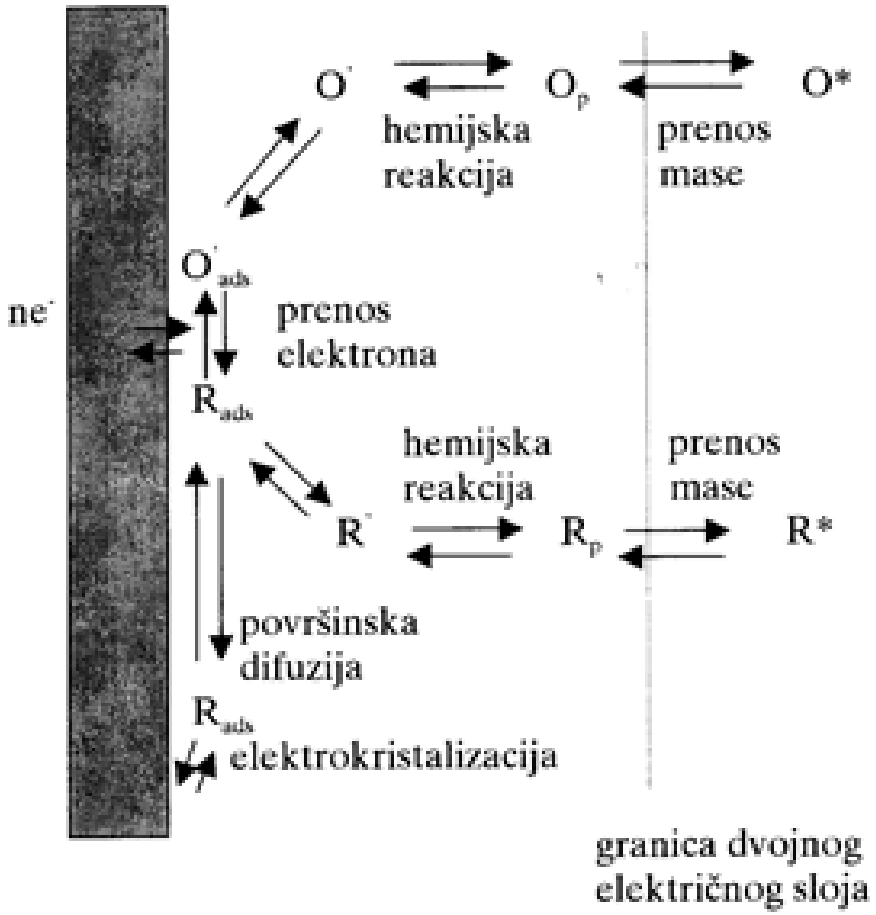
# Jednostavni elektrodni procesi 2

Predavanje 19, 29.04.2020.

**Udžbenik: S. Mentus, Elektrohemija, 2008, strane 196-210 (ne sve strane) + 213-214**

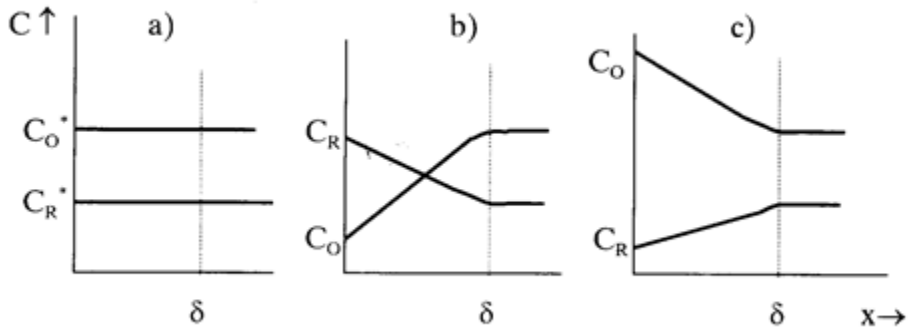
# Priroda sporog stupnja elektrodnog procesa




- **Jednostavni elektrodni procesi određeni**
  - Jednovremenim prenosom elektrona
  - Prenosom mase
  - Kombinacijom ova dva
- **Složeni elektrodni procesi – spori stupanje je bilo šta drugo**

# Jednačina stacionarne I-E krive kada su prenos elektrona i prenos mase (jednovremeno) spori stupnjevi

$$j = j_0 \left( \frac{C_R}{C_R^*} e^{\frac{\beta n F \eta}{RT}} - \frac{C_O}{C_O^*} e^{-\frac{(1-\beta) n F \eta}{RT}} \right)$$




$$j = -nFD_O \frac{dC_O}{dx} \approx -nFD_O \frac{C_O^* - C_O}{\delta_O} \Rightarrow j_{l,c} = -nFD_O \frac{C_O^*}{\delta_O}$$

**Granična difuziona struja**

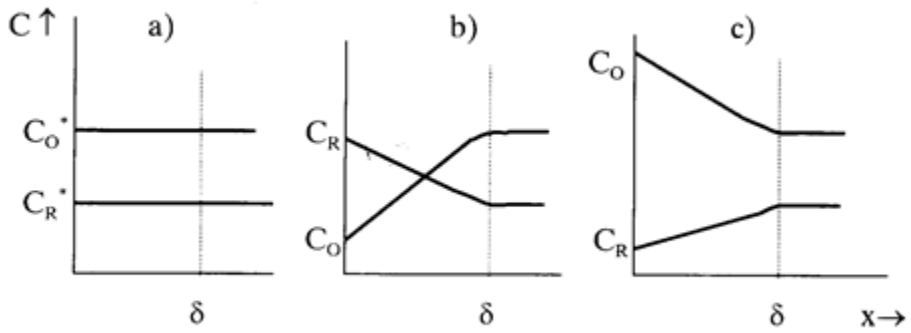
Debljina difuzionog sloja

$$j = nFD_R \frac{dC_R}{dx} \approx nFD_R \frac{C_R^* - C_R}{\delta_R} \Rightarrow j_{l,a} = nFD_R \frac{C_R^*}{\delta_R}$$

**Ako je $C_x$ 0**

# Jednačina stacionarne I-E krive kada su prenos elektrona i prenos mase (jednovremeno) spori stupnjevi

$$j = j_0 \left( \frac{C_R}{C_R^*} e^{\frac{\beta n F \eta}{RT}} - \frac{C_O}{C_O^*} e^{-\frac{(1-\beta) n F \eta}{RT}} \right)$$




$$j = -nFD_O \frac{dC_O}{dx} \approx -nFD_O \frac{C_O^* - C_O}{\delta_O} \quad + \quad j_{l,c} = -nFD_O \frac{C_O^*}{\delta_O} \quad \Rightarrow \quad \frac{C_O}{C_O^*} = 1 - \frac{j}{j_{l,c}}$$

$$j = nFD_R \frac{dC_R}{dx} \approx nFD_R \frac{C_R^* - C_R}{\delta_R} \quad + \quad j_{l,a} = nFD_R \frac{C_R^*}{\delta_R} \quad \Rightarrow \quad \frac{C_R}{C_R^*} = 1 - \frac{j}{j_{l,a}}$$

# Jednačina stacionarne I-E krive kada su prenos elektrona i prenos mase (jednovremeno) spori stupnjevi

$$j = j_0\left(\frac{C_R}{C_R^*}e^{\frac{\beta nF\eta}{RT}} - \frac{C_O}{C_O^*}e^{-\frac{(1-\beta)nF\eta}{RT}}\right)$$

$$\frac{C_R}{C_R^*} = 1 - \frac{j}{j_{l,a}} \qquad \frac{C_O}{C_O^*} = 1 - \frac{j}{j_{l,c}}$$

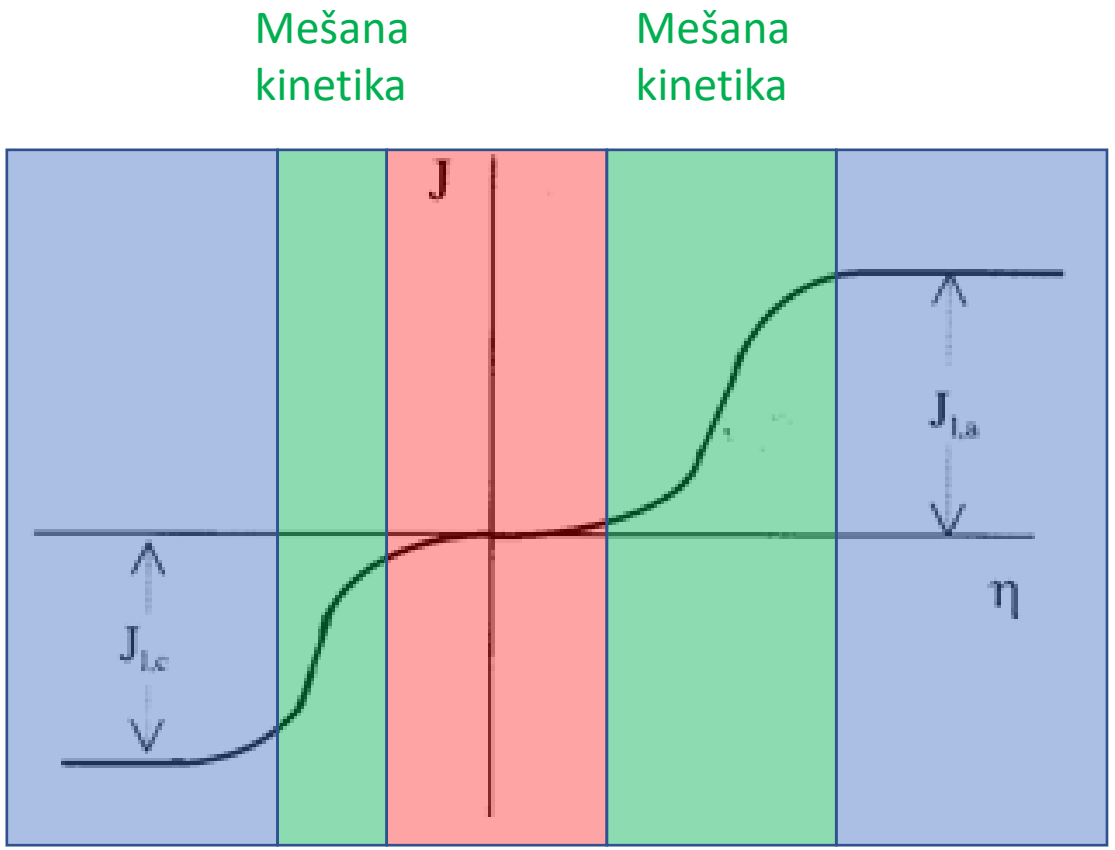
$$j = j_0\left[\left(1 - \frac{j}{j_{l,a}}\right)e^{\frac{\beta nF\eta}{RT}} - \left(1 - \frac{j}{j_{l,c}}\right)e^{\frac{-(1-\beta)nF\eta}{RT}}\right]$$

Stacionarna I-E krive **kvazireverzibilnog** redoks procesa

# Jednačina stacionarne I-E krive kada su prenos elektrona i prenos mase (jednovremeno) spori stupnjevi

$$j = j_0\left[\left(1-\frac{j}{j_{l,a}}\right)e^{\frac{\beta nF\eta}{RT}} - \left(1-\frac{j}{j_{l,c}}\right)e^{\frac{-(1-\beta)nF\eta}{RT}}\right]$$

Stacionarna I-E krive **kvazireverzibilnog** redoks procesa



# Nagib **stacionarne** *I-E* krive kvazireverzibilnog redoks procesa na ravnotežnom potencijalu

$$\frac{j}{j_0} = \frac{j}{j_{l,c}} - \frac{j}{j_{l,a}} + \frac{nF\eta}{RT}$$

$$\left(\frac{\eta}{j}\right)_{\eta=0} = \frac{RT}{nF}\left(\frac{1}{j_0} + \frac{1}{j_{l,a}} - \frac{1}{j_{l,c}}\right)$$

**Iz kinetičkog dela**
**Zavisi od potencijala!!!!!!**

$$\left(\frac{\eta}{j}\right)_{\eta=0} = (R_{ct} + R_{mt,a} + R_{mt,c})_{\eta=0}$$

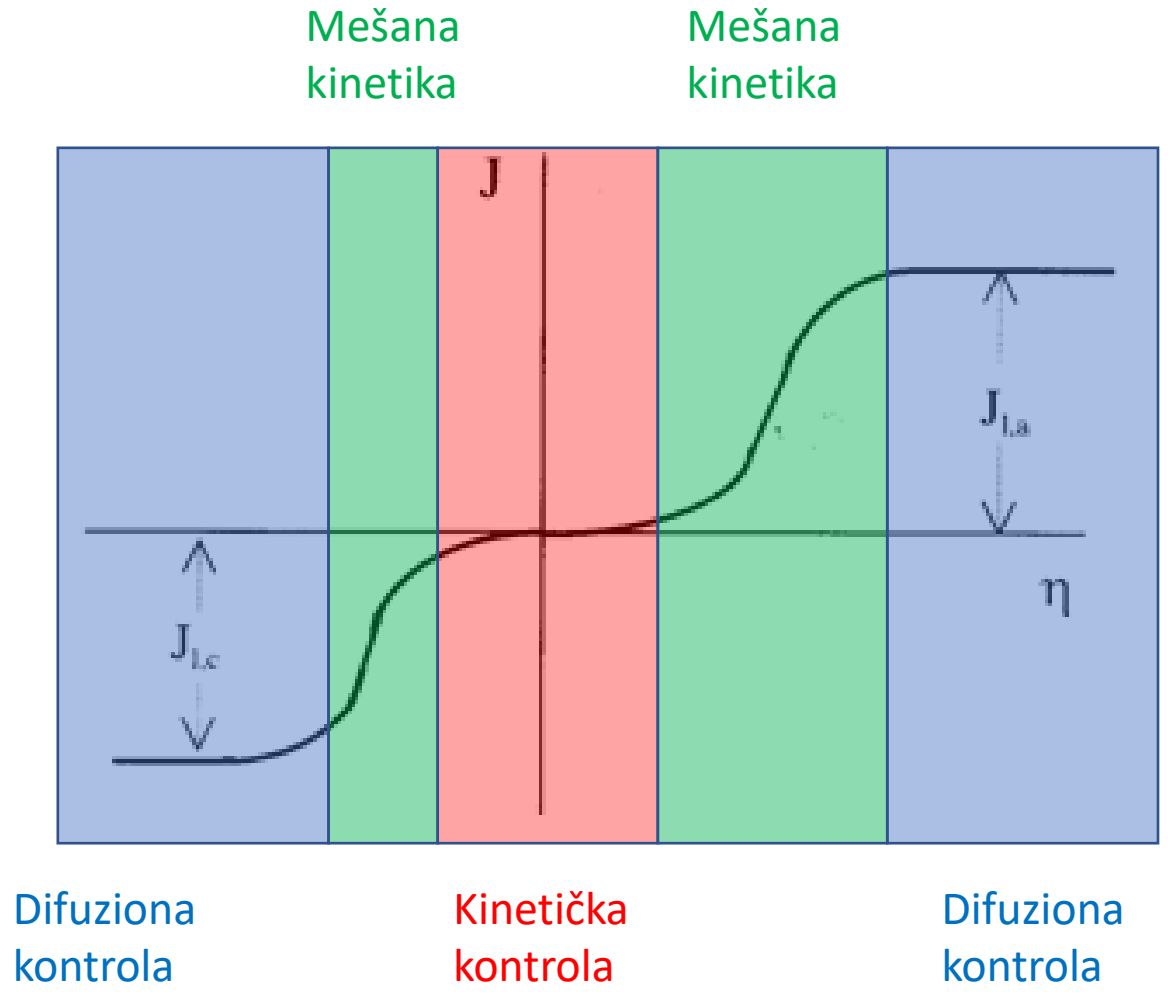
**Iz granične difuzione struje**
**Ne zavisi od potencijala!!!!!!**

Ako su otpori u serijskoj vezi to znači da procesi slede jedan drugog, a ne da se odigravaju paralelno

**Elektroaktivna vrsta mora da difunduje do elektrode da bi došlo do prenosa naelektrisanja**

# Jednačina stacionarne I-E krive kada su prenos elektrona i prenos mase (jednovremeno) spori stupnjevi

Kako se odnose otpori za procese prenosa elektrona i prenosa mase u naznačenim oblastima?

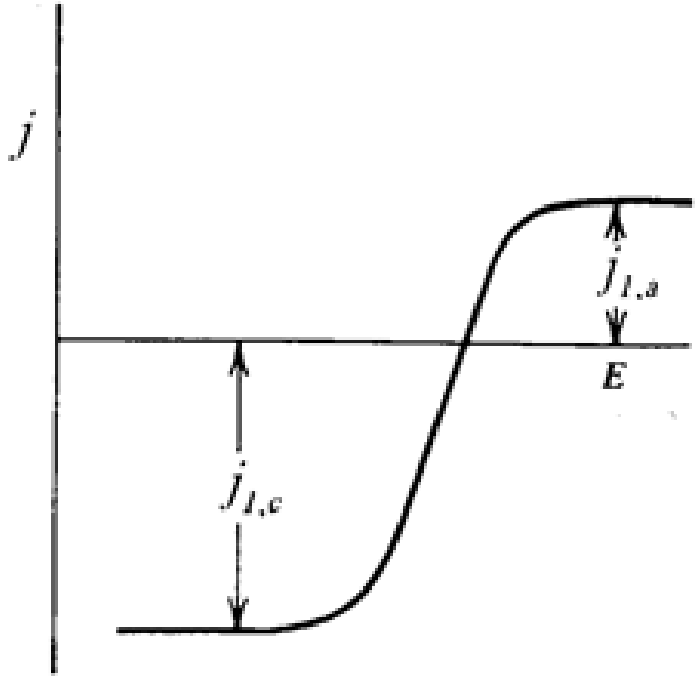


# Jednačina I-E krive kada je prenos mase spori stupanj – **stacionarna** I-E kriva reverzibilnog redoks procesa

- Gustina struje izmene jako velika ($R_{ct}$ jako malo)

$$\left(1-\frac{j}{j_{l,a}}\right)\cdot e^{\frac{\beta nF\eta}{RT}}=\left(1-\frac{j}{j_{l,c}}\right)\cdot e^{\frac{-(1-\beta)nF\eta}{RT}}$$

$$\eta=\frac{RT}{nF}\ln\frac{1-\dfrac{j}{j_{l,c}}}{1-\dfrac{j}{j_{l,a}}}$$



# Jednačina I-E krive kada je prenos mase spori stupanj – **stacionarna** I-E kriva reverzibilnog redoks procesa

- Gustina struje izmene jako velika ($R_{ct}$ jako malo)

$$\eta = \frac{RT}{nF} \ln \frac{1 - \frac{j}{j_{l,c}}}{1 - \frac{j}{j_{l,a}}} \quad + \quad \frac{C_O}{C_O^*} = 1 - \frac{j}{j_{l,c}} \quad + \quad \frac{C_R}{C_R^*} = 1 - \frac{j}{j_{l,a}}$$

$$\eta = \frac{RT}{nF} \ln \frac{C_O}{C_O^*} \frac{C_R^*}{C_R} \quad \Rightarrow \quad \eta = \left( E^{0,'} + \frac{RT}{nF} \ln \frac{C_O}{C_R} \right) - \left( E^{0,'} + \frac{RT}{nF} \ln \frac{C_O^*}{C_R^*} \right)$$

Ravnotežni elektrodni potencijal

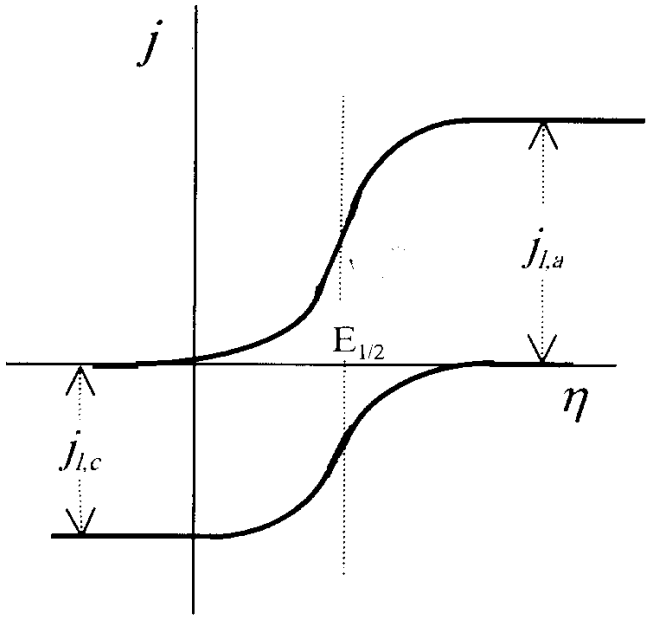
# Jednačina I-E krive kada je prenos mase spori stupanj – **stacionarna** I-E kriva reverzibilnog redoks procesa

$$\eta = \left( E^{0,'} + \frac{RT}{nF} \ln \frac{C_O}{C_R} \right) - \left( E^{0,'} + \frac{RT}{nF} \ln \frac{C_O^*}{C_R^*} \right)$$

$$C_O = (j - j_{l,c}) \frac{\delta_O}{nFD_O} \qquad C_R = (j_{l,a} - j) \frac{\delta_R}{nFD_R}$$

$$E = E^{0'} + \frac{RT}{nF} \ln \frac{D_R \delta_O}{D_O \delta_R} + \frac{RT}{nF} \ln \frac{j - j_{l,c}}{j_{l,a} - j}$$

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{j - j_{l,c}}{j_{l,a} - j}$$ Polutalasni potencijal



# Nagib I-E krive reverzibilnog redoks procesa na ravnotežnom potencijalu

$$\left(\frac{\eta}{j}\right)_{\eta=0} = \frac{RT}{nF}\left(\frac{1}{j_{l,a}} - \frac{1}{j_{l,c}}\right) = (R_{mt,a} + R_{mt,c})_{\eta=0}$$

Parametre sporog prenosa mase računamo iz graničnih difuzionih struja

$$j_0 = \frac{RT}{nF(R_{ct})_{\eta=0}}$$

**Ogromna gustina struje izmene!!!!!!!**

Zanemarljiv otpor za prenos naelektrisanja

**Šta znači „ogromna“?**

# Određivanje parametara sporog prenosa elektrona

| | Ireverzibilni proces | Kvazireverzibilni proces | Reverzibilni proces |
|---|---|---|---|
| | $j = j_0 \cdot \left( e^{\frac{\beta nF\eta}{RT}} - e^{\frac{-(1-\beta)nF\eta}{RT}} \right)$ | $j = j_0 \left[ \left( 1 - \frac{j}{j_{l,a}} \right) e^{\frac{\beta nF\eta}{RT}} - \left( 1 - \frac{j}{j_{l,c}} \right) e^{\frac{-(1-\beta)nF\eta}{RT}} \right]$ | $\eta = \frac{RT}{nF} \ln \frac{1 - \frac{j}{j_{l,c}}}{1 - \frac{j}{j_{l,a}}}$ |
| CT | $\beta$ i $j_0$ | $\beta$ i $j_0$ | *nema* |
| MT | *nema* | $j_{l,a}$ *i* $j_{l,c}$ | $j_{l,a}$ *i* $j_{l,c}$ |

MT – čitamo sa *I-E* krive

CT – radimo Tafelovu analizu

# Tafelova analiza – ireverzibilni proces

- Tafelova jednačina (1905) – $\eta = a + b\log j$

$$\frac{j_a}{j_c} = e^{\frac{nF\eta}{RT}} \qquad \frac{j_a}{j_c} = 10^{\frac{nF\eta}{2,303RT}}$$

**Veće od 100 ili manje od 0,01 (merimo samo anodnu ili katodnu komponentu)**

$$|\eta| > \frac{2 \cdot 2,3RT}{nF} \approx \frac{120}{n}\ \text{mV}$$

# Tafelova analiza – ireverzibilni proces

- Tafelova jednačina (1905) – ***η = a + b*log*j***

$$\ln j = \ln j_0 + \frac{\beta n F \eta}{RT}$$

$$\eta = \frac{-RT}{\beta n F} \ln j_0 + \frac{RT}{\beta n F} \ln j$$

$$\eta = \frac{-2{,}3RT}{\beta n F} \log j_0 + \frac{2{,}3RT}{\beta n F} \log j$$

$$\eta = \frac{-2{,}3RT}{\beta n F} \log j_0 + \frac{2{,}3RT}{\beta n F} \log j$$

***η =*** ***a*** ***+ b*** ***log j***

**Tafelov nagib**

# Tafelova analiza – ireverzibilni proces

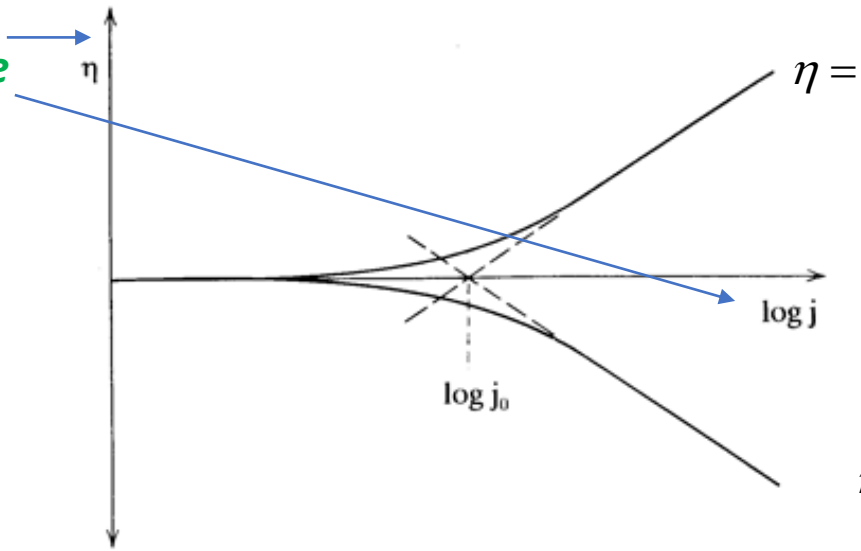
- Tafelova jednačina (1905) – ***η = a + blogj***

$$a_a = \frac{-2{,}3RT}{\beta nF}\log j_0 \qquad \frac{\mathrm{d}\eta}{\mathrm{dlogj}} = b_a = \frac{2{,}3RT}{\beta nF}$$

$$b_a = |b_c| = \frac{120}{n}\ mV$$

**Na sobnoj temperaturi**
**β = 0,5**

***Tafelove koordinate***




$$\eta = \frac{-2{,}3RT}{\beta nF}\log j_0 + \frac{2{,}3RT}{\beta nF}\log j$$

***Anodna grana***

$$\eta = \frac{2{,}3RT}{(1-\beta)nF}\log j_0 - \frac{2{,}3RT}{(1-\beta)nF}\log j$$

***Katodna grana***

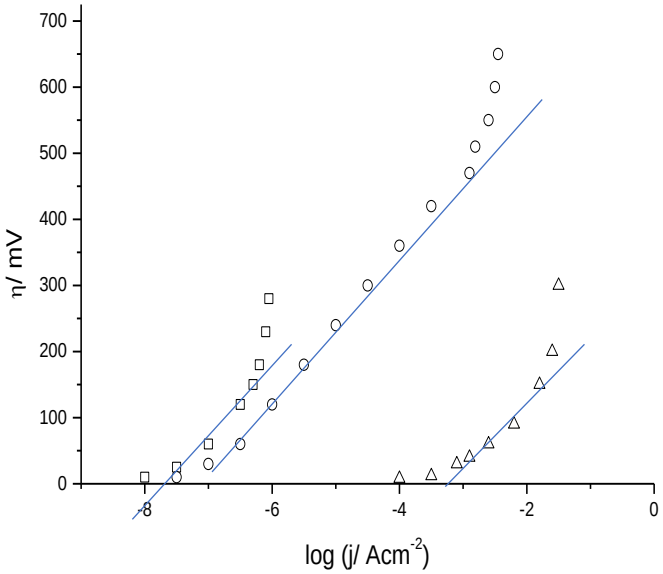
# Tafelova analiza – kvazireverzibilni proces

- Tafelova jednačina (1905) – ***η = a + b log j***

$$j = j_0\left[\left(1-\frac{j}{j_{l,a}}\right)e^{\frac{\beta nF\eta}{RT}} - \left(1-\frac{j}{j_{l,c}}\right)e^{\frac{-(1-\beta)nF\eta}{RT}}\right]$$

***Anodna grana***

$$\eta = -\frac{RT}{\beta nF}\ln j_0 + \frac{RT}{\beta nF}\ln\left(\frac{j}{1-\frac{j}{j_{l,a}}}\right)$$




$$\eta = \frac{RT}{(1-\beta)nF}\ln j_0 - \frac{RT}{(1-\beta)nF}\ln\left(\frac{j}{1-\frac{j}{j_{l,c}}}\right)$$

***Korekcija na prenos mase***

# Uticaj temperature na kinetiku elektrodne reakcije

$$k_a = Ae^{\frac{-\Delta G_c^{\#} + \beta nFE}{RT}}$$

Raste sa povećanjem temperature

$$k_a = Ae^{\frac{-\Delta H^{\#}}{RT}} e^{\frac{\Delta S^{\#}}{R}} e^{\frac{\beta nFE}{RT}}$$

$$\frac{\partial \ln j_a}{\partial (1/T)} = -\frac{\Delta H^{\#} + \beta nFE}{R}$$

Određivanje energije aktivacije