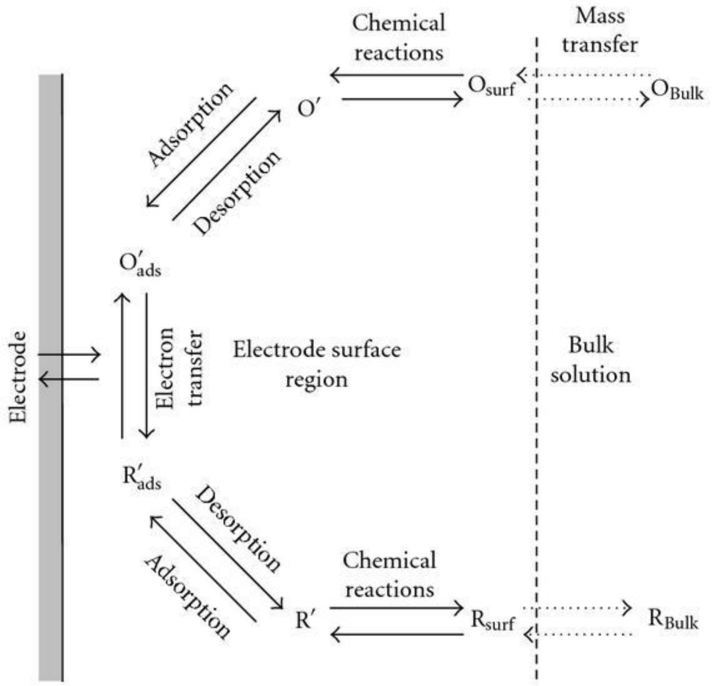
3.2 – Kinetics of electroplating

3.1. Electrodeposition mechanism

Overview

Electrodeposition is governed by 5 fundamental processes

1) Charge transfer kinetics: Butler-Volmer
2) Mass transfer: migration, diffusion, convection
3) Coupled chemical reactions
4) Adsorption and diffusion of adions
5) Crystallisation: nucleation and growth



3.2. Electrodeposition kinetics

1) One-step reaction – 1st order kinetics

$$O + e^{-} \underset{k_{ox}}{\overset{k_{red}}{\rightleftarrows}} R$$

Write the rate of reduction and the rate of oxidation

3.2. Electrodeposition kinetics

1) One-step reaction – 1st order kinetics

$$Ox + ze^- \underset{k_{Ox}}{\overset{k_{Red}}{\rightleftarrows}} Red$$

$$v_{Red} = -\frac{d[Ox]}{dt} = k_{Red}[Ox] \qquad v_{Ox} = -\frac{d[Red]}{dt} = k_{red}[Red]$$

$$Q = nzF = \int i(t).dt$$

where F is the Faraday constant $F = e.\mathcal{N}_A = 96485\ C.mol^{-1}$

From the Faraday law, determine the reduction and oxidation currents

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$$Q = nzF = \int i(t).dt \Leftrightarrow i = zF\frac{dn}{dt}$$

where F is the Faraday constant $F = e.\mathcal{N}_A = 96485\ C.mol^{-1}$

$$i_{Red} = zFk_{Red}[Ox] \qquad i_{Ox} = zFk_{Ox}[Red]$$

3.2. Electrodeposition kinetics

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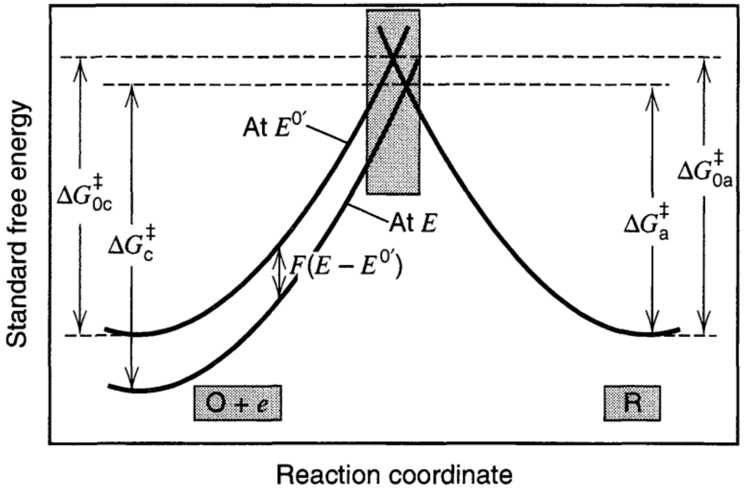
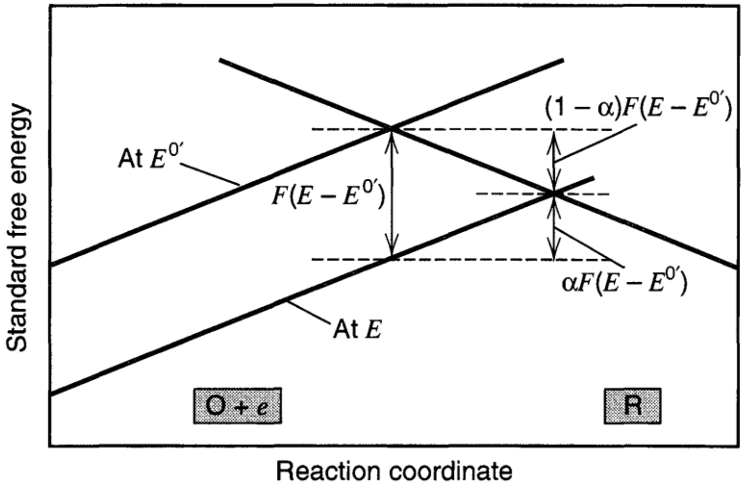
k_{Red} and k_{Ox} are kinetic constants that satisfy the Arrhenius law





3.2. Electrodeposition kinetics

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k_{Red} and k_{Ox} are kinetic constants that satisfy the Arrhenius law

$$k_{Red} = \beta_{Red} \cdot exp^{\frac{-\Delta G^*_{Red}}{RT}} \qquad k_{Ox} = \beta_{Ox} \cdot exp^{\frac{-\Delta G^*_{Ox}}{RT}}$$

$$\Delta G^*_{Red} = \Delta G^*_{\chi,\,Red} + \alpha zF\Delta\phi \qquad \Delta G^*_{Ox} = \Delta G^*_{\chi,\,Ox} - (1-\alpha)zF\Delta\phi$$

Chemical
Potential independent

Electrochemical
Potential dependent

$$i_{Red} = zF[Ox]\beta_{Red}\, exp^{\frac{-\Delta G^*_{\chi,\,Red}}{RT}} exp^{\frac{-\alpha zF\Delta\phi}{RT}} \qquad i_{Ox} = zF[Red]\beta_{Ox}\, exp^{\frac{-\Delta G^*_{\chi,\,Ox}}{RT}} exp^{\frac{(1-\alpha)zF\Delta\phi}{RT}}$$

3.2. Electrodeposition kinetics

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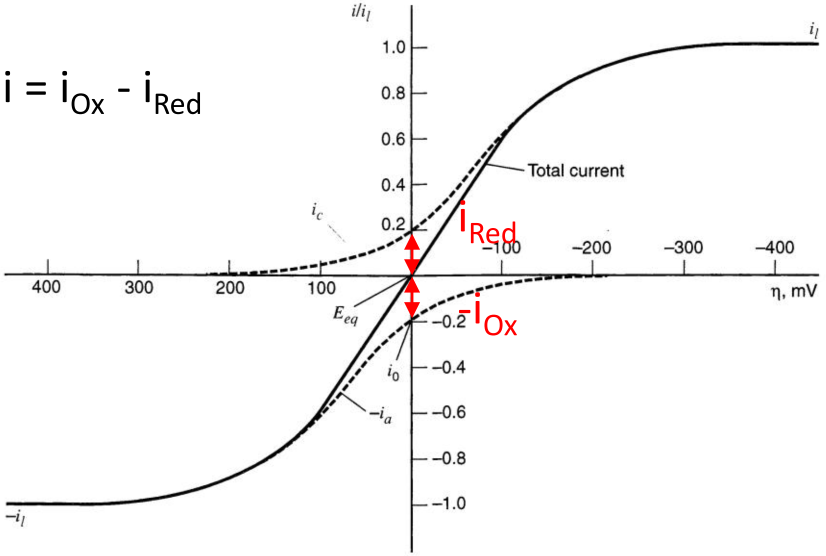
Net current: $i = i_{Ox} - i_{Red}$



At equilibrium potential $(\Delta\phi = \Delta\phi_{eq})$, $i_{Red} = i_{Ox} = i_0$ the exchange current density

3.2. Electrodeposition kinetics

1) One-step reaction – 1st order kinetics

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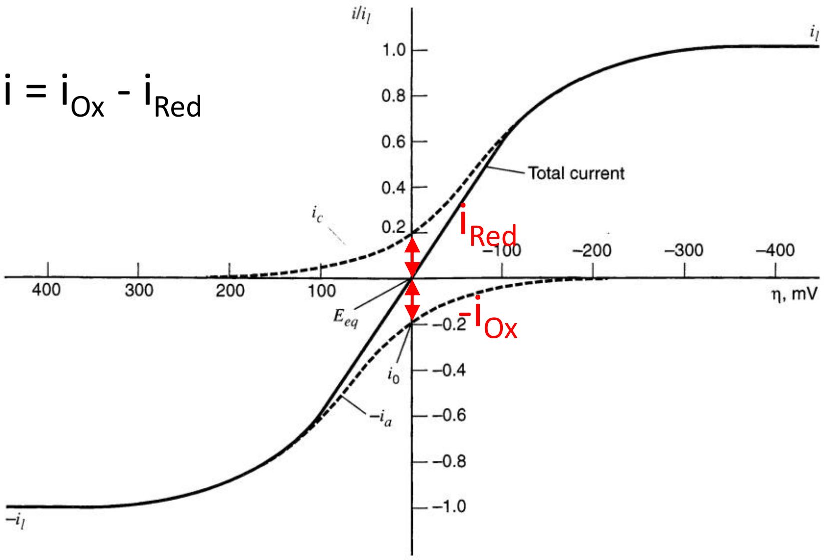
$$\boldsymbol{i_0} = zF[Ox]\beta_{Red}\, exp^{\frac{-\Delta G^*_{\chi,Red}}{RT}}\, exp^{\frac{-\alpha zF\Delta\phi_{eq}}{RT}} = zF[Red]\beta_{Ox}\, exp^{\frac{-\Delta G^*_{\chi,Ox}}{RT}}\, exp^{\frac{(1-\alpha)zF\Delta\phi_{eq}}{RT}}$$

Net current: $i = i_{Ox} - i_{Red}$



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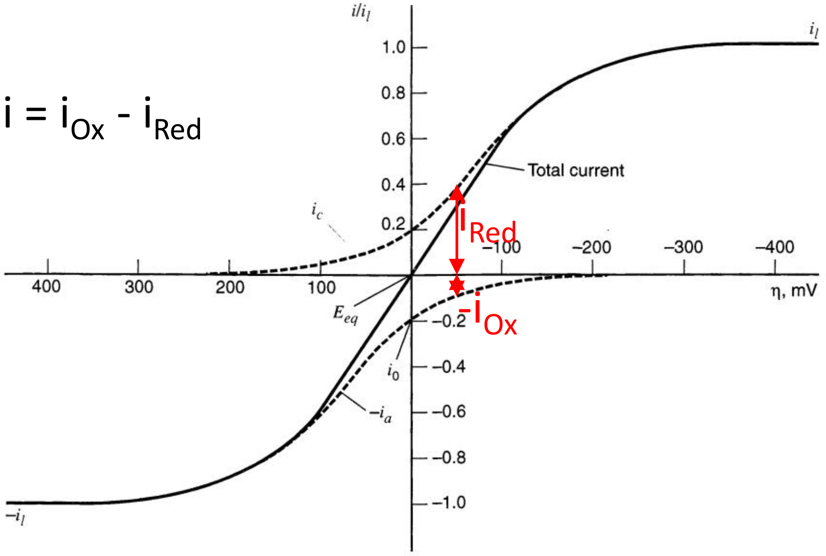


Out of equilibrium potential $(\Delta\phi = \Delta\phi_{eq} + \eta)$, express i as a function of i_0

3.2. Electrodeposition kinetics

1) One-step reaction – 1st order kinetics

$$Ox + ze^- \underset{k_{Ox}}{\overset{k_{Red}}{\rightleftarrows}} Red$$

$$i_{Red} = zF[Ox]\beta_{Red}\, exp^{\frac{-\Delta G^*_{\chi,Red}}{RT}} exp^{\frac{-\alpha zF\Delta\phi}{RT}} \qquad i_{Ox} = zF[Red]\beta_{Ox}\, exp^{\frac{-\Delta G^*_{\chi,Ox}}{RT}} exp^{\frac{(1-\alpha)zF\Delta\phi}{RT}}$$

Out of equilibrium: $\Delta\phi = \Delta\phi_{eq} + \eta$

$$i = i_{Ox} - i_{Red}$$

$$i = \left\{zF[Red]\beta_{Ox} \cdot exp^{\frac{-\Delta G^*_{\chi,Ox}}{RT}} exp^{\frac{(1-\alpha)zF\Delta\phi_{eq}}{RT}}\right\} exp^{\frac{(1-\alpha)zF\eta}{RT}} - \left\{zF[Ox]\beta_{Red} \cdot exp^{\frac{-\Delta G^*_{\chi,Red}}{RT}} exp^{\frac{-\alpha zF\Delta\phi_{eq}}{RT}}\right\} \Delta\phi_{eq} exp^{\frac{-\alpha zF\eta}{RT}}$$

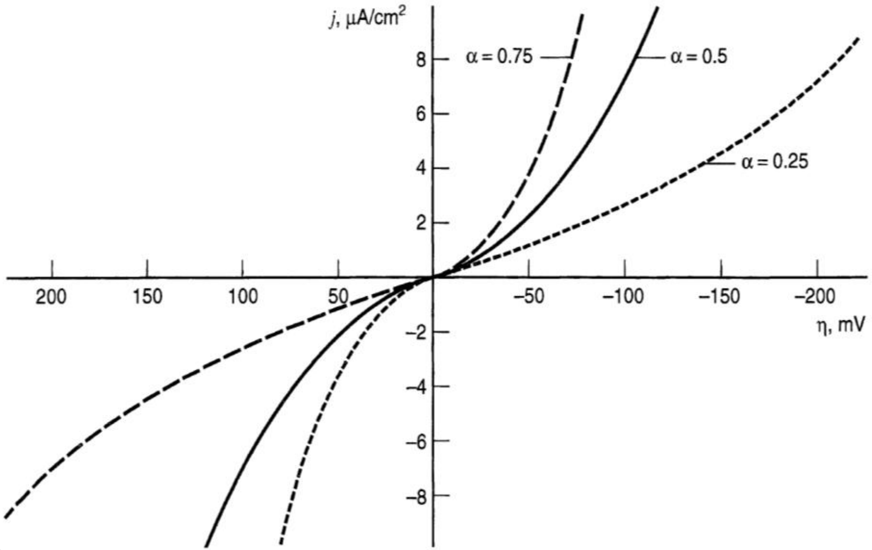
$$i = i_0\left(exp^{\frac{(1-\alpha)zF\eta}{RT}} - exp^{\frac{-\alpha zF\eta}{RT}}\right)$$

Butler-Volmer equation

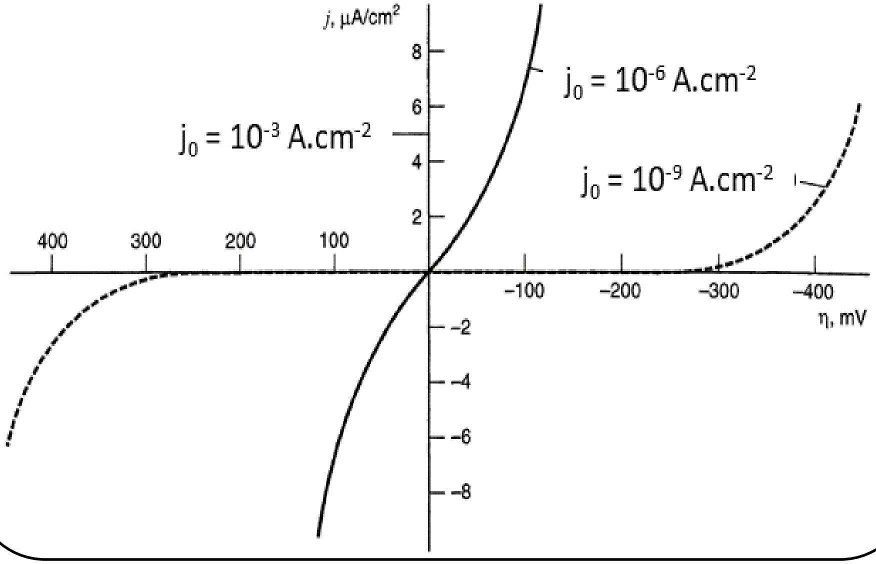
3.2. Electrodeposition kinetics

1) One-step reaction – 1st order kinetics

Effect of the transfer coefficient α



Effect of the exchange current i_0



$$i = i_0\left(exp^{\frac{(1-\alpha)zF\eta}{RT}} - exp^{\frac{-\alpha zF\eta}{RT}}\right)$$

Butler-Volmer equation

3.2. Electrodeposition kinetics

1) One-step reaction – 1st order kinetics

Low overpotential approximation: $\frac{-\alpha zF\eta}{RT} \ll 1$ (linearize the exponentials)

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Butler-Volmer equation

3.2. Electrodeposition kinetics

1) One-step reaction – 1st order kinetics

Low overpotential approximation: (linearize the exponential)

$$\frac{-\alpha zF\eta}{RT} \ll 1 \rightarrow exp^{\frac{-\alpha zF\eta}{RT}} \approx 1 - \frac{-\alpha zF\eta}{RT} \quad and \quad \frac{(1-\alpha)zF\eta}{RT} \ll 1 \rightarrow exp^{\frac{(1-\alpha)zF\eta}{RT}} \approx 1 + \frac{(1-\alpha)zF\eta}{RT}$$

Linear approximation: $i = i_0 \cdot \boxed{\frac{zF\eta}{RT}}$

$$i = i_0\left(\boxed{exp^{\frac{(1-\alpha)zF\eta}{RT}} - exp^{\frac{-\alpha zF\eta}{RT}}}\right)$$

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1) One-step reaction – 1st order kinetics

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Linear approximation: $i = i_0 \cdot \frac{zF\eta}{RT}$

High cathodic overpotential approximation: (express the Tafel equation $\eta = a + b \cdot \log|i|$)

$$i = i_0\left(exp^{\frac{(1-\alpha)zF\eta}{RT}} - exp^{\frac{-\alpha zF\eta}{RT}}\right)$$

Butler-Volmer equation

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1) One-step reaction – 1st order kinetics

Low overpotential approximation: (linearize the exponential)

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Linear approximation: $i = i_0 \cdot \frac{zF\eta}{RT}$

High cathodic overpotential approximation: (express the Tafel equation $\eta = a + b \cdot \log|i|$)

$$exp^{\frac{-\alpha zF\eta}{RT}} \gg exp^{\frac{(1-\alpha)zF\eta}{RT}} \qquad i \approx ic = i_0 \cdot exp^{\frac{-\alpha zF\eta}{RT}}$$

$$\eta = \frac{RT}{\alpha zF}(\ln i_0 - \ln i_c)$$

Tafel equation: $\eta = \frac{RT}{\alpha zF}\ln i_0 - \frac{RT}{\alpha zF}\ln i_c$

$$i = i_0\left(exp^{\frac{(1-\alpha)zF\eta}{RT}} - exp^{\frac{-\alpha zF\eta}{RT}}\right)$$

Butler-Volmer equation

3.2. Electrodeposition kinetics

2) Mass transfer limitation

$$i = i_0\left(\frac{[Red]^{el}}{[Red]^0}exp^{\frac{(1-\alpha)zF\eta}{RT}} - \frac{[Ox]^{el}}{[Ox]^0}exp^{\frac{-\alpha zF\eta}{RT}}\right)$$

Extended Butler-Volmer equation

In electroplating : $i = i_c = i_0\frac{[Ox]^{el}}{[Ox]^0}exp^{\frac{-\alpha zF\eta}{RT}}$

If $[Ox]^{el} \mapsto 0$, the current density j_c is strictly related to the molar flow φ_c: $j_c = zF\varphi_c$

Cations are transfered to the electrode by **convection**, **migration**, and **diffusion**

3.2. Electrodeposition kinetics

2) Mass transfer limitation

Cations are transfered to the electrode by **migration**, **diffusion,** and **convection**

Migration: All ions j will contribute to the ionic conductivity: $\kappa = F\sum_j |z_j| \mu_j C_j$

where μ_j is the ion mobility

Migration current of cation c: $i_c = \frac{|z_c|\mu_c C_c}{\sum_j |z_j| \mu_j C_j} \mapsto 0$ for large κ

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Diffusion:

Fick's laws for molar flows: $\varphi_c = -D_c \nabla C_c$ and $\frac{\partial C_c}{\partial t} = D_c \nabla^2 C_c$

For linear diffusion: $j = zFD\frac{\partial C}{\partial x}$

V) Electrodeposition mechanism and kinetics

2) Mass transfer limitation

The current density j_c is related to the molar flow φ_c: $j_c = zF\ \varphi_c$

Cations are transfered to the electrode by **migration**, **diffusion,** and **convection**

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For linear diffusion: $j = zFD\frac{\partial C}{\partial x}$

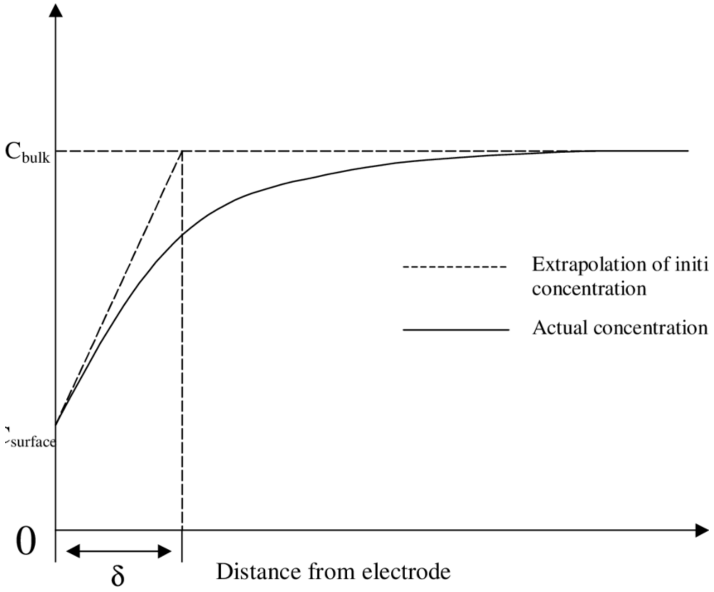
Convection: Forced agitation of the electrolyte

$$\varphi_c = \varphi_{diffusive} + \varphi_{advective}$$
$$\varphi_c = -D_c \nabla C_c + v\nabla C$$

V) Electrodeposition mechanism and kinetics

2) Mass transfer limitation

Nernst diffusion layer for a planar electrode



$$j = zFD\frac{C^{sol} - C^{el}}{\delta}$$

V) Electrodeposition mechanism and kinetics

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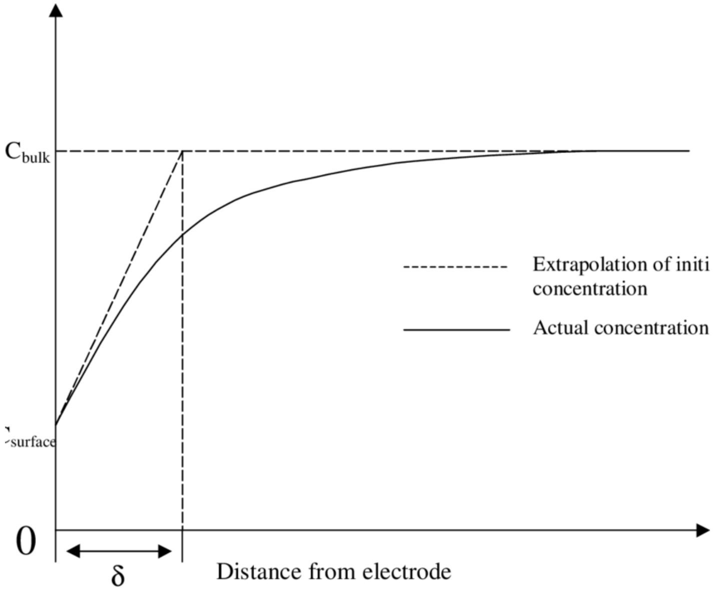
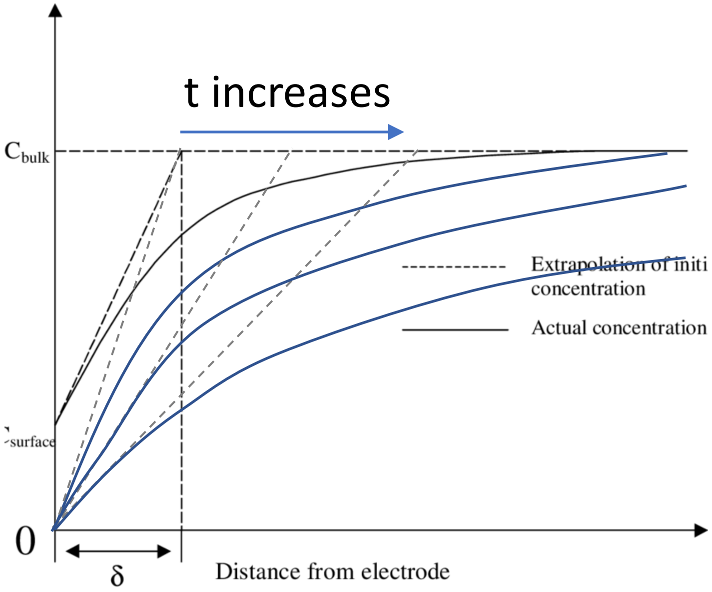




$$j = zFD\frac{C^{sol} - C^{el}}{\delta}$$

High overpotentials → $C^{el} \rightarrow 0$

Solution to Fick's second law: $\delta = \sqrt{\pi D t}$

Cottrell law: $j_{lim} = zFC^{sol}\sqrt{\frac{D}{\pi t}}$

V) Electrodeposition mechanism and kinetics

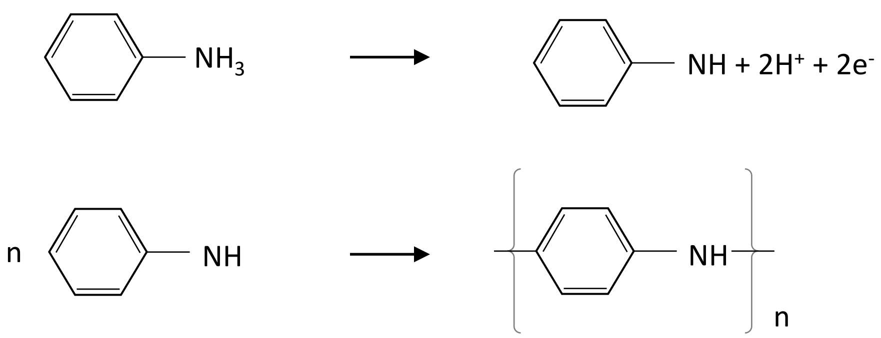
3) Chemical-electrochemical reactions

C-EC coupling: reduction of a metalorganic complex $[ML_x]^{z+}$

1) $[ML_x]^{n+} \rightarrow M^{z+} + xL^{m-}$ complexation constant independent of potential

2) $M^{z+} + ze^- \rightarrow M^0$ the slower process defines the reaction kinetics

EC-C coupling: polymerization of aniline



Oxidation of aniline monomer

Polymerization