Voltametrija

Cottrellova jednadžba

Fickov zakon

$$\frac{\partial c_{\mathrm{O}}(x,t)}{\partial t} = D_{\mathrm{O}} \frac{\partial^2 c_{\mathrm{O}}(x,t)}{\partial x^2}$$

Rubni uvjeti

$$c_{\mathrm{O}}(x,0) = c_{\mathrm{O}}^*$$

$$\lim_{x\to\infty} c_{\mathrm{O}}(x,t) = c_{\mathrm{O}}^*$$

$$c_{\mathrm{O}}(0,t) = 0, \qquad t > 0$$

Rješavanje diferencijale jednadžbe

Laplaceova transformacija

$$L\big(F(t)\big) = \bar{F}(s) \equiv \int_0^\infty e^{-st} F(t)dt$$

Korisne značajke Laplaceove transformacije:

$$L\left\{\frac{dF(t)}{dt}\right\} = s\bar{F}(s) - F(0)$$

$$L\left\{\frac{\partial F(x,t)}{\partial x}\right\} = \frac{\partial \bar{F}(x,s)}{\partial x}$$

Osnovna jednadžba:

$$\frac{\partial c_{\mathrm{O}}(x,t)}{\partial t} = D_{\mathrm{O}} \frac{\partial^2 c_{\mathrm{O}}(x,t)}{\partial x^2}$$

Nakon transformacije:

$$\frac{\partial^2 \overline{c_{\mathrm{O}}}\,(x,s)}{\partial x^2} - \frac{s}{D_{\mathrm{O}}} \overline{c_{\mathrm{O}}}(x,s) = -\frac{c_{\mathrm{O}}^*}{D_{\mathrm{O}}}$$

Riješavamo traženjem: CF

$$\frac{\partial^2 \overline{c_{\mathrm{O,CF}}}(x,s)}{\partial x^2} - \frac{s}{D_{\mathrm{O}}} \overline{c_{\mathrm{OCF}}}(x,s) = 0$$

$$\overline{c_{\mathrm{O}}}(x,s) = \mathrm{CF} + \mathrm{PI}$$

PI $\overline{c_{\mathrm{O,PI}}}(x,s) = k$

Nalaženjem CF i PI te uvrštavanjem rubnih uvjeta dobivamo:

$$\overline{c_O}(x,s) = \frac{c_O^*}{s} - \frac{c_O^*}{s} e^{-x\sqrt{s/D_O}}$$

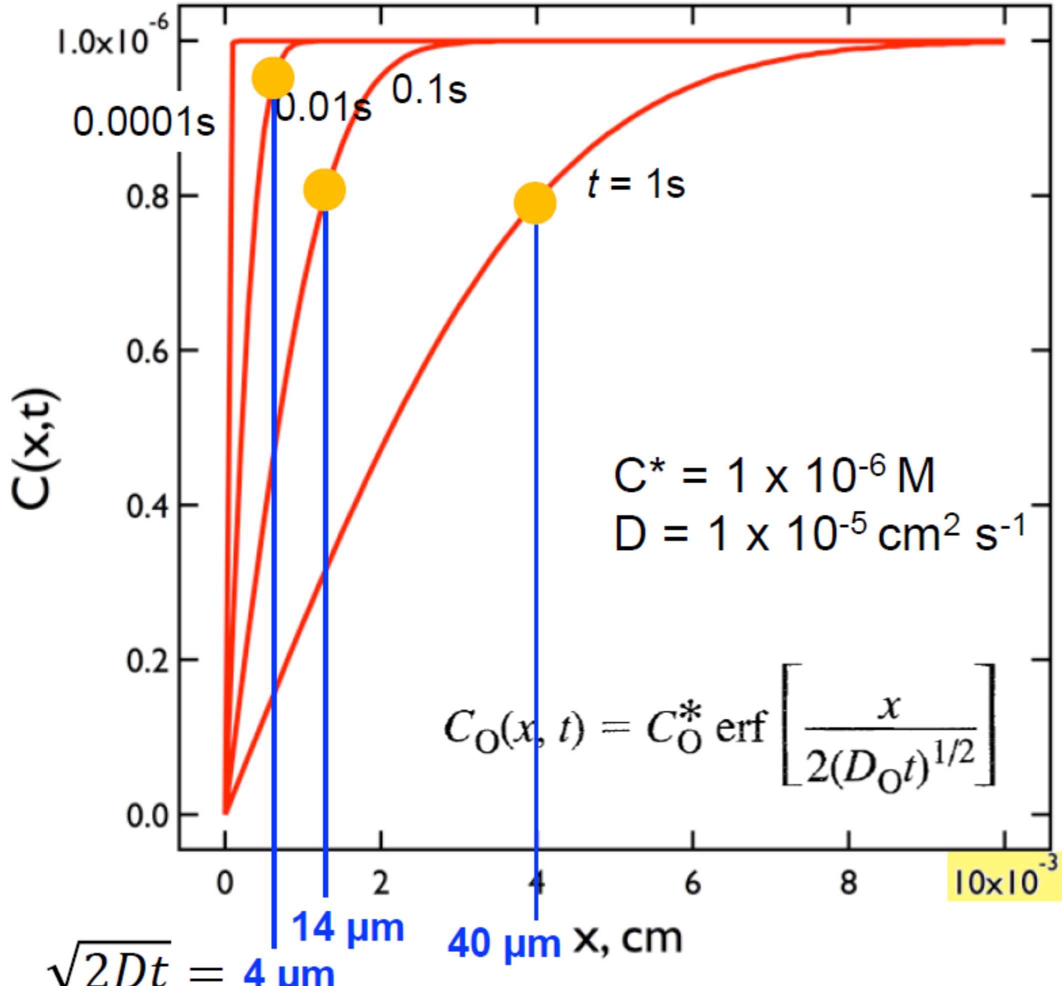
Inverzna Laplaceova transformacija daje rješenje jednadžbe

Koncentracijski profil u difuzijski kontroliranim uvjetima na planarnoj elektrodi

$$\boldsymbol{c_O(x,t) = c_O^*\, erf\left(\frac{x}{2\sqrt{tD_O}}\right)}$$

$$l = \sqrt{2D_0 t}$$

Debljina difuzijskog sloja


1.0x10^-6
0.8
0.6
0.4
0.2
0.0
C(x,t)
0.0001s
0.01s
0.1s
t = 1s
C* = 1 x 10^-6 M
D = 1 x 10^-5 cm^2 s^-1
$C_O(x, t) = C_O^* \operatorname{erf}\left[\frac{x}{2(D_O t)^{1/2}}\right]$
0
2
4
6
8
10x10^-3
x, cm
14 μm
40 μm
$\sqrt{2Dt}$ = 4 μm

Iz koncentracijskog profila uvrštavanjem u 1. Fickov zakon dolazimo do difuzijskog toka J_{O}

$$J_{\mathrm{O}} = -D_{\mathrm{O}} \frac{\partial c_{\mathrm{O}}(x,t)}{\partial x}$$

$$\frac{d}{dx}\,\mathrm{erf}(x) = \frac{2}{\pi^{1/2}}\, e^{-x^2}$$

$$J_{\mathrm{O}} = D_{\mathrm{O}} c_{\mathrm{O}}^{*} \frac{1}{2\sqrt{tD_{\mathrm{O}}}} \frac{2}{\sqrt{\pi}}\, e^{\frac{-x^2}{4tD_{\mathrm{O}}}}$$

$$J_{\mathrm{O}}(0,t) = c_{\mathrm{O}}^{*} \sqrt{\frac{D_{\mathrm{O}}}{\pi t}}$$

Cottrellova jednadžba

Planarna elektroda

$$\boldsymbol{i = zFA\,J(0,t) = zFAc_{O}^{*}\sqrt{\frac{D_{O}}{\pi t}}}$$

Slučaj sferične difuzije

Ovisnost struje o vremenu na stacionarnoj sferičnoj elektrodi

- Riješava se na analogan način uz prelazak na polarne koordinate

$$\boldsymbol{i = zFAc_O^* \sqrt{\frac{D_O}{\pi t}} + \frac{zFAD_O c_O^*}{r}}$$

„Utjecaj sferičnosti” izražen u slučaju elektroda malih dimenzija i kod dugotrajnih stacionarnih eksperimenata (KŽE uz sporo kapanje žive, VŽK, UME)

Ultramikroelektrode

- dimenzija manjih od difuzijskog sloja (max 25 µm, min 100 ili čak 10 nm)
- stacionarni mod mjerenja omogućen malim dimenzijama

$$i_s(sfera) = \frac{zFAD_O c_O^*}{r} = 4\pi r z F D_O c_O^*$$

$$i_s(disk) = 4rzFD_O c_O^*$$

$$i_s(cilindar) = \frac{2zFAD_O c_O^*}{r \ln t}$$

“Niski” potencijal

Na analogan način, rješava se i slučaj niskog potencijala pri kojem su pri površini elektrode koncentracije oksidirane i reducirane vrste definirane Nernstovom jednadžbom

Potrebno u obzir uzeti i difuziju reducirane vrste

- s površine elektrode u otopinu u slučaju nastajanja topljive vrste (iona)
- u unutrašnjost živine kapi ukoliko nastaje amalgam

$$\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2} \qquad \frac{\partial C_R(x,t)}{\partial t} = D_R \frac{\partial^2 C_R(x,t)}{\partial x^2}$$

$$C_O(x,0) = C_O^* \qquad C_R(x,0) = 0$$

$$\lim_{x\to\infty} C_O(x,t) = C_O^* \qquad \lim_{x\to\infty} C_R(x,t) = 0$$

$$\overline{C}_O(x,s) = \frac{C_O^*}{s} + A(s)\, e^{-\sqrt{s/D_O}\,x}$$

$$\overline{C}_R(x,s) = B(s)\, e^{-\sqrt{s/D_R}\,x}$$

$$D_O \left(\frac{\partial \bar{C}_O(x,s)}{\partial x} \right)_{x=0} + D_R \left(\frac{\partial \bar{C}_R(x,s)}{\partial x} \right)_{x=0} = 0$$

Dobivamo B

$$\frac{C_O^*}{s} + A(s) = -\xi \theta A(s)$$

Slijedi iz reverzibilnosti

$$\bar{C}_O(x,s) = \frac{C_O^*}{s} - \frac{C_O^* e^{-(s/D_O)^{1/2}x}}{s(1+\xi\theta)}$$

$$\bar{C}_R(x,s) = \frac{\xi C_O^* e^{-(s/D_R)^{1/2}x}}{s(1+\xi\theta)}$$

$$i = z\,F\,A\,c_O^* \frac{\sqrt{D_O/\pi t}}{1 + \sqrt{\frac{D_O}{D_R}}\; e^{\frac{zF(E-E^\circ)}{RT}}}$$

Ultramikroelektrode

Moguće provesti voltametrijski eksperiment ustaljenog stanja

$$i_s = z\,F\,A\,D_O c_O^* \frac{1}{r\left(1 + \frac{D_O}{D_R} e^{\frac{zF(E-E^\circ)}{RT}}\right)}$$

Struja na stacionarnoj sferičnoj (vrijedi i za disk) mikroelektrodi pri potencijalnu *E* u vremenu t_s pri kojem se uspostavlja ustaljeno stanje (nema promjene struje s vremenom)

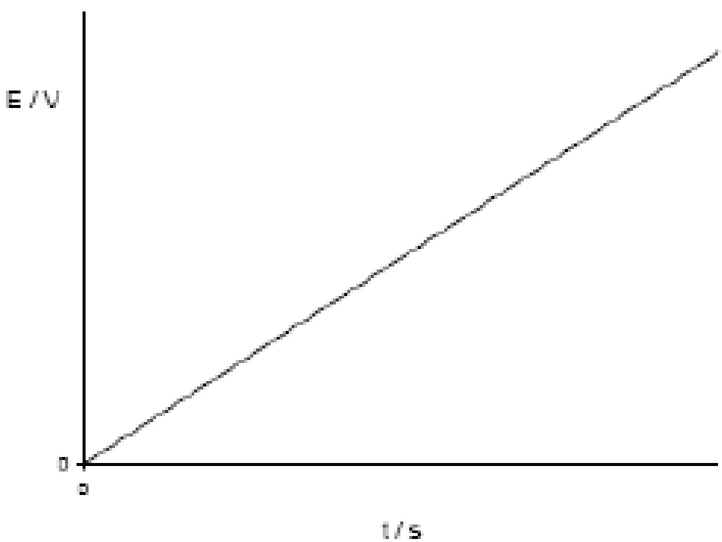
$$E = E_{1/2} + \frac{RT}{zF} \ln \frac{i_d - i}{i} \qquad E_{1/2} = E^\circ + \frac{RT}{zF} ln \frac{D_O}{D_R}$$

Ponašanje analogno kapajućoj živinoj elektrodi uz „linearnu” ovisnost poluvalnog potencijala o omjeru difuzijskih koeficijenata O i R

Voltametrija linearne promjene potencijala
(*Linear Sweep Voltametry)*

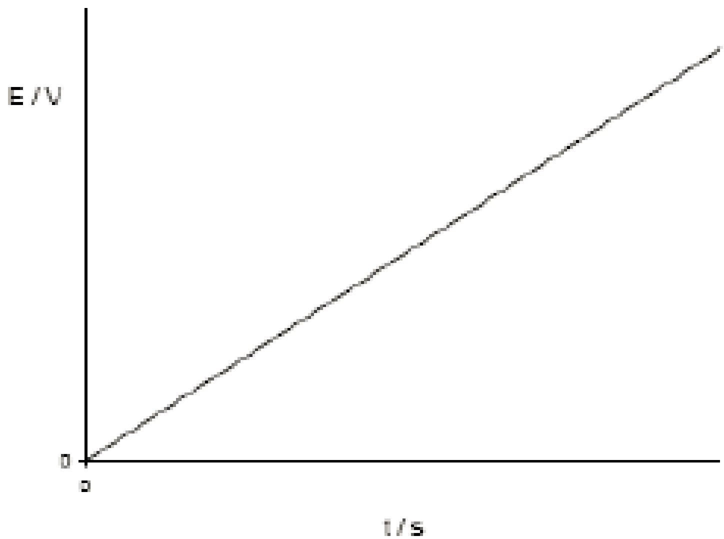
Dosadašnji slučajevi - konstantni potencijal

Što se događa ukoliko tijekom eksperimenta mijenjamo potencijal?

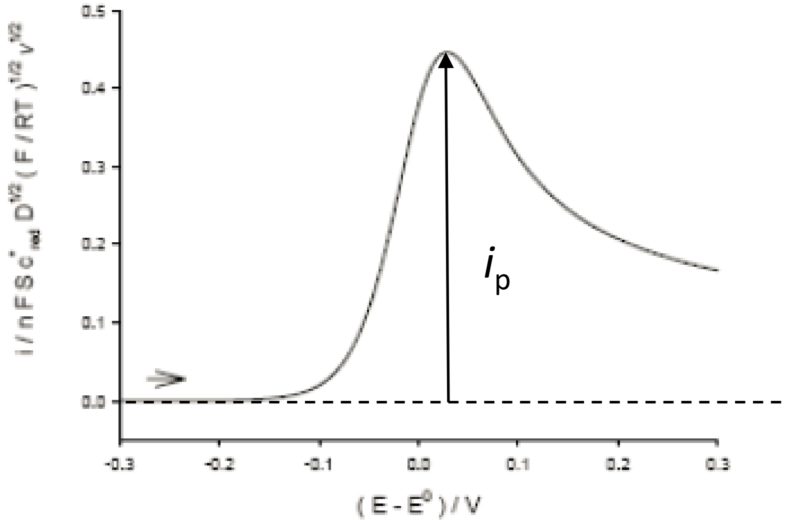


Voltametrija linearne promjene potencijala
(*Linear Sweep Voltametry)*

pobuda



odziv (reverzibilni slučaj!)



$$E_p = E_{1/2} \pm 1{,}11RT/zF$$

Pozitivan pomak za anodni pik, a negativan za katodni

$$i_p = 0.446z\ F\ A\ c_O^* \sqrt{\frac{zFvD_O}{RT}}$$

Anodni pik!, v - brzina promjene potencijala!

Voltametrija linearne promjene potencijala
(*Linear Sweep Voltametry)*

Slučaj linearne promjene potencijala za stacionarnu planarnu elektrodu

$E = E_i - vt$ $\quad E_i -$ početni potencijal $\quad v -$ brzina promjene potencijala (rampa)

$$\int_0^t \frac{i}{\sqrt{t-\tau}}\, d\tau = z\, F\, A\, c_{\mathrm{O}}^* \frac{\sqrt{\pi D_{\mathrm{O}}}}{1 + \sqrt{\frac{D_{\mathrm{O}}}{D_{\mathrm{R}}}}\; e^{\frac{zF(E_i - vt - E^\circ)}{RT}}}$$

Struja se najčešće prevodi u bezdimenzijsku veličinu i odgovarajuća funkcija se numerički integrira čime se dobiva vremenska ovisnost struje

$$i = zF\, A\, c_{\mathrm{O}}^* \sqrt{\frac{\pi z F v D_{\mathrm{O}}}{RT}}\, \chi(t)$$

χ(t) – funkcija čije se vrijednosti dobivaju numeričkim integriranjem

Maksimalna struja (*peak current*)
Randels-Ševčikova jednadžba

$$|i_p| = 0.446 zF\, A\, c_{\mathrm{O}}^* \sqrt{\frac{F v D_{\mathrm{O}}}{RT}}$$

Potencijal (katodnog) maksimuma

$$E_p = E_{1/2} - 1{,}11 RT/zF$$

$$\frac{i_p}{c_0 v^{1/2}} = kz^{3/2} D_O^{1/2} = k'$$

Temelj određivanja c_O ili D_O

Provjera reverzibilnosti elektrodne reakcije

Potencijal vrha vala (pika)

$$E_p = E_{1/2} - 0{,}0285/z$$

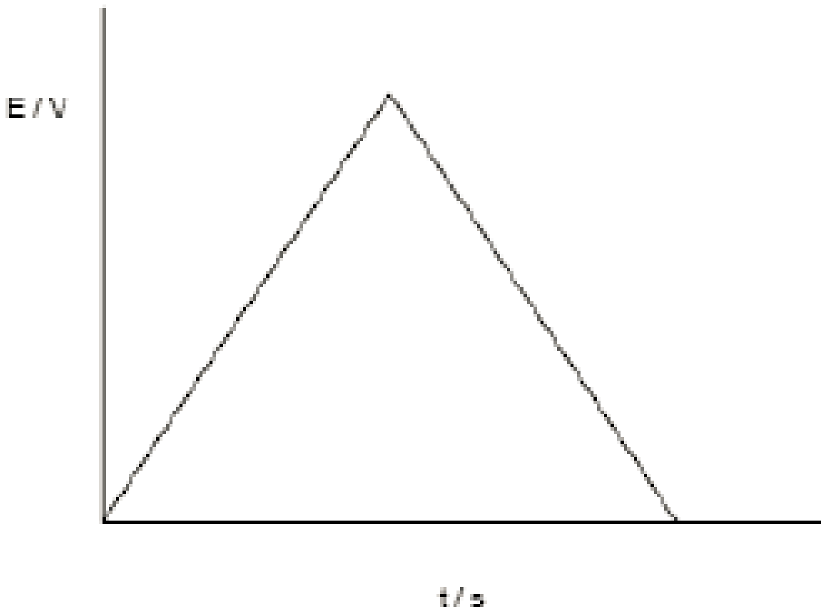
Potencijal polovice vrha vala (pika)

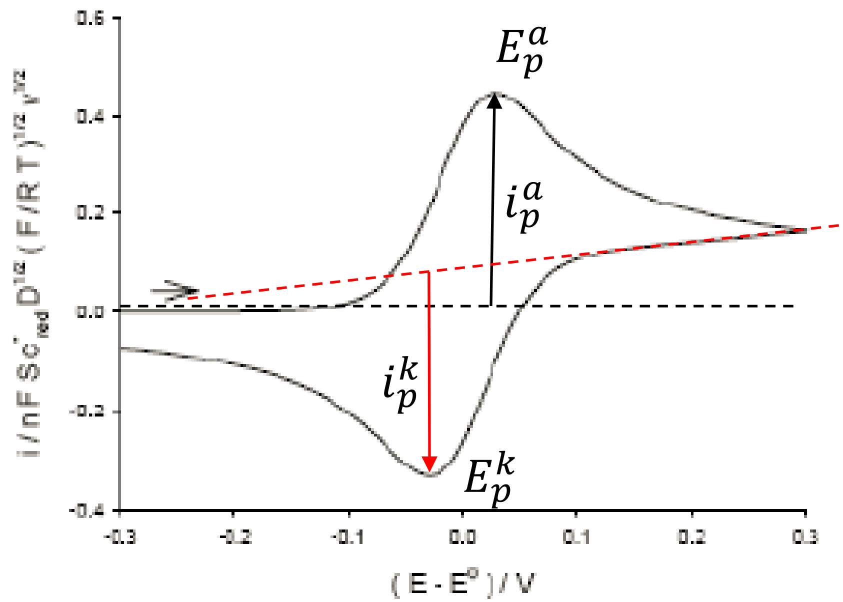
$$E_{p/2} = E_{1/2} + 0{,}028/z$$

$$E_p - E_{p/2} = 0{,}0565/z$$

Ciklička voltametrija

Što ako se smjer promjene potencijala „okrene” nakon postizanja E_p?

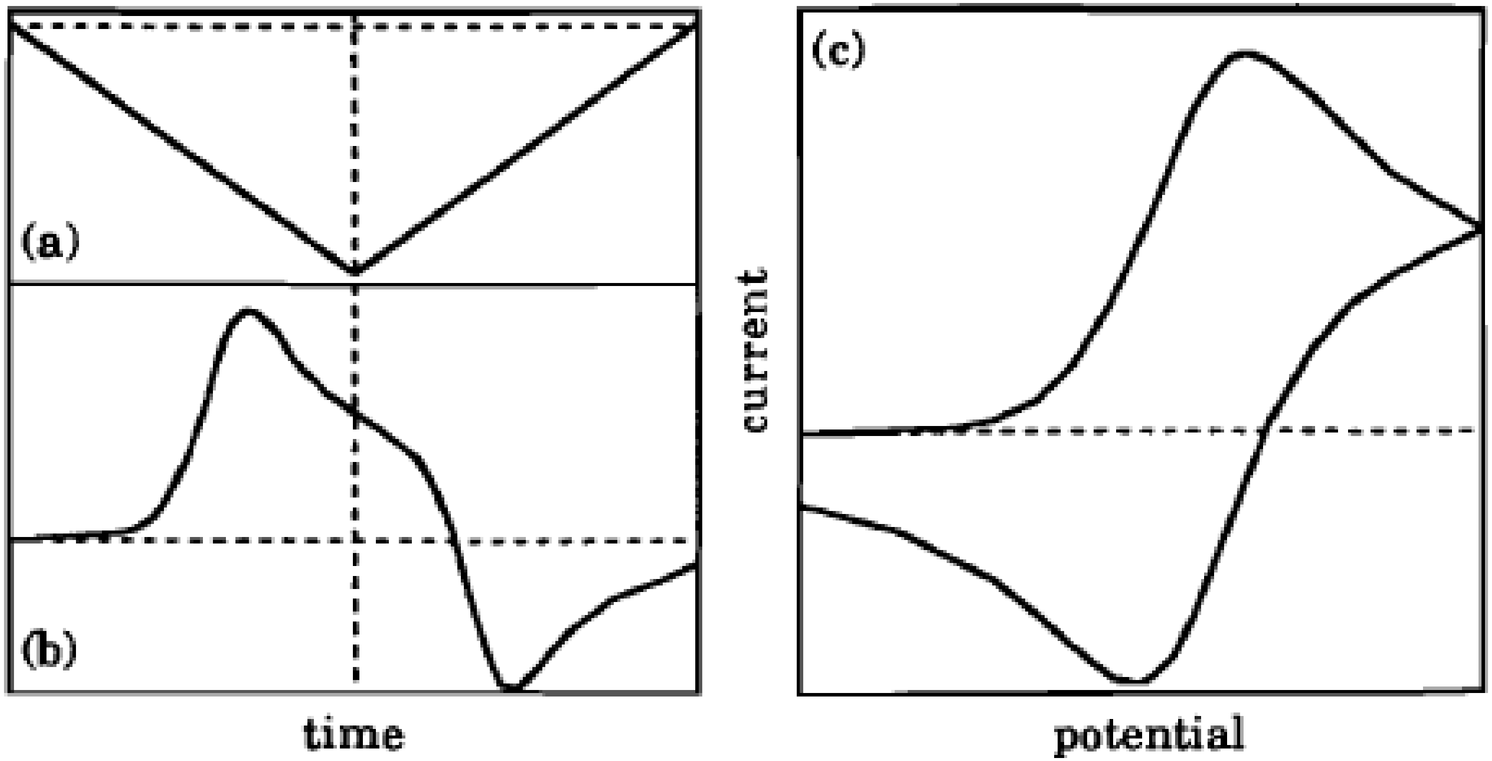




$$E_p^a - E_p^k = \frac{57\text{mV}}{z}$$

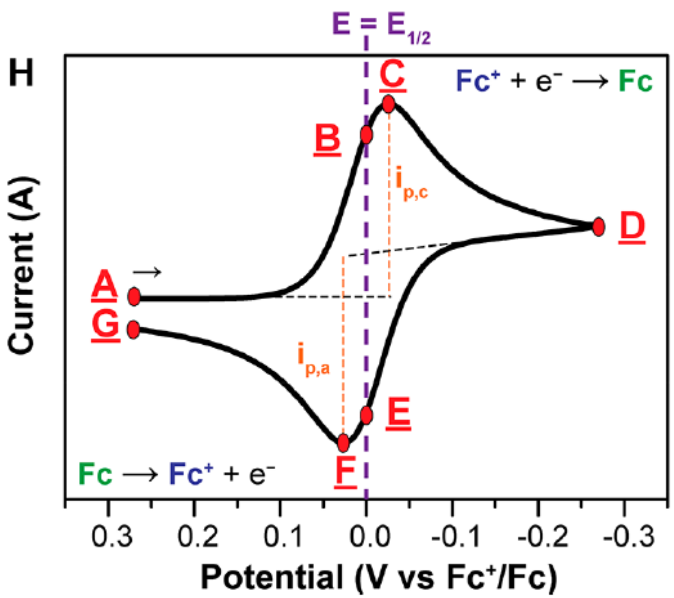
$$\left|i_p^a\right| = \left|i_p^k\right|$$

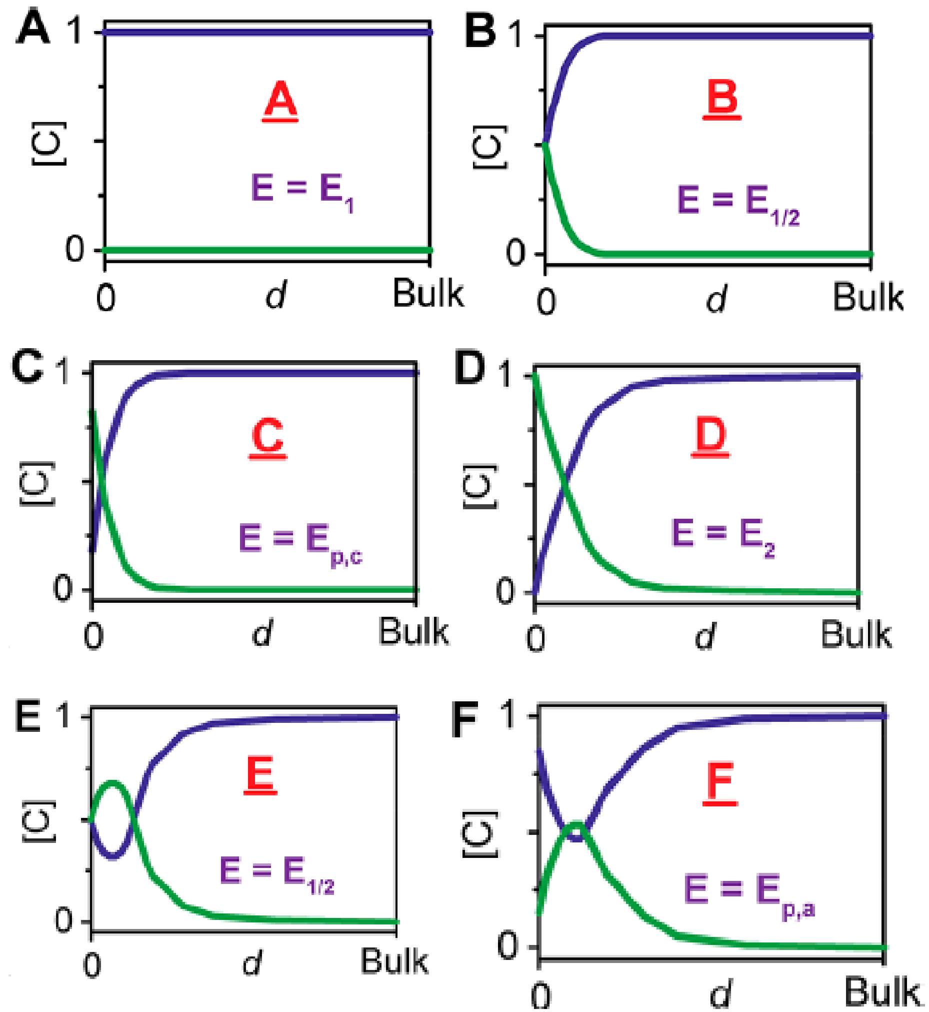
Ciklička voltametrija

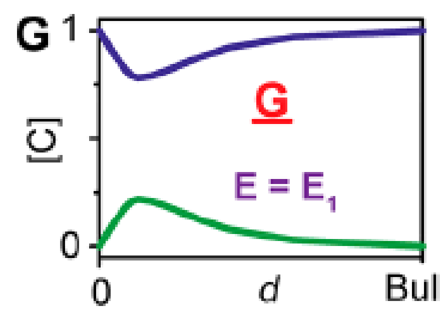


Ciklička voltametrija

Koncentracijski profili tijekom snimanja cikličkog voltamograma.

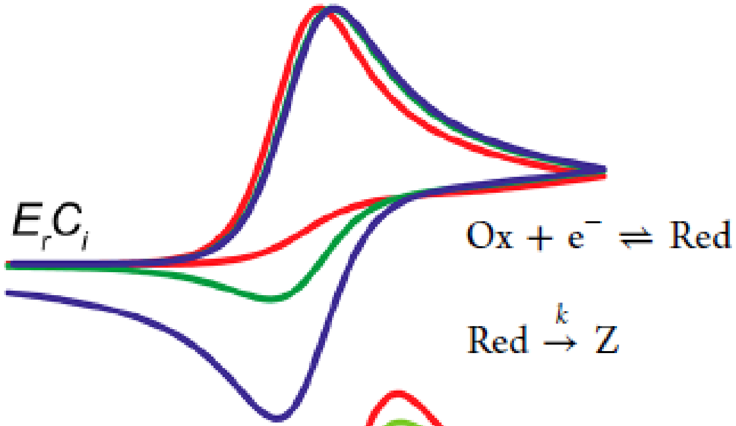




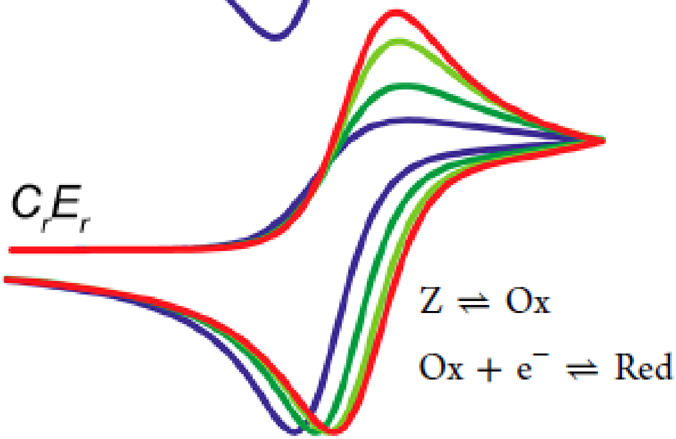


A Practical Beginner's Guide to Cyclic Voltammetry

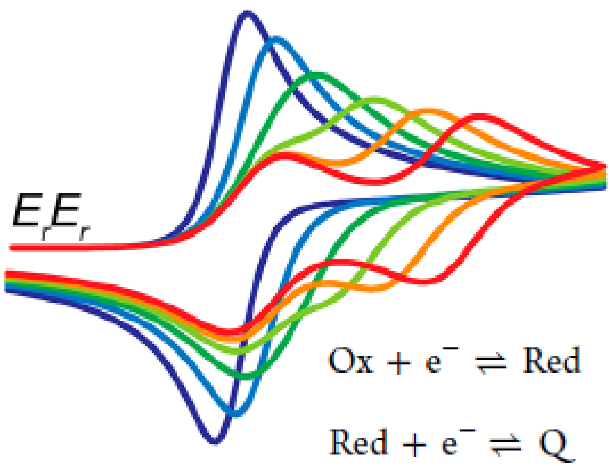
Noémie Elgrishi, Kelley J. Rountree, Brian D. McCarthy, Eric S. Rountree, Thomas T. Eisenhart, and Jillian L. Dempsey*



- Ireverzibilna kemijska promjena produkta reverzibilne elektrokemijske reakcije
- Prikazani ciklički voltamogrami: Različite brzine promjene potencijala



- Reverzibilna elektrokemijska reakcija produkta reverzibilne kemijske reakcije
- Prikazani ciklički voltamogrami: Različite konstante brzine unaprijedne (kemijske) reakcije



- Dvije uzastopne elektrokemijske reakcije
- Prikazani ciklički voltamogrami: Različita razlika u poluvalnim potencijalima elektrokemijskih reakcija

Reaction Parameters Influencing Cobalt Hydride Formation Kinetics: Implications for Benchmarking H_2-Evolution Catalysts

Noémie Elgrishi, Daniel A. Kurtz, and Jillian L. Dempsey*

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290, United States

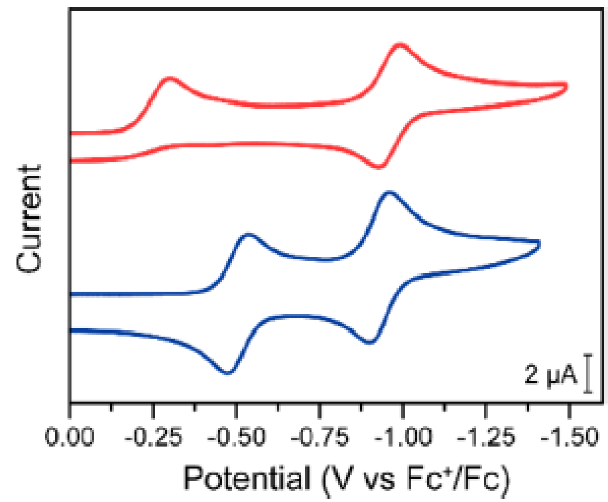
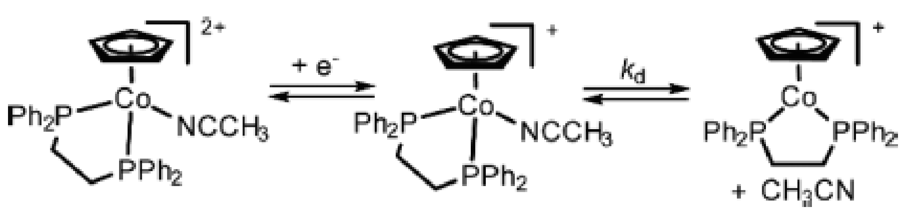
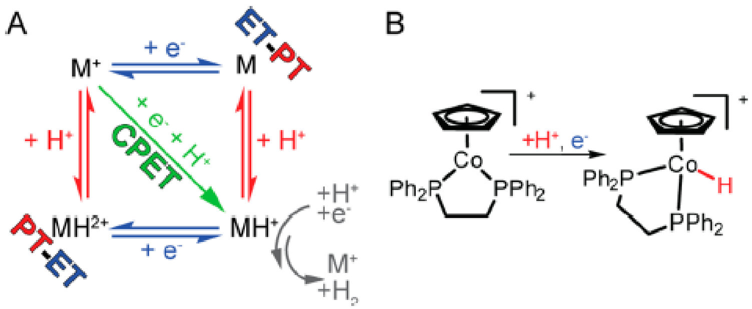


Figure 1. CVs of $[Co(Cp)(dppe)(CH_3CN)](PF_6)_2$ in CH_3CN (0.5 mM, blue trace) and in CH_2Cl_2 (0.5 mM, red trace). The voltammograms were recorded at 100 mV/s in 0.25 M $[Bu_4N][PF_6]$.



Scheme 1



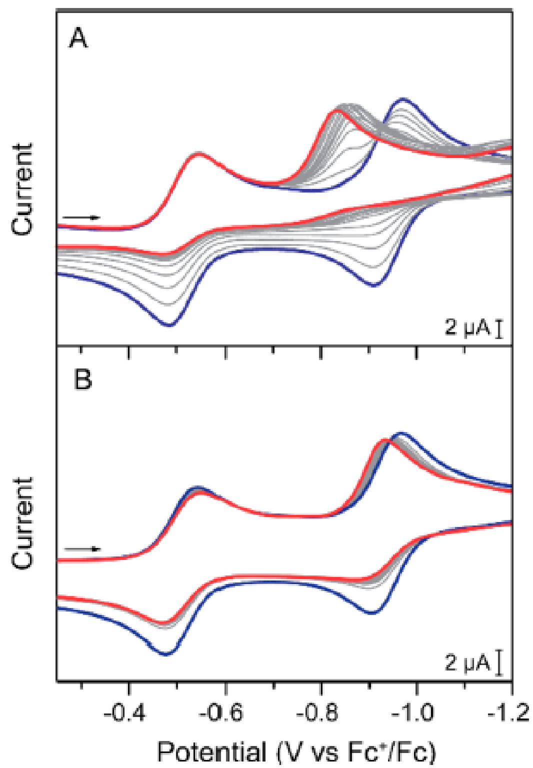
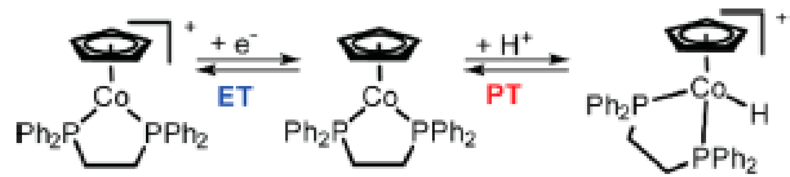
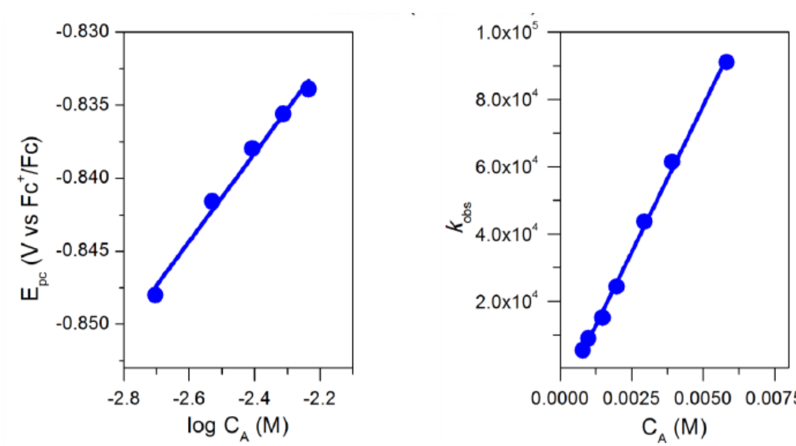


Figure 2. CVs of $[Co(Cp)(dppe)(CH_3CN)](PF_6)_2$ in the absence of a proton source (blue) and as (A) 4-cyano-anilinium ($pK_a = 7$)[26] or (B) benzoic acid ($pK_a = 21.51$)[27] is titrated into an CH_3CN solution (gray to red). The voltammograms were recorded at 100 mV/s in 0.25 M $[Bu_4N][PF_6]$.

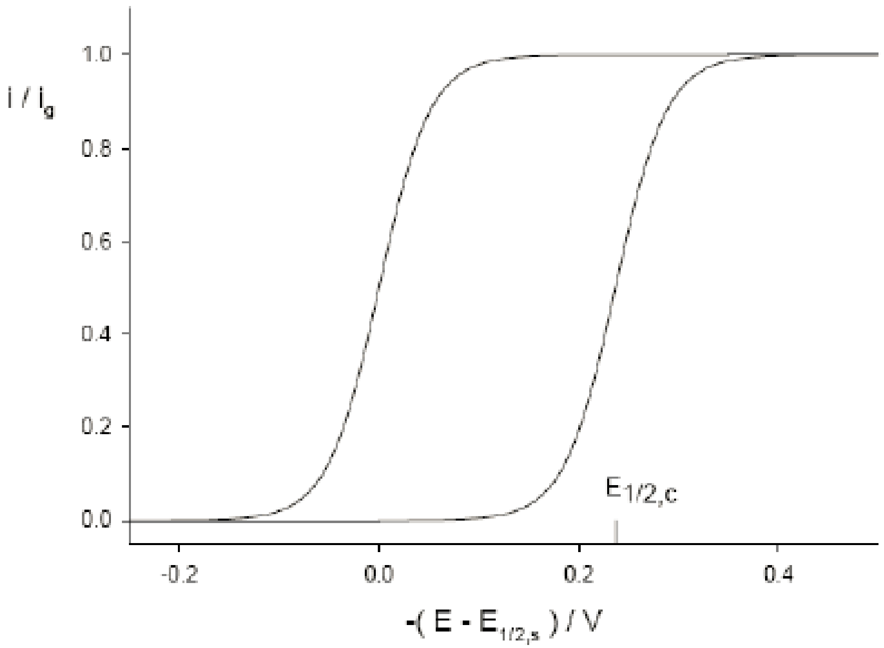


$$E_p = E_{1/2} - \frac{RT}{F}(0.78) + \frac{RT}{2F}\ln\left(\frac{k_{obs}RT}{Fv}\right)$$

$$k_{obs} = k_{PT}C_A$$



Polarografsko / voltametrijsko određivanje konstanti ravnoteže kompleksiranja

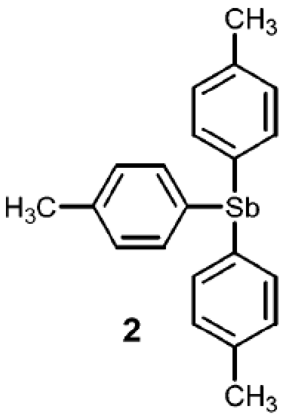


$$E_{1/2,c} = E_{1/2,s} - \frac{RT}{nF} \ln \{1 + \beta_1 [L]\}$$

$$E_{1/2,c} = E_{1/2,s} - \frac{RT}{nF} \ln\left(1 + \beta_1[L^-] + \beta_2[L^-]^2 + \beta_3[L^-]^3 + \ldots\right)$$

Cyclic Voltammetric Study of Intramolecular and Intermolecular Hypervalent Organoantimony Complexes with Sb···N Bonding

Katsuyoshi Hoshino,*,† Tomohisa Ogawa,† Shuji Yasuike,*,§ Hiroko Seki,‡ Jyoji Kurita,§ Tatsuhiro Tokunaga,‡ and Kentaro Yamaguchi‡



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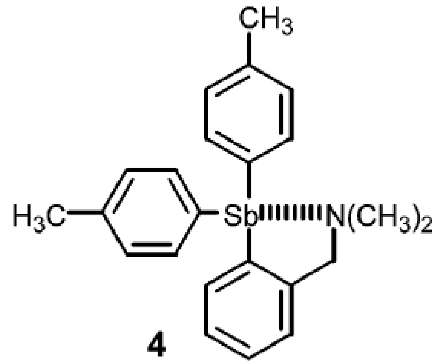

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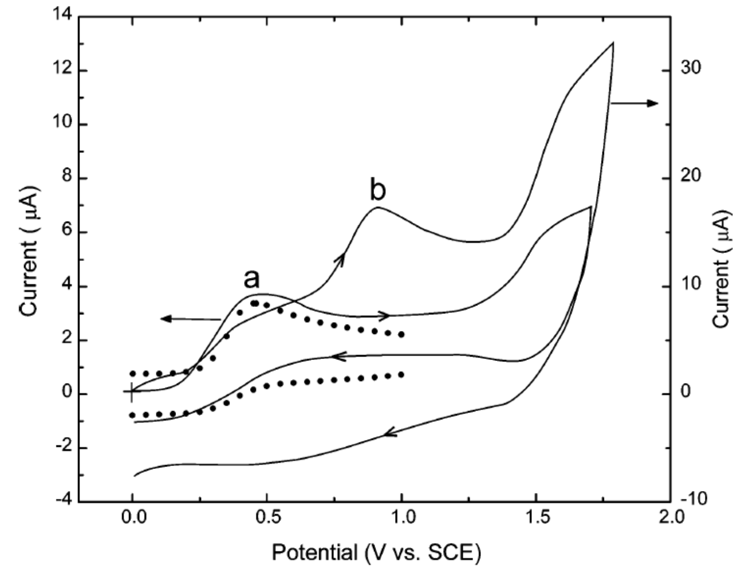
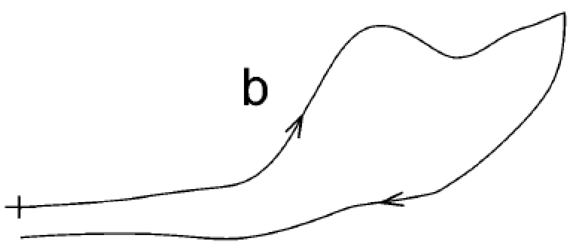




$$R_3Sb \rightarrow R_3Sb^{+}OH$$

$$\mathbf{4}_N \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathbf{4}_B$$

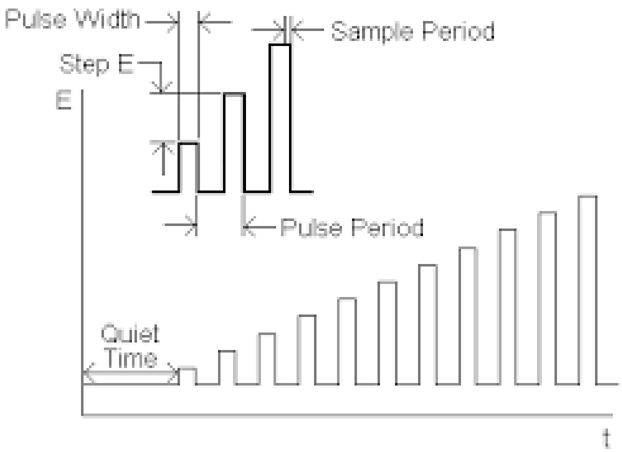
$$\mathbf{4}_B \rightarrow \mathbf{4}_B{}^{+}\text{-OH}$$

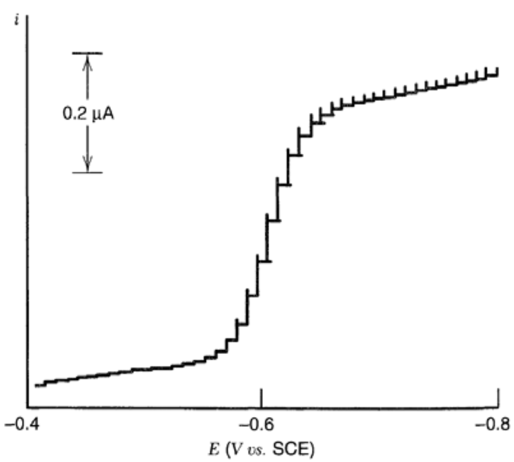
$$i_d/i_k = 1.02 + \frac{0.531\sqrt{b}}{K\sqrt{l}}$$

$$\text{with } b = \frac{\alpha n_a F v}{RT},\ l = k_f + k_b, \text{ and } K = k_f/k_b$$

Pulsne voltametrijske tehnike

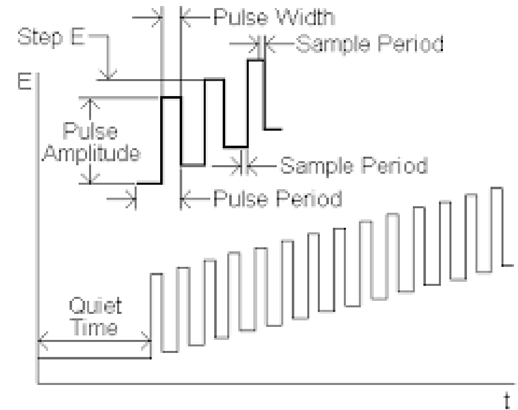
„Normalna”

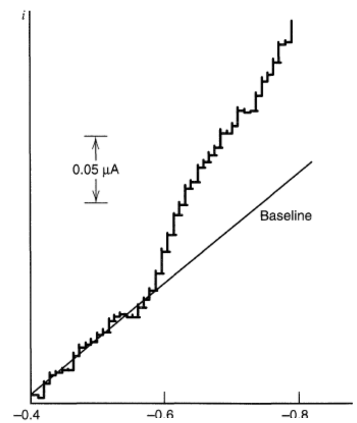


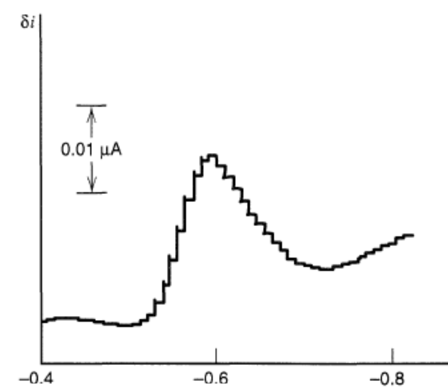


$$i_d = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}(\tau - \tau')^{1/2}}$$

Diferencijalna



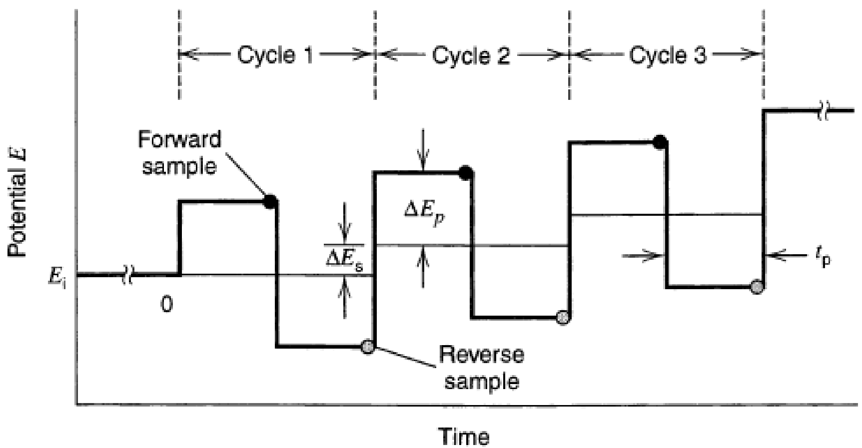


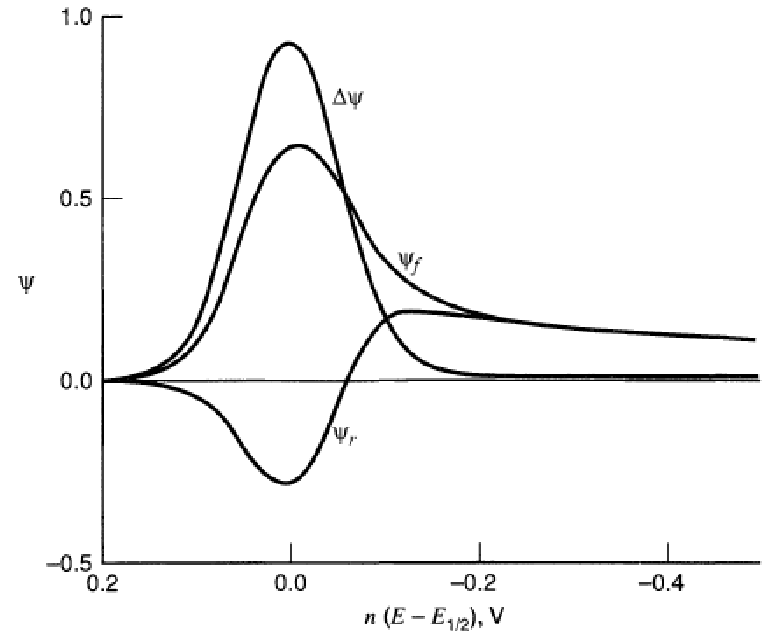


$$E_{max} = E^{0'} + \frac{RT}{nF}\ln\left(\frac{D_R}{D_O}\right)^{1/2} - \frac{\Delta E}{2} = E_{1/2} - \frac{\Delta E}{2}$$

$$(\delta i)_{max} = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}(\tau - \tau')^{1/2}} \cdot \left(\frac{1-\sigma}{1+\sigma}\right) \qquad \sigma = \exp\left(\frac{nF}{RT}\frac{\Delta E}{2}\right)$$

Pravokutnovalna voltametrija
(*Square Wave Voltametry*)



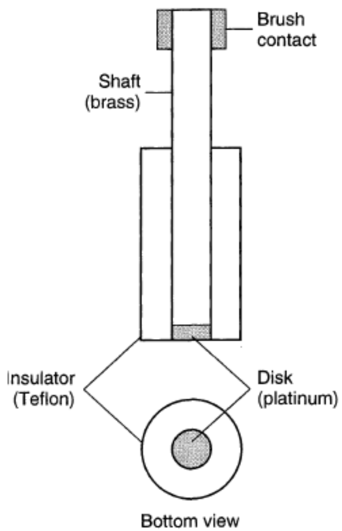


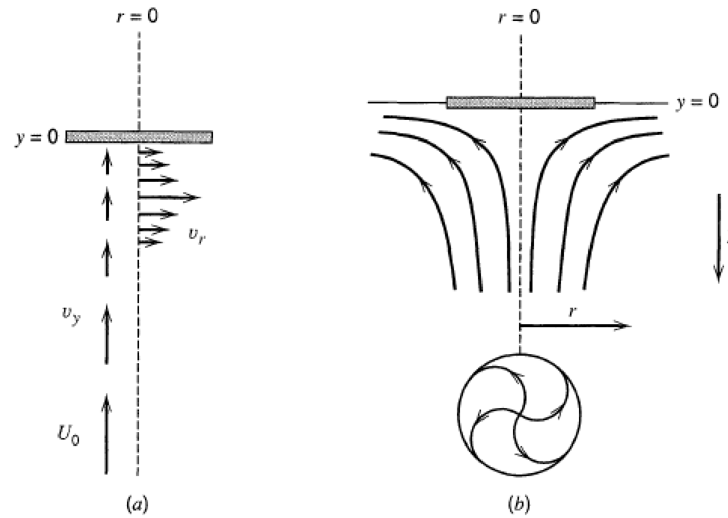
$$\Delta i_p = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t_p^{1/2}}\,\Delta\psi_p$$

Hidrodinamički kontrolirani uvjeti

$$\mathbf{J}_j = -D_j \nabla C_j - \frac{z_j F}{RT} D_j C_j \nabla \phi + C_j \mathbf{v}$$

Rotirajuća disk elektroda





Levicheva jednadžba

$$i_{l,c} = 0.62 n F A D_O^{2/3} \omega^{1/2} \nu^{-1/6} C_O^*$$

Rotirajuća disk elektroda
- ravnotežni uvjeti (reverzibilni proces)

$$i = 0.62nFAD_O^{2/3}\omega^{1/2}\nu^{-1/6}[C_O^* - C_O(y=0)]$$

$$i = i_{l,c}\left[\frac{C_O^* - C_O(y=0)}{C_O^*}\right]$$

$$\boxed{E = E_{1/2} + \frac{RT}{nF}\ln\frac{(i_{l,c} - i)}{(i - i_{l,a})}}$$

$$\boxed{E_{1/2} = E^{0'} + \frac{RT}{nF}\ln\left(\frac{D_R}{D_O}\right)^{2/3}}$$