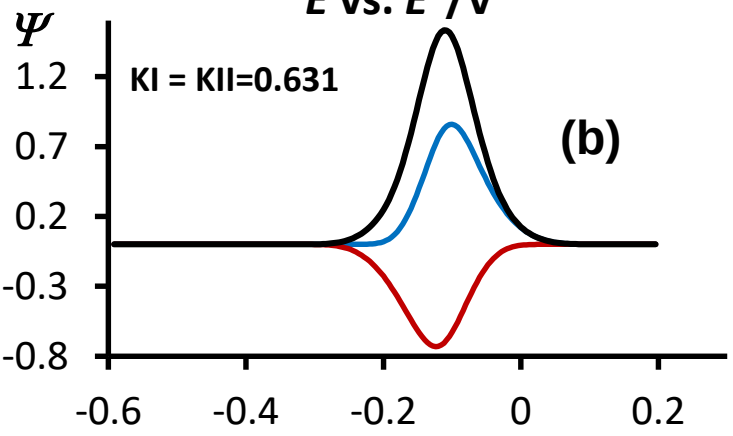


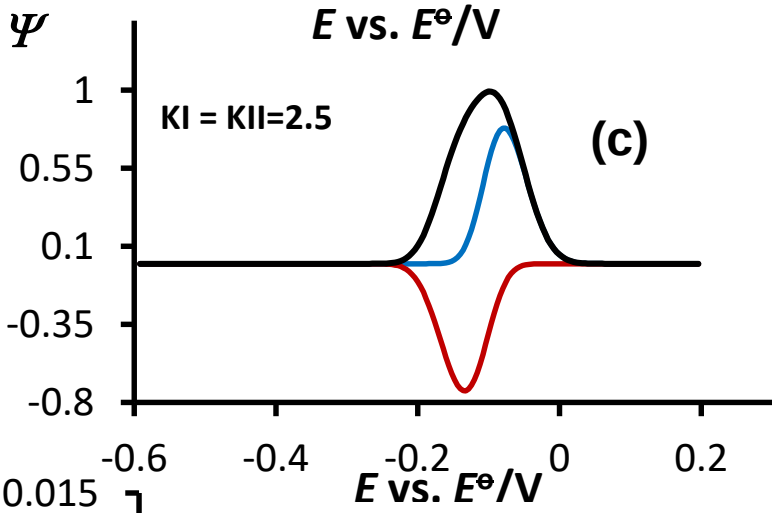


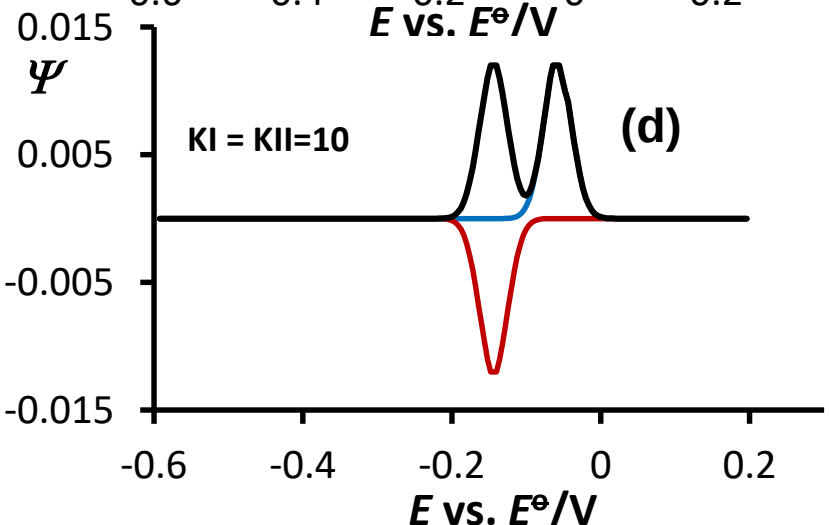


Surface EE Mechanism With both Electron Transfer Steps Occuring At Same Potential

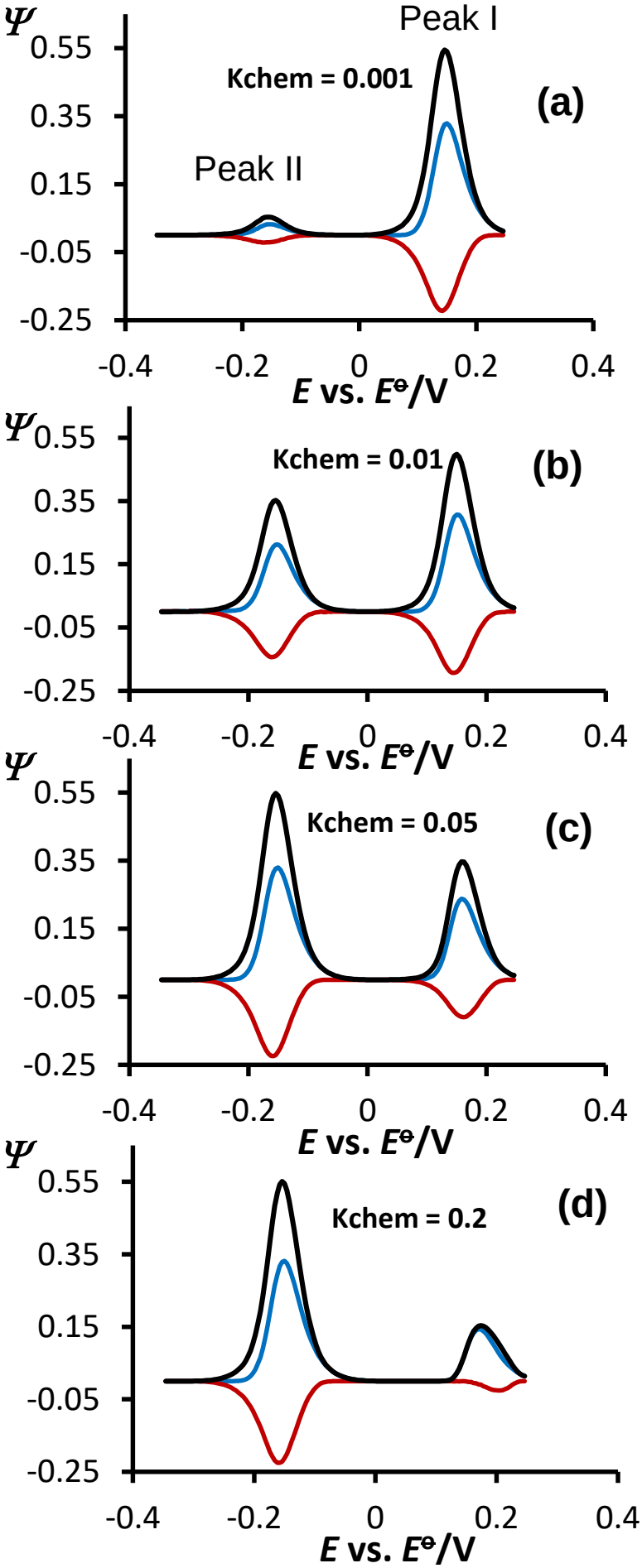


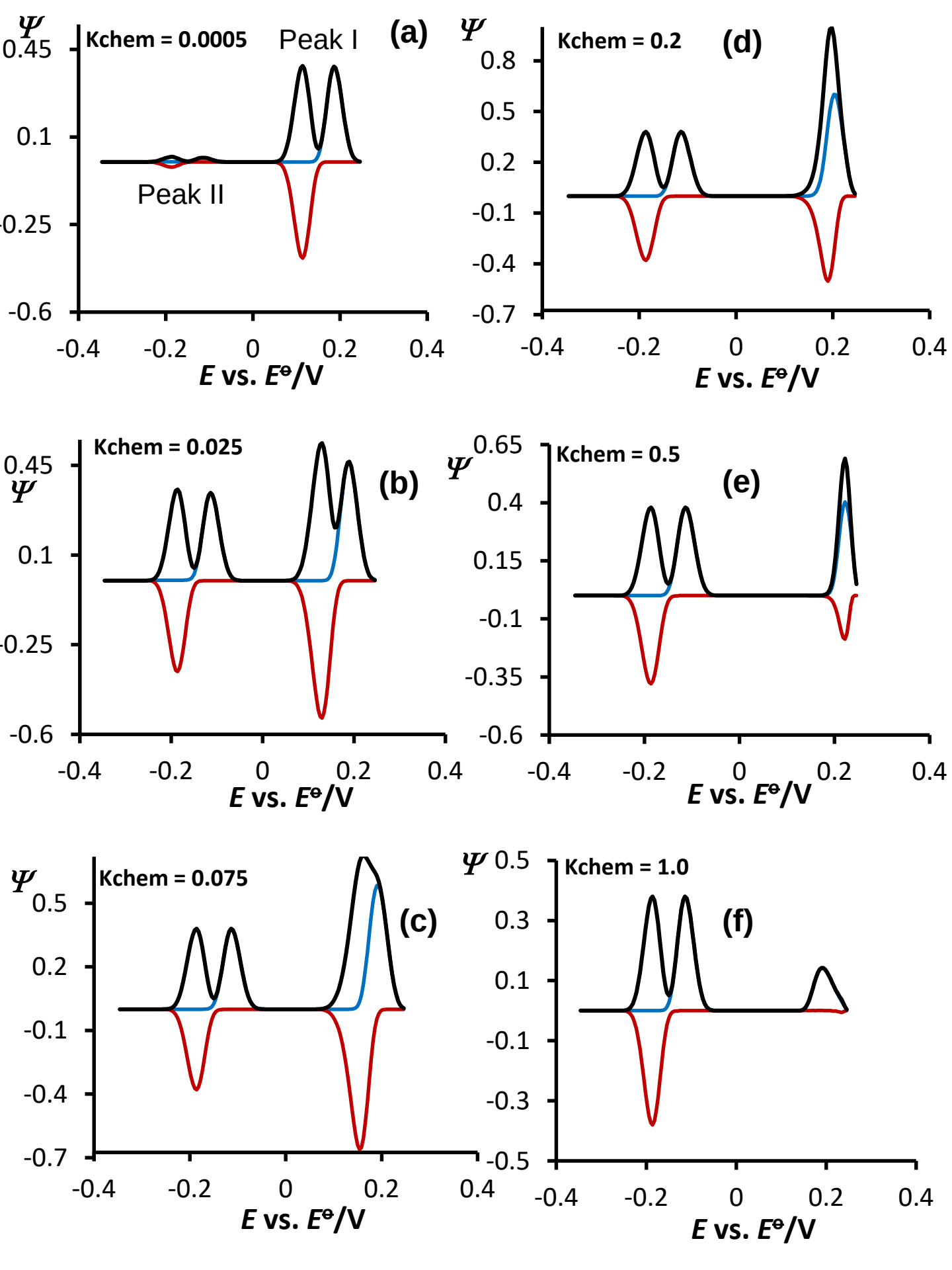


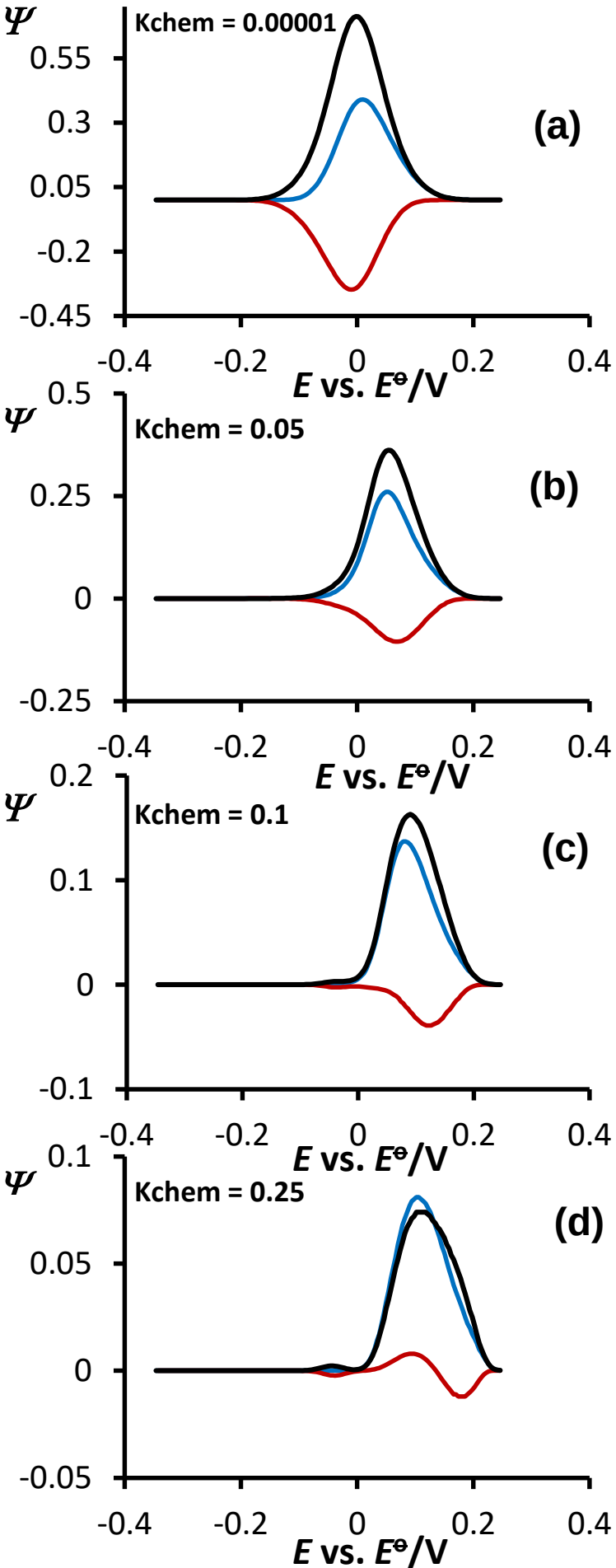


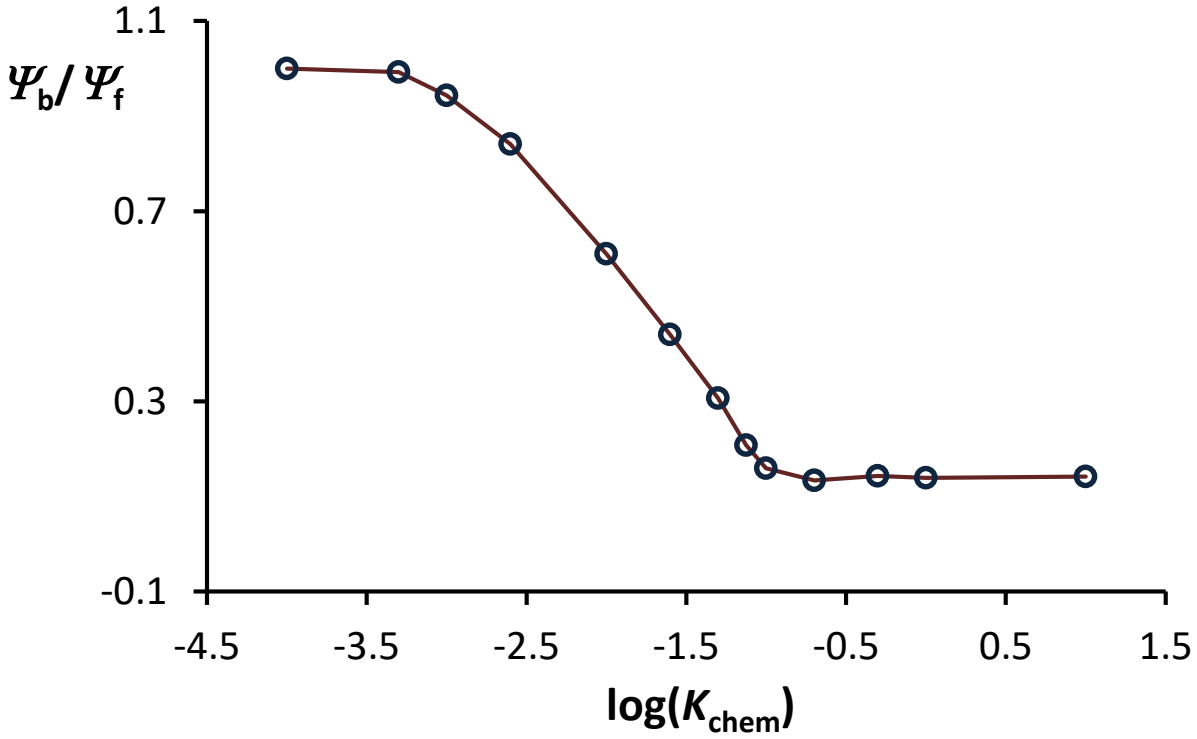


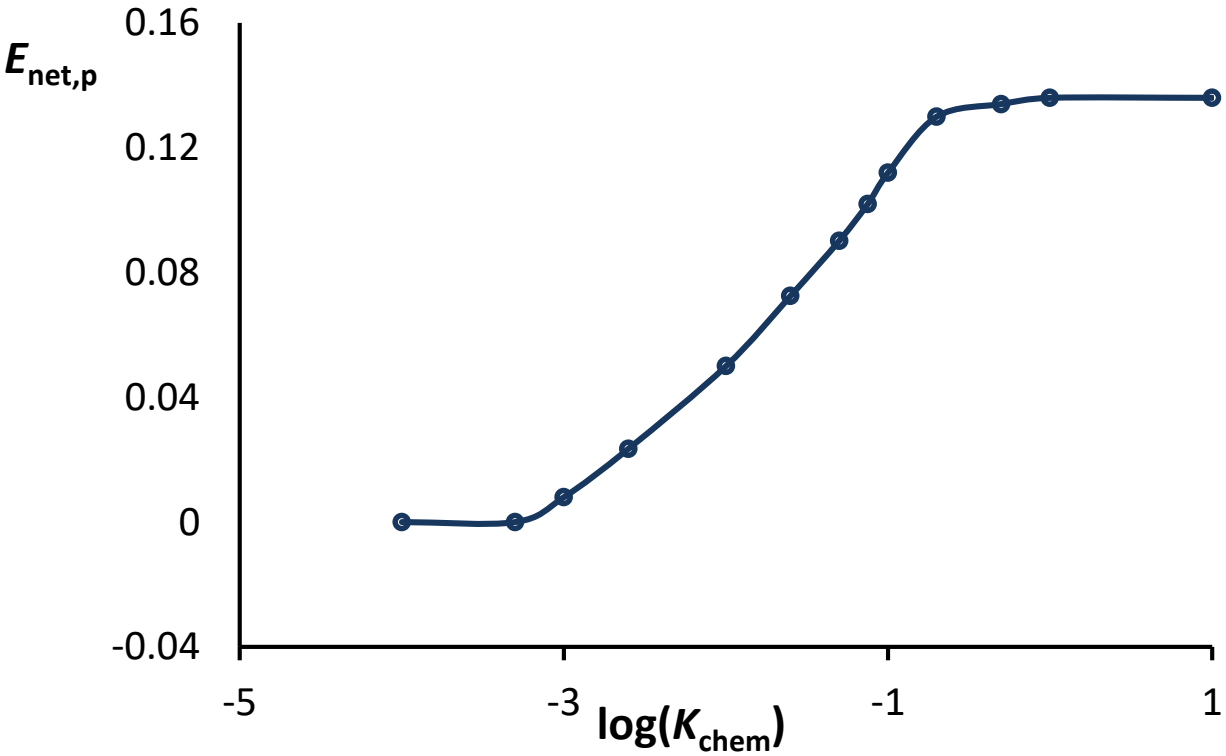
Surface ECE Mechanism With Irreversible Chemical Step Bridging Both Electron Transfer Steps

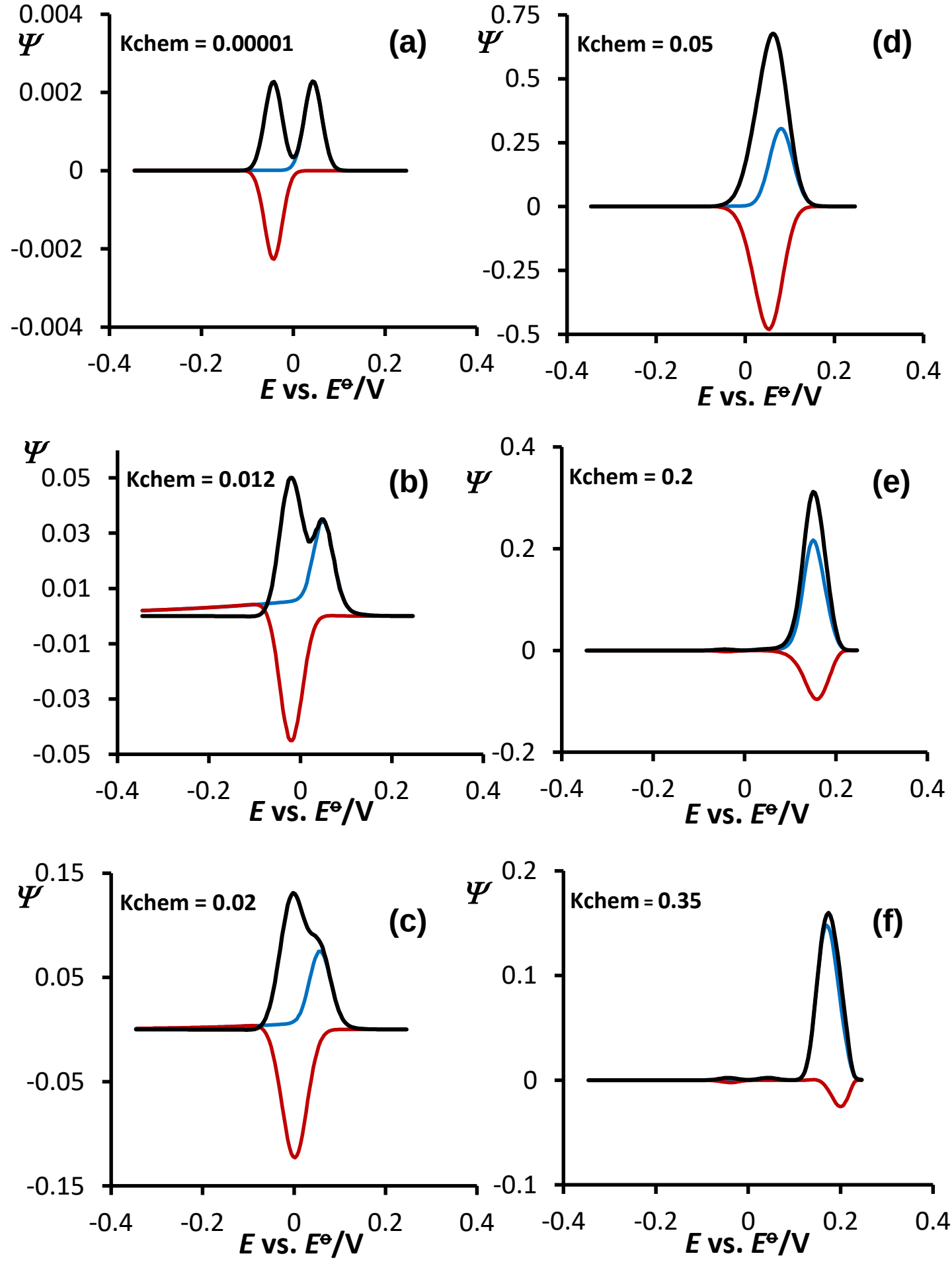



Kchem = 0.0005
Peak I
Peak II
(a)
Ψ
0.45
0.1
-0.25
-0.6
-0.4
-0.2
0
0.2
0.4
E vs. Eᵉ/V
Kchem = 0.2
(d)
0.8
0.5
0.2
-0.1
-0.4
-0.7
Kchem = 0.025
(b)
Kchem = 0.5
(e)
0.65
0.4
0.15
-0.1
-0.35
-0.6
Kchem = 0.075
(c)
Kchem = 1.0
(f)
0.5
0.3
-0.3
-0.5

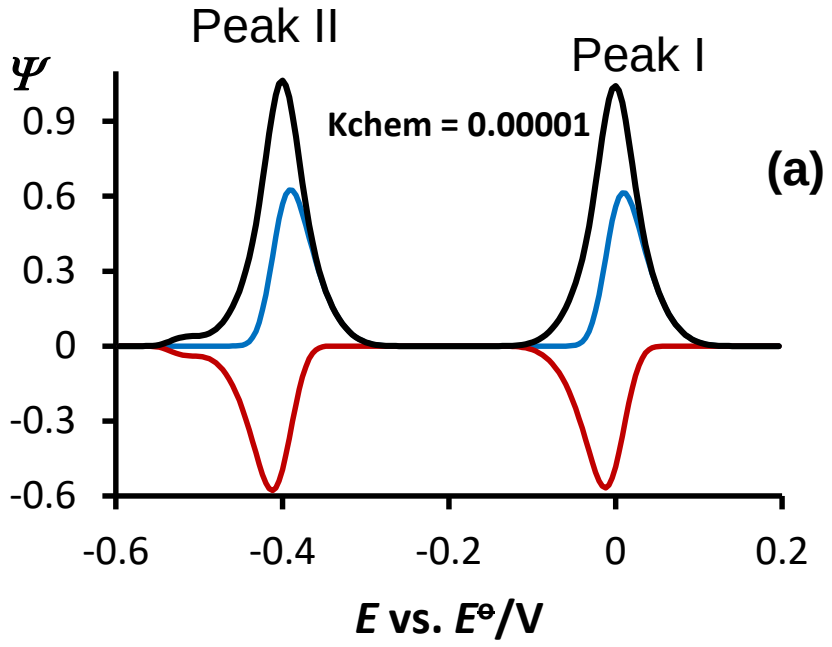

Ψ
Kchem = 0.00001
0.55
0.3
0.05
-0.2
-0.45
(a)
-0.4
-0.2
0
0.2
0.4
E vs. E⁰/V
Ψ
Kchem = 0.05
0.5
0.25
0
-0.25
(b)
-0.4
-0.2
0
0.2
0.4
E vs. E⁰/V
Ψ
Kchem = 0.1
0.2
0.1
0
-0.1
(c)
-0.4
-0.2
0
0.2
0.4
E vs. E⁰/V
Ψ
Kchem = 0.25
0.1
0.05
0
-0.05
(d)
-0.4
-0.2
0
0.2
0.4
E vs. E⁰/V

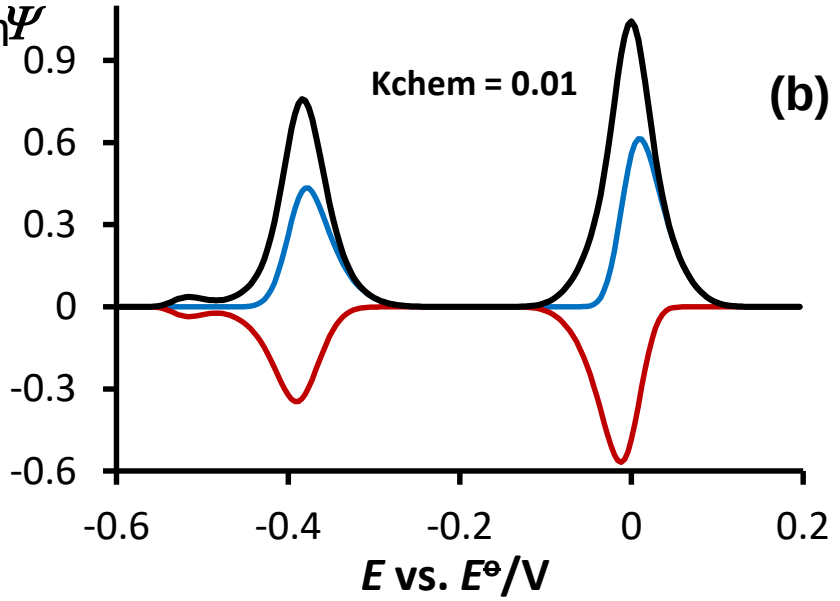

1.1
Ψ_b / Ψ_f
0.7
0.3
-0.1
-4.5
-3.5
-2.5
-1.5
-0.5
0.5
1.5
log(K_{chem})

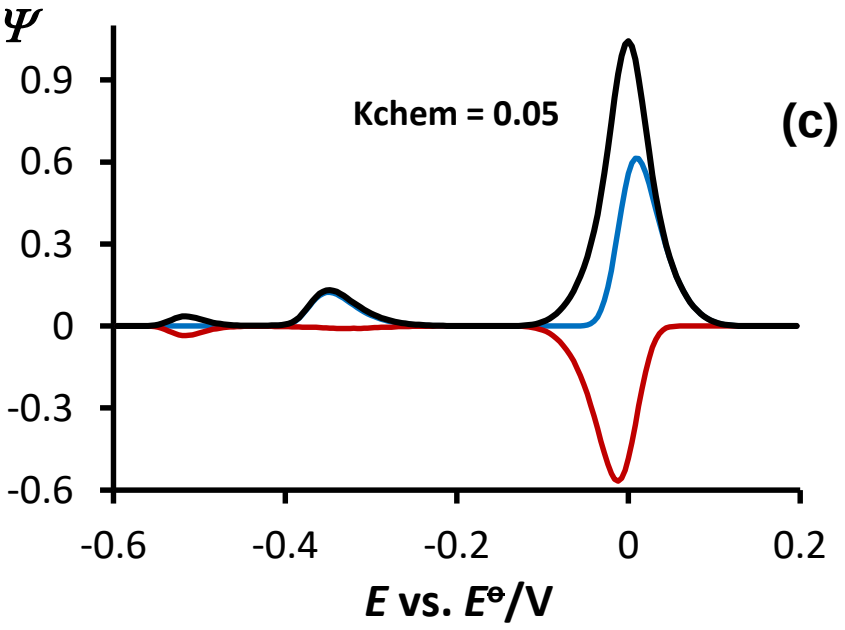

0.16
$E_{net,p}$
0.12
0.08
0.04
0
-0.04
-5
-3
-1
1
log(K_{chem})

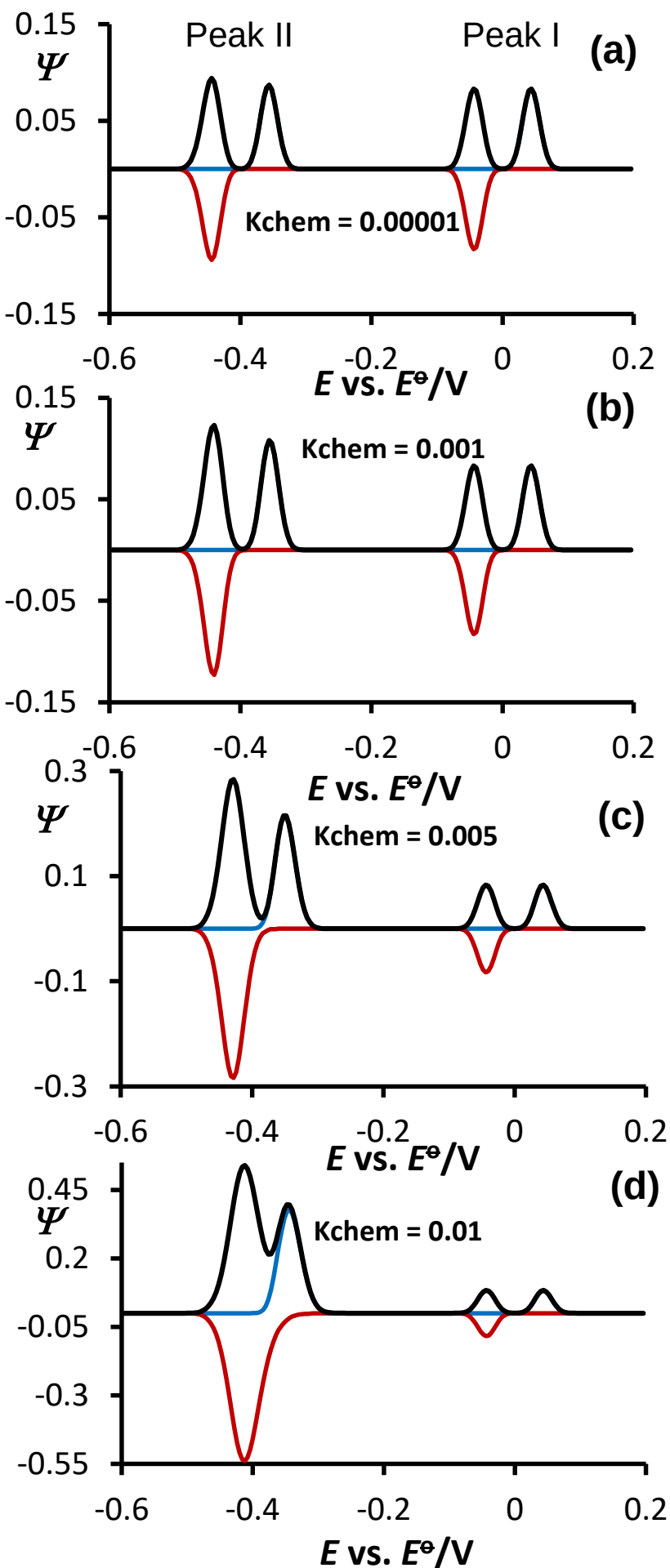

Ψ
Kchem = 0.00001
(a)
0.004
0.002
0
-0.002
-0.004
-0.4
-0.2
0
0.2
0.4
E vs. E⁰/V
Ψ
Kchem = 0.05
(d)
0.75
0.5
0.25
0
-0.25
-0.5
-0.4
-0.2
0
0.2
0.4
E vs. E⁰/V
Ψ
Kchem = 0.012
(b)
0.05
0.03
0.01
-0.01
-0.03
-0.05
-0.4
-0.2
0
0.2
0.4
E vs. E⁰/V
Ψ
Kchem = 0.2
(e)
0.4
0.2
0
-0.2
-0.4
-0.2
0
0.2
0.4
E vs. E⁰/V
Ψ
Kchem = 0.02
(c)
0.15
0.05
-0.05
-0.15
-0.4
-0.2
0
0.2
0.4
E vs. E⁰/V
Ψ
Kchem = 0.35
(f)
0.2
0.1
0
-0.1
-0.4
-0.2
0
0.2
0.4
E vs. E⁰/V

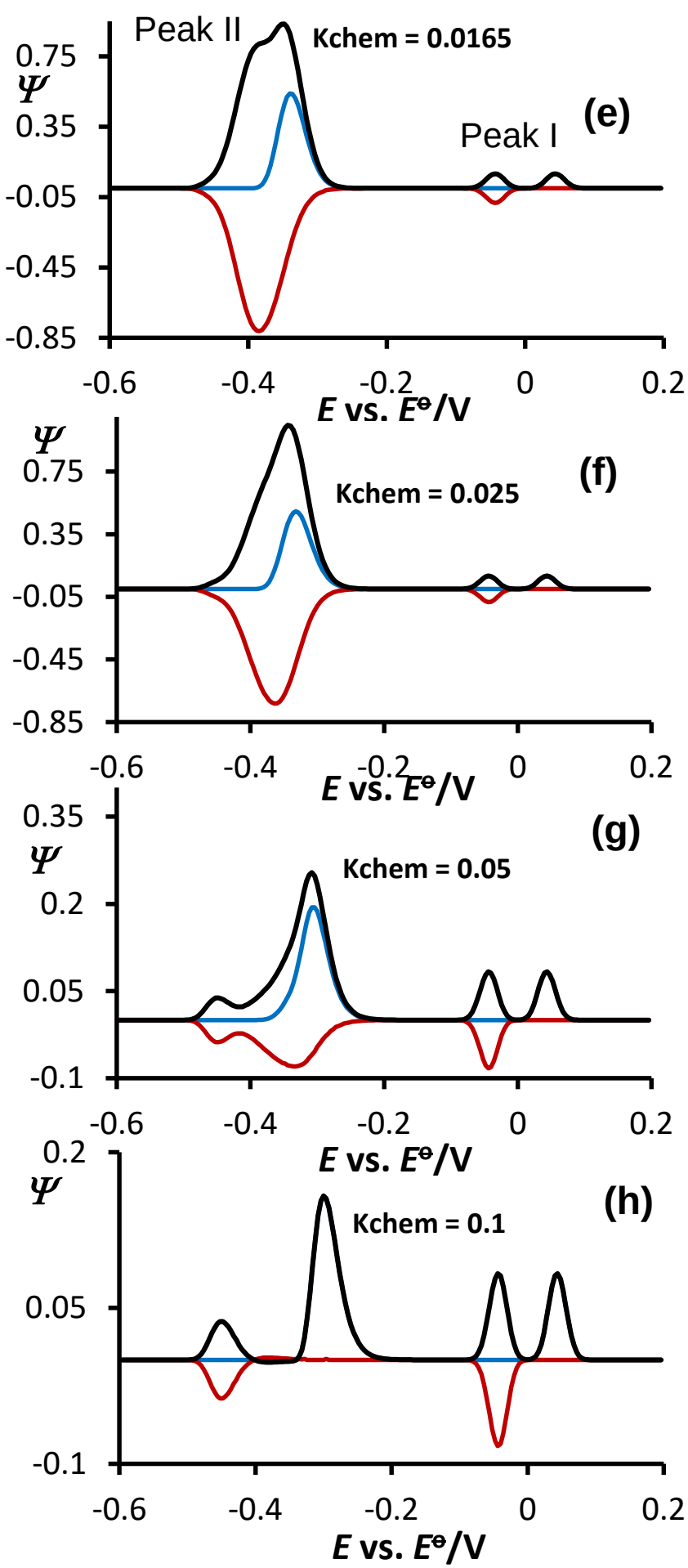
Surface EECrev mechanism

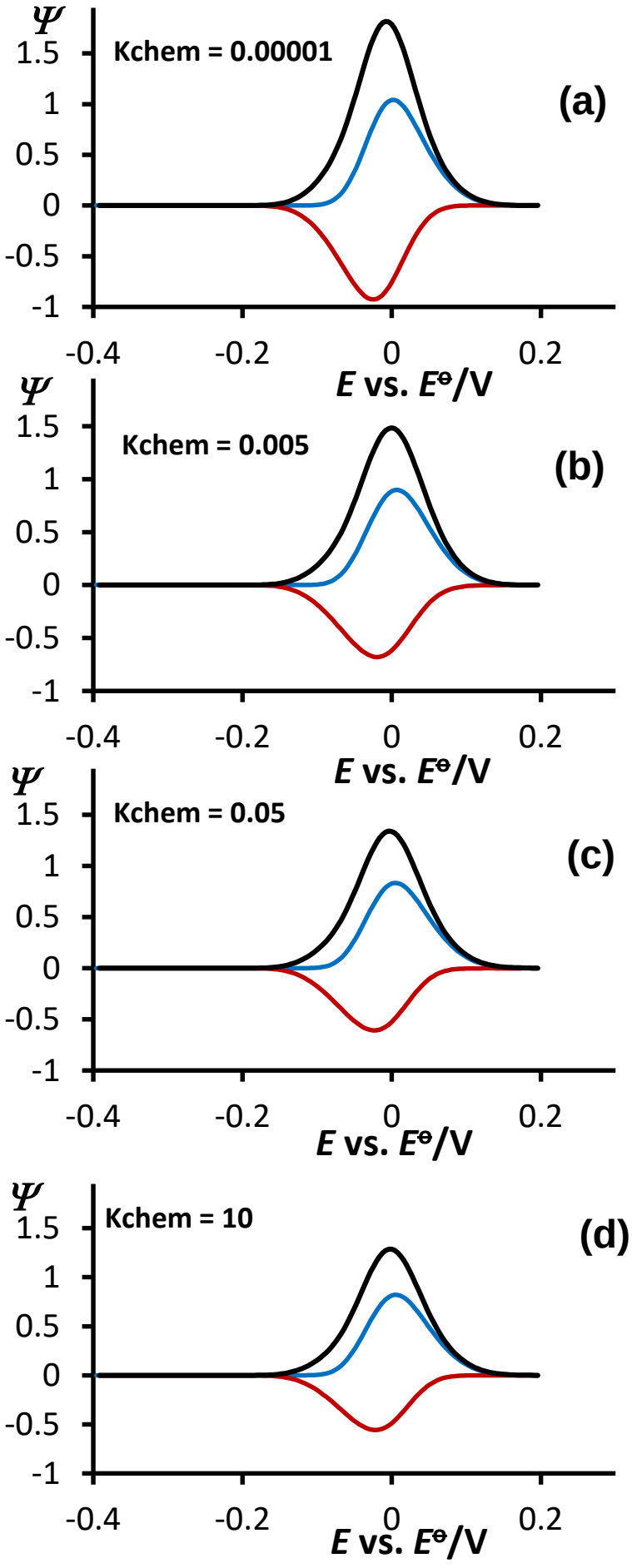


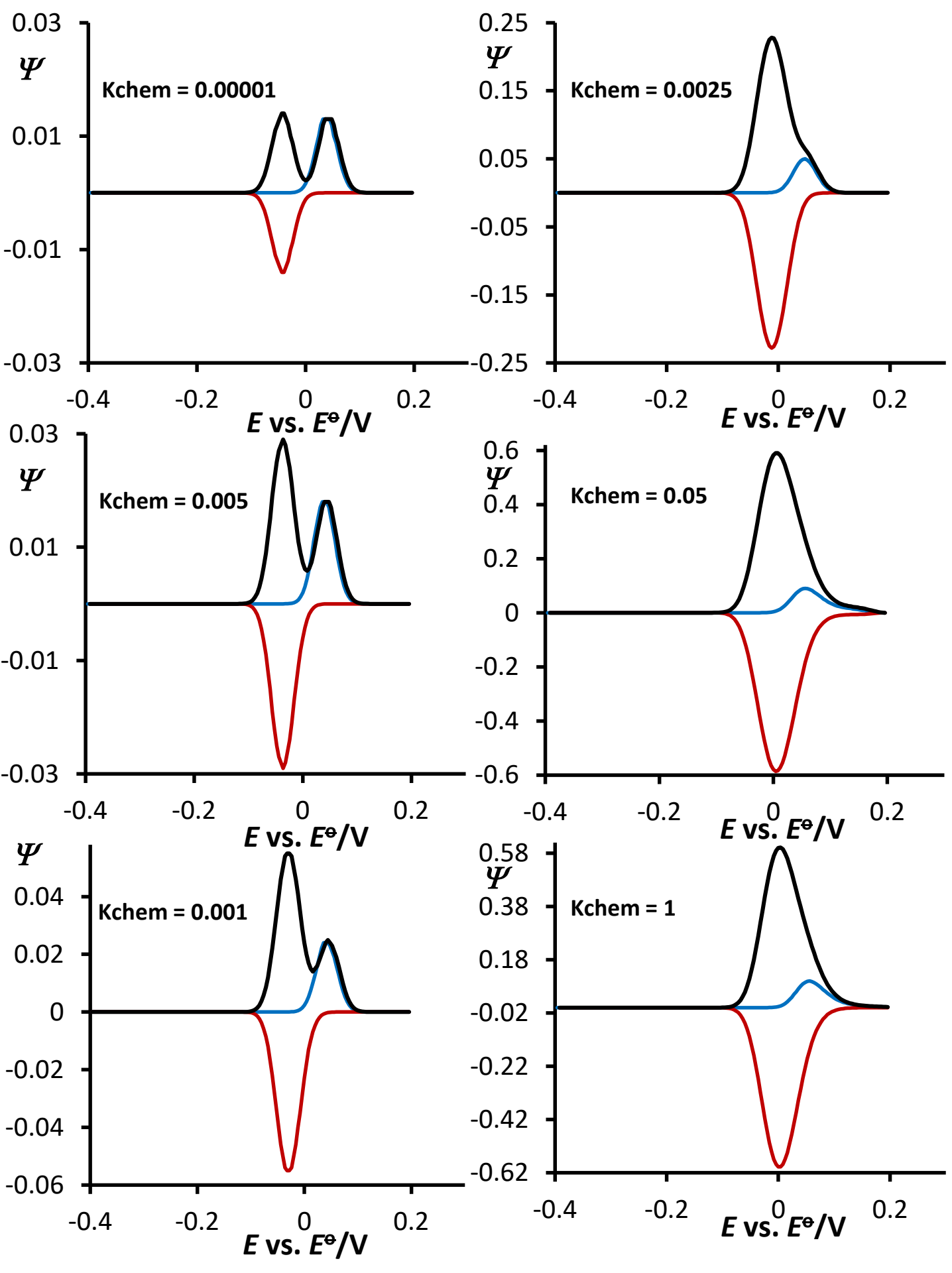




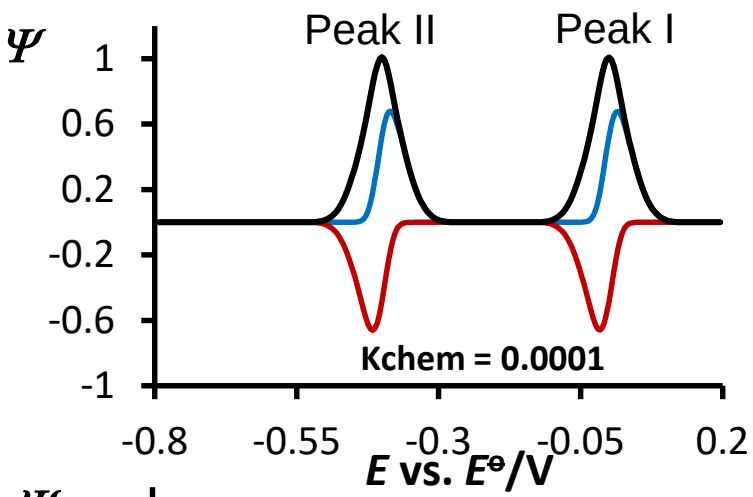

Peak II
Peak I
(a)
Ψ
0.15
0.05
-0.05
-0.15
Kchem = 0.00001
-0.6
-0.4
-0.2
0
0.2
E vs. E⁰/V
(b)
Kchem = 0.001
(c)
0.3
0.1
-0.1
-0.3
Kchem = 0.005
(d)
0.45
0.2
-0.05
-0.3
-0.55
Kchem = 0.01

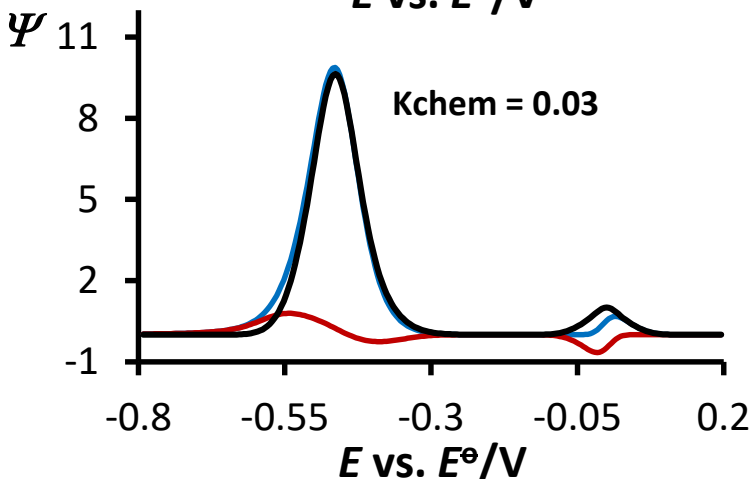

Peak II
Kchem = 0.0165
Peak I
(e)
0.75
Ψ
0.35
-0.05
-0.45
-0.85
-0.6
-0.4
-0.2
0
0.2
E vs. E⁰/V
Ψ
(f)
Kchem = 0.025
0.75
0.35
-0.05
-0.45
-0.85
-0.6
-0.4
-0.2
0
0.2
E vs. E⁰/V
0.35
Ψ
(g)
Kchem = 0.05
0.2
0.05
-0.1
-0.6
-0.4
-0.2
0
0.2
E vs. E⁰/V
0.2
Ψ
(h)
Kchem = 0.1
0.05
-0.1
-0.6
-0.4
-0.2
0
0.2
E vs. E⁰/V

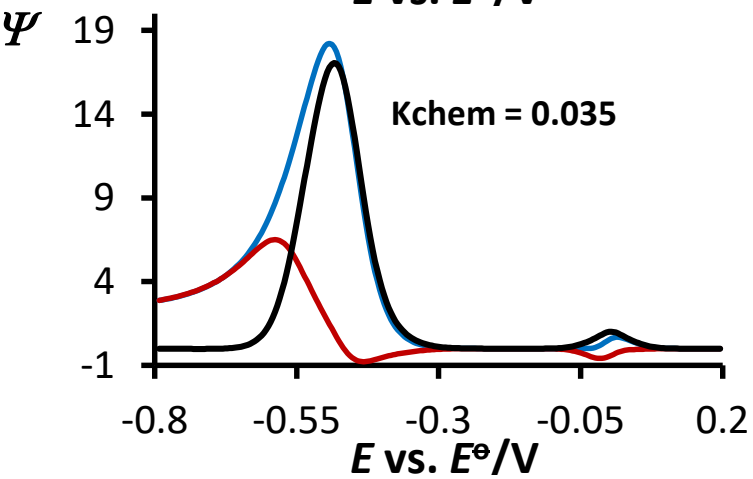

Ψ
Kchem = 0.00001
(a)
1.5
1
0.5
0
-0.5
-1
-0.4
-0.2
0
0.2
E vs. E⊖/V
Ψ
Kchem = 0.005
(b)
E vs. E⊖/V
Ψ
Kchem = 0.05
(c)
E vs. E⊖/V
Ψ
Kchem = 10
(d)
E vs. E⊖/V

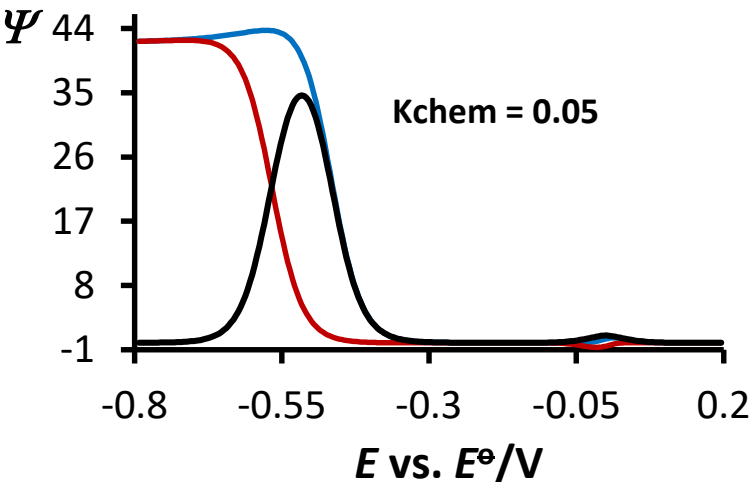

Kchem = 0.00001
Ψ
0.03
0.01
-0.01
-0.03
-0.4
-0.2
0
0.2
E vs. E⁰/V
Kchem = 0.0025
Ψ
0.25
0.15
0.05
-0.05
-0.15
-0.25
-0.4
-0.2
0
0.2
E vs. E⁰/V
Kchem = 0.005
Ψ
0.03
0.01
-0.01
-0.03
-0.4
-0.2
0
0.2
E vs. E⁰/V
Kchem = 0.05
Ψ
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.4
-0.2
0
0.2
E vs. E⁰/V
Kchem = 0.001
Ψ
0.04
0.02
0
-0.02
-0.04
-0.06
-0.4
-0.2
0
0.2
E vs. E⁰/V
Kchem = 1
Ψ
0.58
0.38
0.18
-0.02
-0.22
-0.42
-0.62
-0.4
-0.2
0
0.2
E vs. E⁰/V

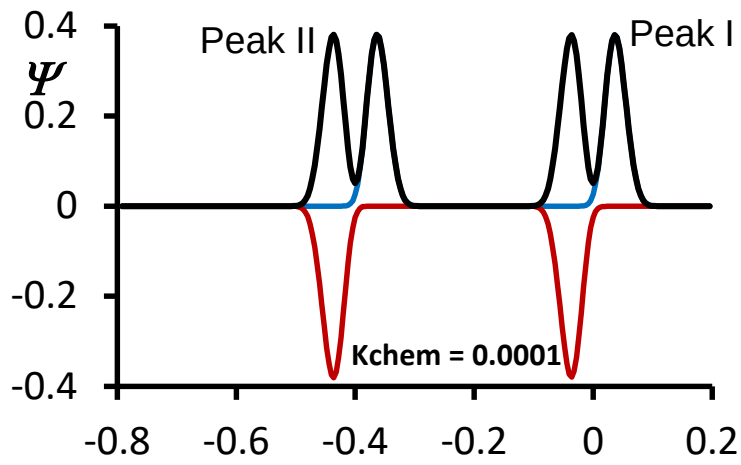
Surface EECatalytic mechanism

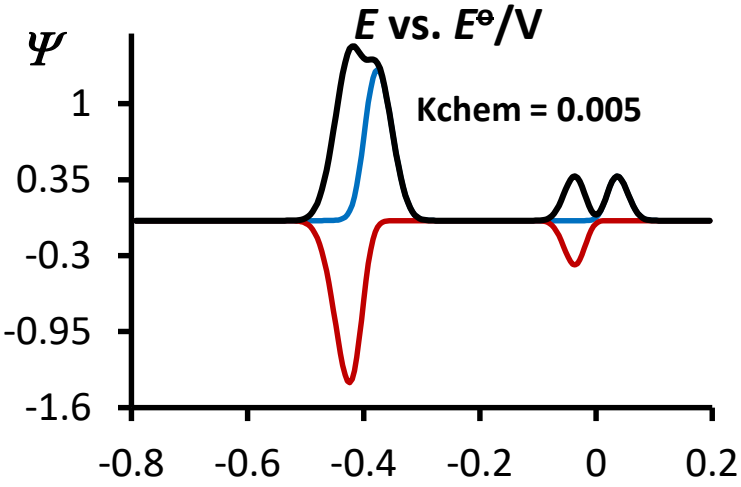


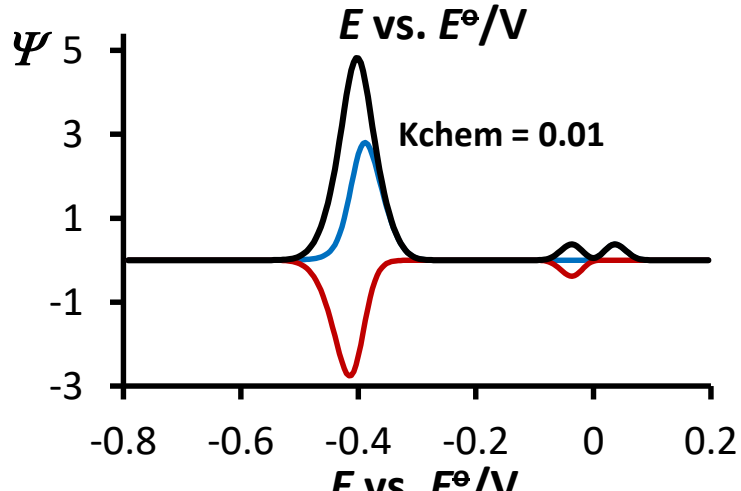


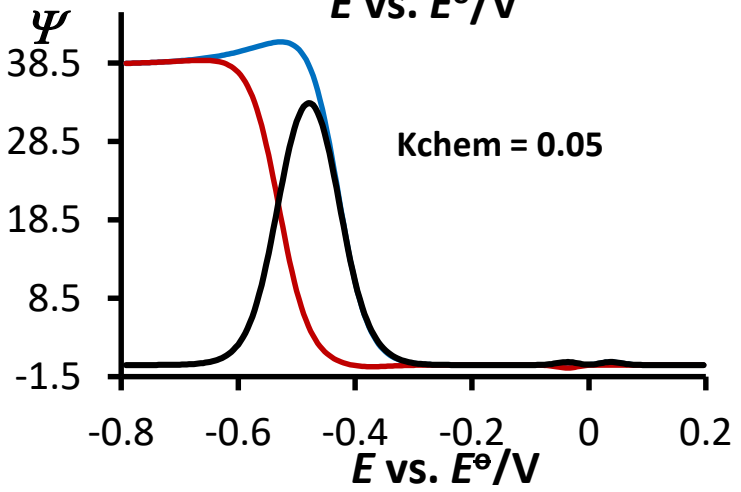


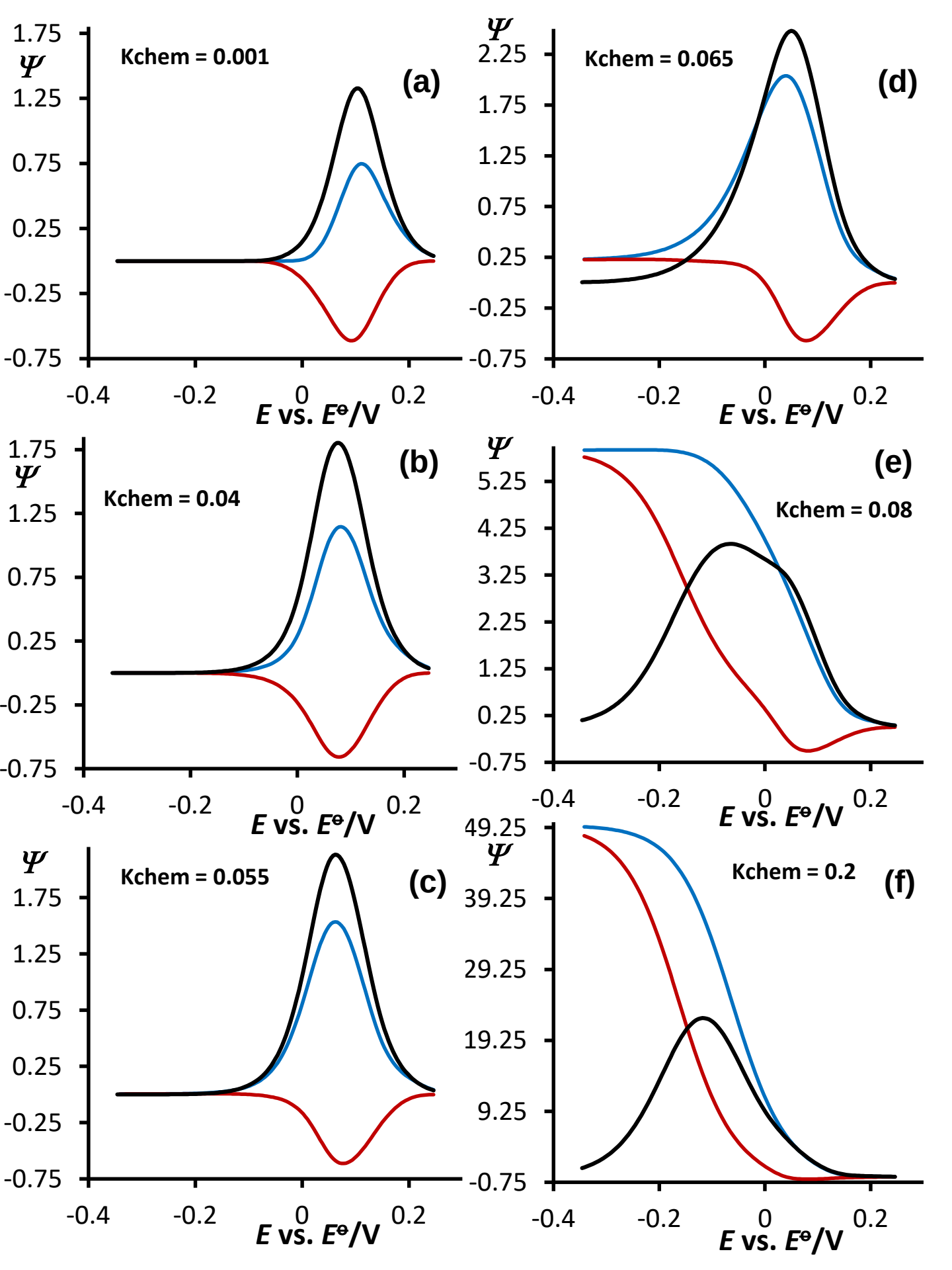


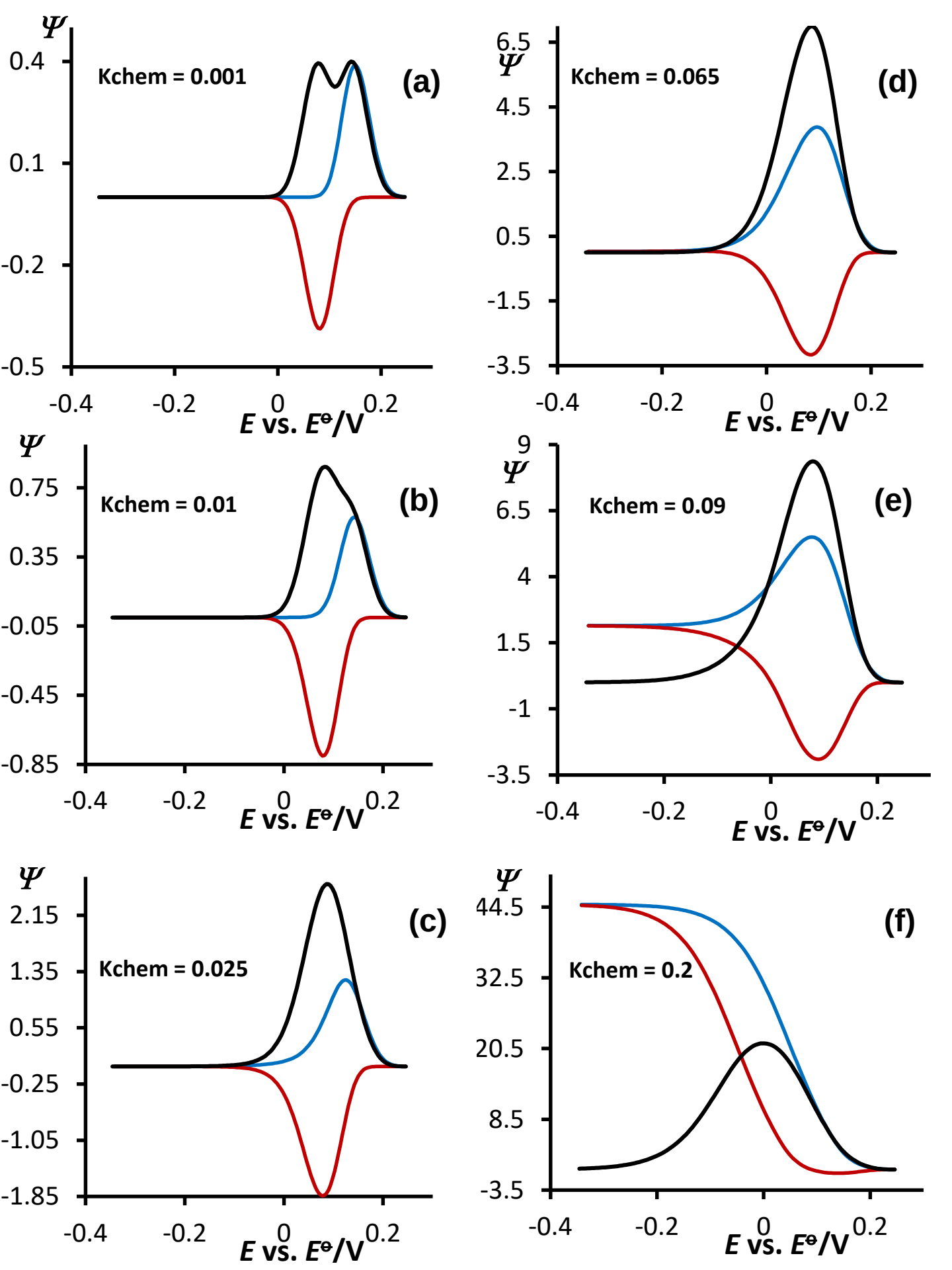

Peak II
Peak I
Ψ
0.4
0.2
0
-0.2
-0.4
Kchem = 0.0001
-0.8
-0.6
-0.4
-0.2
0
0.2
E vs. E⁰/V


Ψ
1
0.35
-0.3
-0.95
-1.6
Kchem = 0.005
-0.8
-0.6
-0.4
-0.2
0
0.2
E vs. E⁰/V


Ψ
5
3
1
-1
-3
Kchem = 0.01
-0.8
-0.6
-0.4
-0.2
0
0.2
E vs. E⁰/V


Ψ
38.5
28.5
18.5
8.5
-1.5
Kchem = 0.05
-0.8
-0.6
-0.4
-0.2
0
0.2
E vs. E⁰/V


Kchem = 0.001
(a)
Kchem = 0.065
(d)
Kchem = 0.04
(b)
Kchem = 0.08
(e)
Kchem = 0.055
(c)
Kchem = 0.2
(f)
Ψ
E vs. E⁰/V
1.75
1.25
0.75
0.25
-0.25
-0.75
2.25
5.25
4.25
3.25
49.25
39.25
29.25
19.25
9.25
-0.4
-0.2
0
0.2


Ψ
0.4
0.1
-0.2
-0.5
Kchem = 0.001
(a)
-0.4
-0.2
0
0.2
E vs. E⁰/V
Ψ
0.75
0.35
-0.05
-0.45
-0.85
Kchem = 0.01
(b)
-0.4
-0.2
0
0.2
E vs. E⁰/V
Ψ
2.15
1.35
0.55
-0.25
-1.05
-1.85
Kchem = 0.025
(c)
-0.4
-0.2
0
0.2
E vs. E⁰/V
Ψ
6.5
4.5
2.5
0.5
-1.5
-3.5
Kchem = 0.065
(d)
-0.4
-0.2
0
0.2
E vs. E⁰/V
Ψ
9
6.5
4
1.5
-1
-3.5
Kchem = 0.09
(e)
-0.4
-0.2
0
0.2
E vs. E⁰/V
Ψ
44.5
32.5
20.5
8.5
-3.5
Kchem = 0.2
(f)
-0.4
-0.2
0
0.2
E vs. E⁰/V

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