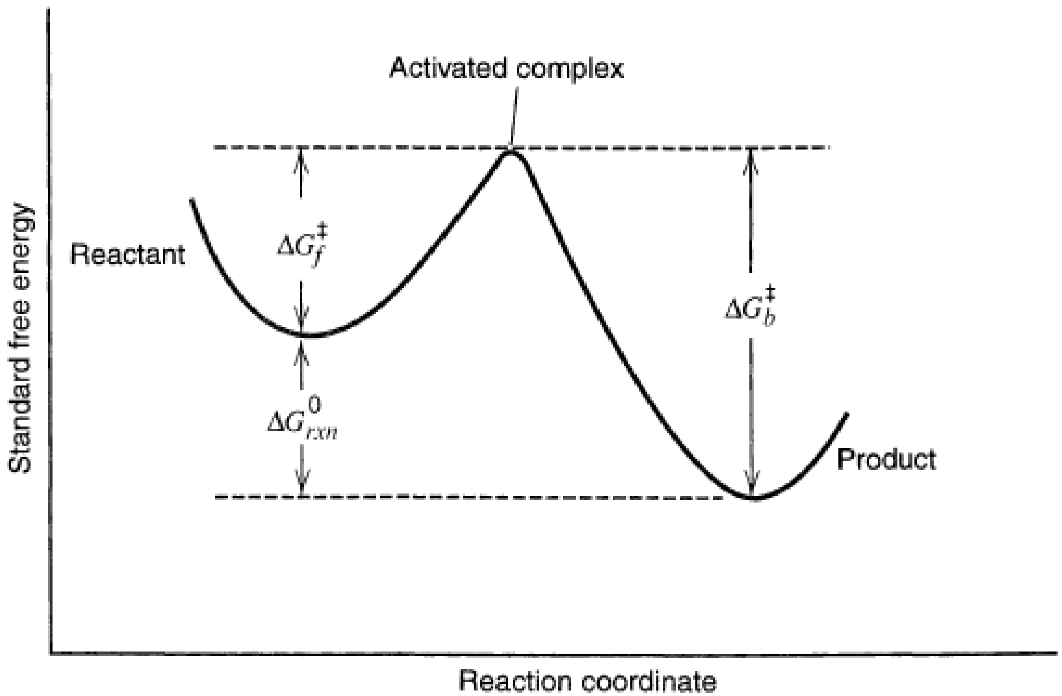
Kinetika elektrodnih reakcija

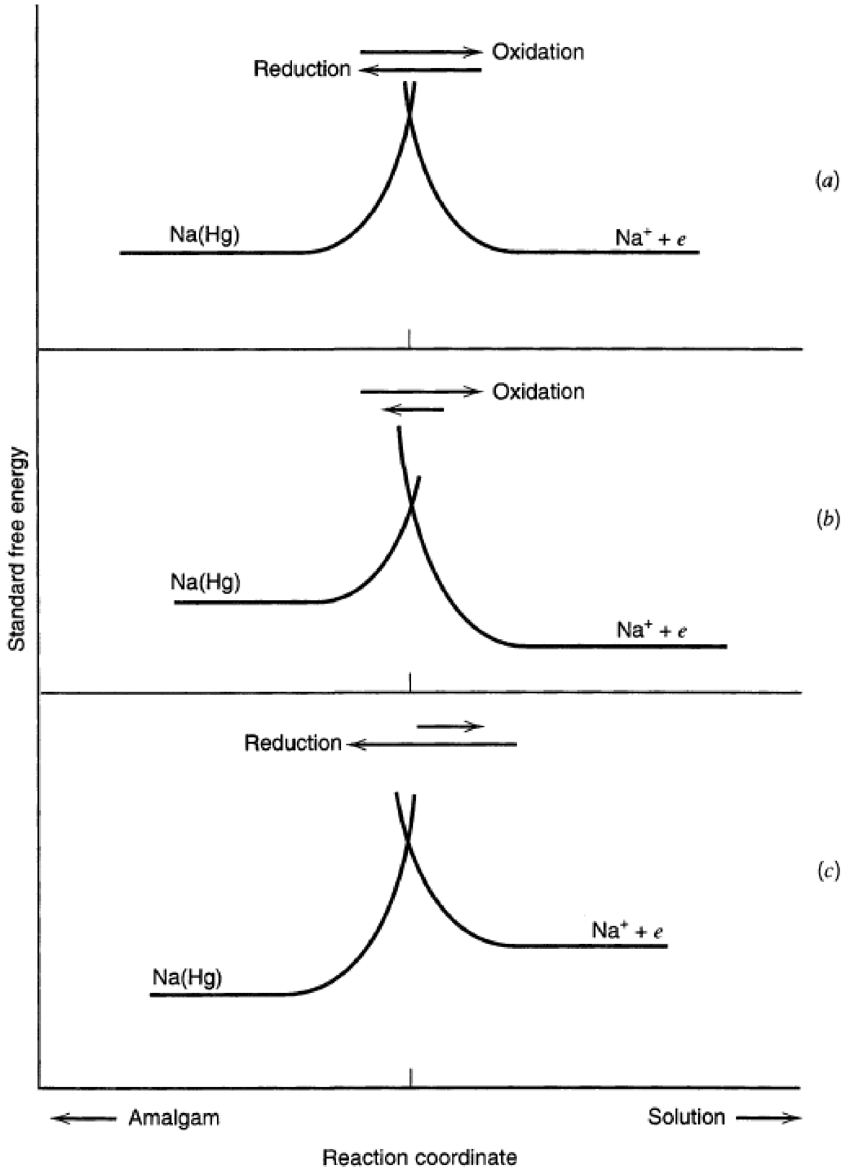
Butler-Volmer Model

Teorija prijelaznog stanja



Prijelazno stanje u slučaju heterogenih reakcija (na elektrodi)

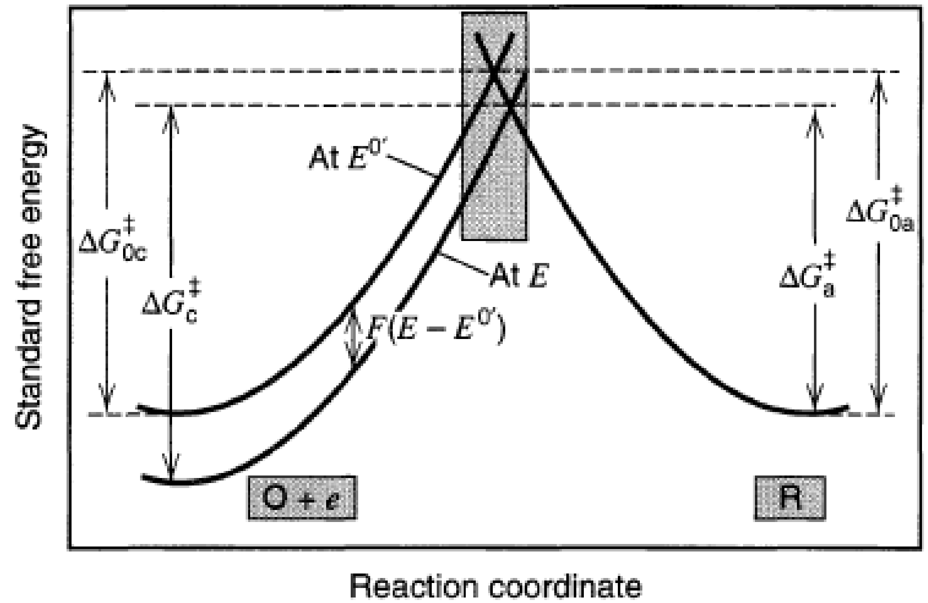
Utjecaj potencijala elektrode na energetsku barijeru?

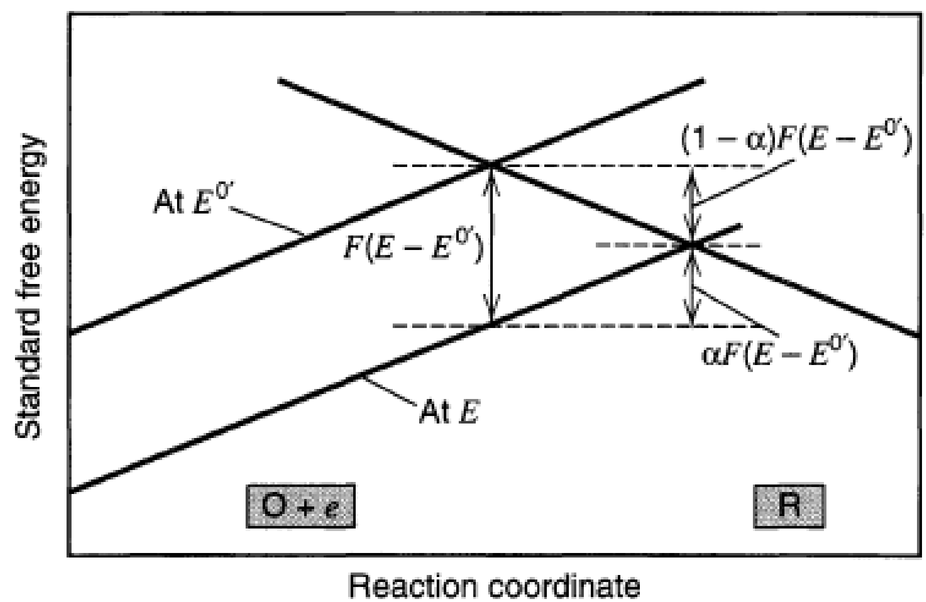


Utjecaj potencijala elektrode na energetsku barijeru

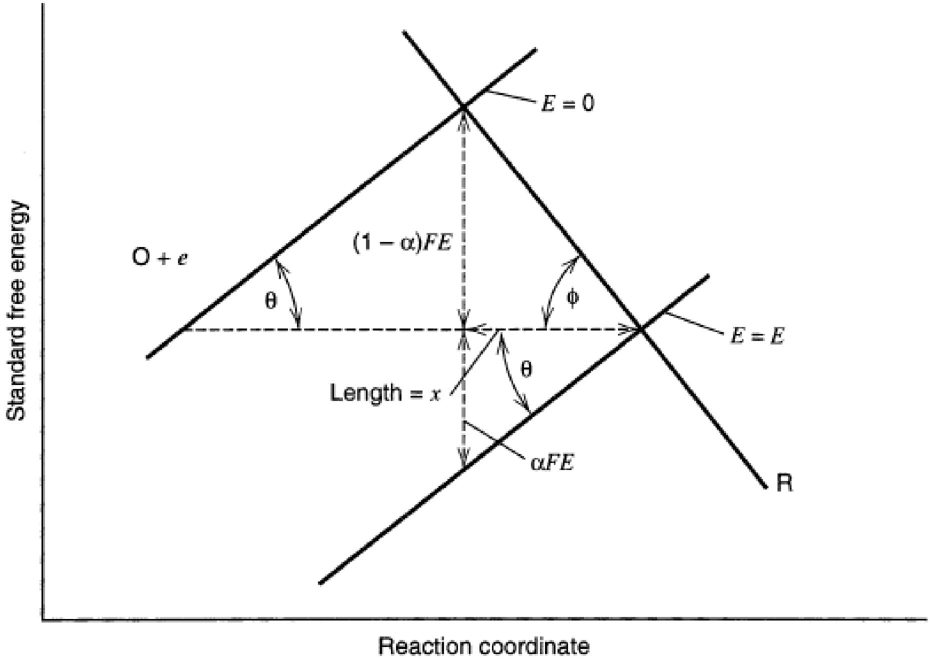
$$\Delta G_c^{\ddagger} = \Delta G_{0c}^{\ddagger} + \alpha F(E - E^{0'})$$

$$\Delta G_a^{\ddagger} = \Delta G_{0a}^{\ddagger} - (1 - \alpha)F(E - E^{0'})$$





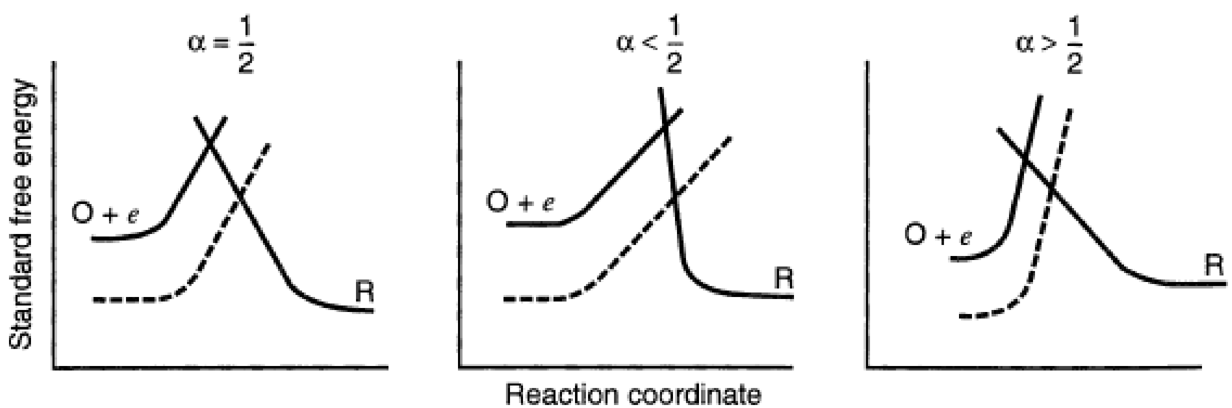
Značenje prijelaznog koeficijenta α?



$$\tan\theta = \alpha FE/x$$

$$\tan\phi = (1-\alpha)\,FE/x$$

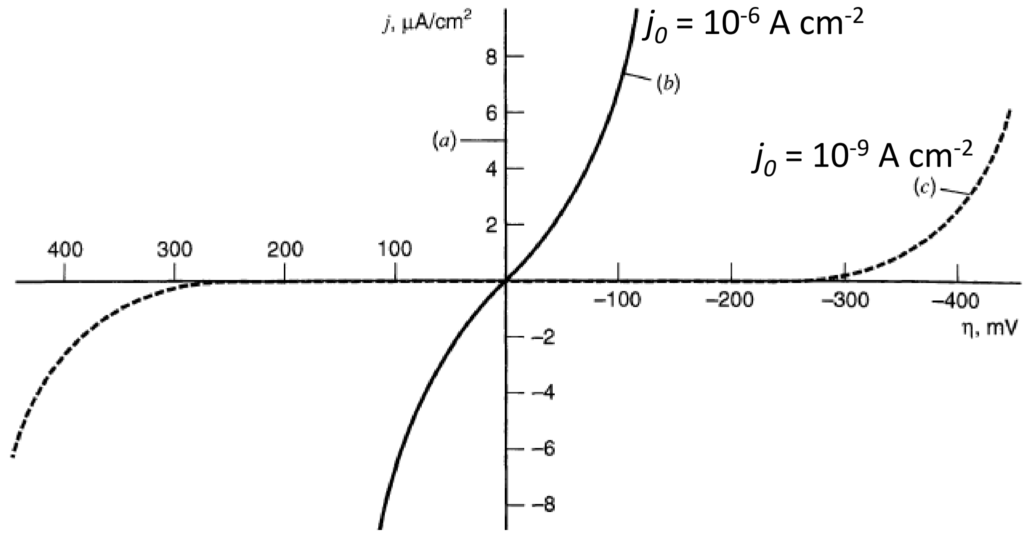
$$\alpha = \frac{\tan\ \theta}{\tan\ \phi + \ \tan\ \theta}$$



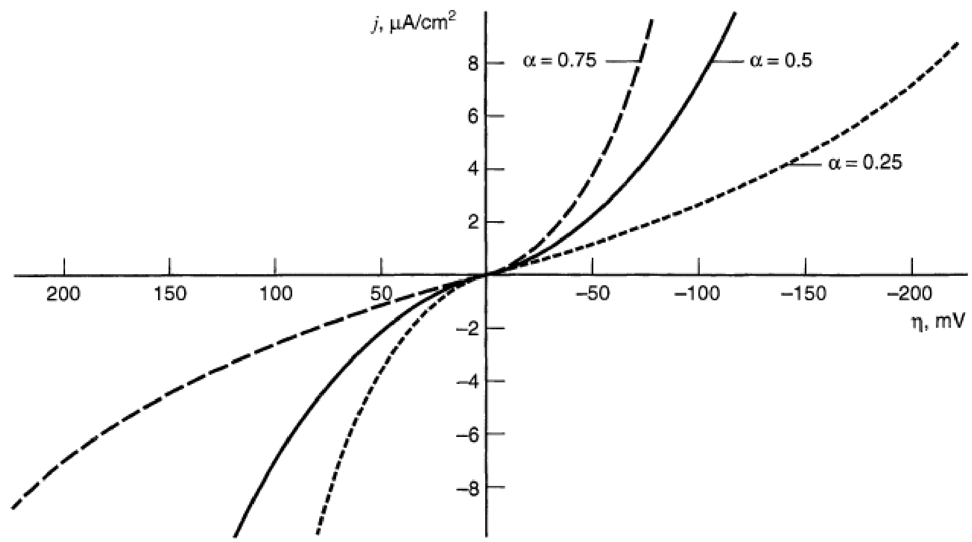
Butler-Volmerova jednadžba

$$i = i_0\left[e^{-\alpha f\eta} - e^{(1-\alpha)f\eta}\right]$$

Utjecaj gustoće struje izmjene

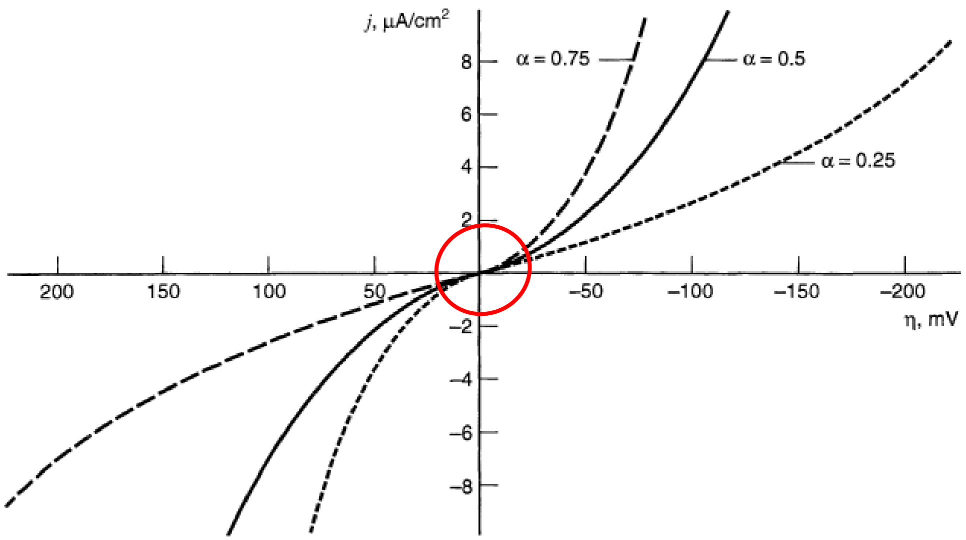


Utjecaj koeficijenta prijelaza



Male vrijednosti prenapona - linearne karakteristike ovisnosti i *vs*. *η*
Ekspanzija u Taylorov red i zadržavanje prva dva člana

$$i = -i_0 f \eta$$



Tafelova jednadžba

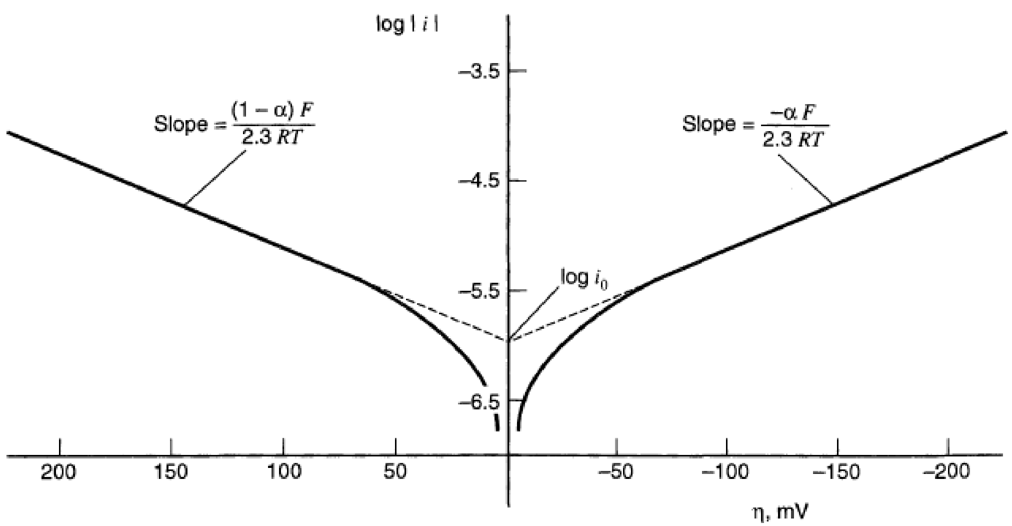
$$\eta = a + b \log i$$

$$i = i_0 e^{-\alpha f \eta}$$

Jedan od doprinosa u B-V jednadžbi (katodni ili anodni) je dominantan

$$\eta = \frac{RT}{\alpha F} \ln i_0 - \frac{RT}{\alpha F} \ln i$$

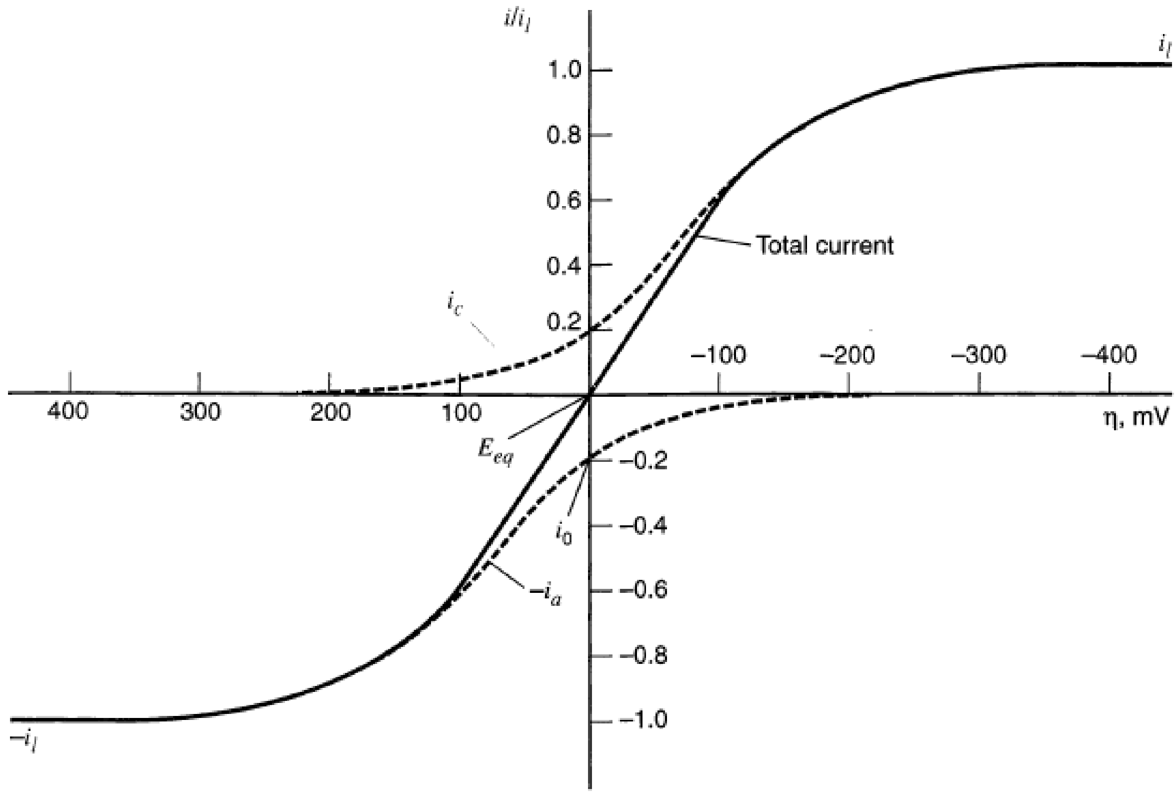
Tafelov dijagram



Difuzijski kontrolirani uvjeti?

$$\boxed{i = i_0\left[\frac{C_O(0,t)}{C_O^*}e^{-\alpha f\eta} - \frac{C_R(0,t)}{C_R^*}e^{(1-\alpha)f\eta}\right]}$$

$$\frac{i}{i_0} = \left(1 - \frac{i}{i_{l,c}}\right)e^{-\alpha f\eta} - \left(1 - \frac{i}{i_{l,a}}\right)e^{(1-\alpha)f\eta}$$



Drugi pristupi određivanju relevantnih parametara

Direktno mjerenje i_0

$$\log i_0 = \log FAk^0 + \log C_O^* + \frac{\alpha F}{2.3RT} E^{0'} - \frac{\alpha F}{2.3RT} E_{eq}$$

$$\frac{d \log (i_0/C_O^*)}{d \log (C_R^*/C_O^*)} = \alpha$$

Allen-Hickling (uzima u obzir quasireverzibilni dio krivulje

$$i = i_0 e^{-\alpha f \eta} (1 - e^{f\eta})$$

$$\log \frac{i}{1 - e^{f\eta}} = \log i_0 - \frac{\alpha F \eta}{2.3RT}$$

$$\bar{C}_{\mathrm{O}}(x, s) = \frac{C_{\mathrm{O}}^{*}}{s} + A(s)e^{-(s/D_{\mathrm{O}})^{1/2}x}$$

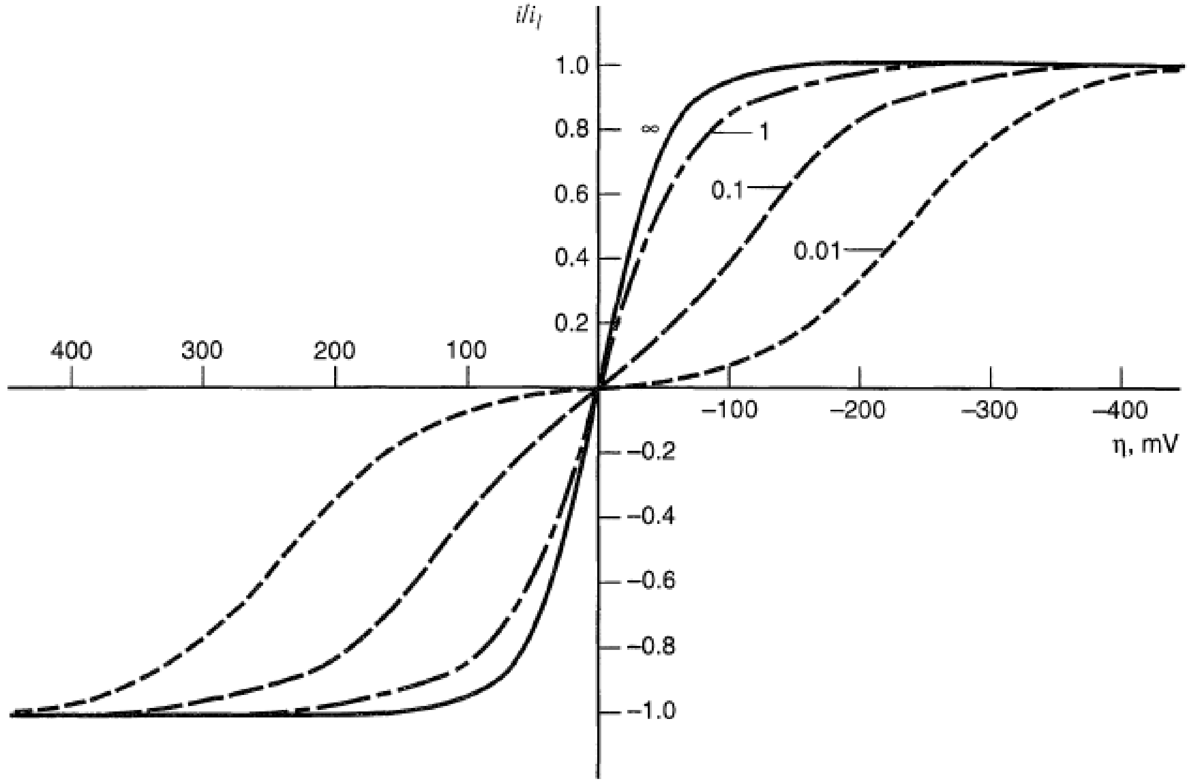
$$\bar{C}_{\mathrm{R}}(x, s) = -\xi A(s)e^{-(s/D_{\mathrm{R}})^{1/2}x}$$

$$\frac{i}{FA} = D_{\mathrm{O}}\left(\frac{\partial C_{\mathrm{O}}(x, t)}{\partial x}\right)_{x=0} = k_{\mathrm{f}}C_{\mathrm{O}}(0, t) - k_{\mathrm{b}}C_{\mathrm{R}}(0, t)$$

$$A(s) = -\frac{k_{\mathrm{f}}}{D_{\mathrm{O}}^{1/2}}\frac{C_{\mathrm{O}}^{*}}{s(H + s^{1/2})} \qquad H = \frac{k_{\mathrm{f}}}{D_{\mathrm{O}}^{1/2}} + \frac{k_{\mathrm{b}}}{D_{\mathrm{R}}^{1/2}}$$

$$\boxed{i(t) = FA(k_{\mathrm{f}}C_{\mathrm{O}}^{*} - k_{\mathrm{b}}C_{\mathrm{R}}^{*})\exp(H^{2}t)\,\mathrm{erfc}(Ht^{1/2})}$$

Utjecaj omjera i_0 / i_l na ovisnost struje o prenaponu



1. Gustoća struje izmjene (j_0) za neku reakciju na platinskoj elektrodi iznosi 0,79 mA cm^{-2} pri 25 °C. Koliko iznosi gustoća struje ako je prenapon:

a) 5 mV

b) 100 mV

c) – 200 mV

Koeficijent prijelaza iznosi 0,5.

2. Pri proučavanju nekog elektrodnog procesa, uz upotrebu radne mikroelektrode površine 12,7 mm^2, izmjerene su sljedeće vrijednosti prenapona i jakosti struje pri temperaturi 25 °C:

η / mV	−200	−190	−180	−160	−150
$-i$ / mA	1,15	0,87	0,65	0,35	0,25

Iz Tafelova prikaza procijenite α i j_0.

3. Izračunajte graničnu jakost struje („Levichevu struju“) za vodenu otopinu neke elektroaktivne tvari koncentracije 4,0 mol dm^{-3} ($D = 1{,}2 \cdot 10^{-9}$ m^2 s^{-1}, $z = 2$) ako je mjerenje izvedeno pomoću rotirajuće disk elektrode polumjera 2,5 µm koja se okreće brzinom 1200 okretaja u minuti. Kinematička viskoznost otopine iznosi 0,01 cm^2 s^{-1}.