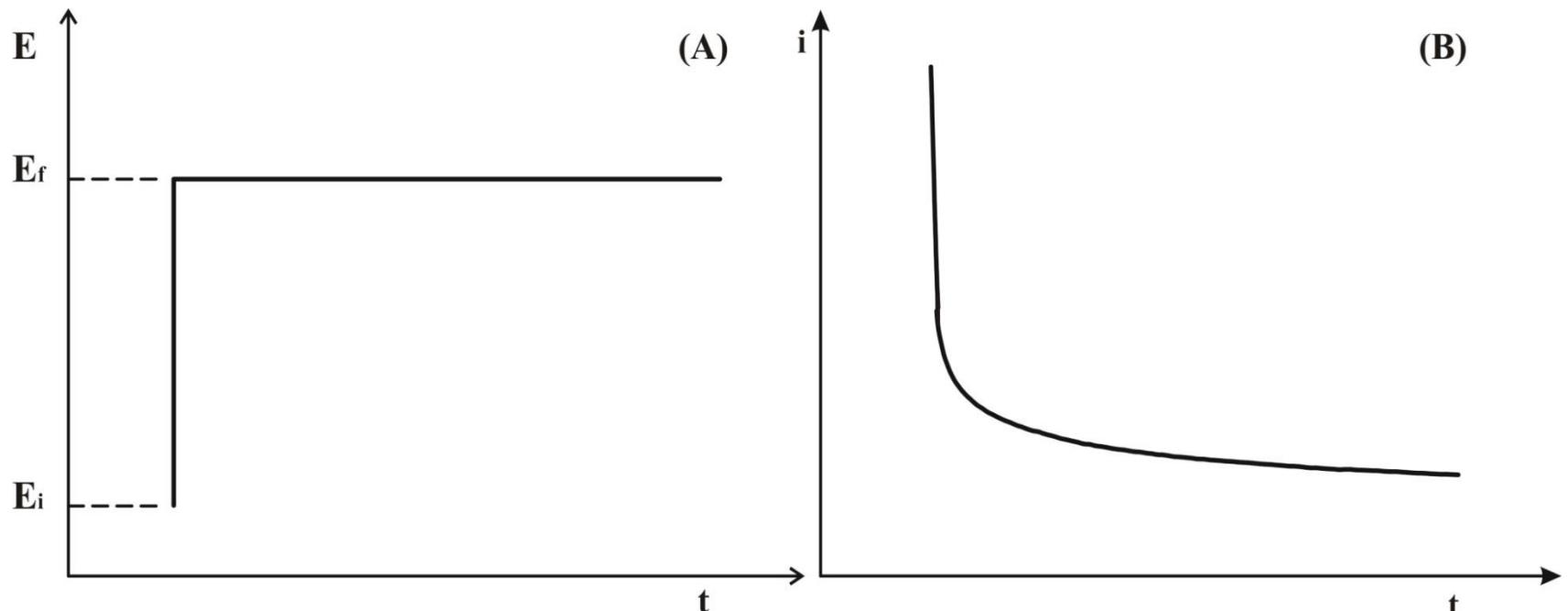


Ispitivanje elektrodne kinetike: stacionarna metoda, polarografija, hronoampermetrija

Predavanje 22, 13.05.2020

Udžbenik: S. Mentus, Elektrohemija, 2008, strane 265-276

HRONOAPMEROMETRIJA



Promena potencijala sa vremenom u hronoampermetriji (A) sa struja vs. vreme odgovorom (B)

- ✓ Reverzibilni procesi
- ✓ Irreverzibilni procesi
- ✓ Kvazireverzibilni procesi

Reverzibilni procesi

$$\frac{dC_o}{dt} = D_o \frac{d^2C_o}{dx^2}$$

Granični uslovi

✓ $C_o(\infty, t) = C_o^*$

✓ $C_o(x, 0) = C_o^*$

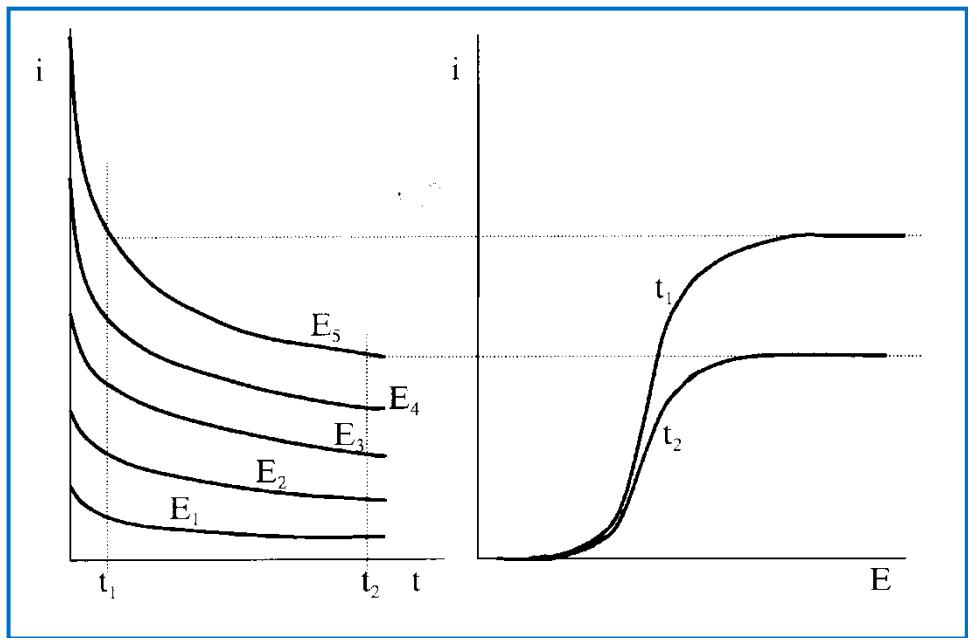
✓ $C_o(0, t) = C_o$ ili b) $C_o(0, t) = 0$

✓ $D \frac{\partial C_o(0, t)}{\partial x} = D \frac{\partial C_R(0, t)}{\partial x}$

Reverzibilni procesi

Jednačina
hronoamperometrijske krive

$$j = \frac{nFD_O^{1/2}C_O^*}{\left(1 + \frac{D_O^{1/2}C_O}{D_R^{1/2}C_R}\right) \cdot \pi^{1/2} t^{1/2}}$$

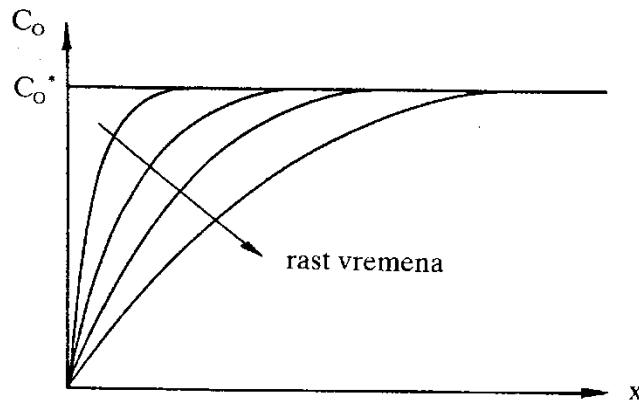


Levo: hronoamperometrijske krive prema jednačini za različite vrednosti naponskog pulsa; Desno: I - E krive dobijene iz hronoamperometrijskih krivih za različita vremena od momenta zadavanja naponskog pulsa.

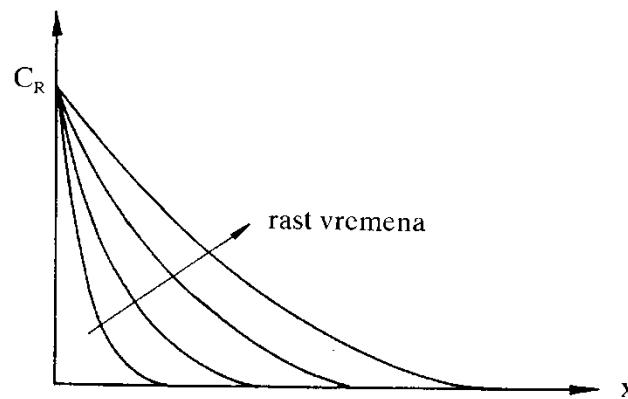
Kotrelova (Cottrell) jednačina

$$i = nFACD^{1/2} \pi^{-1/2} \underline{\underline{t}}^{-1/2}$$

Reverzibilni procesi



$$\left(\frac{dC_O}{dx} \right)_{x=0} = \frac{C_O^*}{\sqrt{\pi D t}}$$



Promena raspodele koncentracija učesnika reverzibilne redoks reakcije, za $C_R^* = 0$, u zavisnosti od rastojanja, x , od površine elektrode, tokom vremena, pri skokovito zadatom potencijalu koji odgovara uslovu $C_O = 0$.

Kvazi-reverzibilni procesi

$$C_R(x,0) = 0$$

Granični uslovi

✓ $C_O(\infty, t) = C_O^*$

✓ $C_O(x,0) = C_O^*$

✓ $C_O(0, t) = C_O$ ili b) $C_O(0, t) = 0$

✓ $D \frac{\partial C_o(0,t)}{\partial x} = D \frac{\partial C_R(0,t)}{\partial x}$

✓ $D \frac{\partial C_o(0,t)}{\partial x} = k_a C_R(0,t) - k_c C_o(0,t)$

Kvazi-reverzibilni procesi

Jednačina
hronoamperometrijske krive

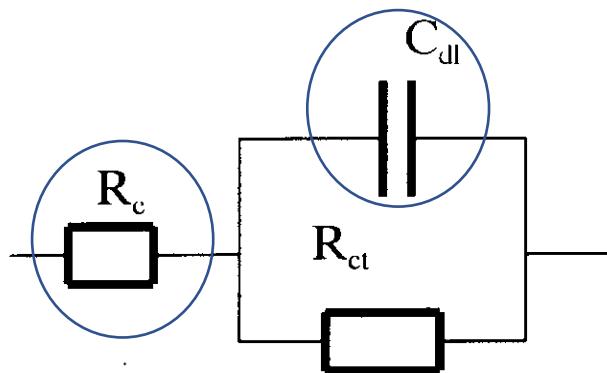
$$j = -nFk_c C_o^* e^{\frac{(k_c + k_a)^2 t}{D}} ercf \frac{(k_a + k_c)}{D^{1/2}}$$

Za male vrednosti y: $e^{y^2} ercf y = 1 - \frac{2y}{\pi^{1/2}}$  $j = -nFk_c C_o^* \left(1 - \frac{2(k_a + k_c)}{\pi^{1/2} D^{1/2}} t^{1/2} \right)$

Za velike vrednosti y: $e^{y^2} ercf y = \frac{1}{y\pi^{1/2}}$  $j = \frac{-nFk_c C_o^* D^{1/2}}{\pi^{1/2} (k_a + k_c) t^{1/2}}$

Blokirajuća elektroda

$$E = jR_e + \frac{q}{C_{dl}} = \frac{dq}{dt} R_e + \frac{q}{C_{dl}}$$



Ekvivalentno kolo jedne elektrode - Re je otpor elektrolita, Rct otpor prenosa elektrona kroz faznu granicu metal/elektrolit, Cdl kapacitet dvojnog električnog sloja granice metal/ elektrolit

$$\frac{dq}{dt} = \frac{-q}{R_e C_{dl}} + \frac{E}{R_e} \quad \frac{q}{R_e C_{dl}} = u \quad q = 0 \text{ za } t = 0$$

$$q = E C_{dl} \left(1 - e^{-\frac{t}{R_e C_{dl}}} \right)$$

$$j_C = \frac{dq}{dt} = \frac{E}{R_e} e^{\frac{-t}{R_e C_{dl}}}$$

$$j_c = E/R_e \text{ za } t = 0$$

$$\text{Vremenska konstanta } \tau = R_e C_{dl}$$

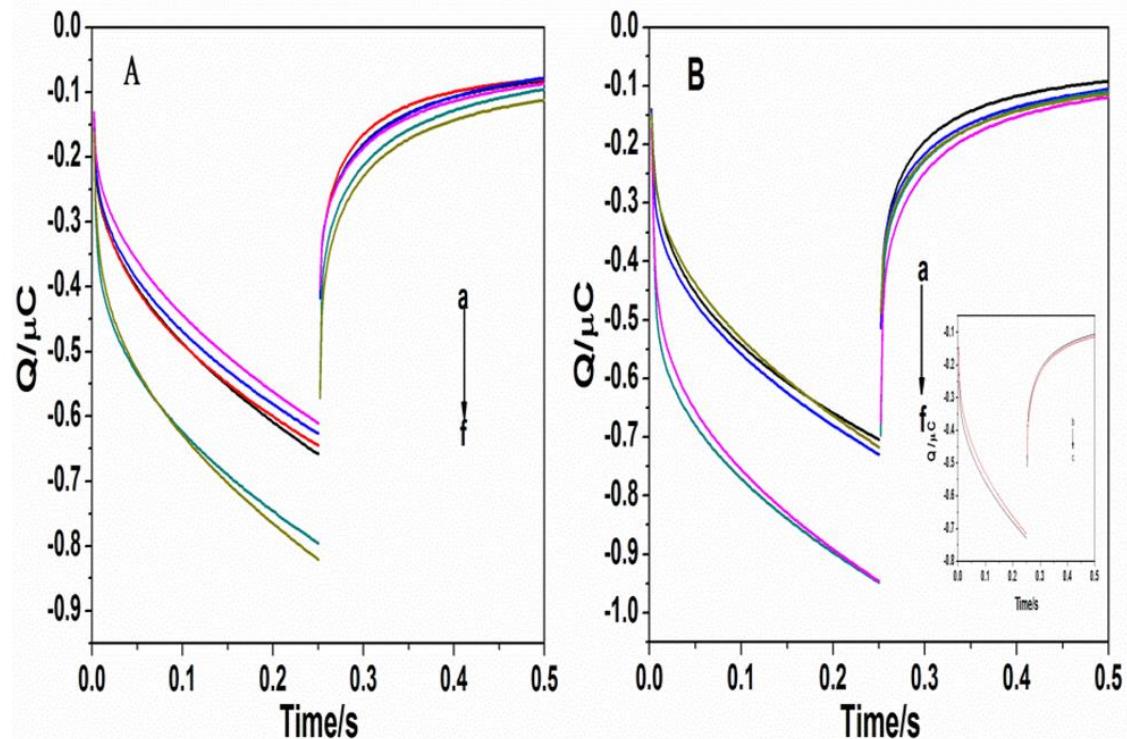
$$R_e \text{ oko } 1 \Omega \text{cm}^2 \text{ i } C_{dl} \text{ oko } 10^{-5} \text{ F cm}^{-2}$$

\downarrow
 τ oko 10^{-5} s

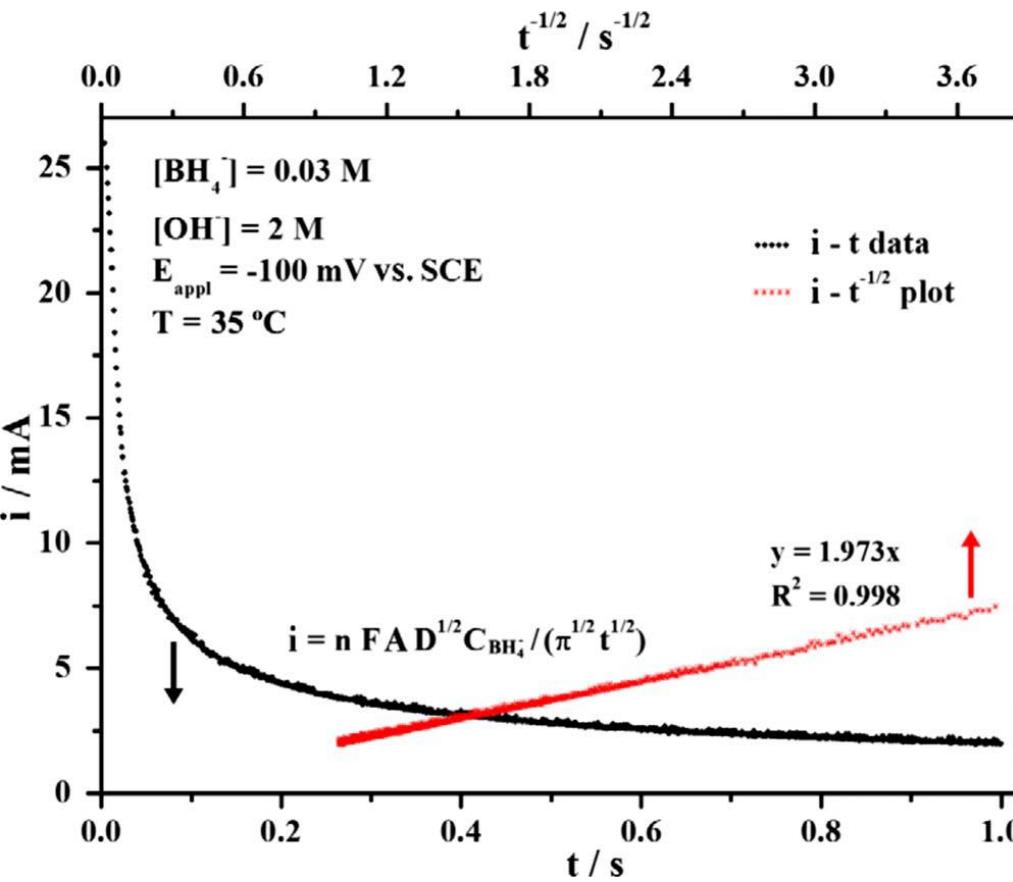
Primena hronoamperometrije

Količina naelektrisanja

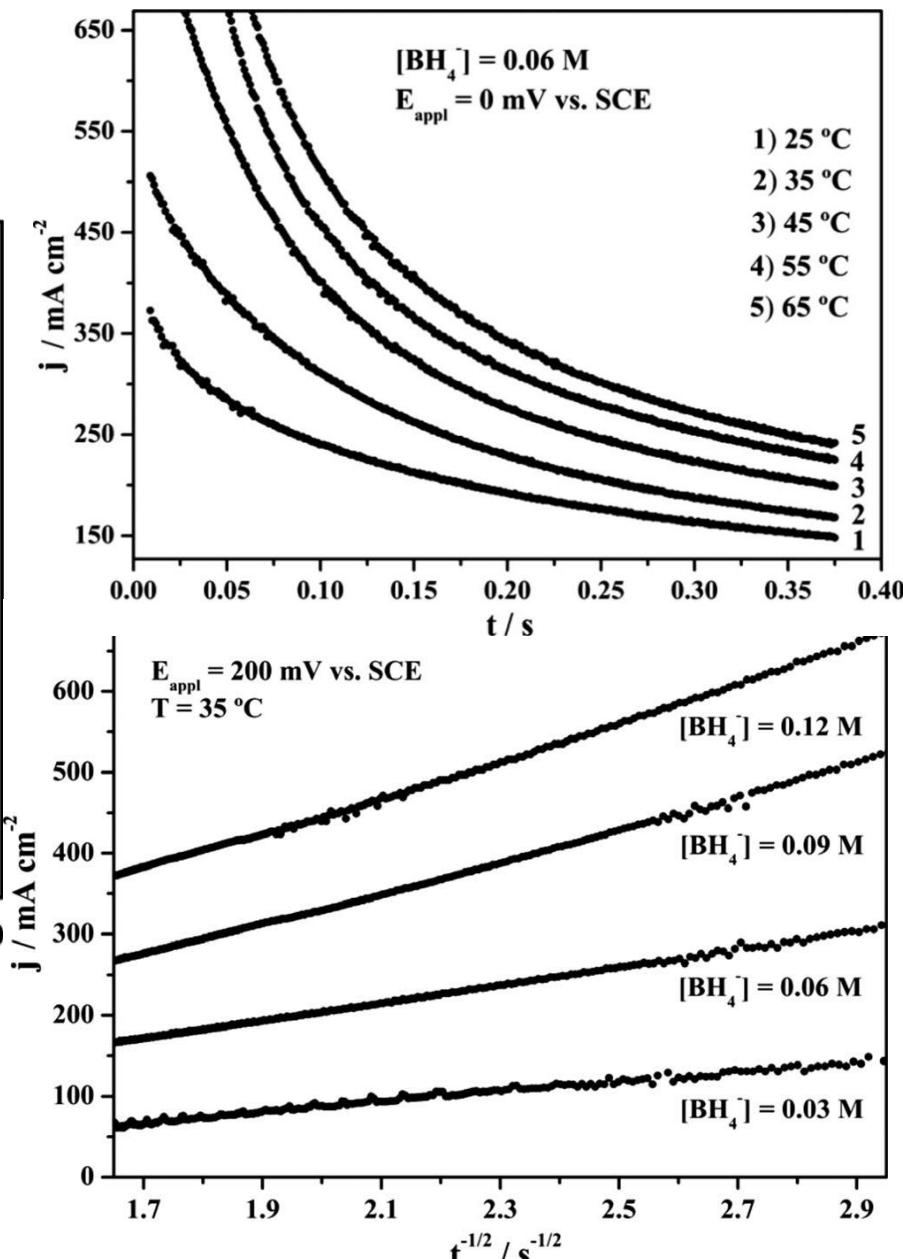
- Q vs t
- Hronokulometrija
- Merenje količine adsorbovanih reaktanata
- Q vs $t^{1/2}$



Kinetički i difuzioni parametri



Current transient for a typical chronoamperometric experiment and corresponding $i-t^{-1/2}$ plot.



Kinetički i difuzioni parametri

F70

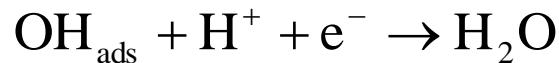
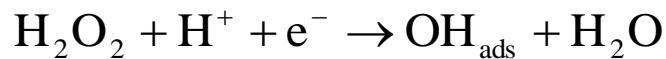
Journal of The Electrochemical Society, **156** (5) F67-F74 (2009)

Table I. Diffusion coefficients ($\text{cm}^2 \text{ s}^{-1}$) calculated using the Cottrell equation.

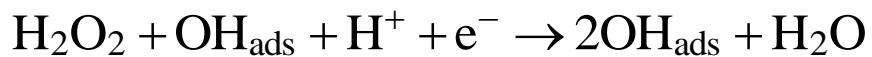
E, mV	[BH ₄ ⁻], M	Temperature, °C				
		25	35	45	55	65
-200	0.03	1.86×10^{-5}	2.33×10^{-5}	2.73×10^{-5}	3.20×10^{-5}	4.47×10^{-5}
	0.06	5.28×10^{-6}	1.19×10^{-5}	2.01×10^{-5}	2.03×10^{-5}	2.82×10^{-5}
	0.09	8.79×10^{-6}	1.42×10^{-5}	1.22×10^{-5}	2.01×10^{-5}	2.92×10^{-5}
	0.12	3.83×10^{-5}	1.68×10^{-5}	8.15×10^{-5}	6.25×10^{-5}	1.41×10^{-5}
	0.03	1.86×10^{-5}	2.31×10^{-5}	2.72×10^{-5}	3.25×10^{-5}	4.29×10^{-5}
	0.06	1.38×10^{-5}	1.80×10^{-5}	2.10×10^{-5}	2.27×10^{-5}	3.05×10^{-5}
-100	0.09	7.92×10^{-6}	1.48×10^{-5}	1.20×10^{-5}	2.81×10^{-5}	3.29×10^{-5}
	0.12	5.43×10^{-5}	1.89×10^{-5}	5.23×10^{-5}	5.22×10^{-5}	1.37×10^{-5}
	0.03	1.84×10^{-5}	2.19×10^{-5}	2.72×10^{-5}	3.33×10^{-5}	4.31×10^{-5}
	0.06	1.32×10^{-5}	1.55×10^{-5}	2.17×10^{-5}	2.78×10^{-5}	3.03×10^{-5}
	0.09	9.49×10^{-6}	1.06×10^{-5}	9.46×10^{-6}	2.33×10^{-5}	2.36×10^{-5}
	0.12	4.78×10^{-5}	1.54×10^{-5}	6.35×10^{-5}	6.35×10^{-5}	2.40×10^{-5}
0	0.03	1.80×10^{-5}	2.16×10^{-5}	2.50×10^{-5}	3.32×10^{-5}	3.99×10^{-5}
	0.06	1.36×10^{-5}	1.63×10^{-5}	1.98×10^{-5}	2.35×10^{-5}	2.67×10^{-5}
	0.09	1.09×10^{-5}	1.43×10^{-5}	1.16×10^{-5}	1.90×10^{-5}	2.78×10^{-5}
	0.12	4.32×10^{-5}	2.17×10^{-5}	5.26×10^{-5}	6.16×10^{-5}	2.62×10^{-5}
	0.03	1.53×10^{-5}	1.32×10^{-5}	1.76×10^{-5}	1.84×10^{-5}	1.84×10^{-5}
	0.06	1.33×10^{-5}	1.44×10^{-5}	1.93×10^{-5}	8.28×10^{-6}	1.14×10^{-6}
100	0.09	6.69×10^{-6}	1.70×10^{-5}	8.02×10^{-6}	2.19×10^{-5}	2.37×10^{-5}
	0.12	4.90×10^{-5}	1.98×10^{-5}	3.67×10^{-5}	6.24×10^{-5}	3.97×10^{-5}
200	0.03					
	0.06					

Elektrokataliza

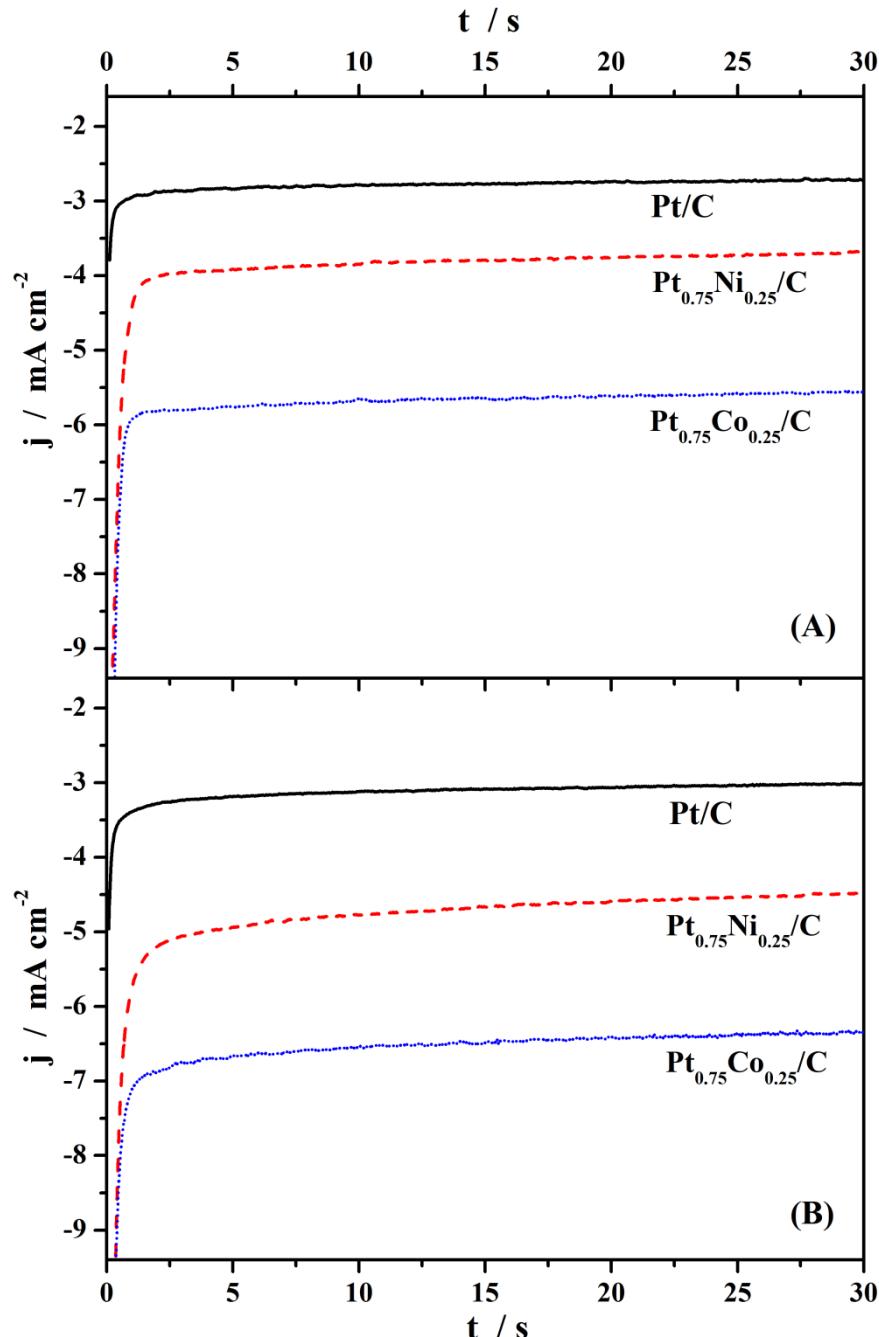
„Normalni“ mehanizam



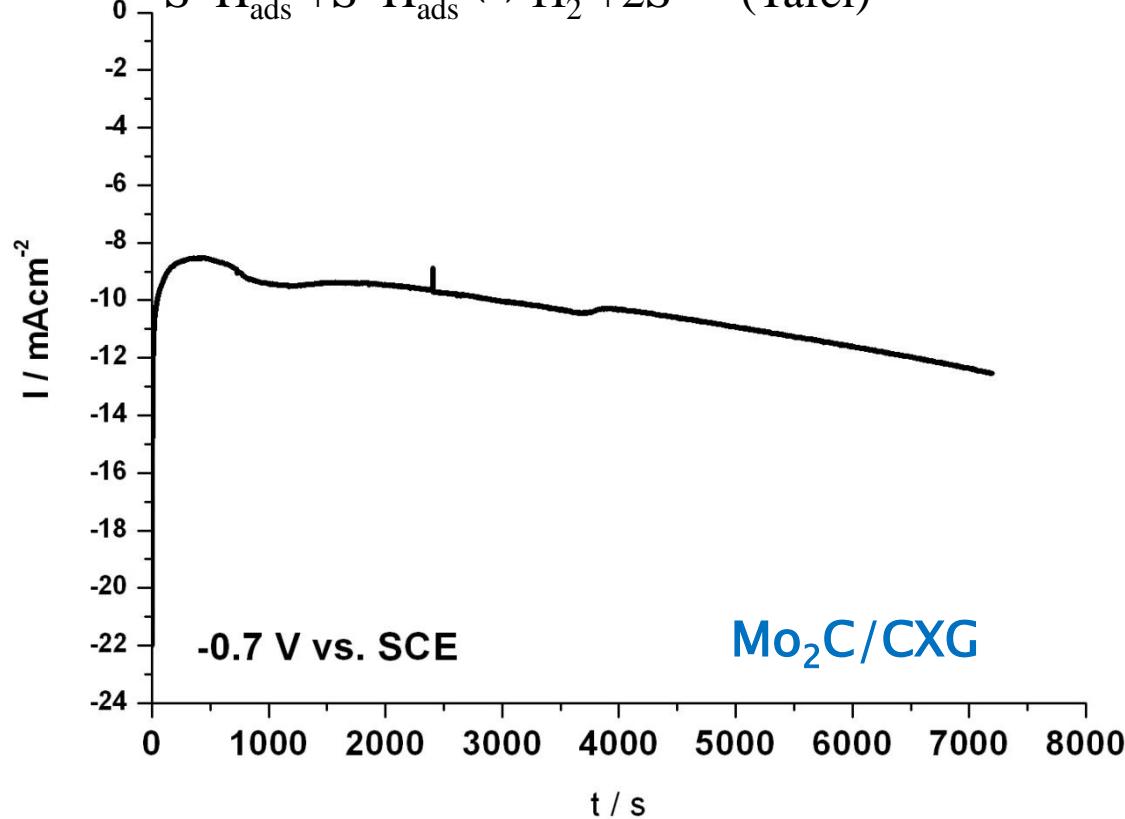
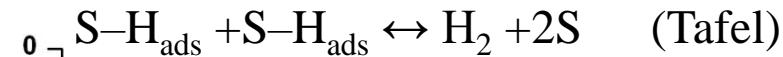
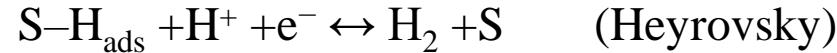
Autokatalitički mehanizam



CA curves for the studied electrocatalysts recorded in 0.03 M H_2O_2 in 0.1 M HClO_4 at the potentials of 0 V (A) and -0.2 V (B), using 1000 rpm rotation speed.

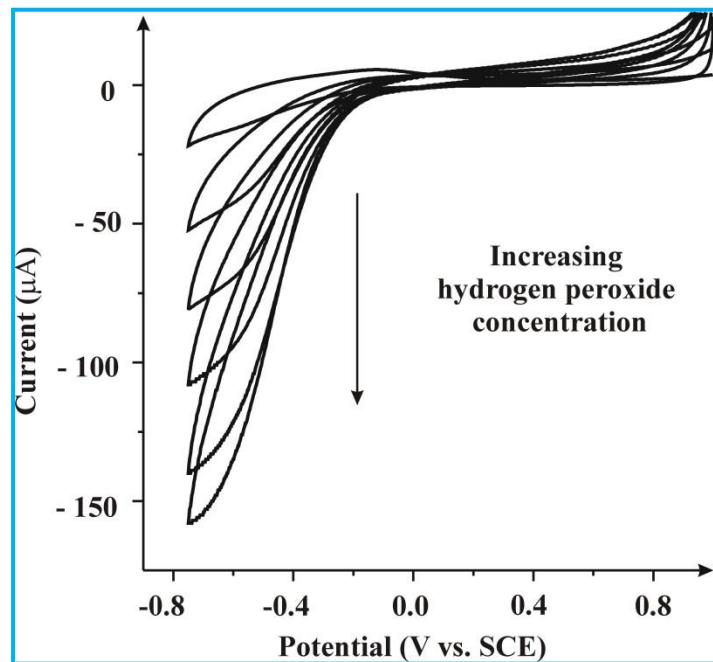


Elektrokataliza



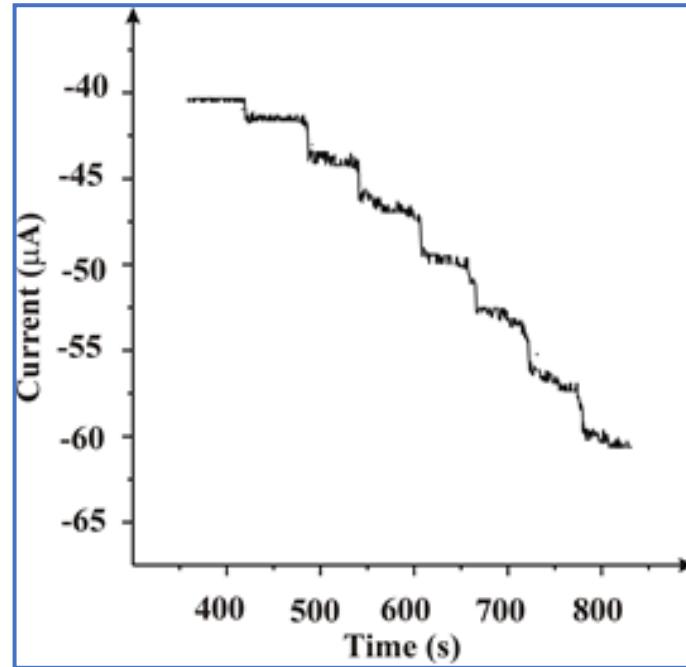
Elektroanaliza

LOD = 3,5 μM



CVs of iron (III) oxide – modified carbon powder epoxy composite electrode, $\text{Fe}_2\text{O}_3+\text{CP-E}$, in pH 7.4 phosphate buffer with increasing hydrogen peroxide concentration in the range 0.5 - 5 mM

LOD = 0,13 μM



Amperometric response observed at the $\text{Fe}_2\text{O}_3/\text{CP-E}$ composite electrode from 0.25 mM additions of hydrogen peroxide to a pH 7.4 phosphate buffer solution at operating potential of -0.75 V vs. SCE

POLAROGRAFIJA

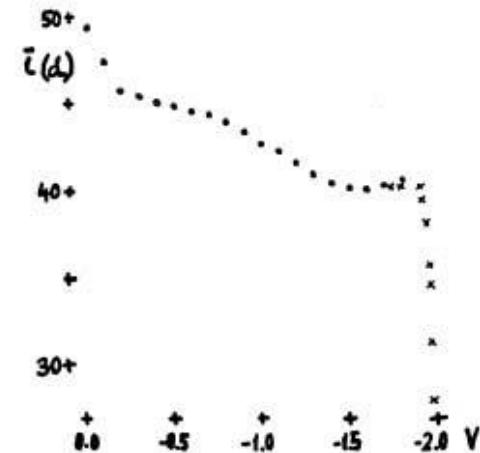
Kapljuća živina elektroda

Brzina polarizacije < 10 mV/s

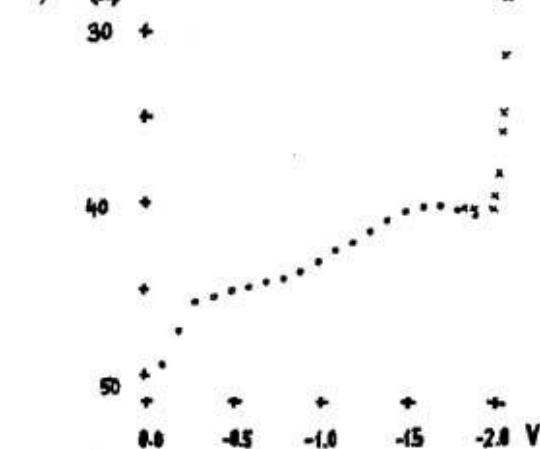
a)

Friday February 10th 1922 afternoon

In NaCl open to air



b)



The first recorded I - E curve copied from Professor Heyrovsky's laboratory notebook (a) and transformed into the nowadays used form (b).

Razvoj polarografije

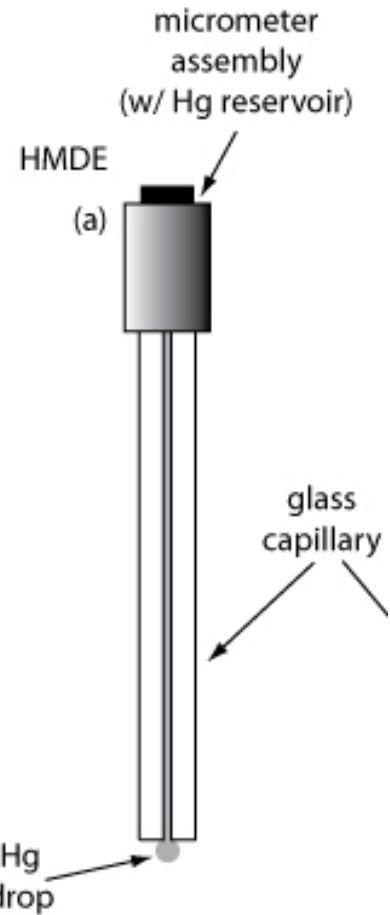
- ✓ 1922. – Jaroslav Hejrovska, polarografsko određivanje kiseonika
- ✓ 1929. – početak komercijalne proizvodnje u Pragu
(projekat *Menhetn*)
- ✓ 1959. Nobelova nagrada za hemiju za „njegovo otkriće i razvoj polarografskih metoda analize“

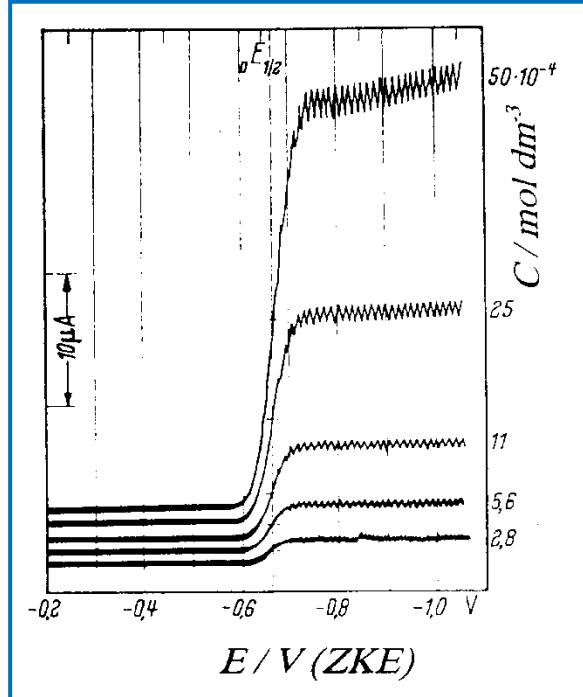
Veličina kapi i brzina isticanja zavise od:

- Veličine otvora kapilare
- Visinske razlike vrha kapilare i nivoa u rezervoaru
- Površinskog napona granice živa/elektrolit

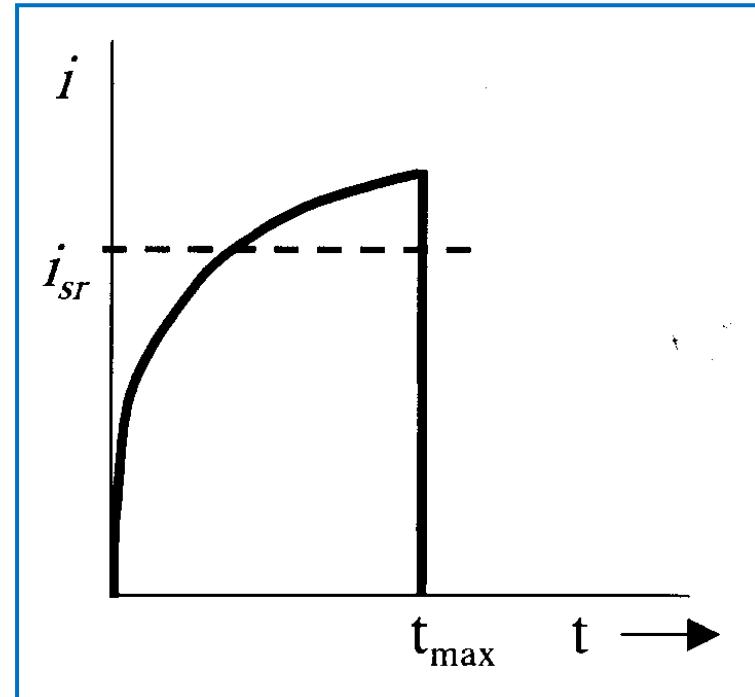
Prednosti kapljuće živine elektrode

- ✓ najveća oblast idealne polarizacije u oblasti od preko 1V
- ✓ kontrolisana površina elektrode
- ✓ nema presićenja metalom koji se katodno izdvaja





Polarogrami redukcije kadmijumovih jona
iz osnovnog elektrolita 1 M KCl.
Koncentracije $CdCl_2$ za svaku krivu
naznačene su na desnoj skali



Promena faradejske struje s vremenom života
živine kapi i srednja struja u polarografiji

Ilkovićeva
jednačina

$$I_l = 708 n D^{1/2} C_i^* m^{2/3} t^{1/6}$$

$$\bar{I}_l = \frac{\int_0^{t_{\max}} I dt}{\int_0^{t_{\max}} dt} = 607 n D^{1/2} t_{\max}^{1/6} C_i^* m^{2/3} = K C_i^*$$

Izvođenje Ilkovičeve jednačine

Kotrelova jednačina

$$I = \frac{nFAD^{1/2}C_o^*}{\pi^{1/2}t^{1/2}}$$

$$mt = \frac{4}{3}r^3\pi d \longrightarrow r = \left(\frac{3mt}{4\pi d} \right)^{1/3}$$

$$A = 4\pi r^2 = 4\pi \left(\frac{3mt}{4\pi d} \right)^{2/3}$$

$$I_i = \frac{nFD_i^{1/2}C_i^*}{\pi^{1/2}t^{1/2}} A = \frac{nFD_i^{1/2}C_i^*}{\pi^{1/2}t^{1/2}} \left[4\pi \left(\frac{3mt}{4\pi\rho} \right) \right]^{2/3}$$

Korekcioni faktor $(7/3)^{1/2}$

$$I = 708nD_i^{1/2} m^{2/3} t^{1/6} (C_i^* - C_i)$$

$$\bar{I} = 607nD_i^{1/2} m^{2/3} t_{\max}^{1/6} (C_i^* - C_i)$$

Kapacitativna struja

$$I = \frac{dq}{dt} = \frac{d(A\sigma)}{dt} = \frac{dA}{dt} C_{i,dl} (E - E_{pzc})$$

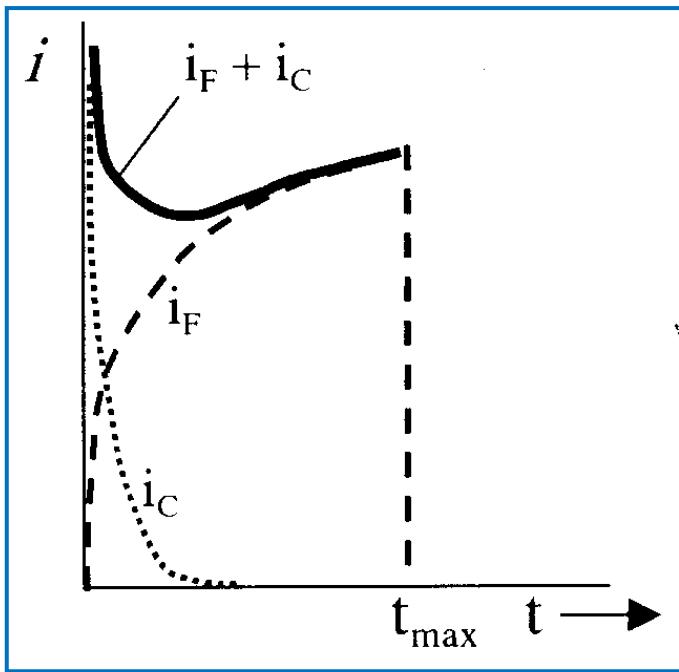
$$A = 4\pi r^2 = 4\pi \left(\frac{3mt}{4\pi d} \right)^{2/3} \quad \xrightarrow{\hspace{1cm}} \quad \frac{dA}{dt} = \frac{8\pi}{3} \left(\frac{3m}{4\pi\rho} \right)^{2/3} t^{-1/3}$$

$$I_c = \frac{8\pi}{3} \left(\frac{3m}{4\pi\rho} \right)^{2/3} t^{-1/3} C_{i,dl} (E - E_{pzc})$$

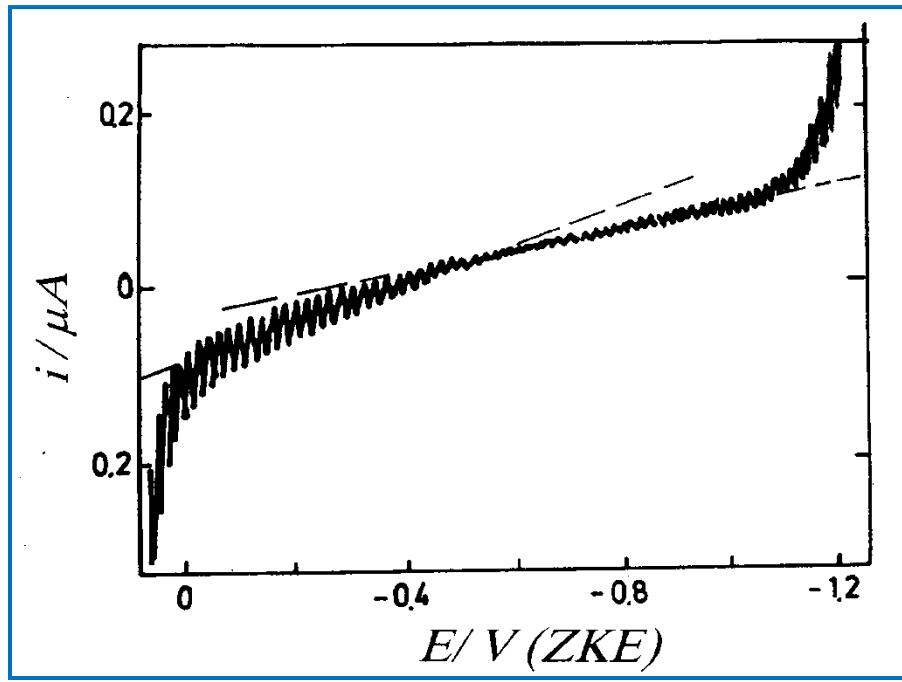
$$I_c = 0,00567 C_{i,dl} (E - E_{pzc}) m^{2/3} t^{-1/3}$$

$$\bar{I}_c = \frac{\int_0^{t_{\max}} I_c dt}{\int_0^{t_{\max}} dt} = 0,000850 C_{i,dl} (E - E_{pzc}) m^{2/3} t_{\max}^{-1/3}$$

Kapacitativna struja



Kapacitivna I_C , faradejska I_F i rezultujuća ($I_F + I_c$) struja.



Osnovna polarografska kriva u $0,1 \text{ M HCl}$.

$$t_{\max} \sim 1 \text{ s}; C_{dl} \sim 10 \text{ } \mu\text{F/cm}^2; \text{ za } E = 1 \text{ V}, I_c \approx 10^{-5} \text{ m}^{2/3}$$

$$D \sim 10^{-5}, I_f \approx 10^{-5} \text{ m}^{2/3}$$

Granica osetljivosti $10^{-5} \text{ mol dm}^{-3}$

Kvalitativna analiza

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

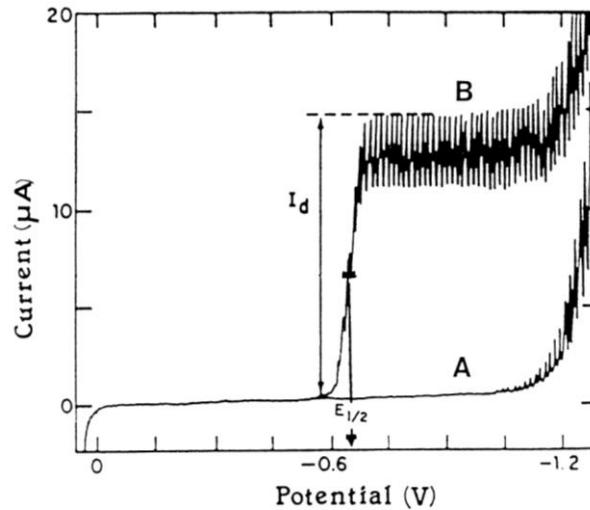


FIGURE 3-2 Polarograms for 1 M hydrochloric acid (Curve A) and 4×10^{-4} M Cd^{+2} in 1 M hydrochloric acid B. i_d represents the limiting current; $E_{1/2}$ is the half-wave potential.

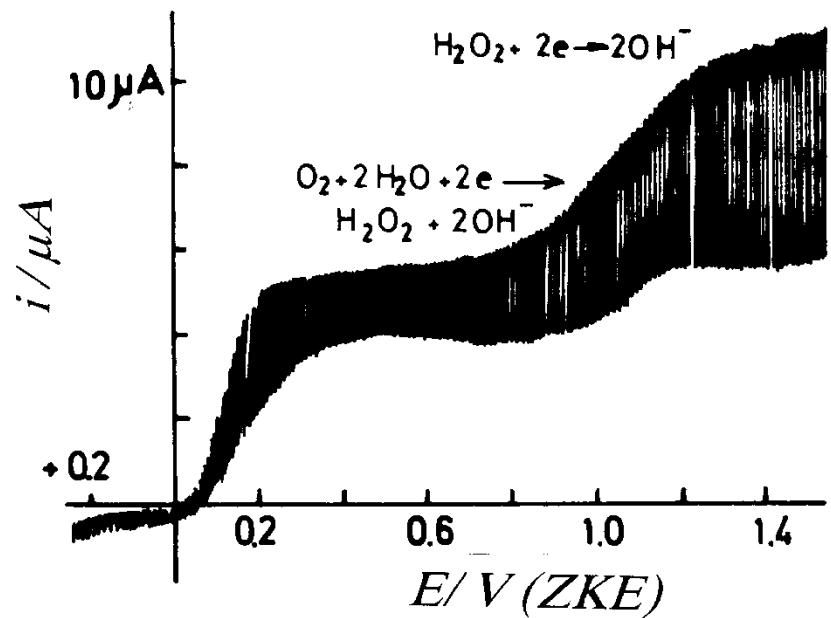
TABLE 3-1 Functional Groups Reducible at the Dropping Mercury Electrode

Class of Compound	Functional Group	$E_{1/2}(\text{V})^a$
Azo	$-\text{N}=\text{N}-$	-0.4
Carbon–carbon double bond ^b	$-\text{C}=\text{C}-$	-2.3
Carbon–carbon triple bond ^b	$-\text{C}\equiv\text{C}-$	-2.3
Carbonyl	$\text{>} \text{C}=\text{O}$	-2.2
Disulfide	$\text{S}-\text{S}$	-0.3
Nitro	NO_2	-0.9
Organic halides	$\text{C}-\text{X}$ ($\text{X}=\text{Br}, \text{Cl}, \text{I}$)	-1.5
Quinone	$\text{C}=\text{O}$	-0.1

^a Against the saturated calomel electrode at pH 7.

^b Conjugated with a similar bond or with an aromatic ring.

Kvantitativna analiza



Polarogram redukcije kiseonika na Pt-elektrodi u $0,1 \text{ M}$ vodenom rastvoru KNO_3 zasićenom vazdušnim kiseonikom

$$\begin{aligned}\operatorname{erfc}(x) &= 1 - \operatorname{erf}(x) \\&= \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-t^2} dt \\&= e^{-x^2} \operatorname{erfcx}(x),\end{aligned}$$