

Voltometrija

Cottrellova jednadžba

Fickov zakon

$$\frac{\partial c_0(x, t)}{\partial t} = D_0 \frac{\partial^2 c_0(x, t)}{\partial x^2}$$

Rubni uvjeti

$$c_0(x, 0) = c_0^*$$

$$\lim_{x \rightarrow \infty} c_0(x, t) = c_0^*$$

$$c_0(0, t) = 0, \quad t > 0$$

Rješavanje diferencijale jednadžbe

Laplaceova transformacija

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

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 jednačba:
$$\frac{\partial c_0(x, t)}{\partial t} = D_0 \frac{\partial^2 c_0(x, t)}{\partial x^2}$$

Nakon transformacije:
$$\frac{\partial^2 \bar{c}_0(x, s)}{\partial x^2} - \frac{s}{D_0} \bar{c}_0(x, s) = -\frac{c_0^*}{D_0}$$

Rješavamo traženjem: CF
$$\frac{\partial^2 \bar{c}_{0,CF}(x, s)}{\partial x^2} - \frac{s}{D_0} \bar{c}_{0,CF}(x, s) = 0$$

$$\bar{c}_0(x, s) = CF + PI$$

PI
$$\bar{c}_{0,PI}(x, s) = k$$

Nalaženjem CF i PI te uvrštavanjem rubnih uvjeta dobivamo:

$$\bar{c}_O(x, s) = \frac{c_O^*}{s} - \frac{c_O^*}{s} e^{-x\sqrt{s/D_0}}$$

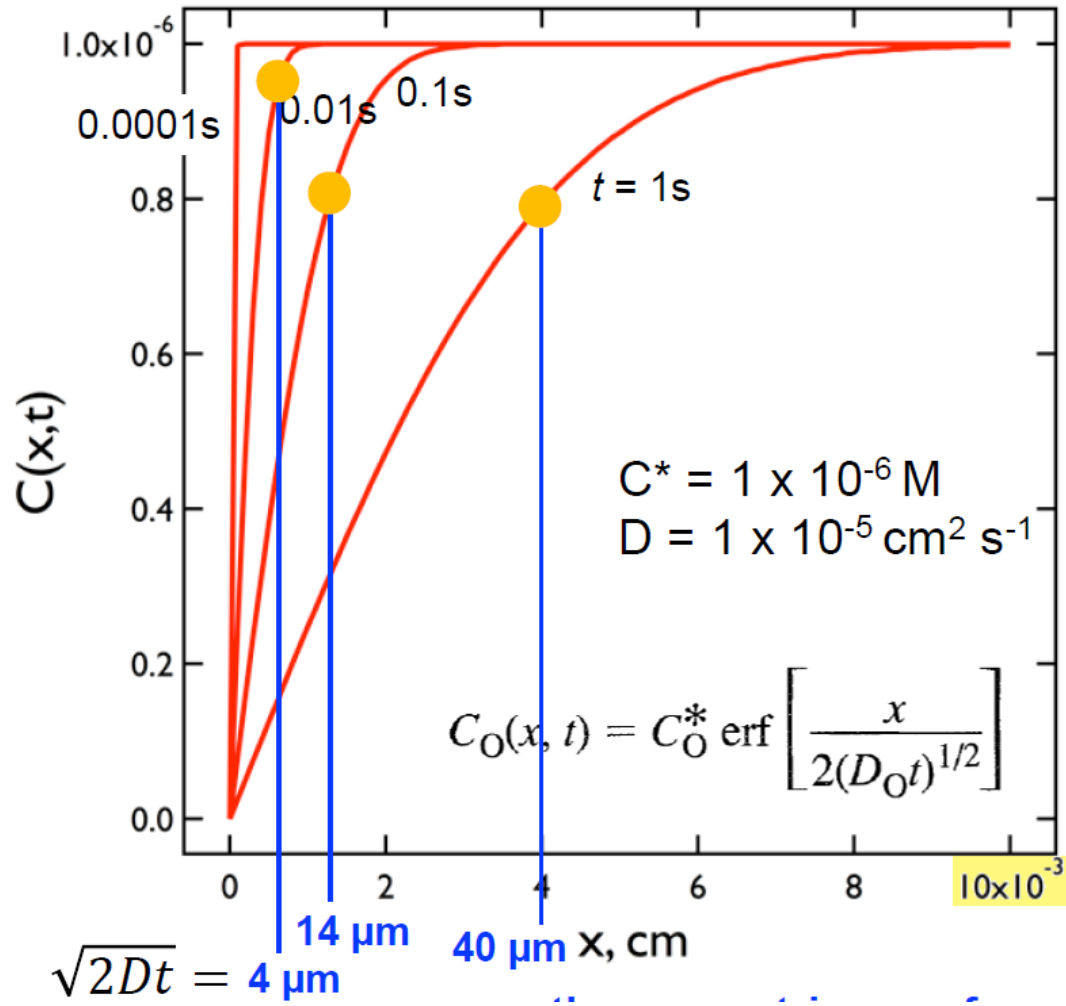
Inverzna Laplaceova transformacija daje rješenje jednadžbe

Koncentracijski profil u difuzijski kontroliranim uvjetima na planarnoj elektrodi

$$c_O(x, t) = c_O^* \operatorname{erf} \left(\frac{x}{2\sqrt{tD_0}} \right)$$

$$l = \sqrt{2D_0t}$$

Debljina difuzijskog sloja



Iz koncentracijskog profila uvrštavanjem u 1. Fickov zakon dolazimo do difuzijskog toka J_0

$$J_0 = -D_0 \frac{\partial c_0(x, t)}{\partial x}$$

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

$$J_0 = D_0 c_0^* \frac{1}{2\sqrt{tD_0}} \frac{2}{\sqrt{\pi}} e^{\frac{-x^2}{4tD_0}}$$

$$J_0(0, t) = c_0^* \sqrt{\frac{D_0}{\pi t}}$$

Cottrellova jednačba

Planarna elektroda

$$i = zFAJ(0, t) = zFAc_0^* \sqrt{\frac{D_0}{\pi t}}$$

“Niski” potencijal

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

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

$$\begin{aligned}\frac{\partial C_{\text{O}}(x, t)}{\partial t} &= D_{\text{O}} \frac{\partial^2 C_{\text{O}}(x, t)}{\partial x^2} & \frac{\partial C_{\text{R}}(x, t)}{\partial t} &= D_{\text{R}} \frac{\partial^2 C_{\text{R}}(x, t)}{\partial x^2} \\ C_{\text{O}}(x, 0) &= C_{\text{O}}^* & C_{\text{R}}(x, 0) &= 0 \\ \lim_{x \rightarrow \infty} C_{\text{O}}(x, t) &= C_{\text{O}}^* & \lim_{x \rightarrow \infty} C_{\text{R}}(x, t) &= 0\end{aligned}$$

$$\begin{aligned}\bar{C}_{\text{O}}(x, s) &= \frac{C_{\text{O}}^*}{s} + A(s) e^{-\sqrt{s/D_{\text{O}}}x} \\ \bar{C}_{\text{R}}(x, s) &= B(s) e^{-\sqrt{s/D_{\text{R}}}x}\end{aligned}$$

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

Dobivamo B

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

Slijedi iz
reverzibilnosti

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

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

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

Slučaj sferične difuzije

Ovisnost struje o vremenu na stacionarnoj sferičnoj elektrodi

- Riješava se na analogan način uz prelazak na polarne koordinate

$$i = zFAc_0^* \sqrt{\frac{D_0}{\pi t}} + \frac{zFAD_0c_0^*}{r}$$

„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

$$i_s(\text{sfera}) = \frac{zFAD_0c_0^*}{r} = 4\pi rzFD_0c_0^*$$

$$i_s(\text{disk}) = 4rzFD_0c_0^*$$

$$i_s(\text{cilindar}) = \frac{2zFAD_0c_0^*}{r \ln t}$$

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 potencijalu E u vremenu t_s pri kojem se uspostavlja ustaljeno stanje (nema promjene struje s vremenom)

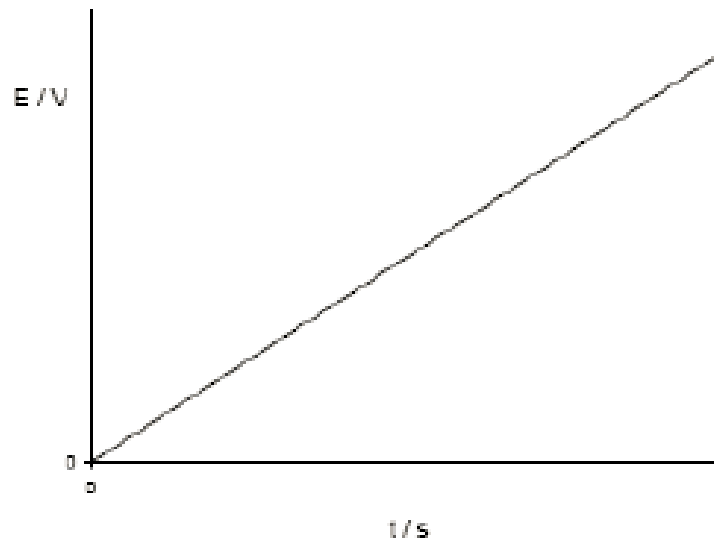
$$E = E_{1/2} + \frac{RT}{zF} \ln \frac{i_d - i}{i} \qquad E_{1/2} = E^\circ + \frac{RT}{zF} \ln \frac{D_O}{D_R}$$

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

Voltometrija linearne promjene potencijala (*Linear Sweep Voltametry*)

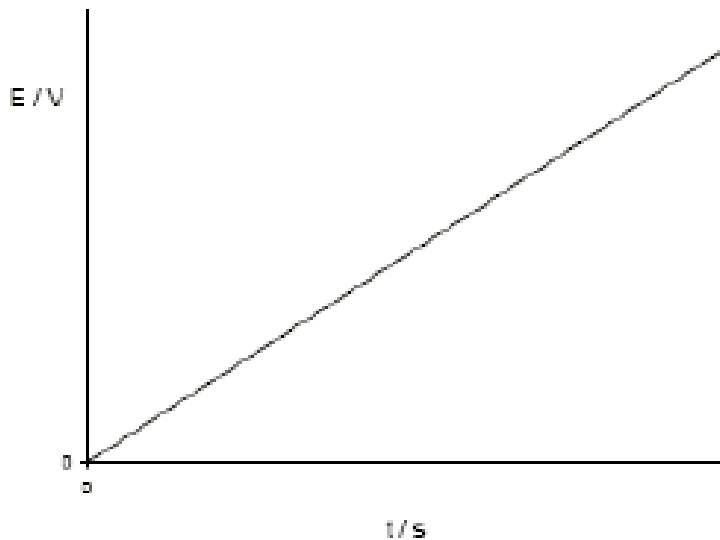
Dosadašnji slučajevi - konstantni potencijal

Što se događa ukoliko tijekom eksperimenta mijenjamo potencijal?



Voltametrija linearne promjene potencijala (Linear Sweep Voltametry)

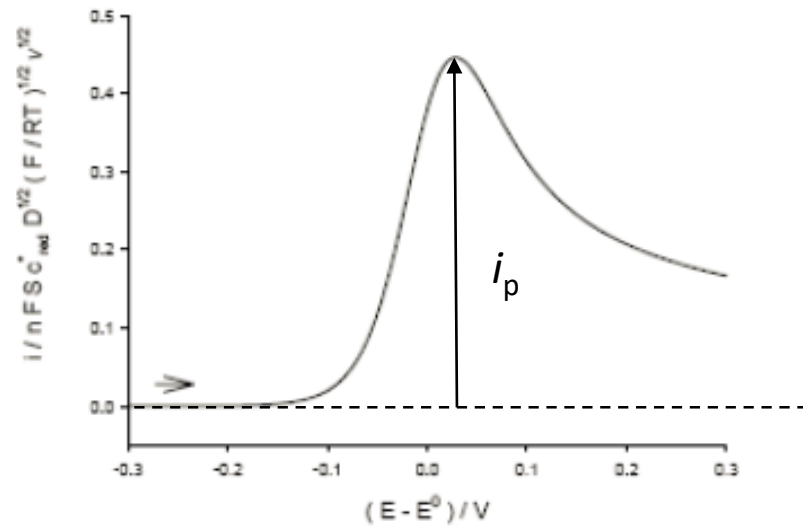
pobuda



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

Pozitivan pomak za anodni pik, a negativan za katodni

odziv (reverzibilni slučaj!)



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

Anodni pik!, v - brzina promjene potencijala!

Voltometrija linearne promjene potencijala (*Linear Sweep Voltametry*)

Slučaj linearne promjene potencijala za stacionarnu planarnu elektrodu

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

$$\int_0^t \frac{i}{\sqrt{t-\tau}} d\tau = z F A c_O^* \frac{\sqrt{\pi D_O}}{1 + \sqrt{\frac{D_O}{D_R}} e^{\frac{zF(E_i-vt-E^\circ)}{RT}}}$$

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

$$i = zF A c_O^* \sqrt{\frac{\pi zFvD_O}{RT}} \chi(t)$$

$\chi(t)$ – funkcija čije se vrijednosti dobivaju numeričkim integriranjem

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

Potencijal (katodnog) maksimuma

$$|i_p| = 0.446zF A c_O^* \sqrt{\frac{zFvD_O}{RT}}$$

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

$$\frac{i_p}{c_0 \nu^{1/2}} = kz^{3/2} D_0^{1/2} = k'$$

Temelj određivanja c_0 ili D_0

Provjera reverzibilnosti
elektrodne reakcije

Potencijal vrha vala (pika)

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

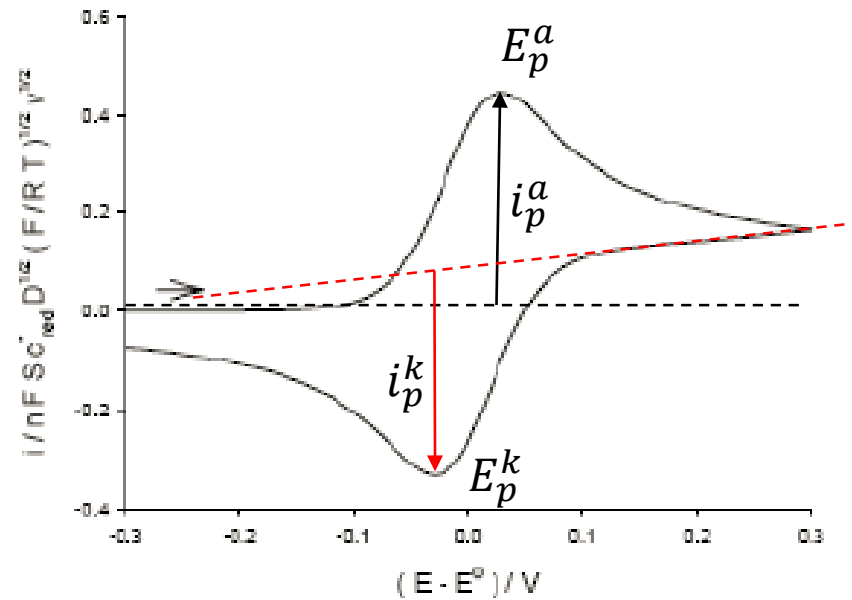
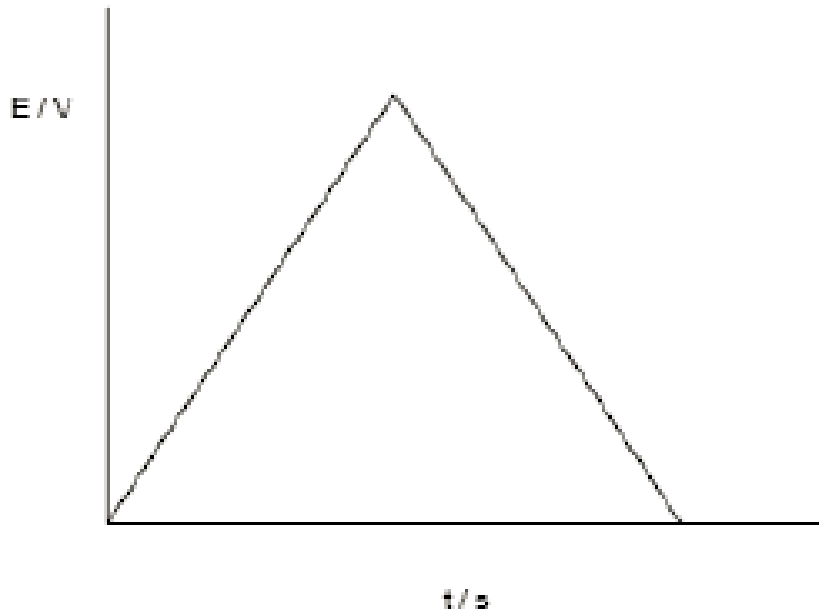
Potencijal polovice vrha vala (pika)

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

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

Ciklička voltametrija

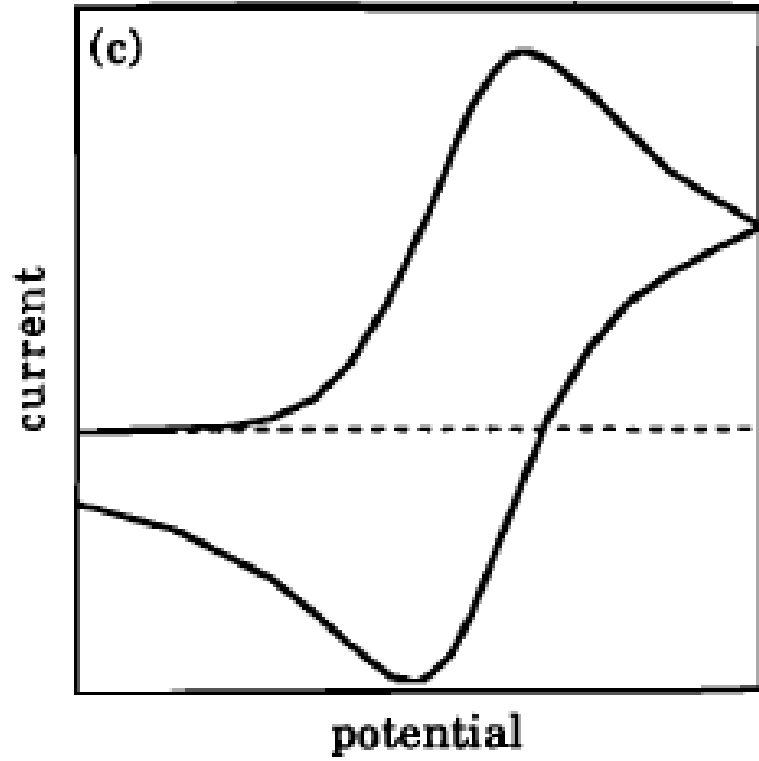
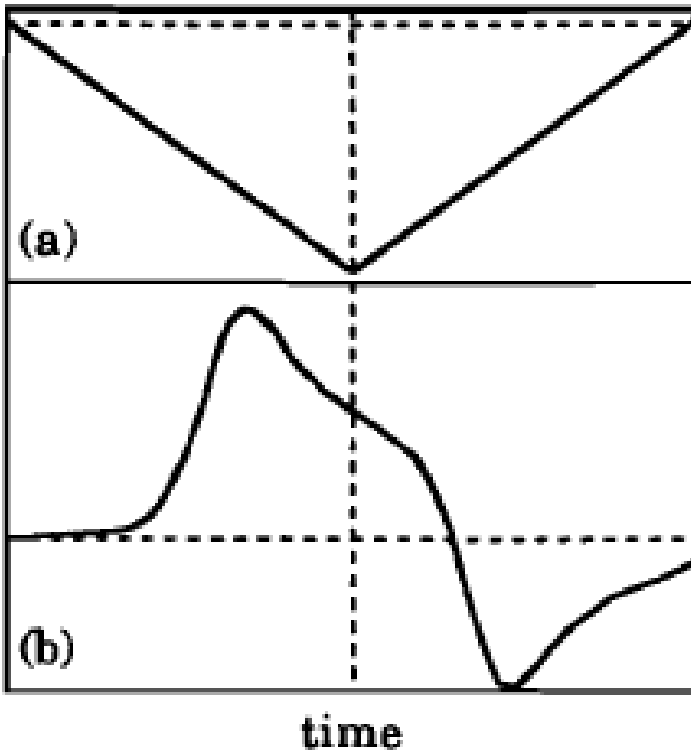
Što ako se smjer promjene potencijala „okrene“ nakon postizanja E_p ?



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

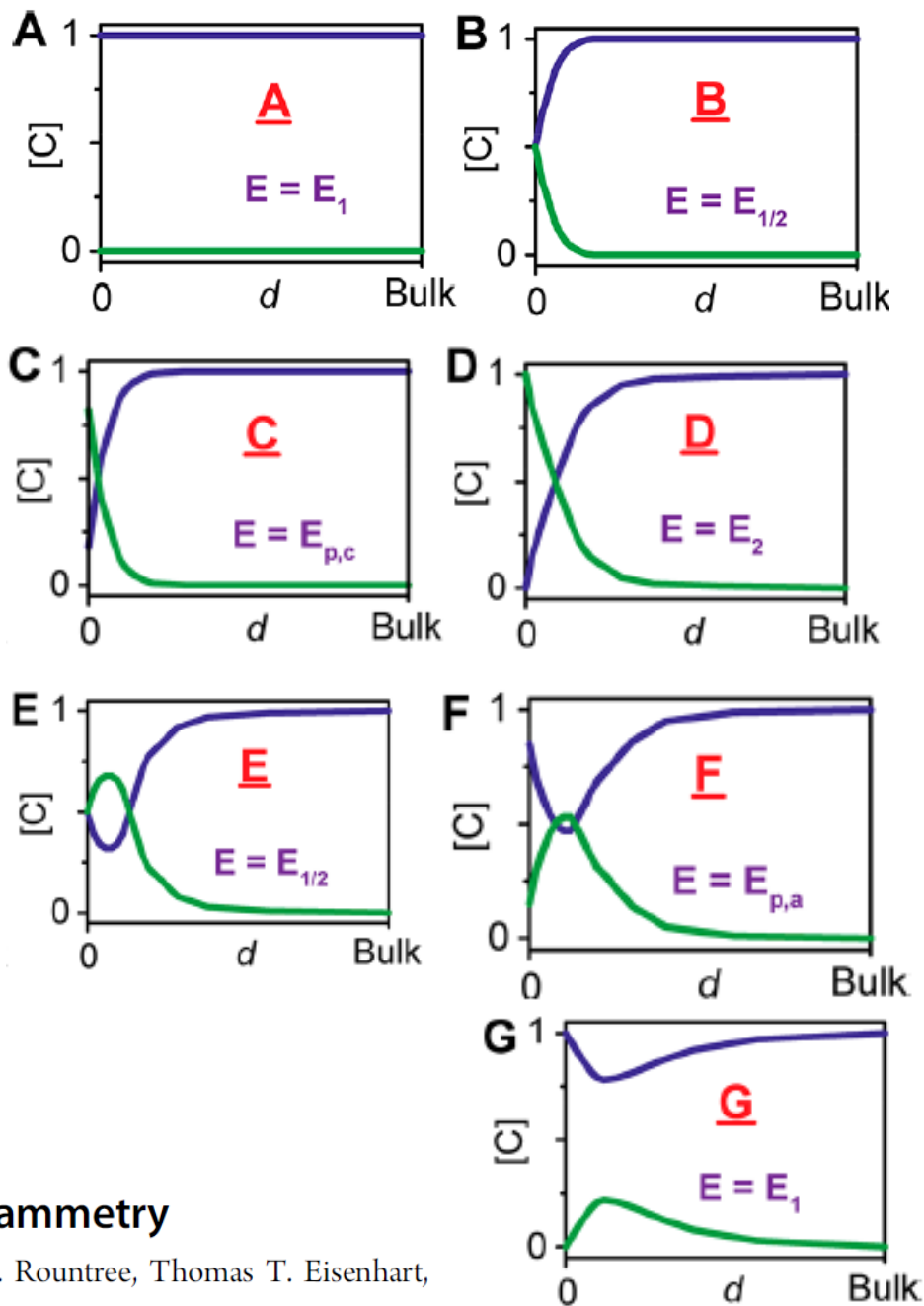
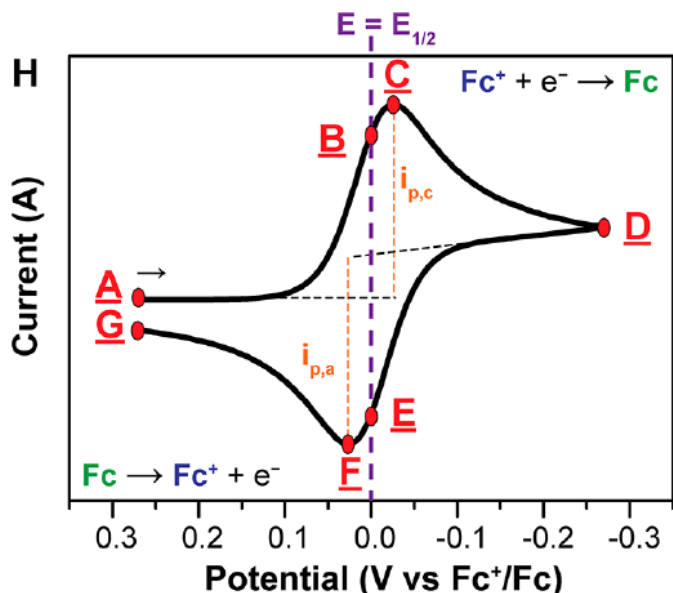
$$|i_p^a| = |i_p^k|$$

Ciklička voltametrija



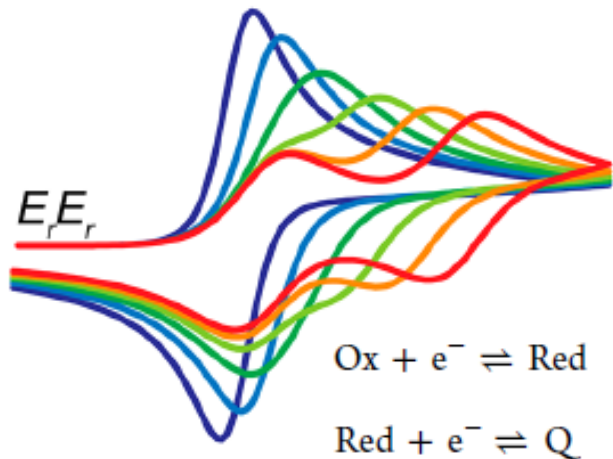
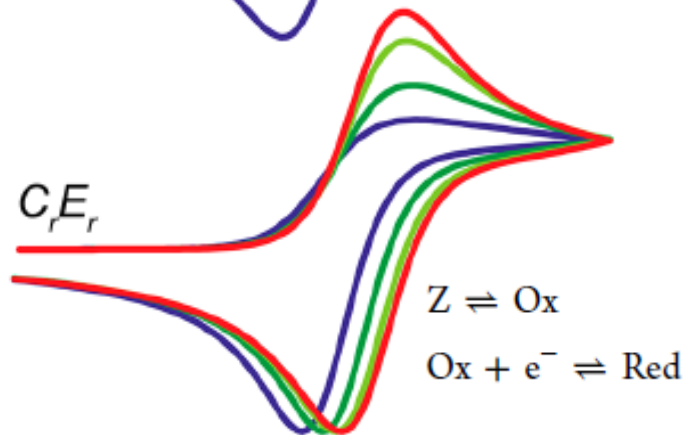
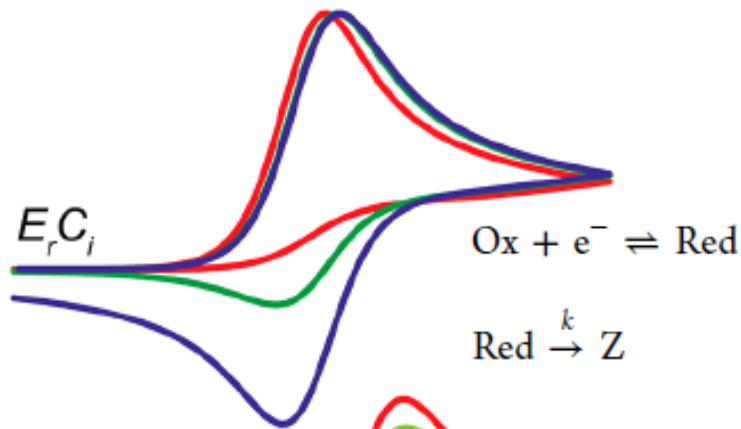
Ciklička voltometrija

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

Electrochemical Studies of the Oxidation Pathways of Catecholamines

M. D. Hawley, S. V. Tatawawadi, S. Piekarski, and R. N. Adams¹

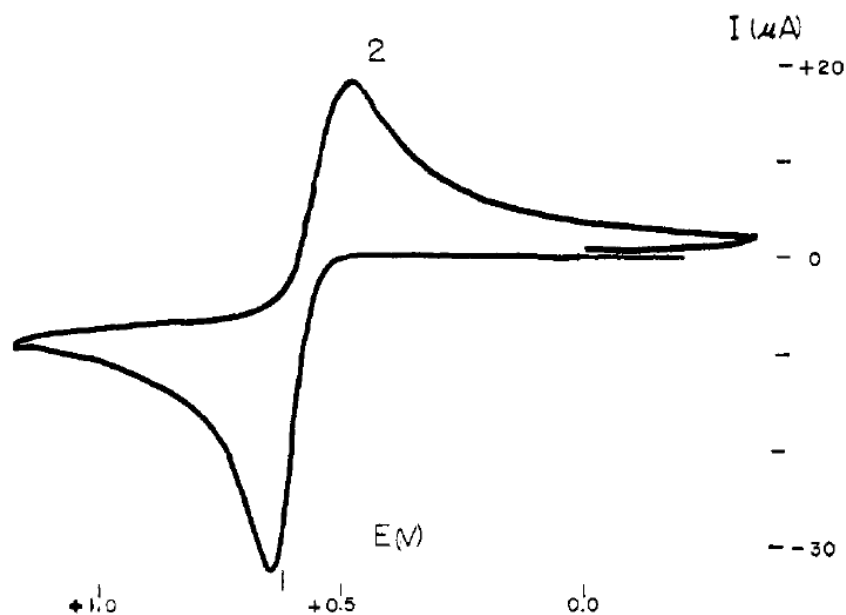
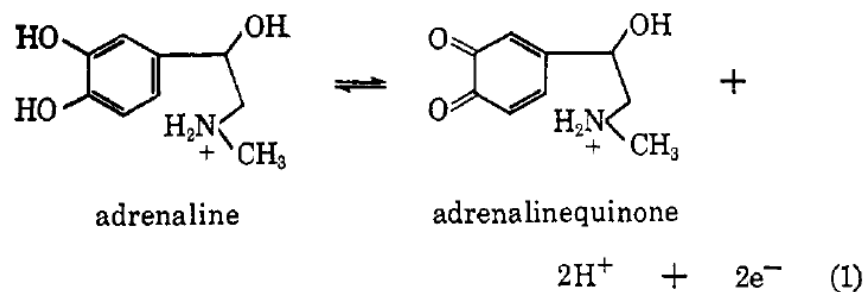


Figure 1. Cyclic voltammety of $1.3 \times 10^{-8} M$ adrenaline in $1.00 M \text{H}_2\text{SO}_4$. Scan rate is 2.40 v/min .

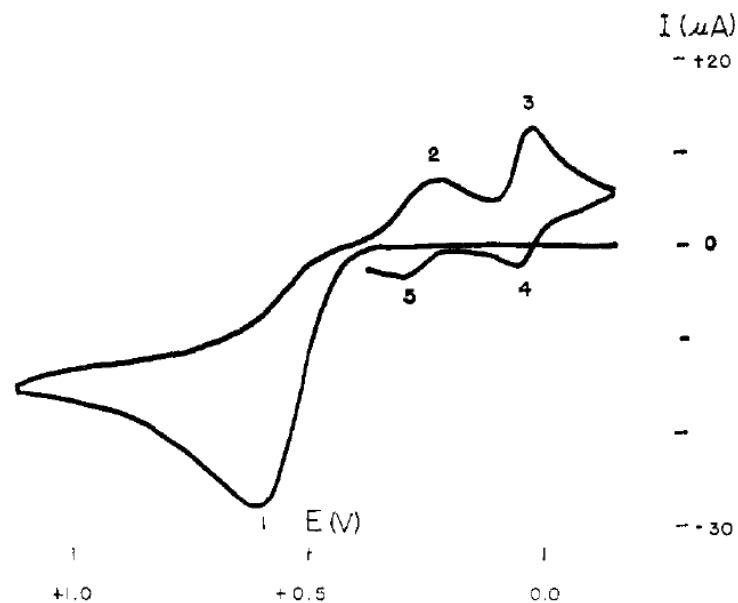


Figure 2. Cyclic voltammety of $1.7 \times 10^{-8} M$ adrenaline at $\text{pH } 3.0$. Scan rate is 2.40 v/min .

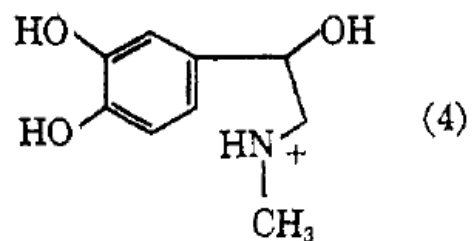
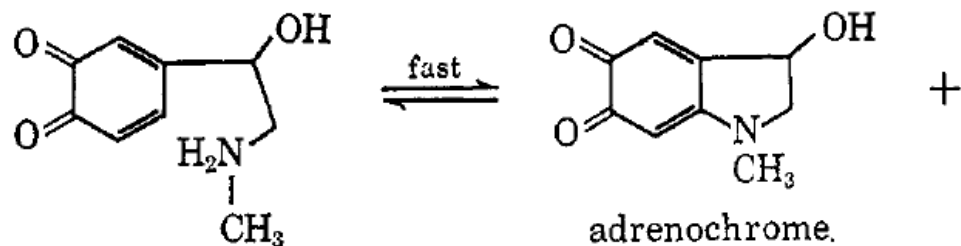
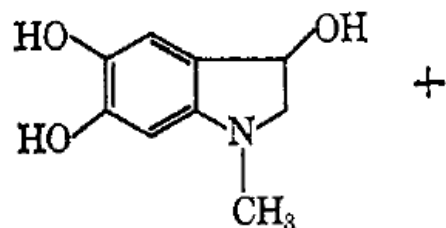
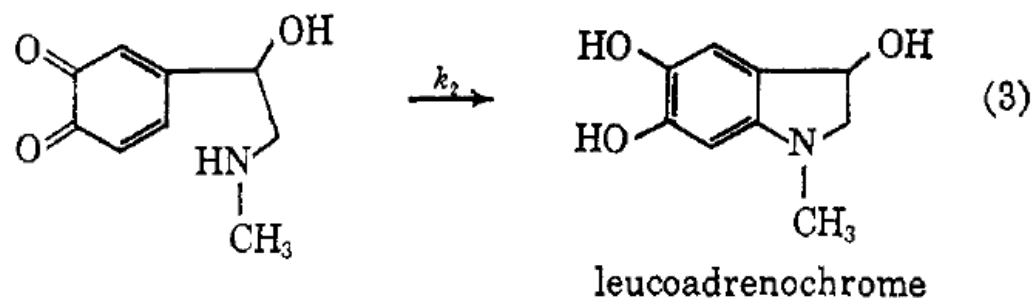
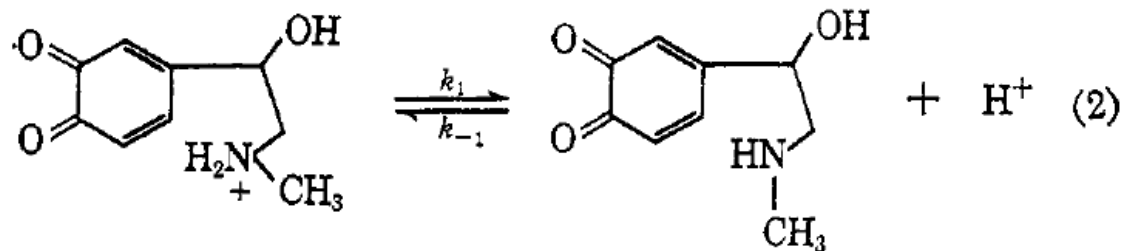
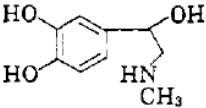
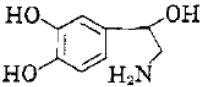
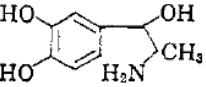
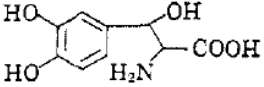
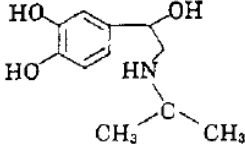


Table II. Cyclization Rate Constants for Oxidized Catecholamines^a

					
pH	Adrenaline	Noradrenaline	α -Methylnoradrenaline	Dopamine	Isoproterenol
3.5	0.025				
4.0	0.098				0.020
4.5	0.27				0.055
5.0	0.99		0.019		0.15
5.5			0.043		
6.0		0.066	0.12		
6.5		0.15	0.23		
7.0		0.36	0.50	0.038	
pK_a	8.88	8.90	8.85	8.92	8.87
$k_2^{a,b}$	7.4×10^3	5×10^1	8.1×10^1	...	1.2×10^8

^a Units of rate constants are sec^{-1} . ^b k_2 calculated as discussed in text (Discussion section), assuming K_a of oxidized catecholamine is the same as the reduced form.

Reaction Parameters Influencing Cobalt Hydride Formation Kinetics: Implications for Benchmarking H₂-Evolution Catalysts

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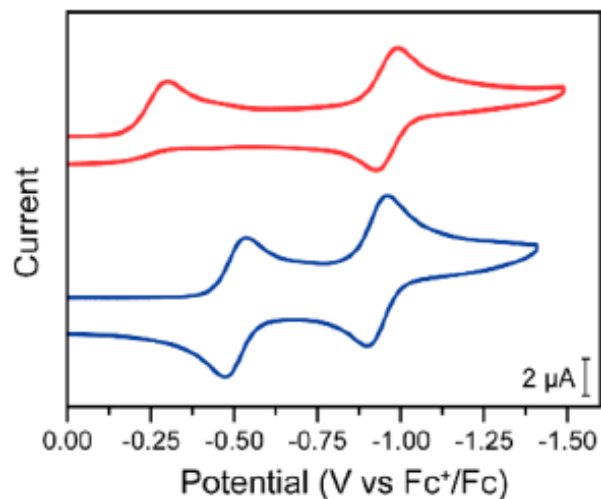
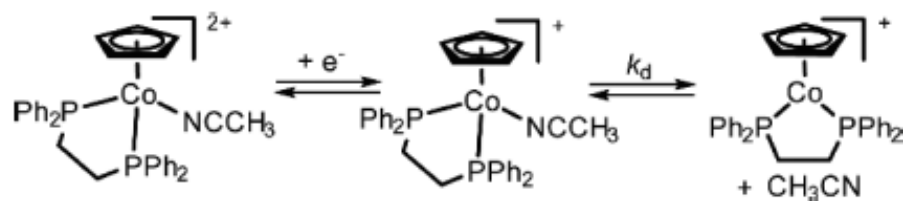


Figure 1. CVs of $[\text{Co}(\text{Cp})(\text{dppe})(\text{CH}_3\text{CN})](\text{PF}_6)_2$ in CH_3CN (0.5 mM, blue trace) and in CH_2Cl_2 (0.5 mM, red trace). The voltammograms were recorded at 100 mV/s in 0.25 M $[\text{Bu}_4\text{N}][\text{PF}_6]$.



Scheme 1

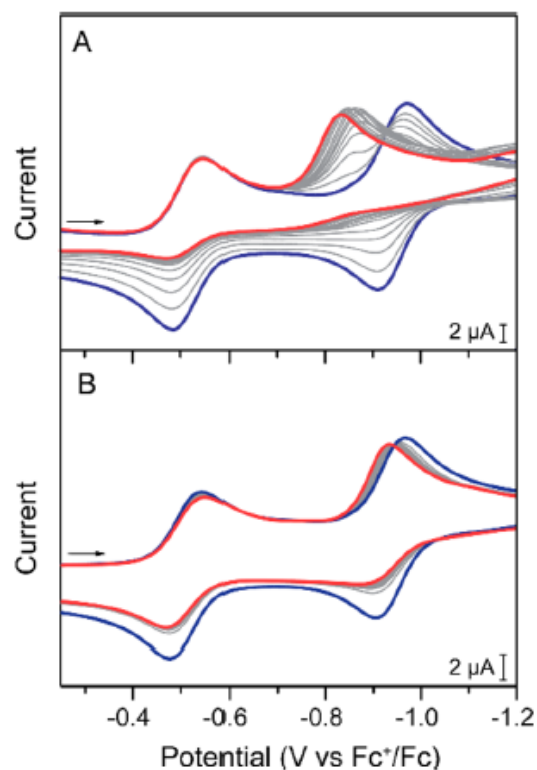
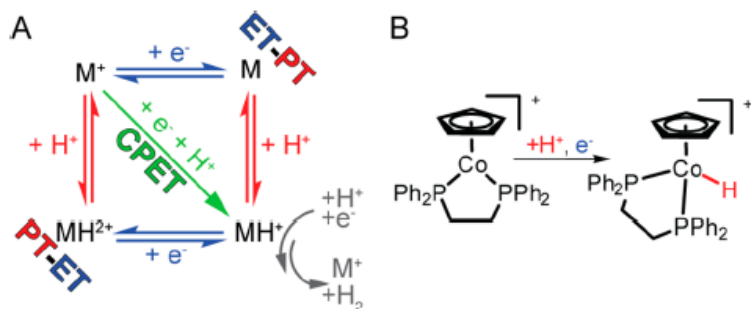
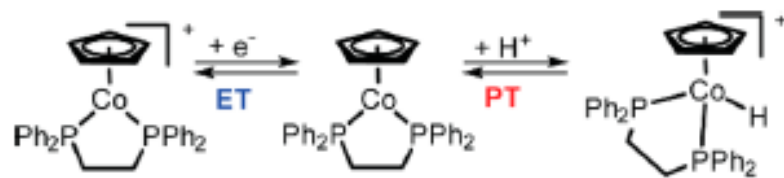
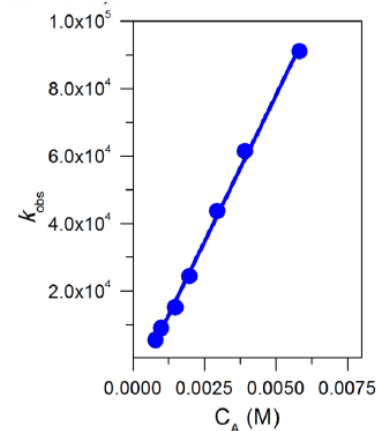
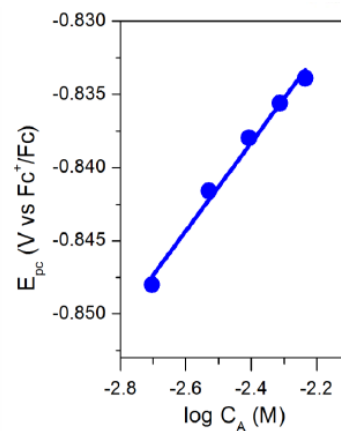


Figure 2. CVs of $[\text{Co}(\text{Cp})(\text{dppf})(\text{CH}_3\text{CN})](\text{PF}_6)_2$ in the absence of a proton source (blue) and as (A) 4-cyano-anilinium ($\text{p}K_a = 7$)²⁶ or (B) benzoic acid ($\text{p}K_a = 21.51$)²⁷ is titrated into an CH_3CN solution (gray to red). The voltammograms were recorded at 100 mV/s in 0.25 M $[\text{Bu}_4\text{N}][\text{PF}_6]$.



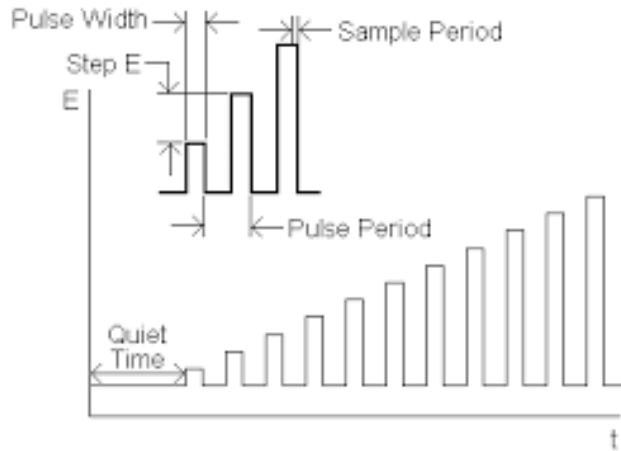
$$E_p = E_{1/2} - \frac{RT}{F}(0.78) + \frac{RT}{2F} \ln\left(\frac{k_{\text{obs}}RT}{Fv}\right)$$

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

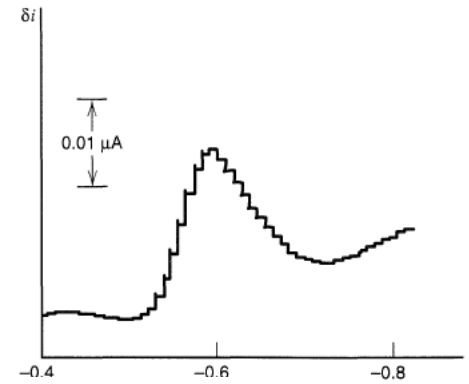
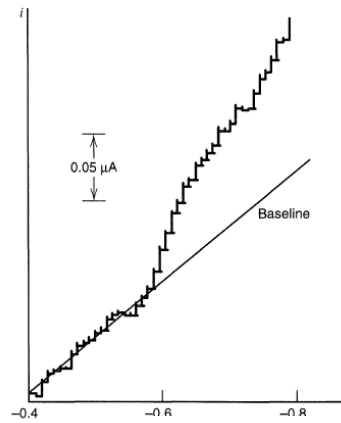
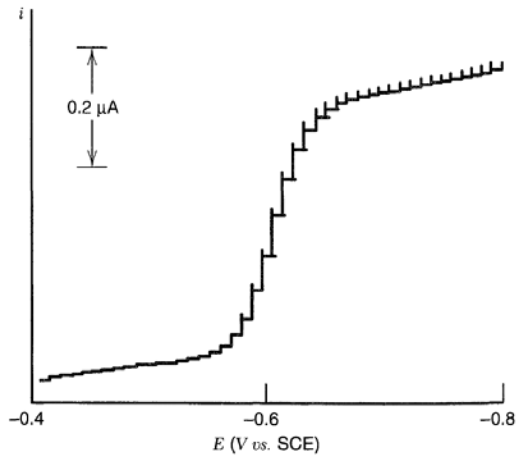
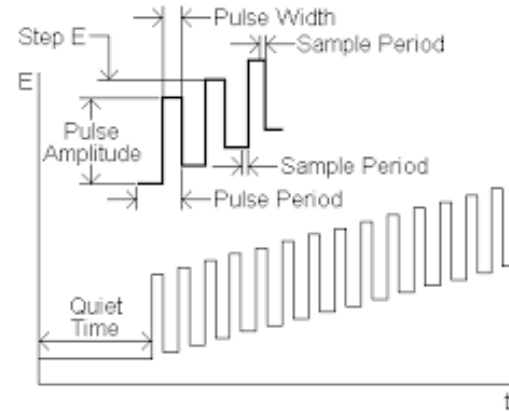


Pulsne voltametrijske tehnike

„Normalna“



Diferencijalna

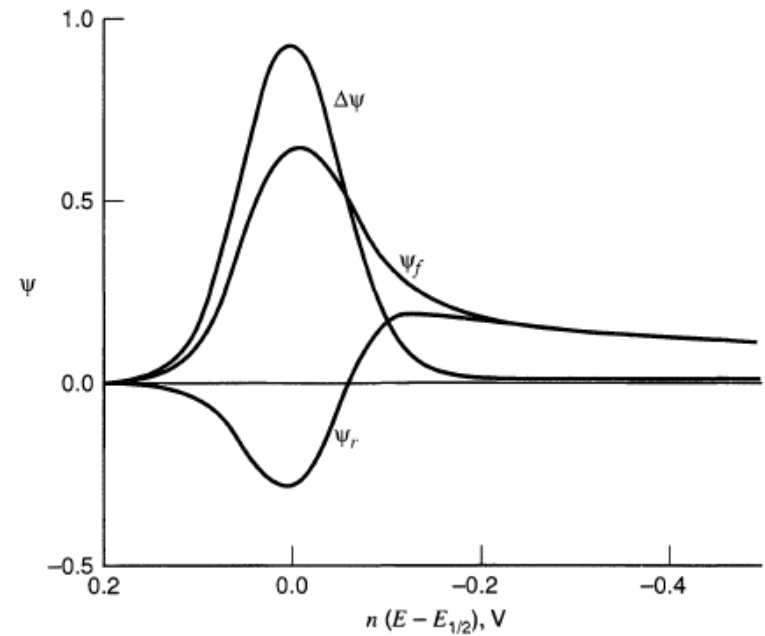
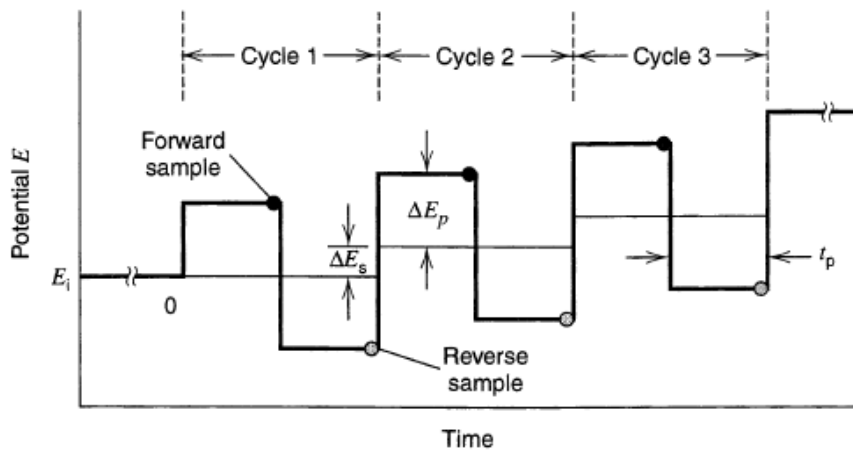


$$E_{\max} = E^{0'} + \frac{RT}{nF} \ln\left(\frac{D_R}{D_O}\right)^{1/2} - \frac{\Delta E}{2} = E_{1/2} - \frac{\Delta E}{2}$$

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

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

Pravokutnovalna voltametrija (Square Wave Voltametry)

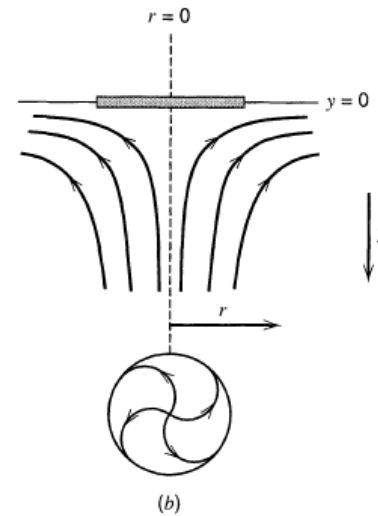
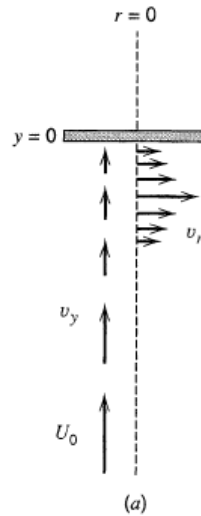
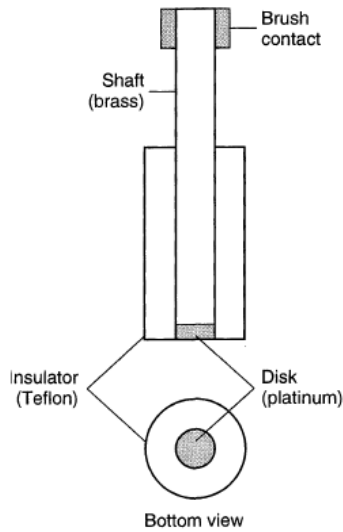


$$\Delta i_p = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t_p^{1/2}} \Delta\psi_p$$

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 jednađba

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

**Rotirajuća disk elektroda
- ravnotežni uvjeti (reverzibilni proces)**

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

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

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

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