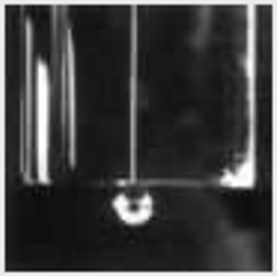
[redacted]

- Tehnika pri kateri spreminjamo napetost $E = f(t)$ in merimo tok i, ki teče skozi indikatorsko mikroelektrodo (Hg, Pt, Au, C,..);
- Iz tokovno napetostne i-E krivulje dobimo informacijo o vrsti analita (E^0, $E_{1/2}$), limitni tok i_1 pa nam da informacijo o koncentraciji:
    - $i_1 = f(z, D, A, m_{Hg}, t, \Delta E, c, ..) = kC$;
- Voltametrija je relativna tehnika – koncentracijo izmerimo na osnovi umerjanja.
- Polarografija je voltametrična tehnika, pri kateri uporabimo Hg kapalno indikatorsko elektrodo (DME).



Nobelova nagrada za kemijo 1959

JAROSLAV HEYROVSKÝ

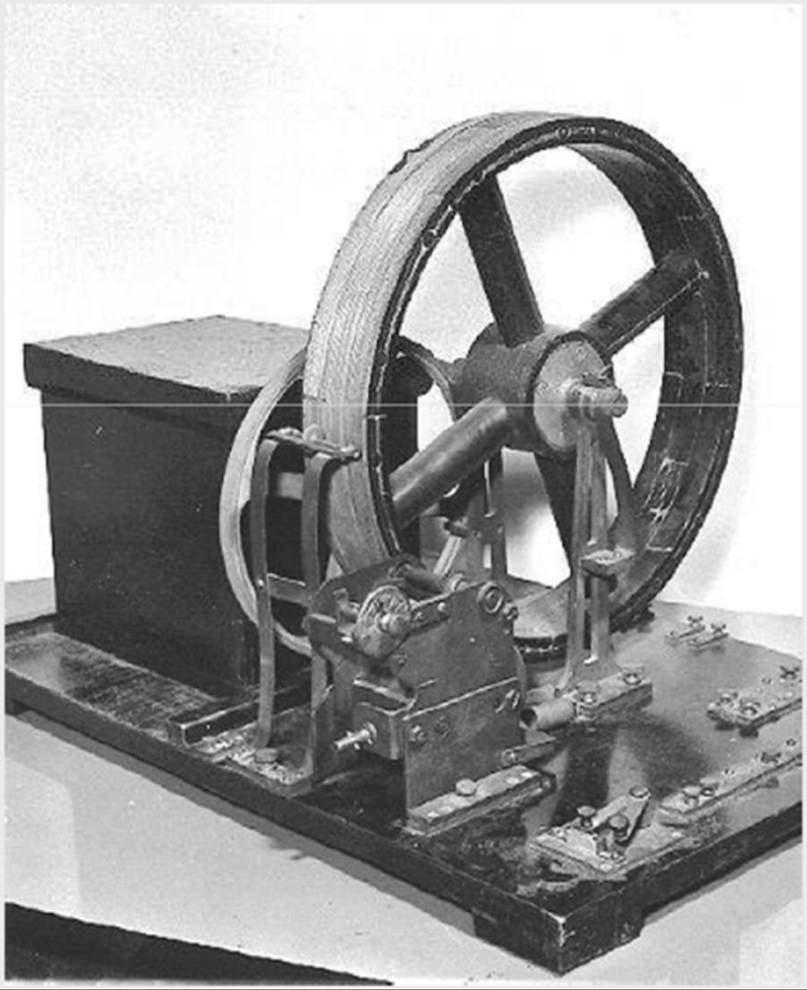
The trends of polarography

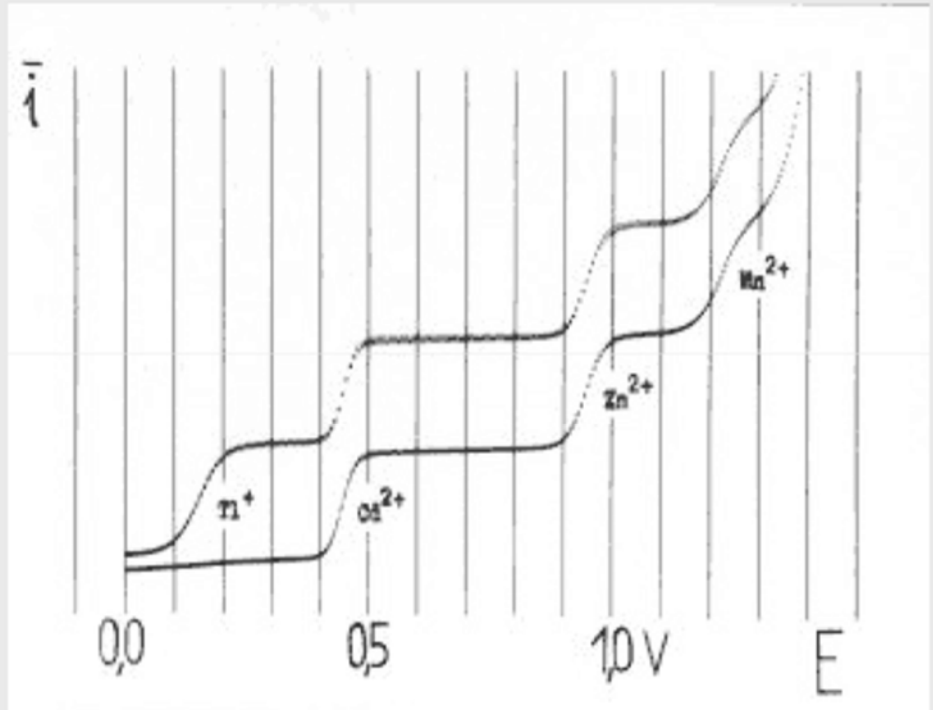
Nobel Lecture, December 11, 1959

The reason why I keep some 38 years to the electrochemical researches with the dropping mercury electrode is its exquisite property as electrode material. Its physical conditions of dropping as well as the chemical changes during the passage of the electric current are well defined, and the phenomena displayed at the dropping mercury electrode proceed with strict reproducibility. Owing to the latter property the processes at the electrode can be exactly expressed mathematically. According to the registering apparatus called "polarograph", which draws automatically curves characteristic of the electrode processes, the electrochemical studies with the dropping mercury electrode and the analytical methods developed on these investigations have been called "polarography".

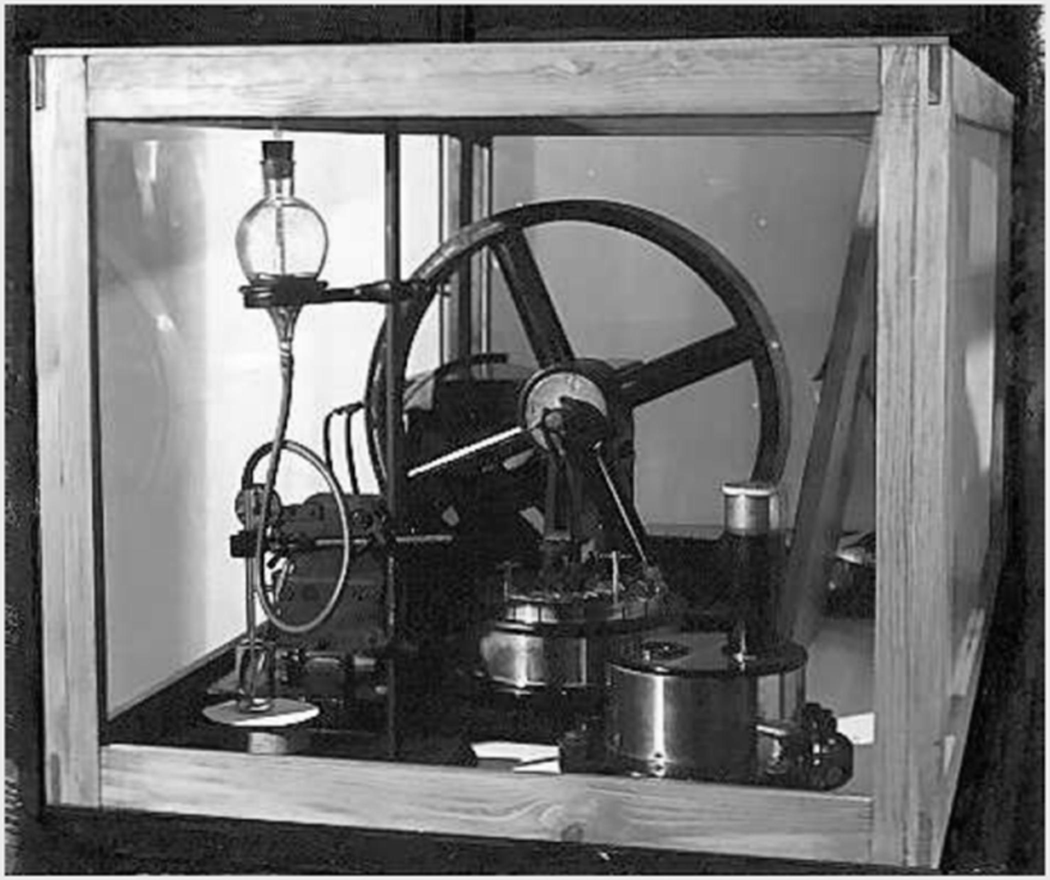
The capillary electrode is normally a 8 cm long, 5-6 mm thick tube with the inner bore of 0.05 to 0.1 mm, from which the drops of mercury fall off every 3 to 6 seconds according to the height of the mercury reservoir which is about 40 cm above the tip of the capillary (Fig. 1).

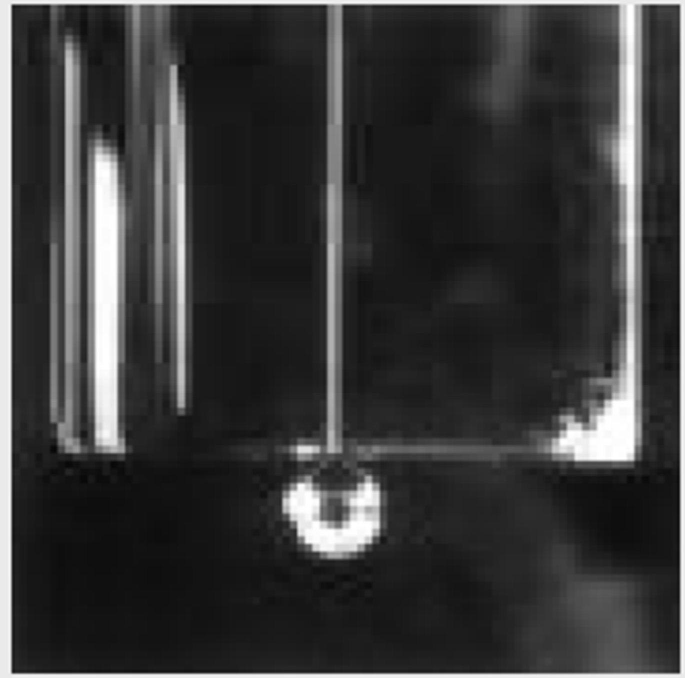
In order that the current passing through this electrode be entirely given by the composition of the solution surrounding it, the second electrode has





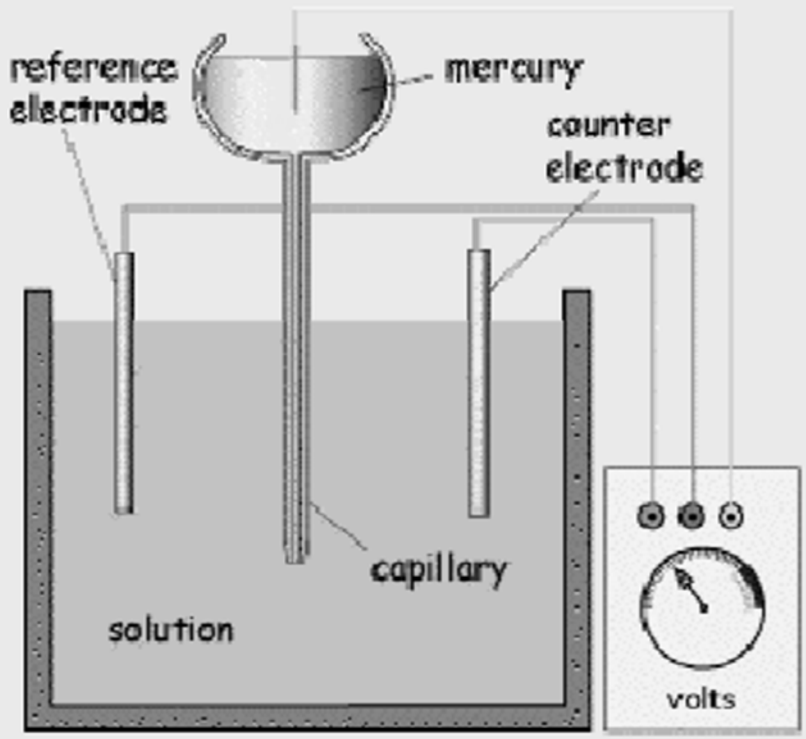
i
Tl+
Cd2+
Zn2+
Mn2+
0,0
0,5
1,0 V
E

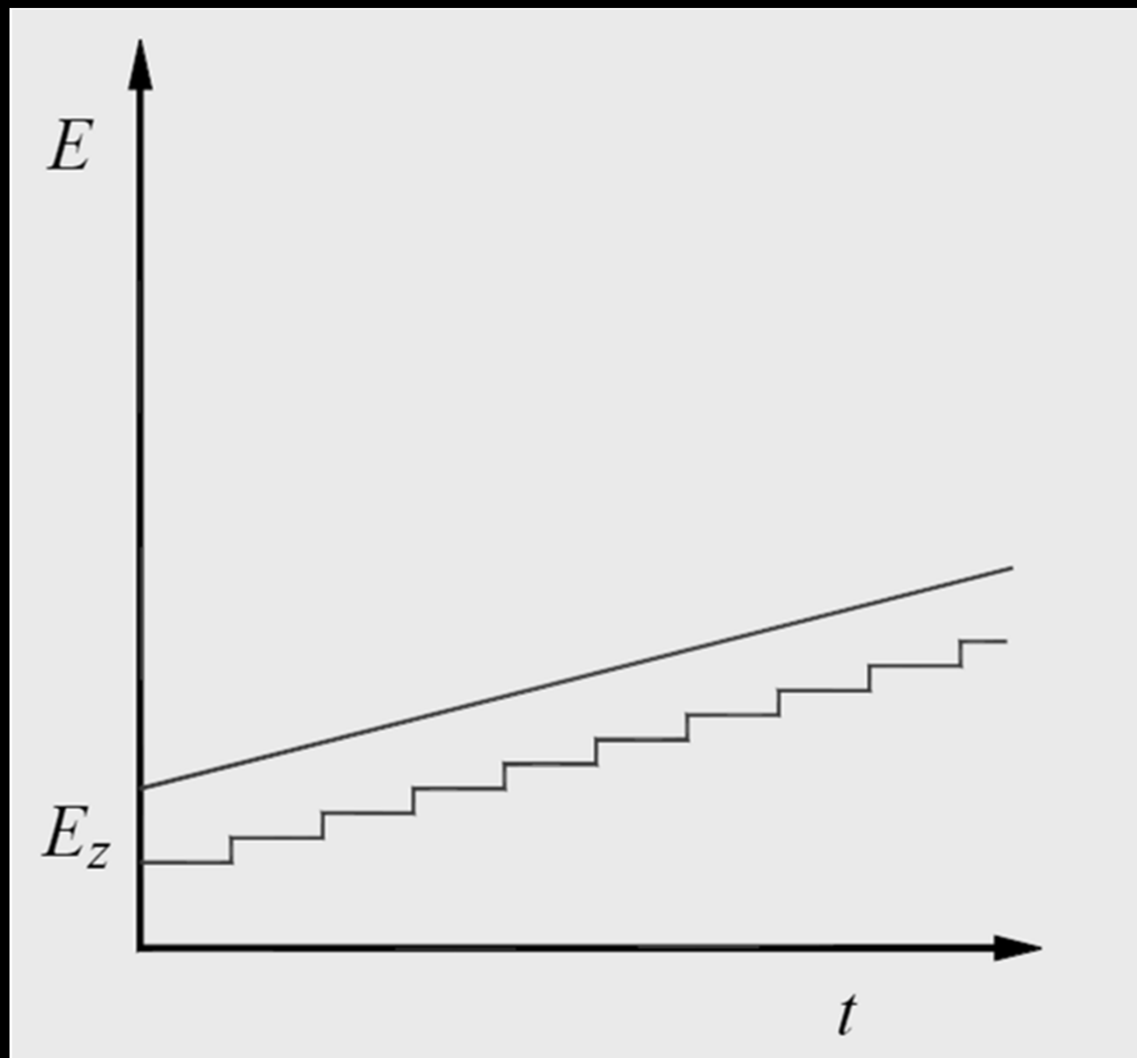




Kapalna Hg lelektroda

A.J. Bard, C.G. Zoski, Voltammetry Retrospective, *Anal. Chem.*, **72** (2000)346 A.


reference electrode
mercury
counter electrode
capillary
solution
volts


E
E_z
t

Ilkovičeva enačba: $i_l = 706\, z D^{1/2} m_\mathrm{f}^{2/3} t^{1/6} C = kC$

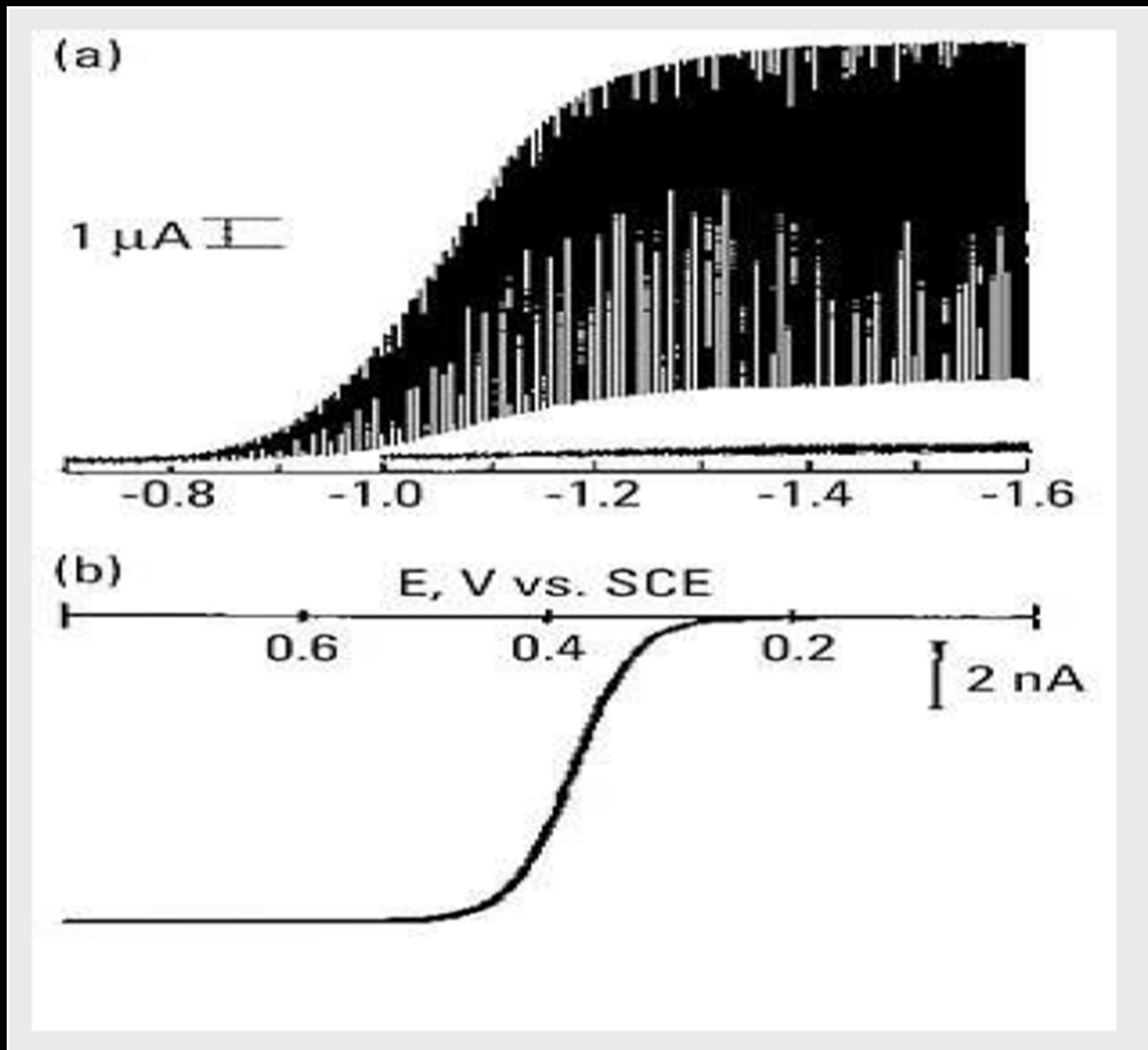
Reverzibilna redukcija: Oks + ze$^-$ = Red; Pb^{2+} + 2e$^-$ = Pb(Hg)

$$E = E^0 - \frac{RT}{zF} \ln \frac{a_{red(0)}}{a_{oks(0)}}$$

$$i = k_\mathrm{oks}\left([\mathrm{Oks}] - [\mathrm{Oks}]_0\right) = k_\mathrm{red}\left([\mathrm{Red}]_0 - [\mathrm{Red}]\right);\ i_l = k_\mathrm{oks}[\mathrm{Oks}];$$

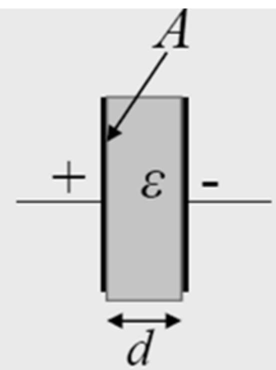
$$[\mathrm{Oks}]_0 = \frac{i_l - i}{k_\mathrm{oks}};\ [\mathrm{Red}]_0 = \frac{i}{k_\mathrm{red}};\ \frac{a_{\mathrm{oks}(0)}}{a_{\mathrm{red}(0)}} = \frac{\gamma_\mathrm{oks} k_\mathrm{red}}{\gamma_\mathrm{red} k_\mathrm{oks}} \cdot \frac{i_l - i}{i};$$

$$E = E_{1/2} + \frac{RT}{zF} \ln \frac{i_l - i}{i};\quad E_{1/2} = E^0 + \frac{RT}{zF} \ln \frac{\gamma_\mathrm{oks} D_\mathrm{red}^{1/2}}{\gamma_\mathrm{red} D_\mathrm{oks}^{1/2}}$$


(a)
1 μA
-0.8
-1.0
-1.2
-1.4
-1.6
(b)
E, V vs. SCE
0.6
0.4
0.2
2 nA

[redacted]

Kapacitivnost: $C_{dl} \propto \dfrac{A\varepsilon}{d}$



Površina kapalne elektrode: $A = 0{,}85\, m^{2/3} t^{2/3}$

$$Q = C_{dl} E^{*}; E^{*} = E_{m} - E$$

$$i_c = \frac{dQ}{dt} = E^{*}\frac{dC_{dl}}{dt} + C_{dl}\frac{dE^{*}}{dt} = E^{*} C_{dl}\frac{dA}{dt} + C_{dl}\frac{dE^{*}}{dt}$$

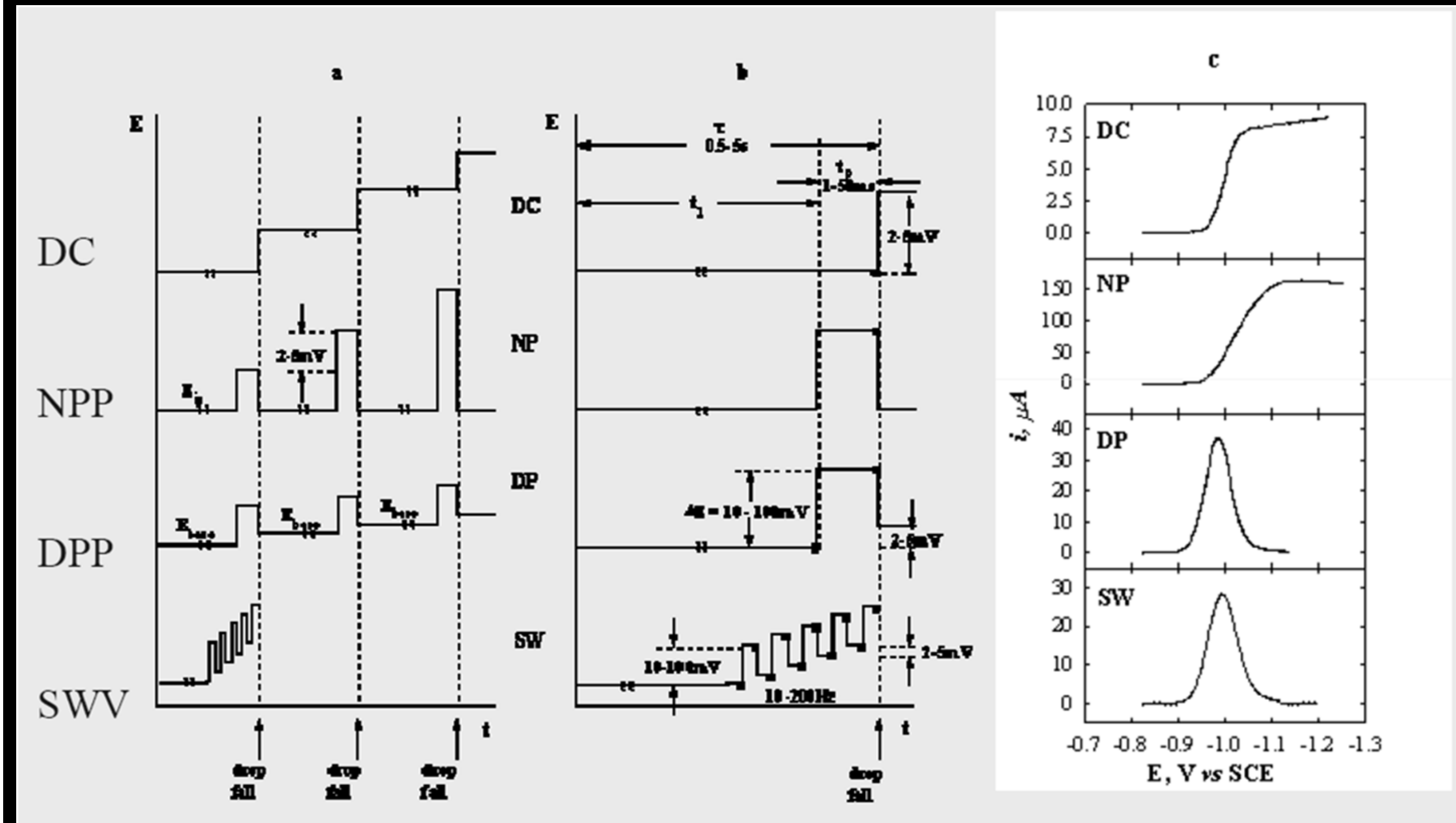
Kapacitivni tok: $i_c = 0{,}85 C_{dl}(E_m - E) m^{2/3} t^{-1/3}$

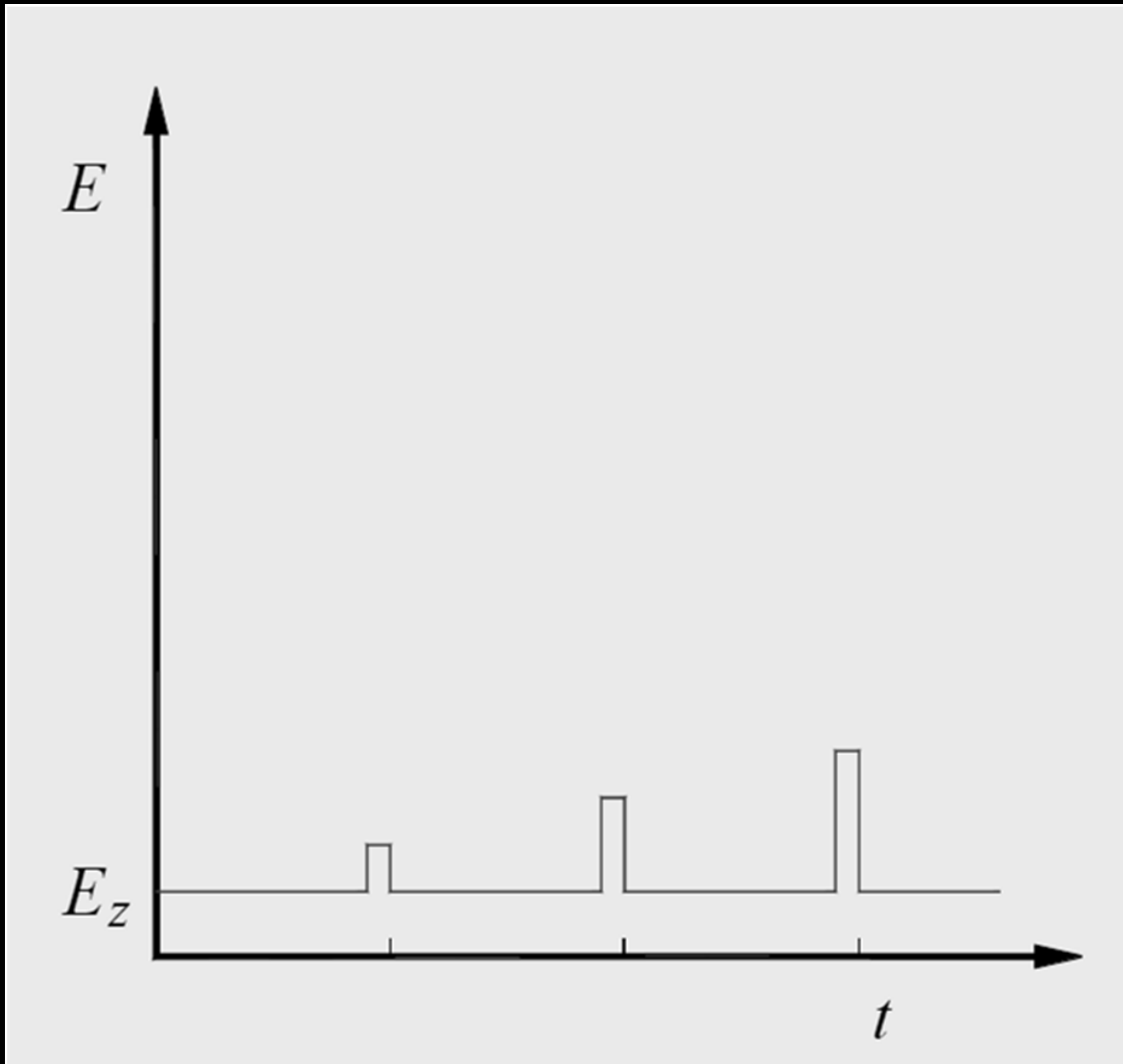
- Nastanek koordinacijske spojine pomakne redukcijo kovine k bolj negativnim napetostim - potrebna je dodatna energija za razgradnjo kompleksa

$$\mathrm{M} + \mathrm{xL} \Leftrightarrow \mathrm{ML_X}; \quad \beta_\mathrm{X} = \frac{[\mathrm{ML_X}]}{[\mathrm{M}][\mathrm{L}]^\mathrm{X}}; \mathrm{ML_X} + \mathrm{ze^-} = \mathrm{M(Hg)} + \mathrm{xL}$$

$$E_{1/2(\mathrm{ML})} - E_{1/2(\mathrm{M})} = -\frac{RT}{zF} \ln \beta_\mathrm{X} [\mathrm{L}]^\mathrm{X}; \qquad C_\mathrm{L} >> C_\mathrm{M}$$

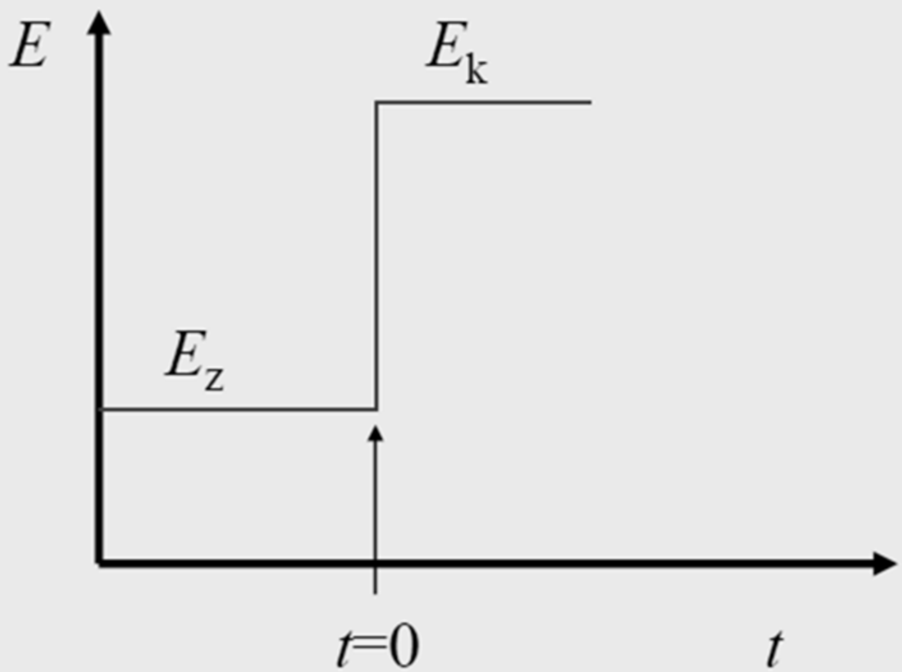
$$\Delta E_{1/2} = f(\beta, [\mathrm{L}]); \qquad \frac{\Delta E_{1/2}}{\Delta \log [\mathrm{L}]} \propto x$$


DC
NPP
DPP
SWV
a
E
t
drop fall
b
E
τ 0.5-5s
t_p 1-50ms
t_1
2-5mV
DC
NP
DP
ΔE = 10 - 100mV
SW
10-100mV
10-200Hz
drop fall
c
DC
NP
DP
SW
i, μA
E, V *vs* SCE
-0.7 -0.8 -0.9 -1.0 -1.1 -1.2 -1.3



E
E z
t

$$\mathrm{O} + z\mathrm{e}^- \underset{k_\mathrm{a}}{\overset{k_\mathrm{k}}{\rightleftharpoons}} \mathrm{R}$$



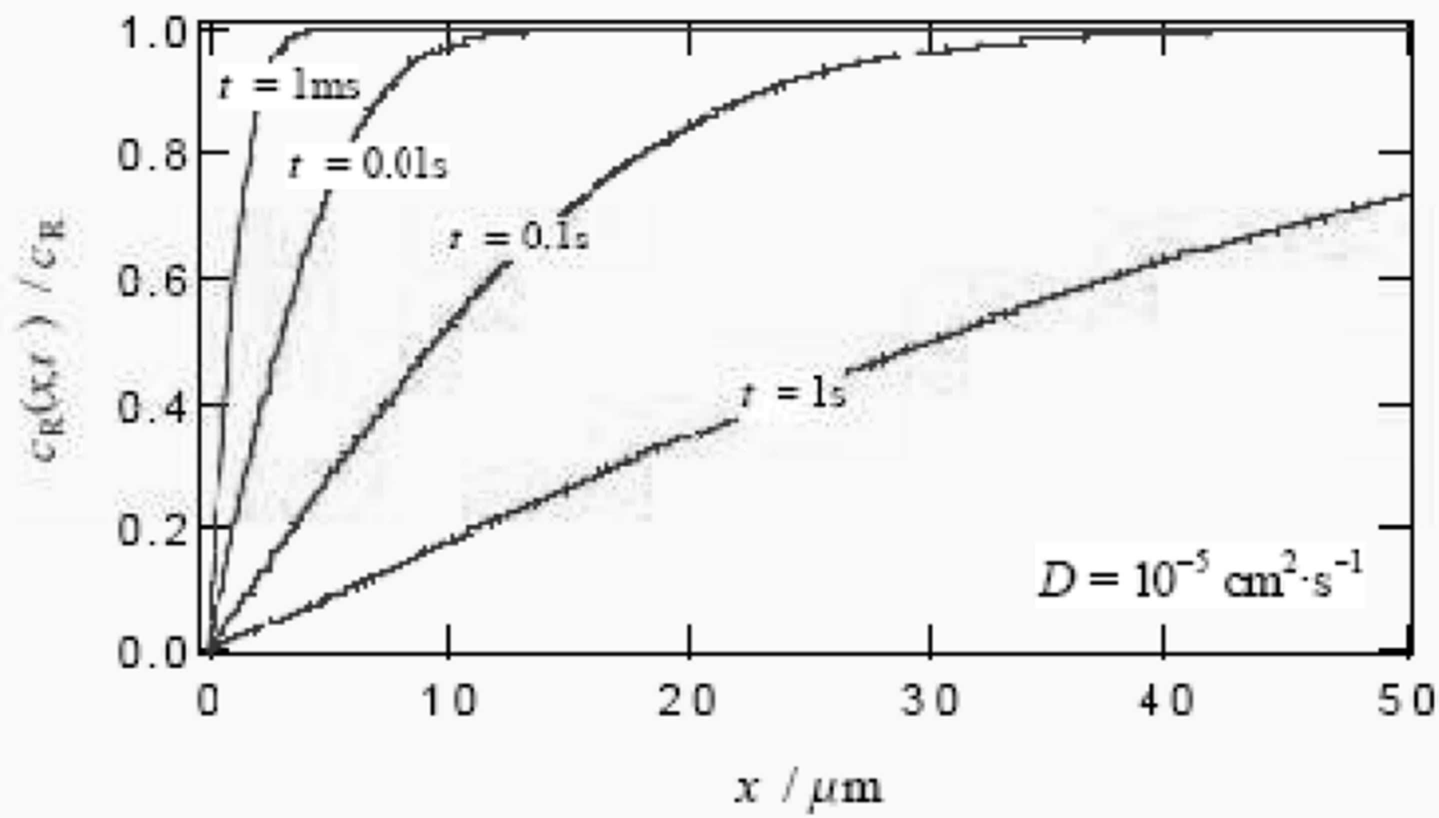
$c_\mathrm{R} = 0,\ E_\mathrm{k} = \eta_\mathrm{c}(-\infty),\ i = i_\mathrm{l}$

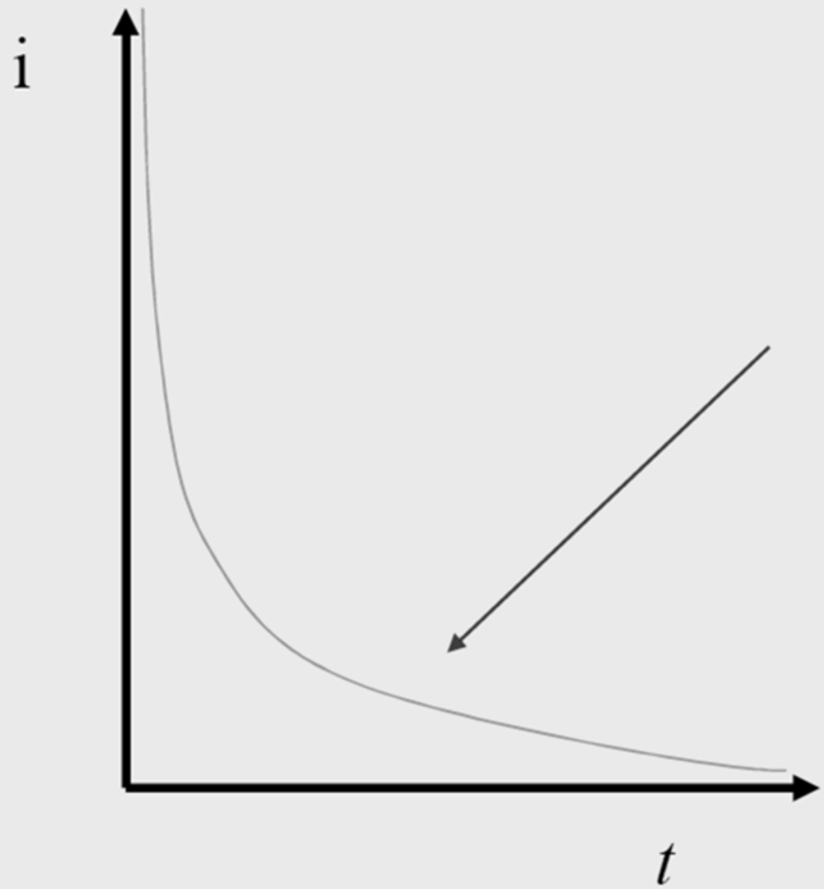
difuzijska kontrola

$$i = \frac{zFAc_\mathrm{O}^{\infty} D_\mathrm{O}^{1/2}}{\pi^{1/2} t^{1/2}}$$

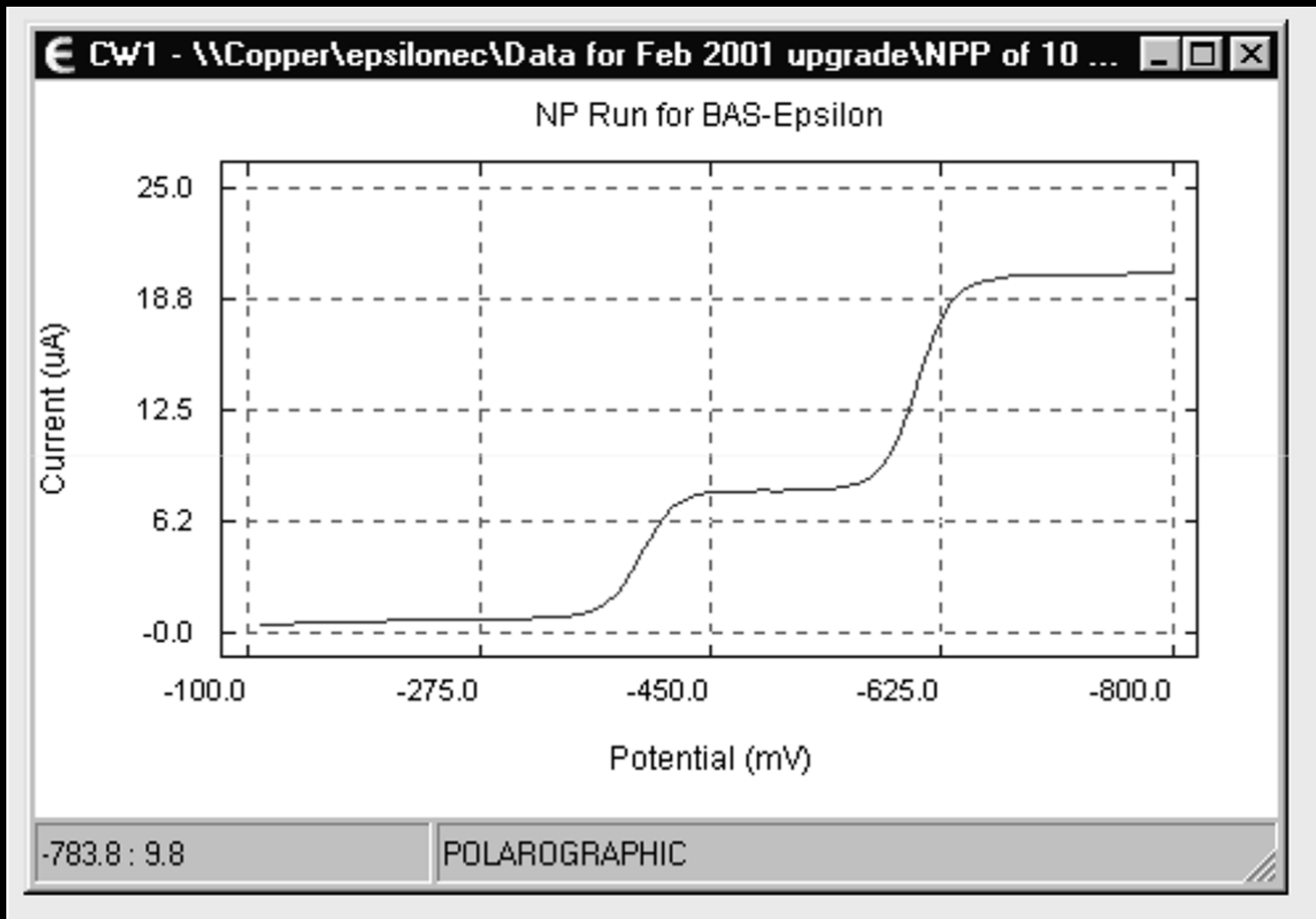
Koncentracijski profil - $f(t)$

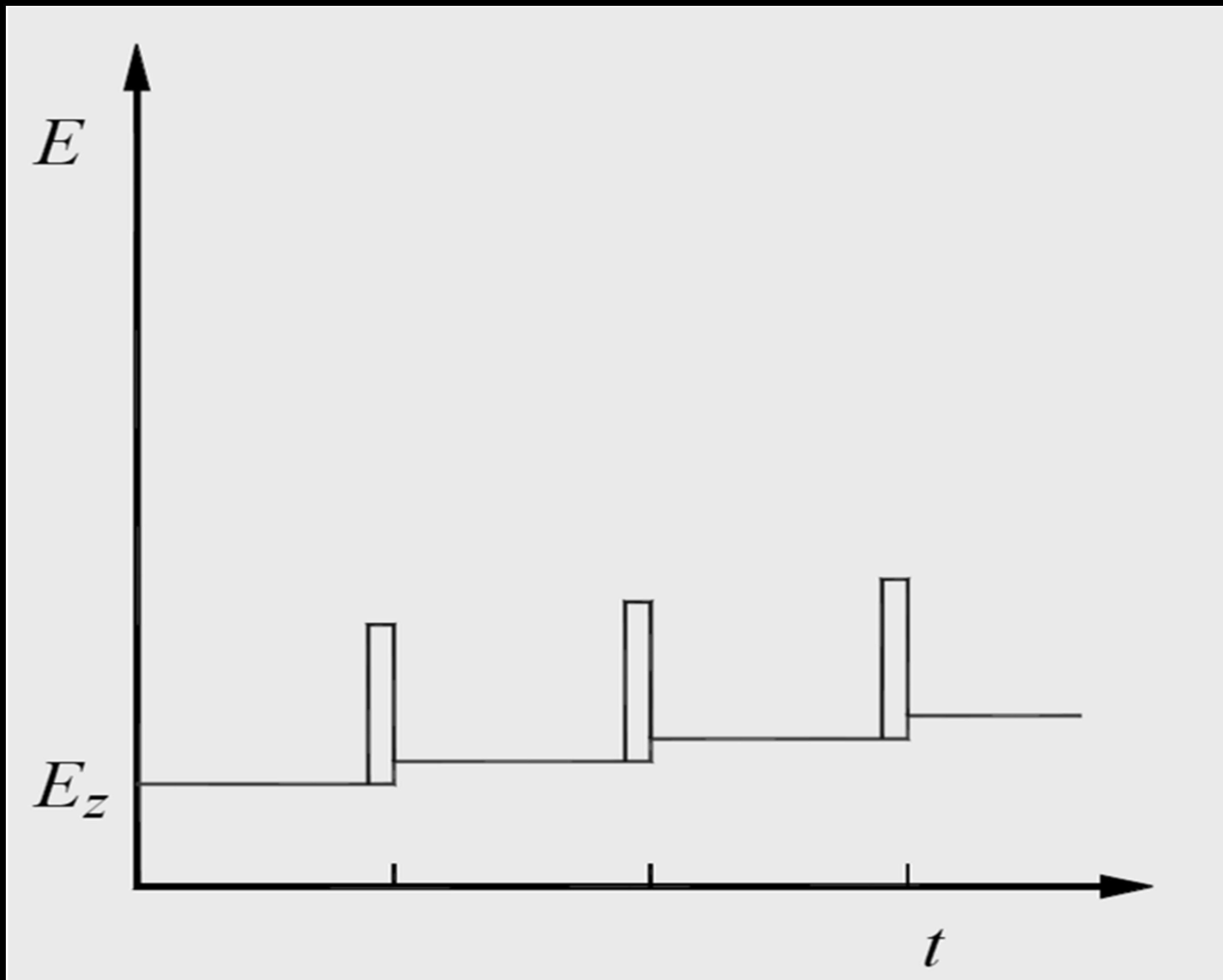
$$c_R(x,t) = c_R \,\mathrm{erf}\left[\frac{x}{2\sqrt{D_R t}}\right]$$

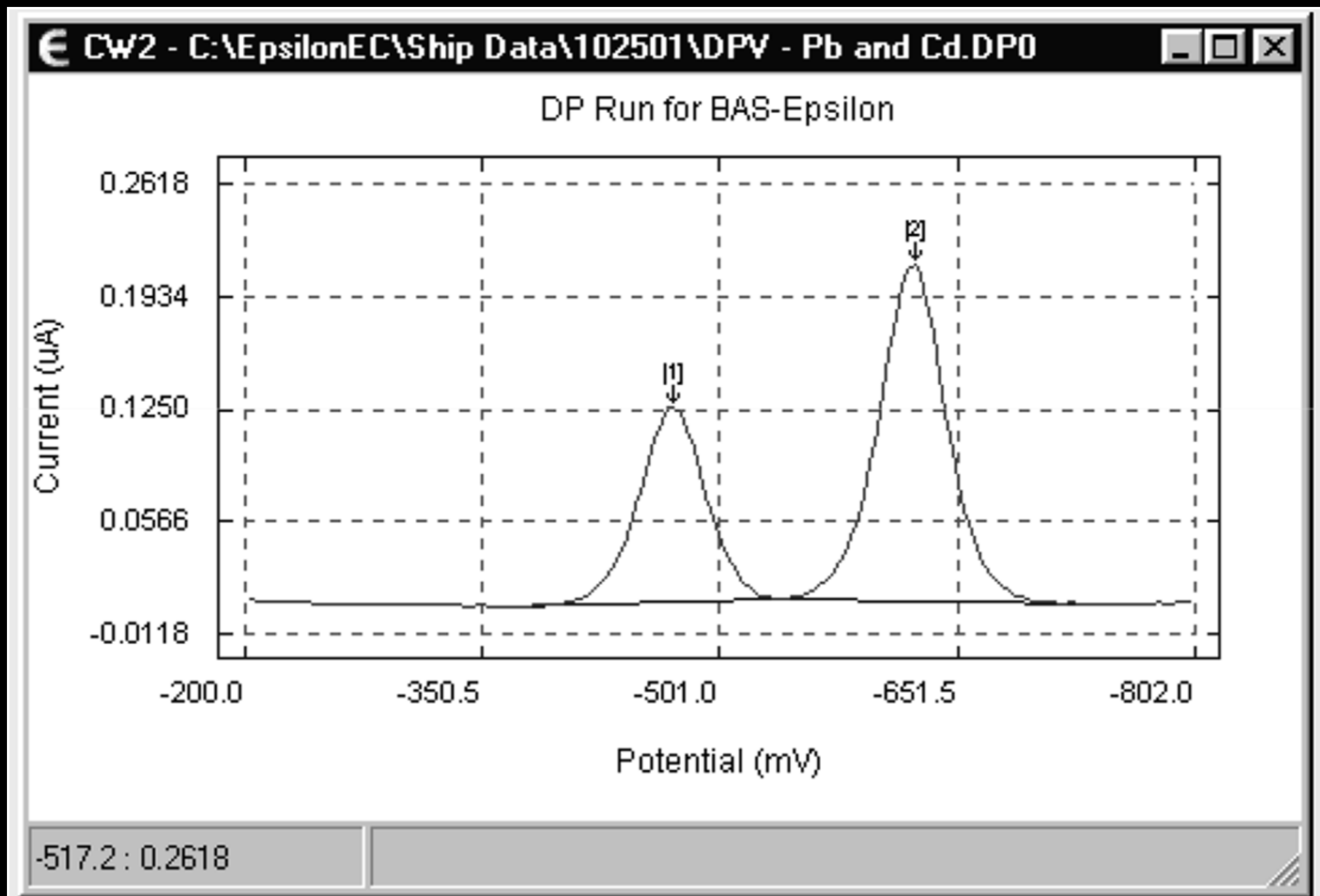


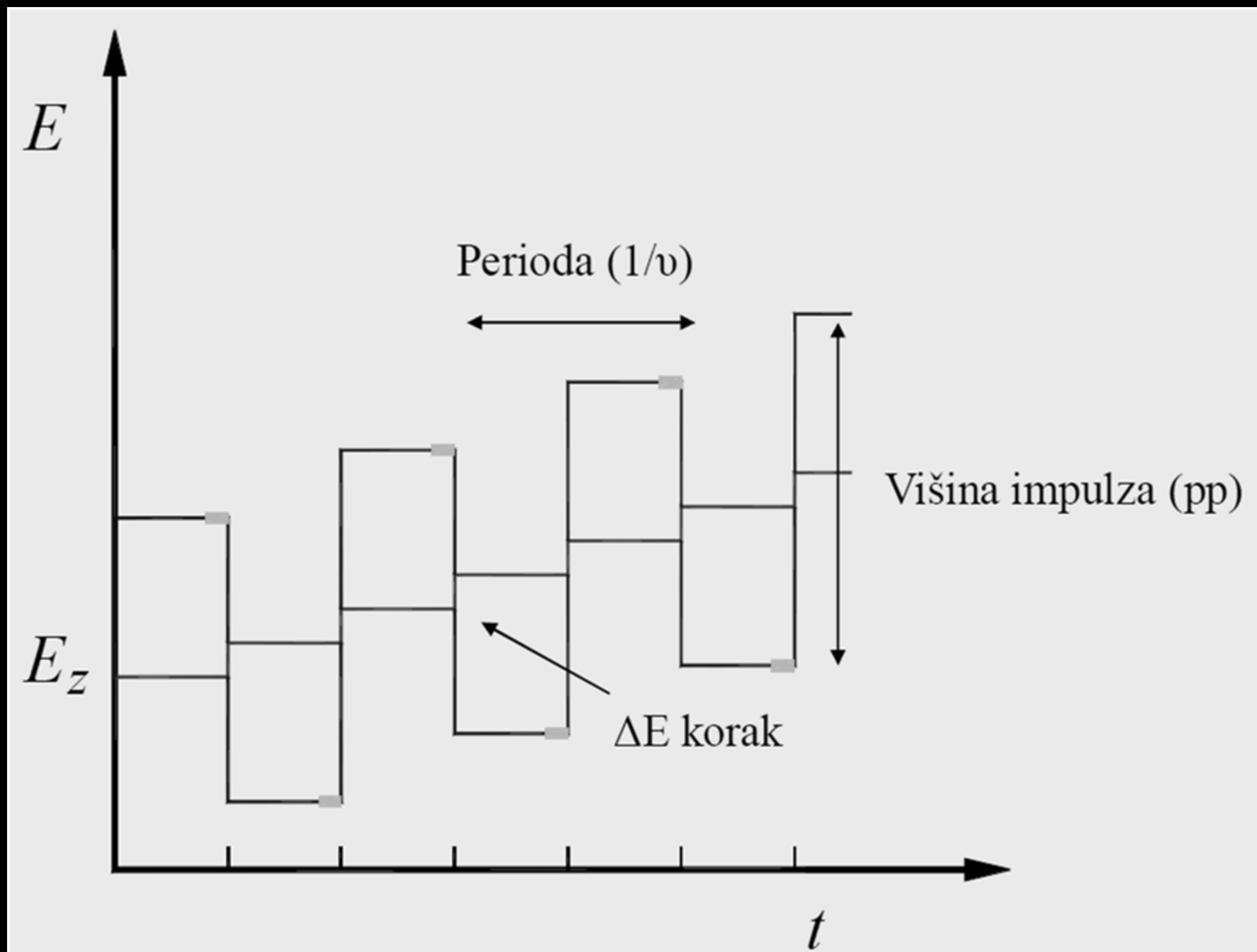


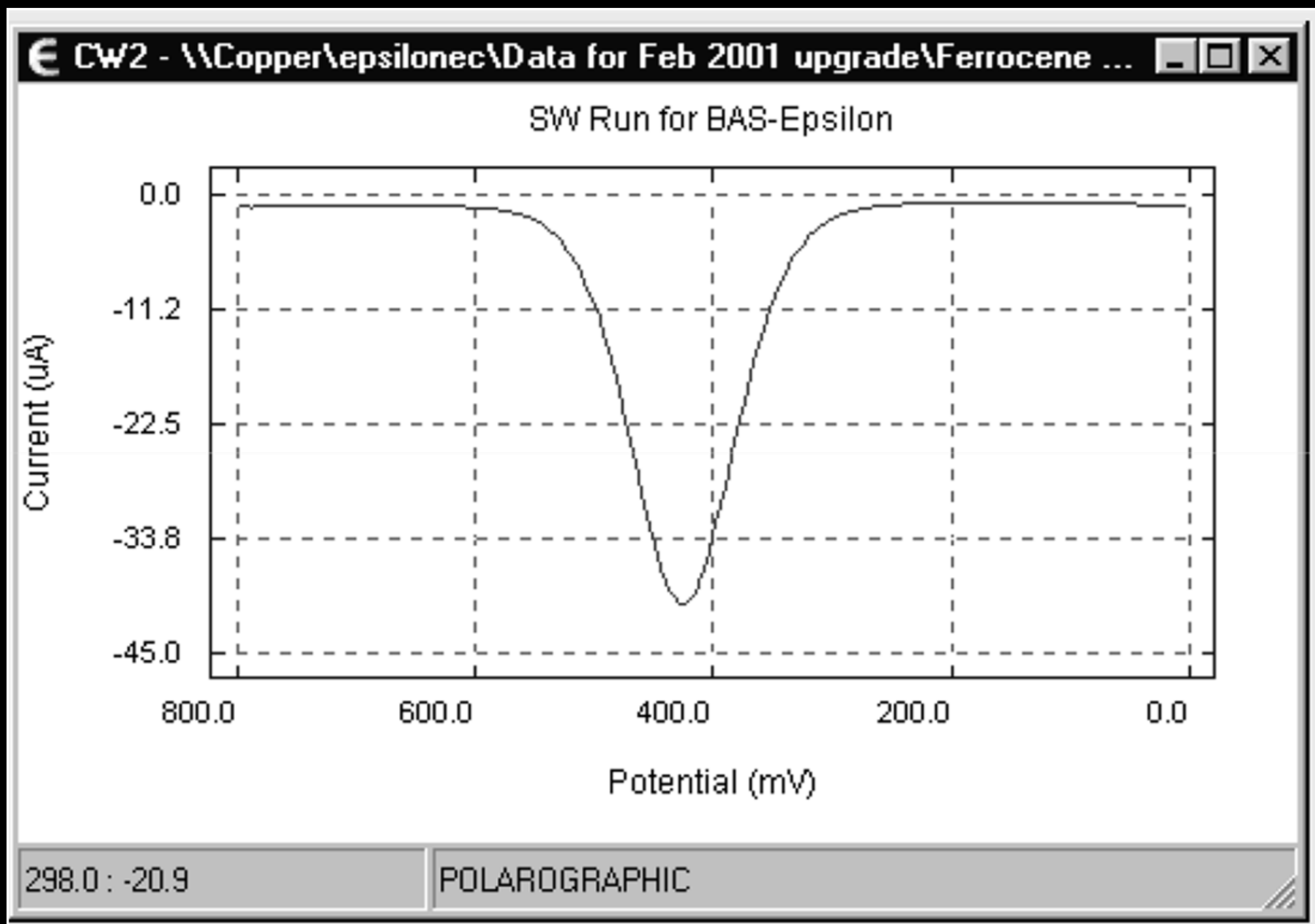
$$i_c = \frac{\Delta E}{R_s} \exp\left(-\frac{t}{R_s C_{dl}} \right)$$


CW1 - \\Copper\epsilonec\Data for Feb 2001 upgrade\NPP of 10 ...
NP Run for BAS-Epsilon
25.0
18.8
12.5
6.2
-0.0
Current (uA)
-100.0
-275.0
-450.0
-625.0
-800.0
Potential (mV)
-783.8 : 9.8
POLAROGRAPHIC

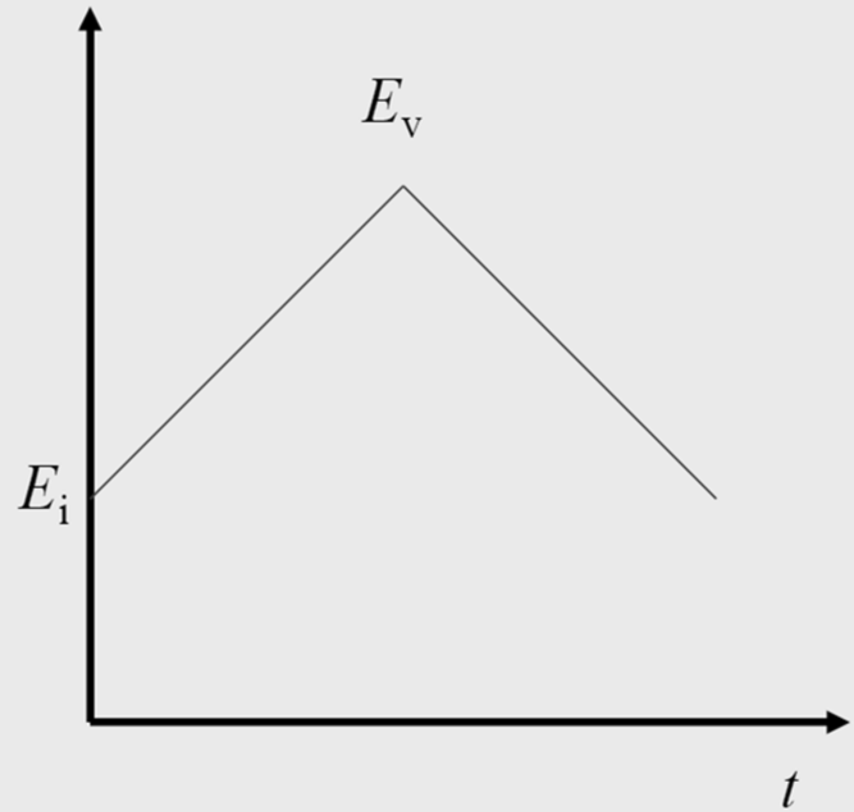

E
Ez
t


CW2 - C:\EpsilonEC\Ship Data\102501\DPV - Pb and Cd.DP0
DP Run for BAS-Epsilon
0.2618
0.1934
0.1250
0.0566
-0.0118
Current (uA)
[1]
[2]
-200.0
-350.5
-501.0
-651.5
-802.0
Potential (mV)
-517.2 : 0.2618

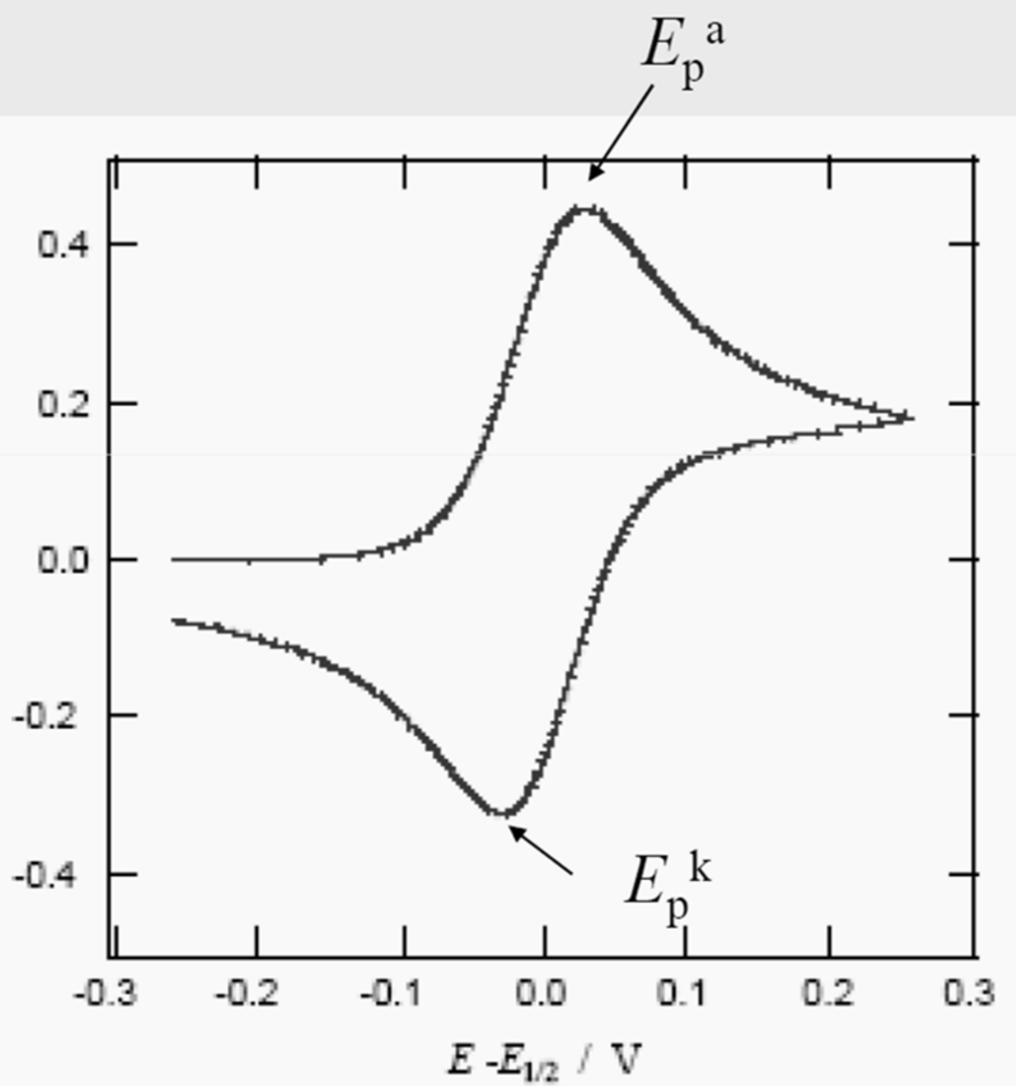

E
E_z
Perioda (1/υ)
Višina impulza (pp)
ΔE korak
t


CW2 - \\Copper\epsilonec\Data for Feb 2001 upgrade\Ferrocene ...
SW Run for BAS-Epsilon
Current (uA)
0.0
-11.2
-22.5
-33.8
-45.0
800.0
600.0
400.0
200.0
0.0
Potential (mV)
298.0 : -20.9
POLAROGRAPHIC

$E(t) = E_i \pm vt$



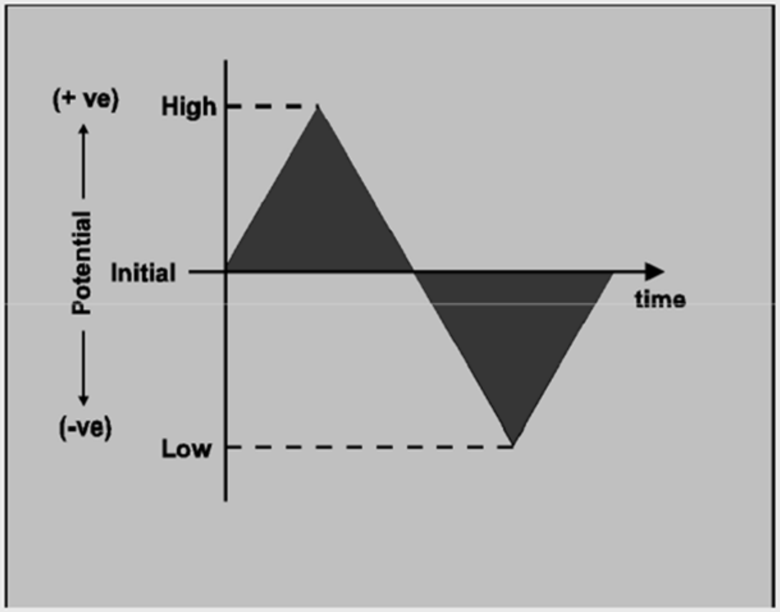
$v = dE/dt$: 10 mV/s – 1 MV/s

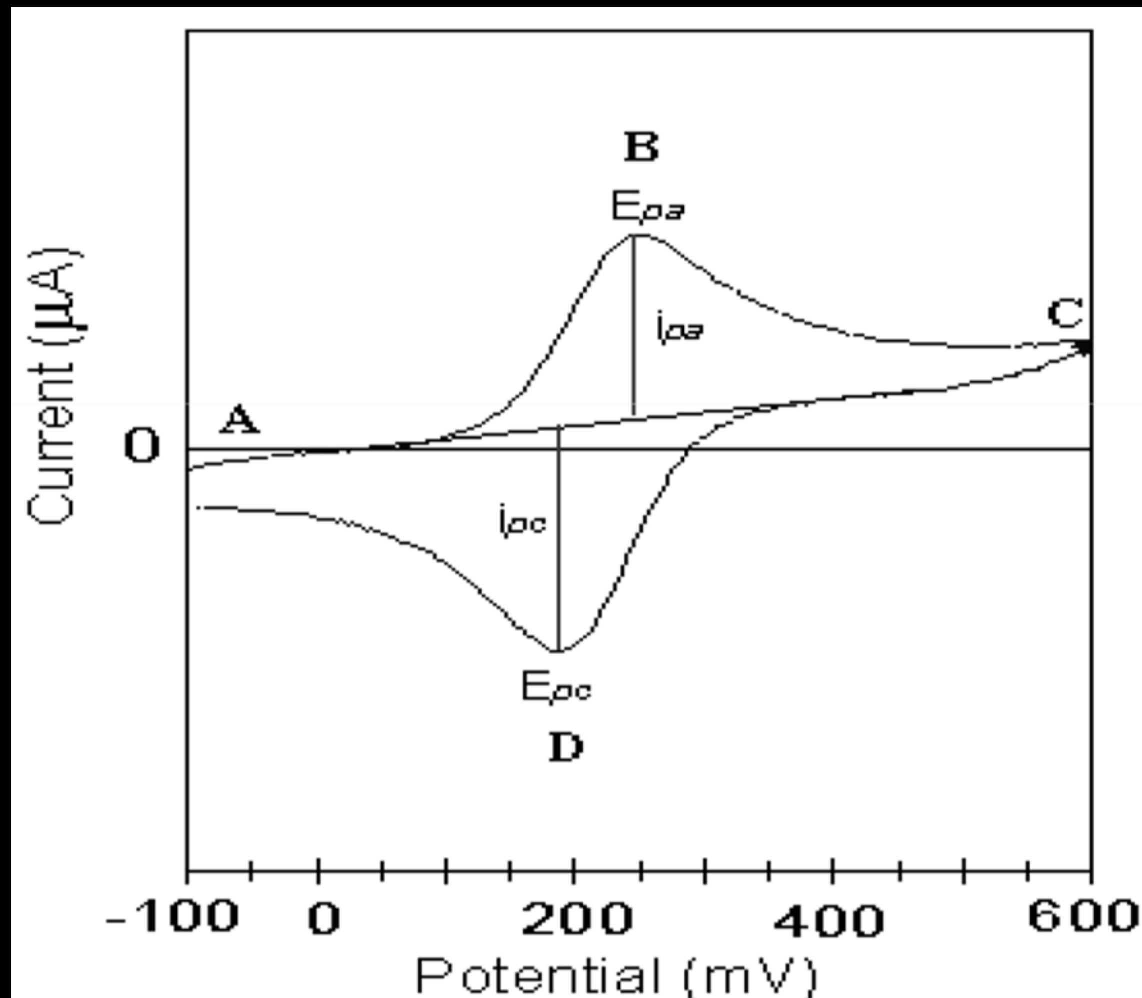


E_p^a
E_p^k
0.4
0.2
0.0
-0.2
-0.4
-0.3
-0.2
-0.1
0.0
0.1
0.2
0.3
$E - E_{1/2}$ / V

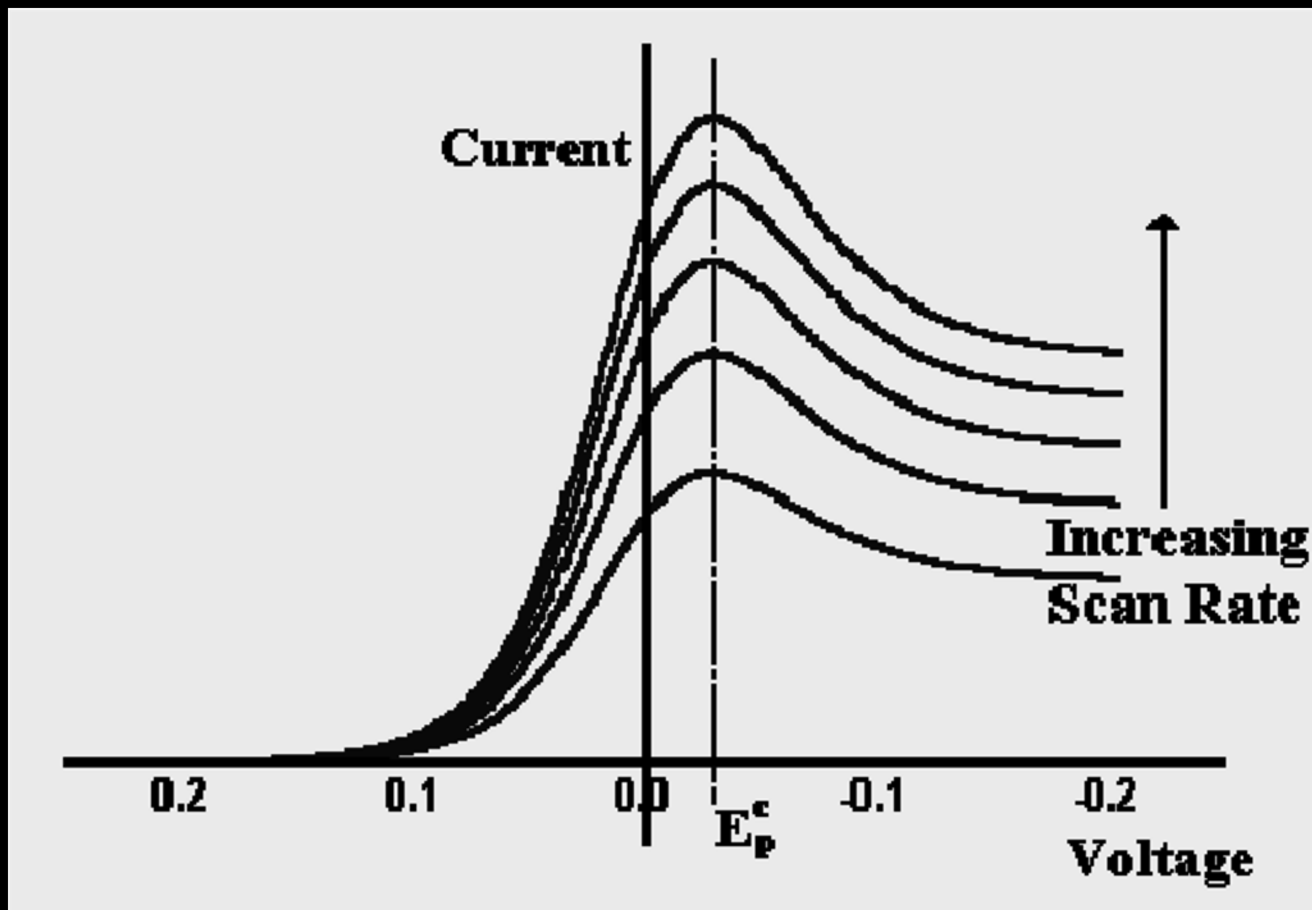
- Merjeneje pričnemo pri napetosti, kjer se na elektrodi nič ne dogaja (i=0).

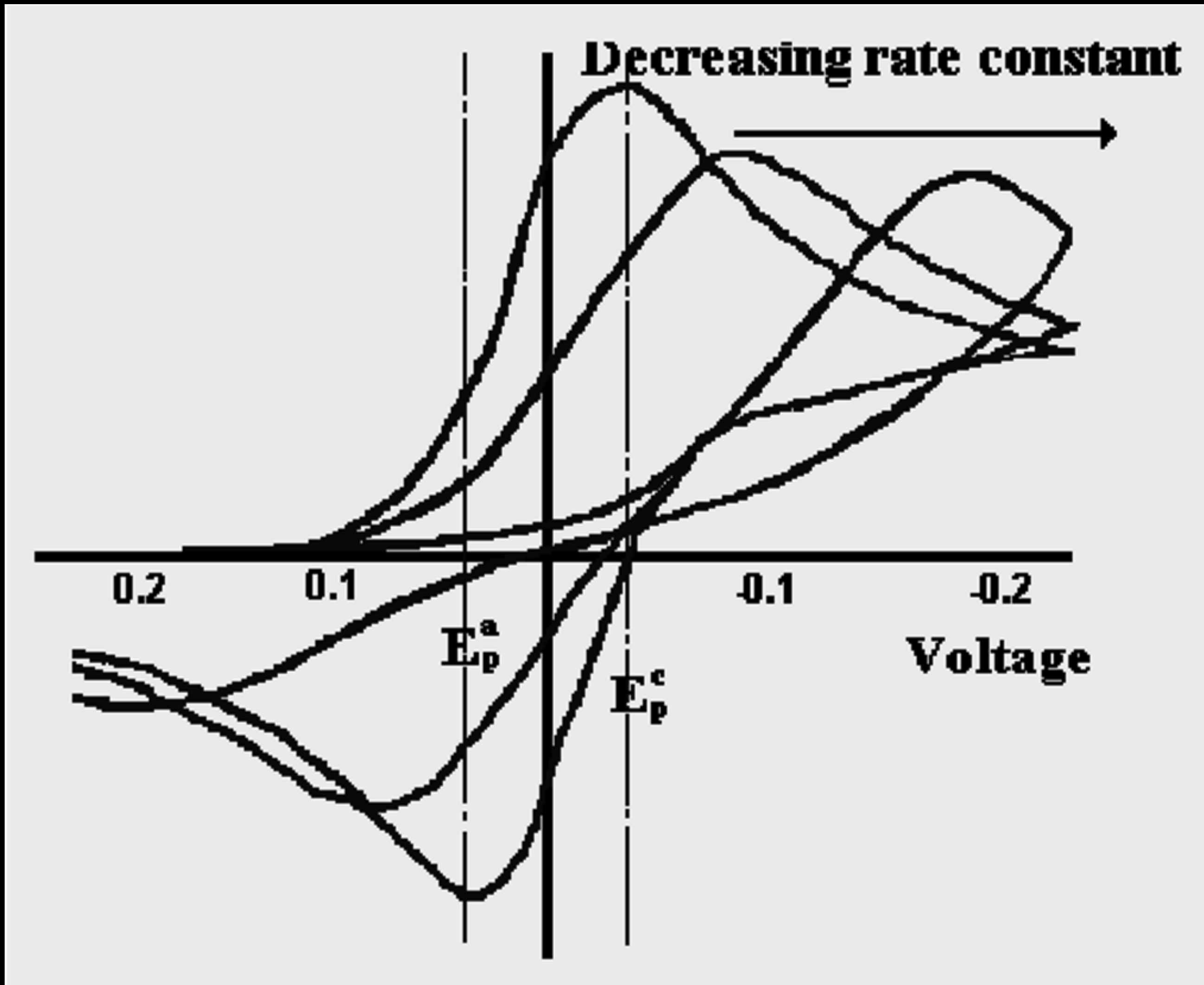
- Pri določeni razkrojni napetosti se začne elektroaktivna snov reducirati (oksidirati) - tok sprva eksponentno narašča in po dosegu maksimuma ($C_{x=0}$= 0) prične padati ($i = k\, t^{-1/2}$).
- Ko se izoblikuje vrh, napetost obrnemo in jo spreminjamo v nasprotni smeri – snov se v obratnem procesu oksidira (reducira).





B
E_{pa}
i_{pa}
C
A
O
i_{pc}
E_{pc}
D
Current (μA)
-100
0
200
400
600
Potential (mV)


Current
Increasing
Scan Rate
0.2
0.1
0.0
-0.1
-0.2
E_p^c
Voltage


Decreasing rate constant
0.2
0.1
-0.1
-0.2
Voltage
E_p^a
E_p^c

- Odlikuje se po visoki občutljivosti in nizki meji zaznave (1.10^{-8} – 1.10^{-12} M)

- Sestoji iz dveh korakov: I. predkoncentriranje, II. inverzni (stripping) proces (merjenje).

- **Anodna striping voltametrija**:

1. $Pb^{2+} + 2e^- + Hg \rightarrow Pb(Hg)$
2. $Pb(Hg) \rightarrow Pb^{2+} + 2e^-$ (oksidacija, anodni proces)

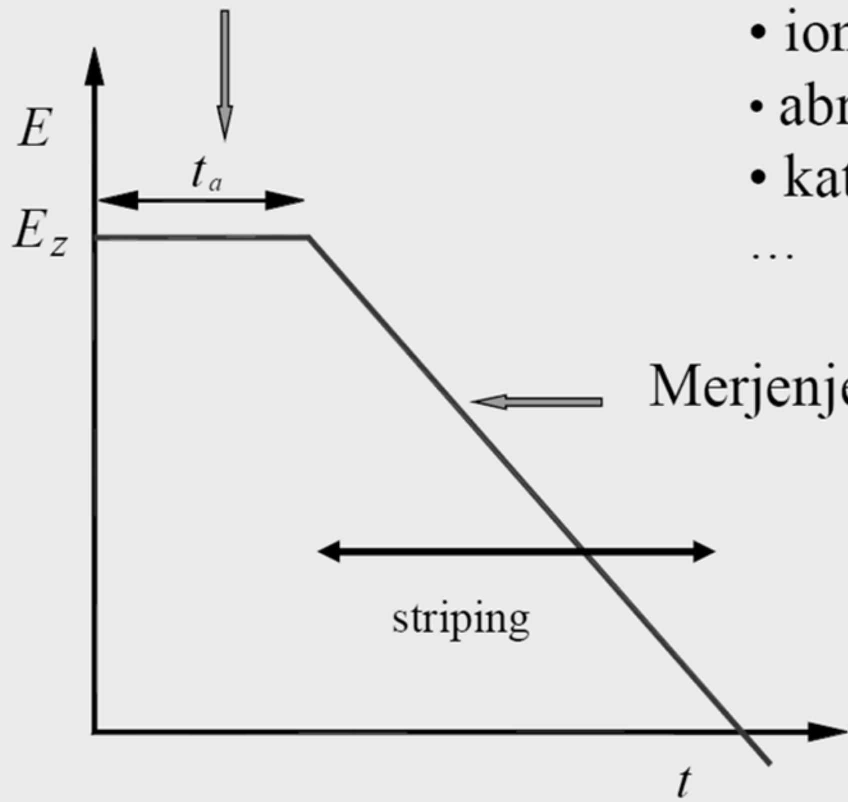
- **Katodna SV**

1. $R\text{-}SH + Ag \rightarrow RS\text{-}Ag + e^-$
2. $RS\text{-}Ag + e^- \rightarrow RS\text{-}H + Ag$ (redukcija)

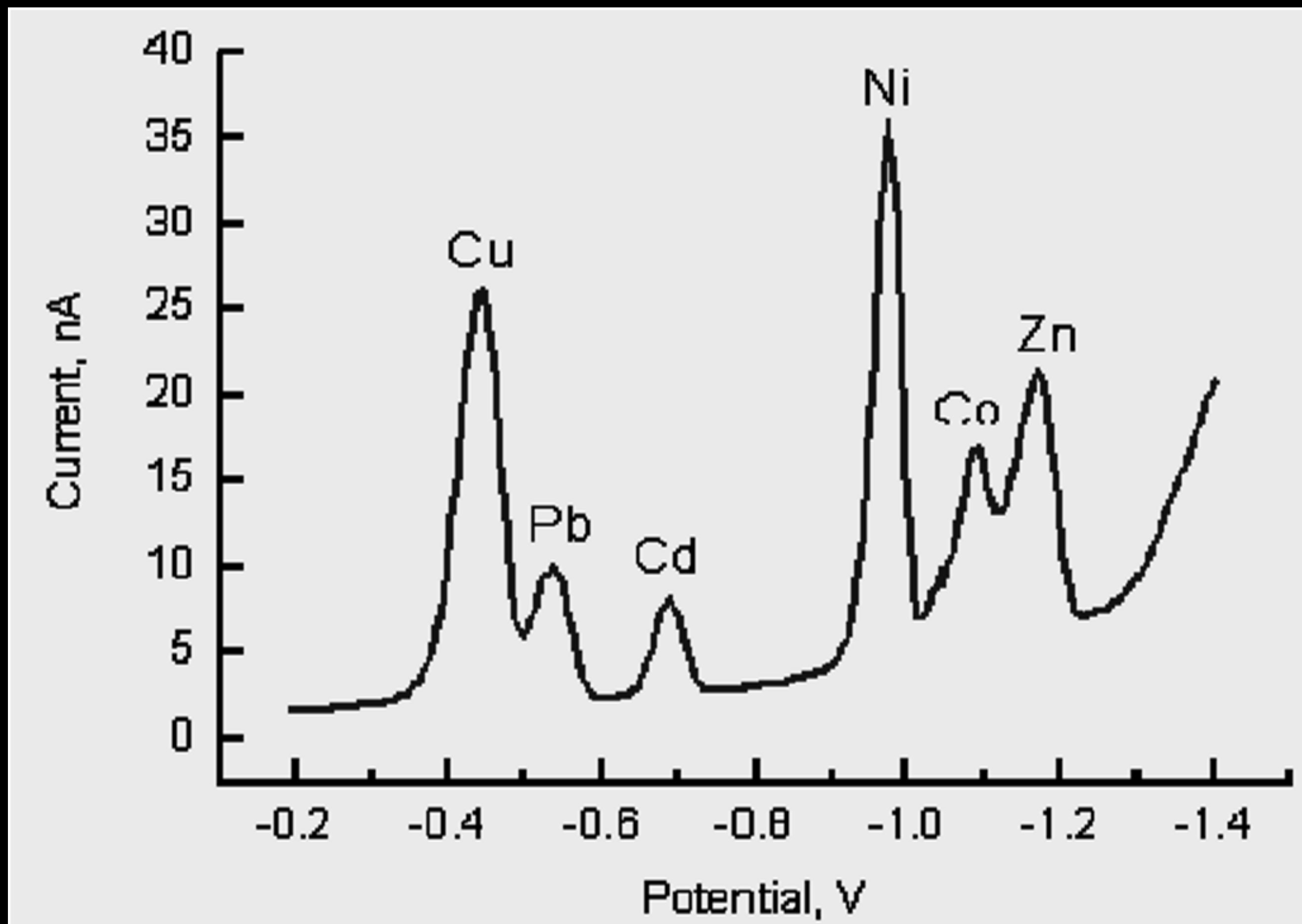
Predkoncentriranje 1-10 min;
aktiven transport (mešanje)

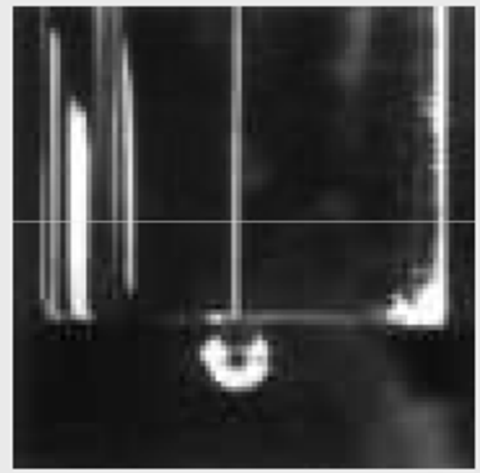
- tvorba amalgamov (ASV),
- adsorpcija (AdSV),
- ionska izmenjava (IexSV),
- abrazivna SV,
- kataliza,

…

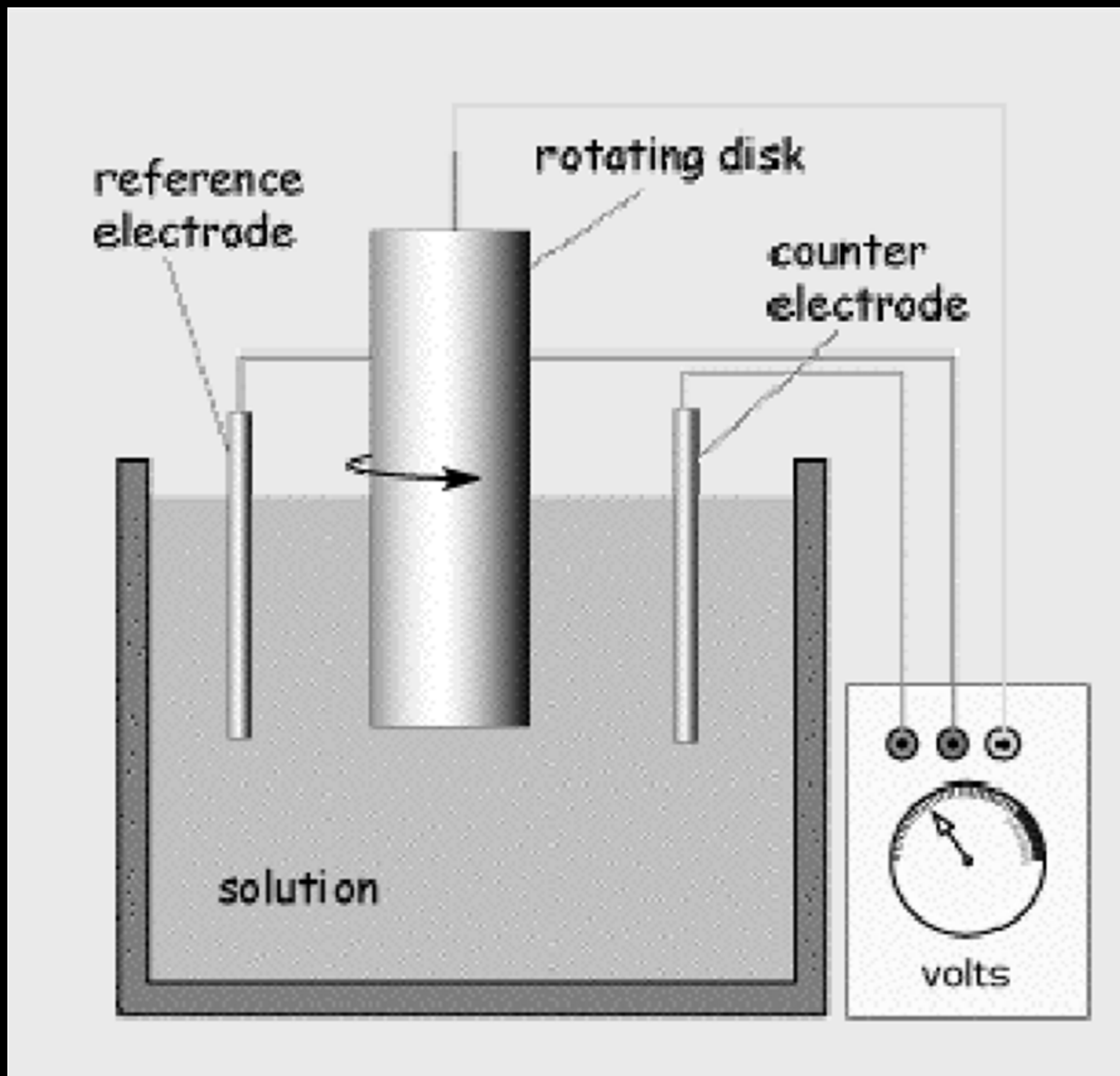


Merjenje (LS, DPP, SWV, ..)

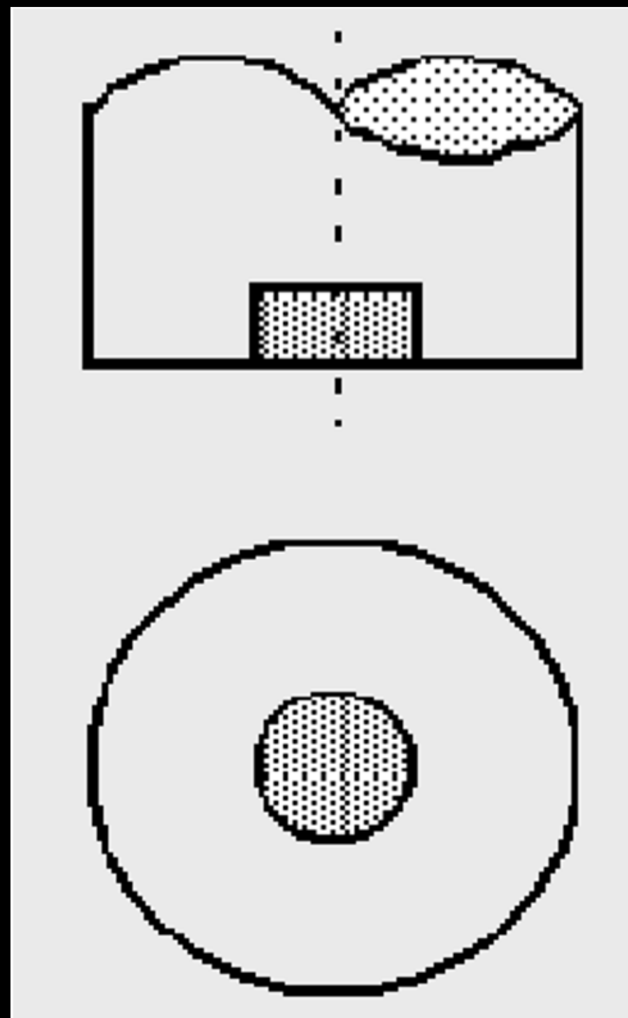

Ni
Cu
Zn
Co
Pb
Cd
40
35
30
25
20
15
10
5
0
Current, nA
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
Potential, V

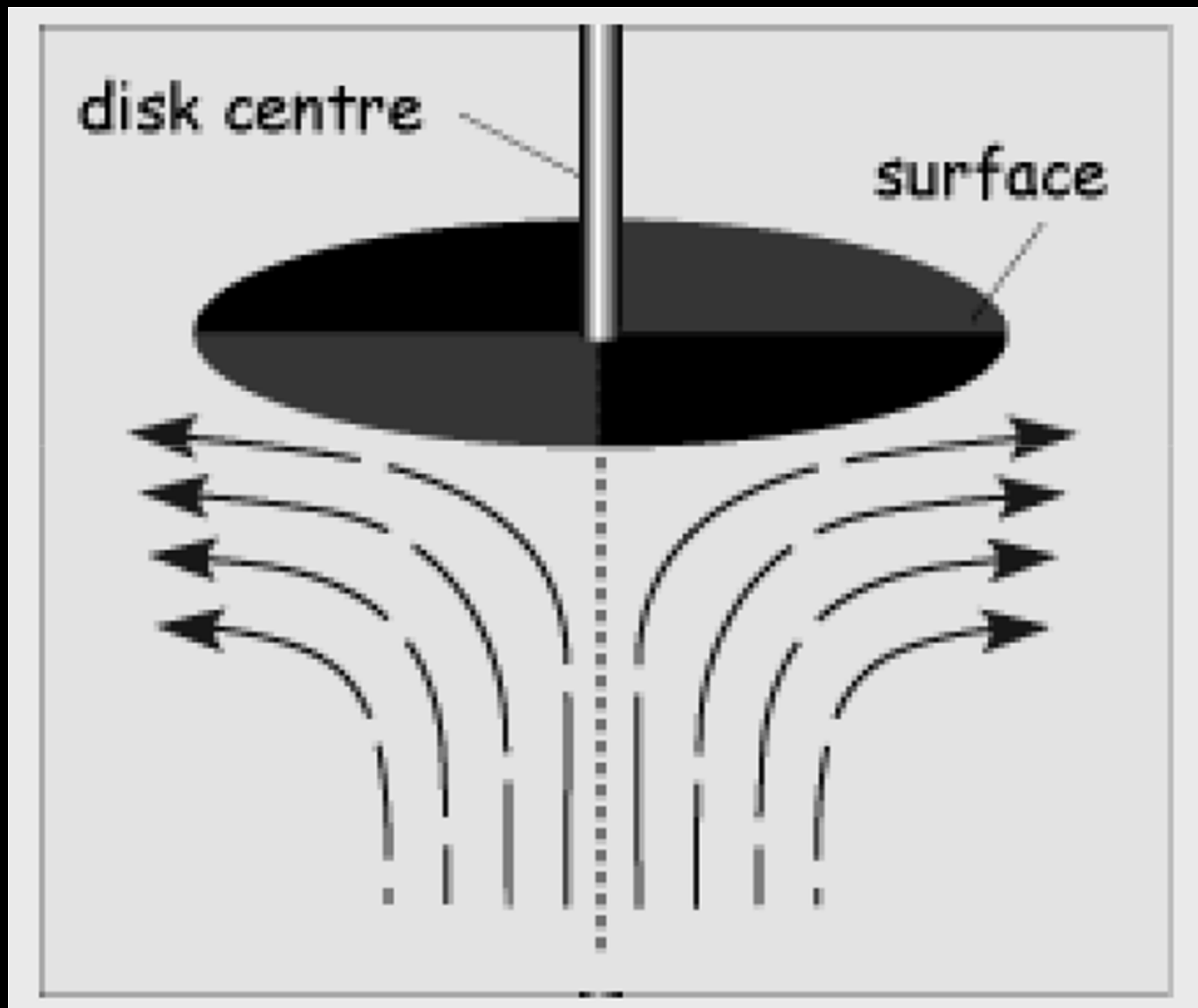


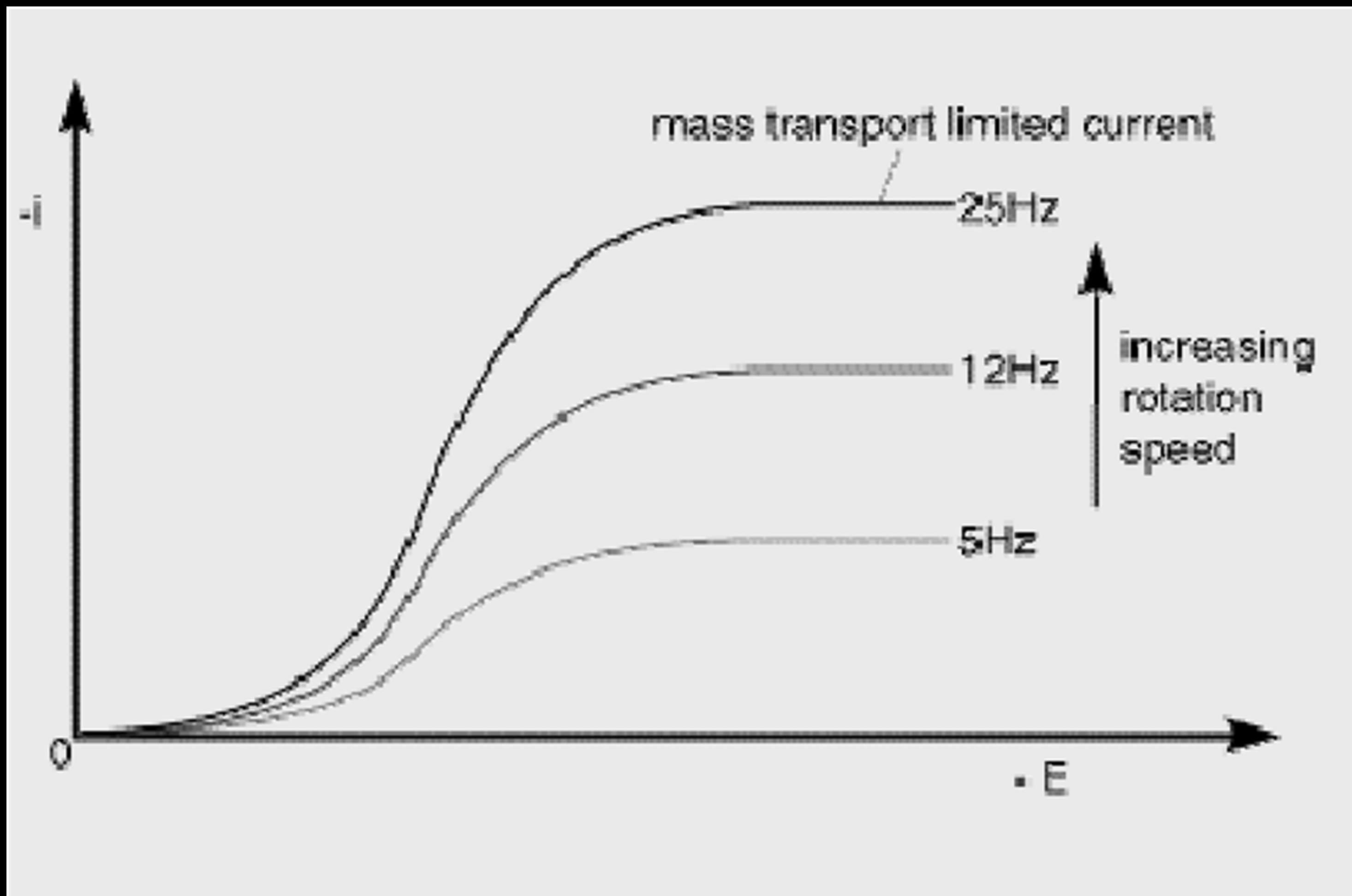
Viseča Hg kapljica –
stacionarna elektroda

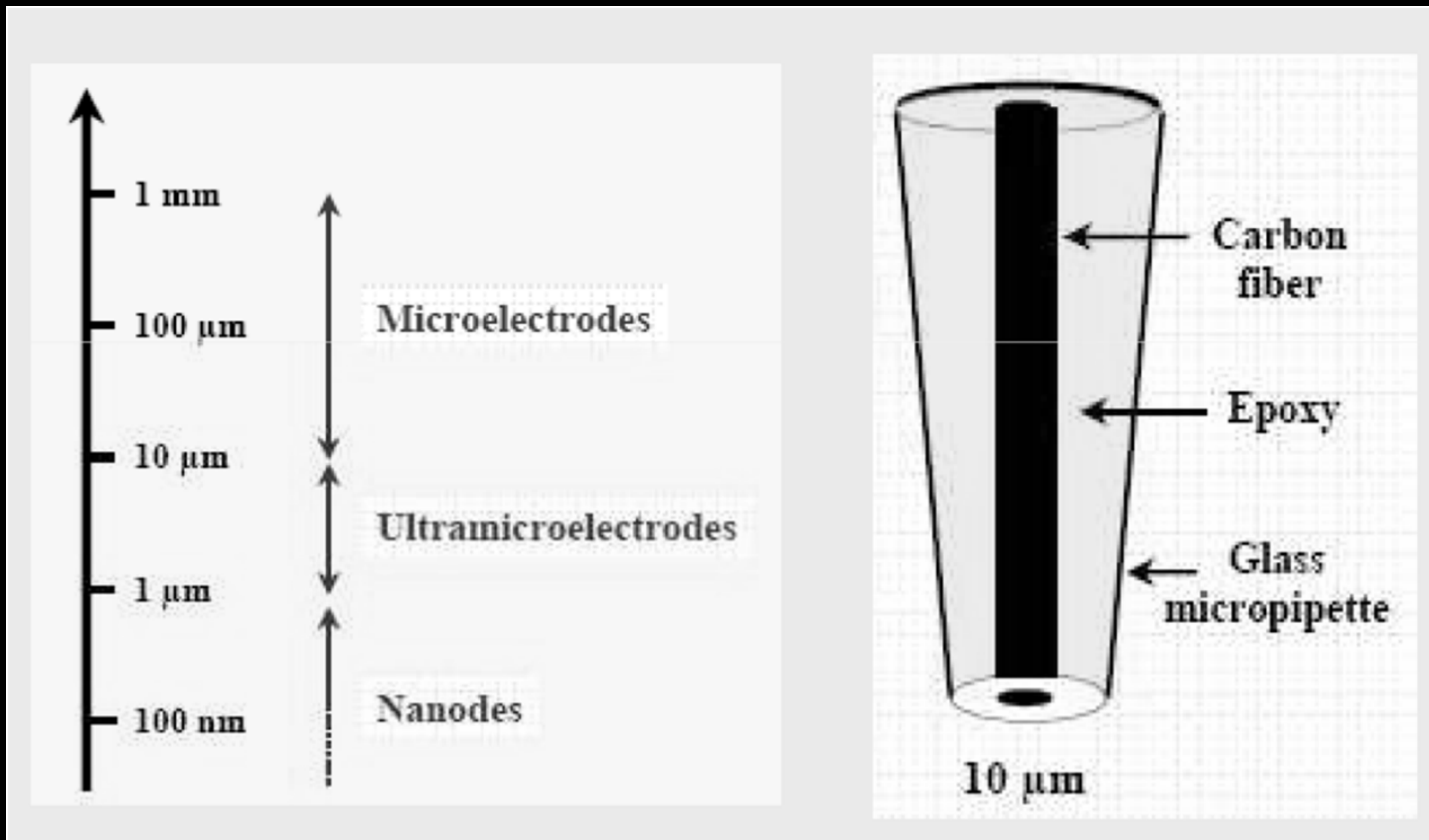


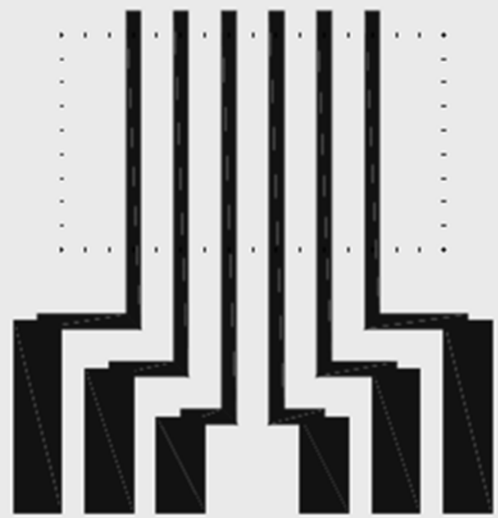
reference electrode
rotating disk
counter electrode
solution
volts




disk centre
surface


mass transport limited current
-i
25Hz
12Hz
5Hz
increasing
rotation
speed
0
E


1 mm
100 µm
10 µm
1 µm
100 nm
Microelectrodes
Ultramicroelectrodes
Nanodes
Carbon fiber
Epoxy
Glass micropipette
10 µm



Independently addressable microarray (IAA)