

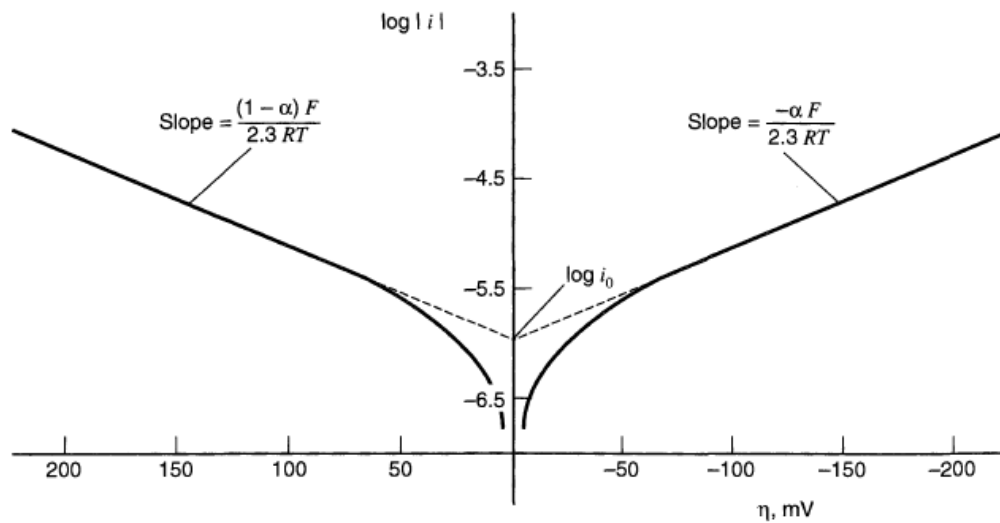
Kinetika elektrodnih reakcija

Butler-Volmer Model

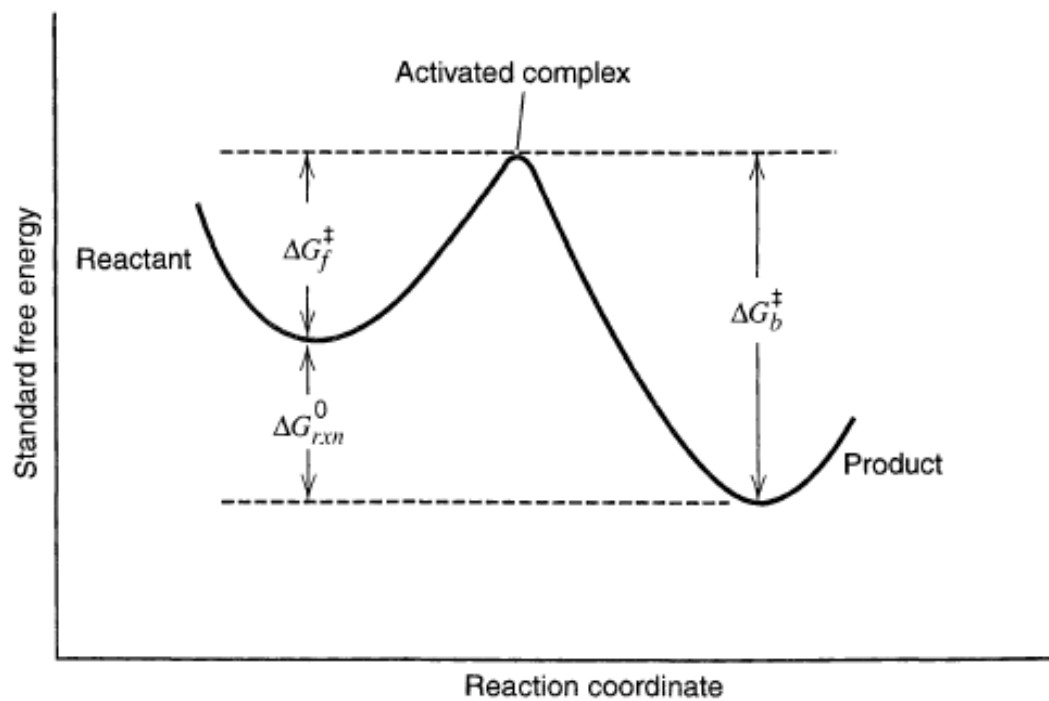
Tafelova rovnice

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

Tafelov diagram

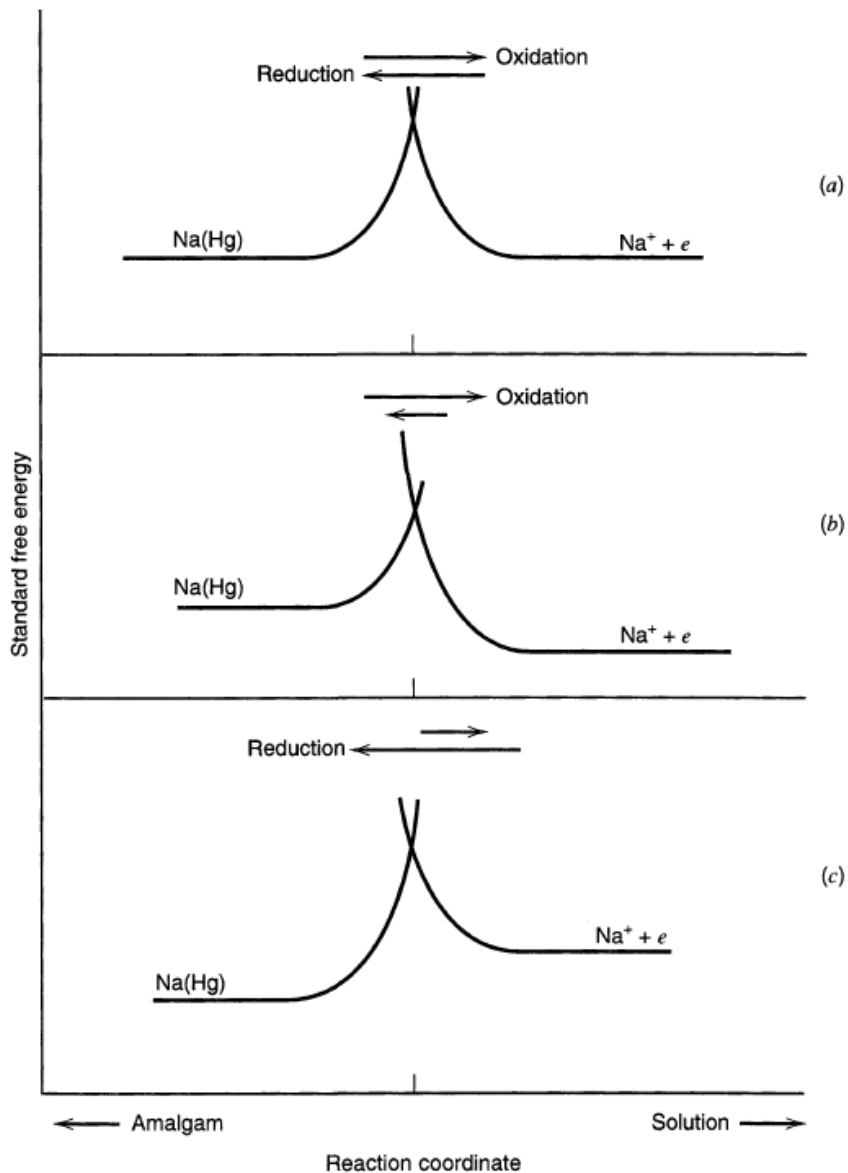


Teorija prijelaznog stanja



Prijelazno stanje u slučaju heterogenih reakcija (na elektrodi)

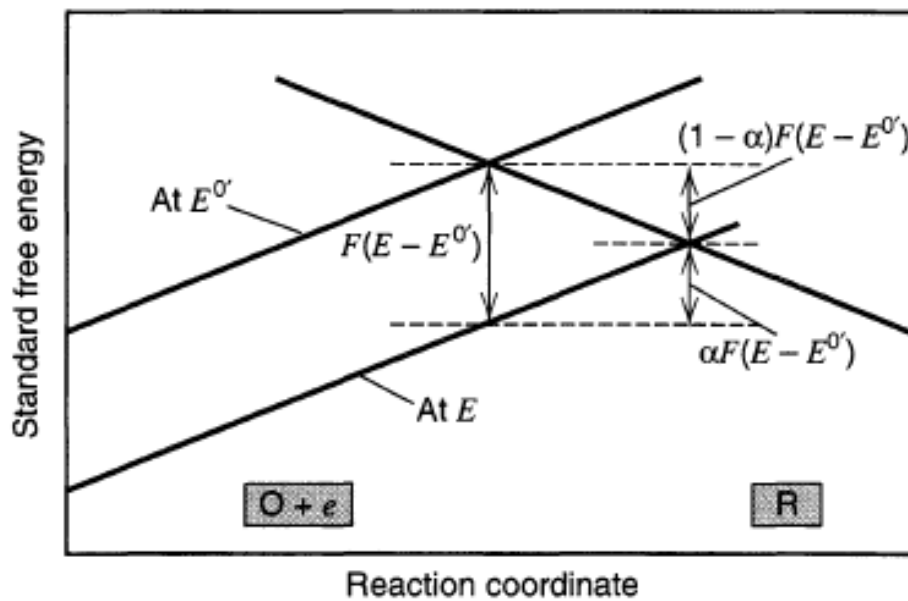
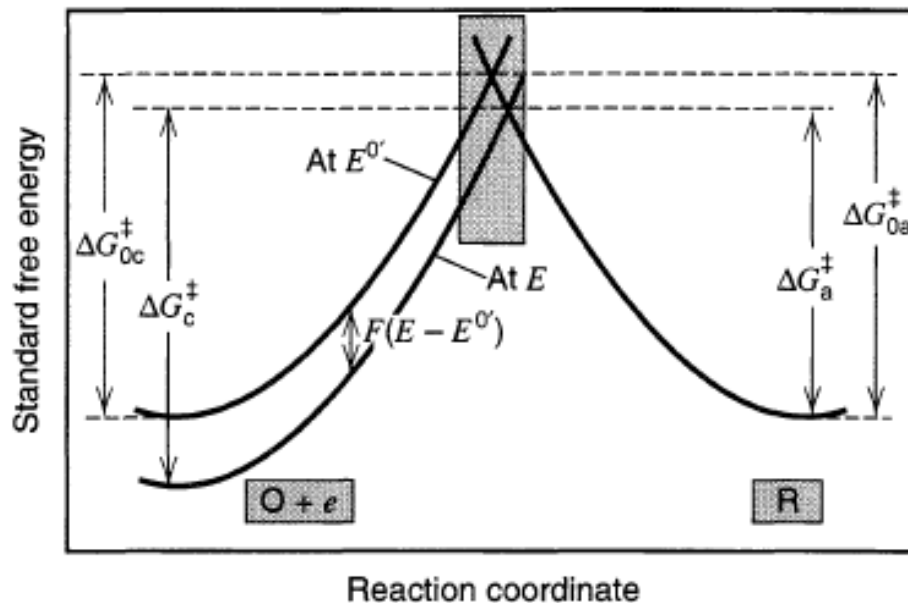
Utjecaj potencijala elektrode na energijsku barijeru?



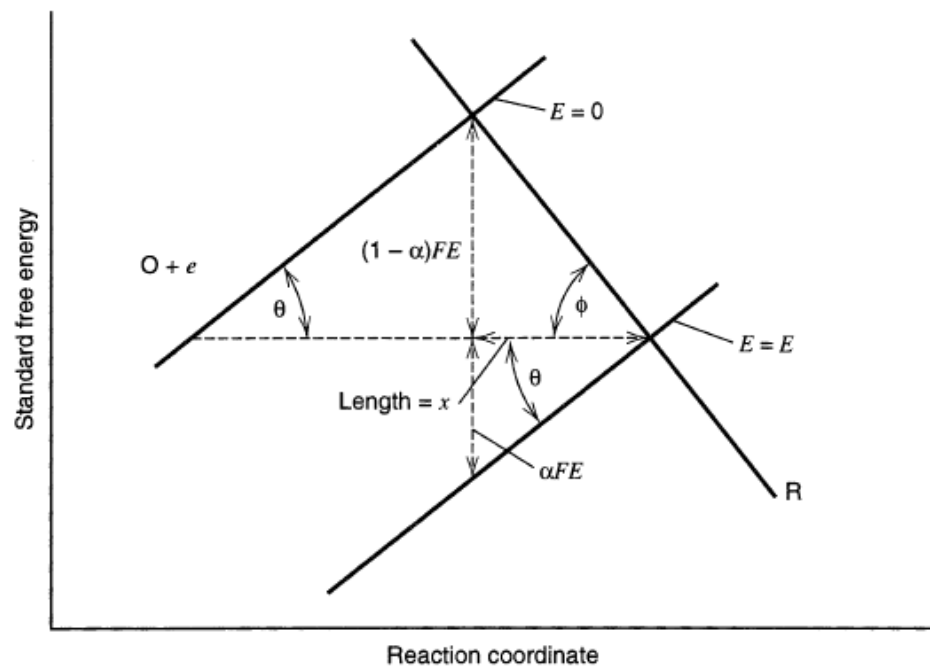
Utjecaj potencijala elektrode na energijsku barijeru

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

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



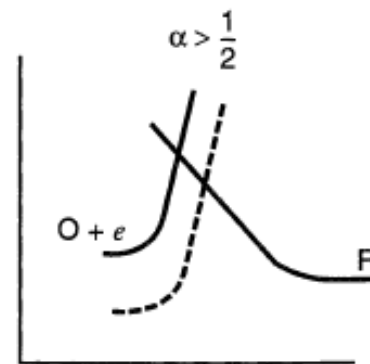
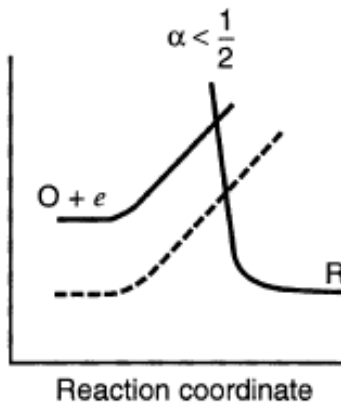
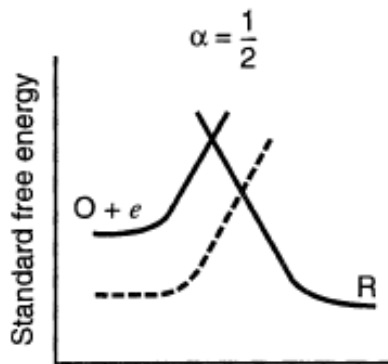
Značenje prijelaznog koeficijenta α ?



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

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

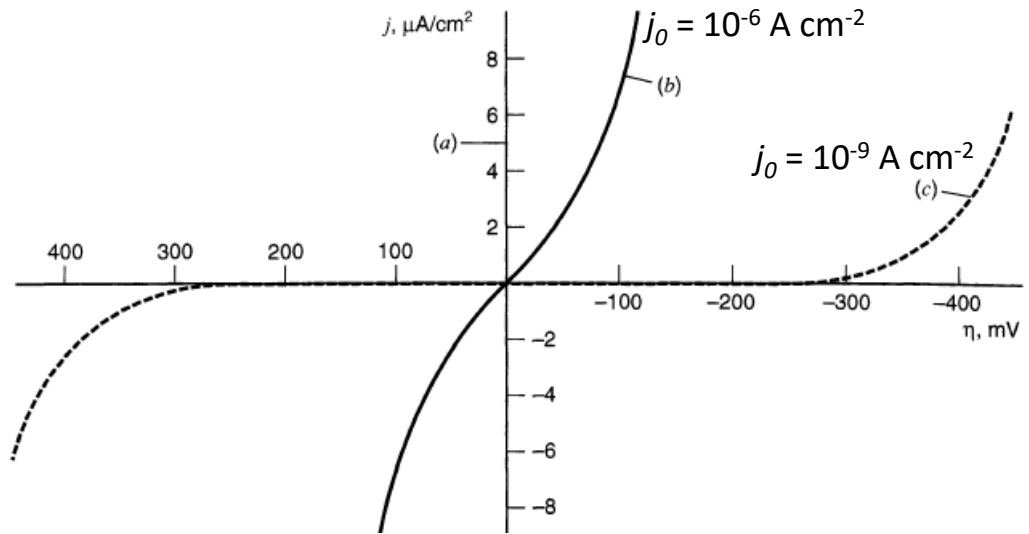
$$\alpha = \frac{\tan \theta}{\tan \phi + \tan \theta}$$



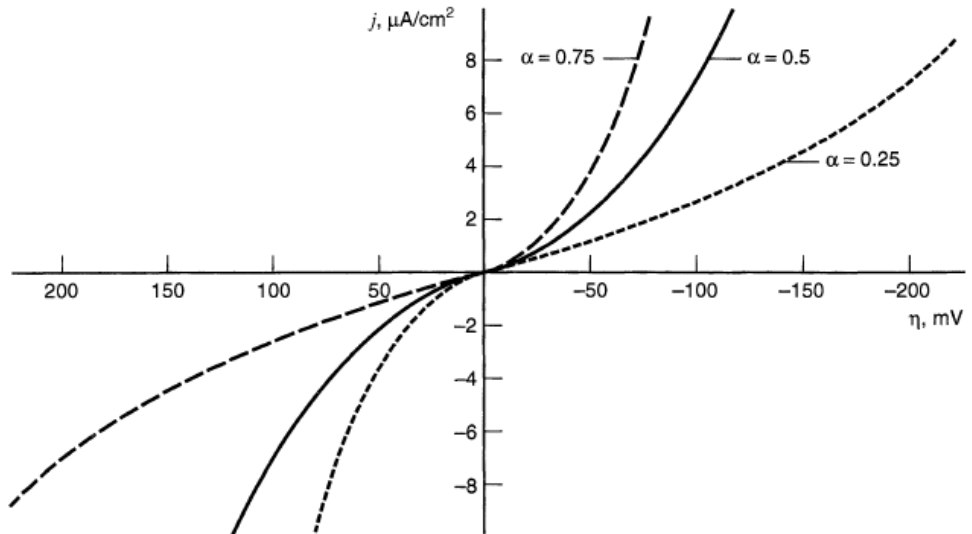
Butler-Volmerova jednadžba

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

Utjecaj gustoće struje izmjene

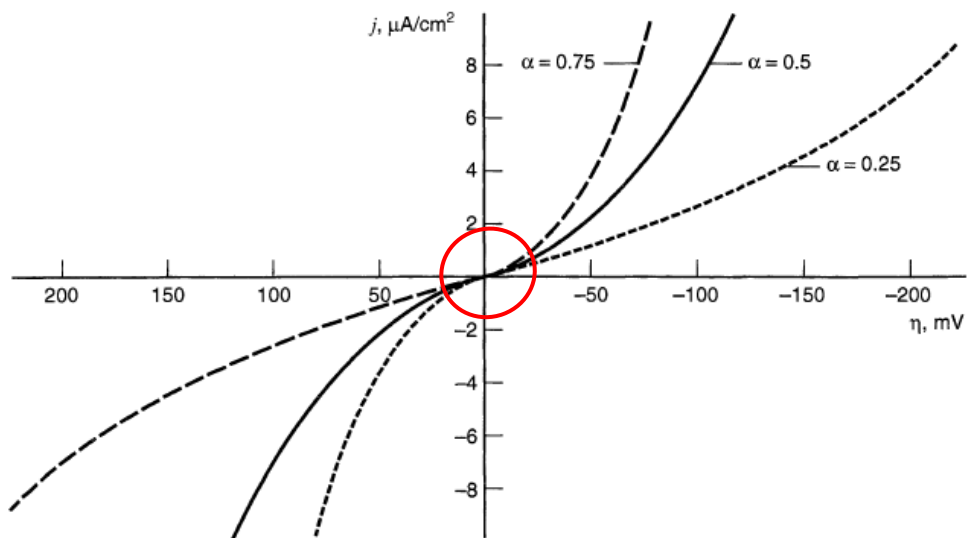


Utjecaj koeficijenta prijelaza



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

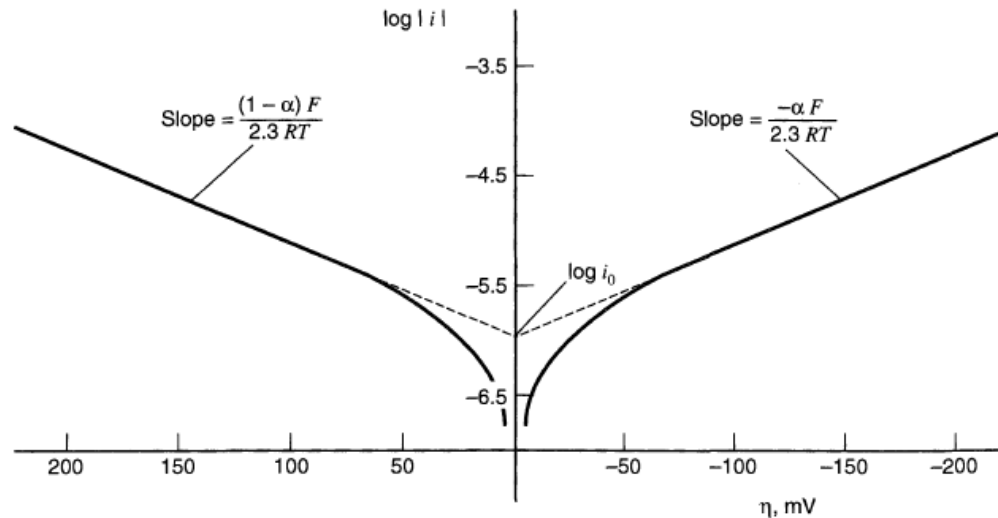
$$\eta = a + b \log i$$

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

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

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

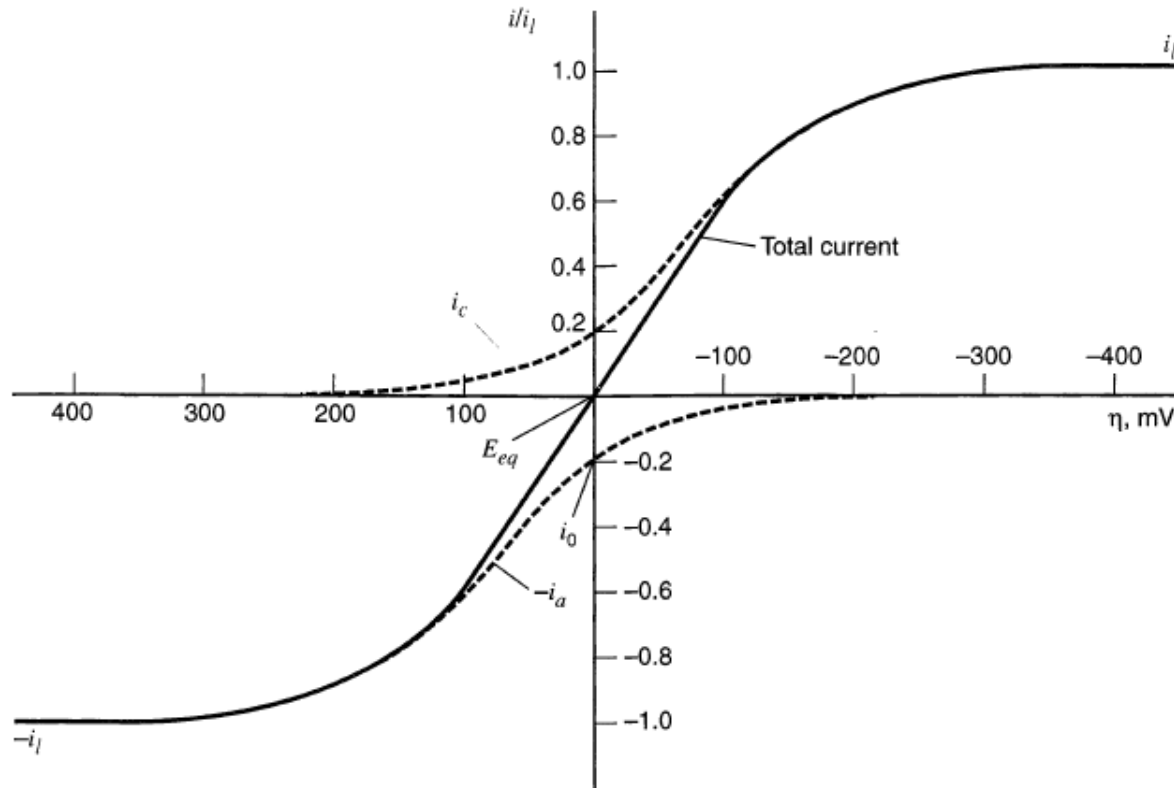
Tafelov dijagram



Difuzijski kontrolirani uvjeti?

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

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



Drugi pristupi određivanju relevantnih parametara

Direktno mjerenje i_0

$$\log i_0 = \log F A k^0 + \log C_{\text{O}}^* + \frac{\alpha F}{2.3RT} E^{0'} - \frac{\alpha F}{2.3RT} E_{\text{eq}}$$

$$\frac{d \log (i_0/C_{\text{O}}^*)}{d \log (C_{\text{R}}^*/C_{\text{O}}^*)} = \alpha$$

Allen-Hickling (uzima u obzir quasireverzibilni dio krivulje)

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

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

Utjecaj omjera i_0 / i_l na ovisnost struje o prenaponu

