Seminar 20/09/2022

Outline

- Some electrochemistry theory
- Results
- Future work

Heterogeneous redox reactions

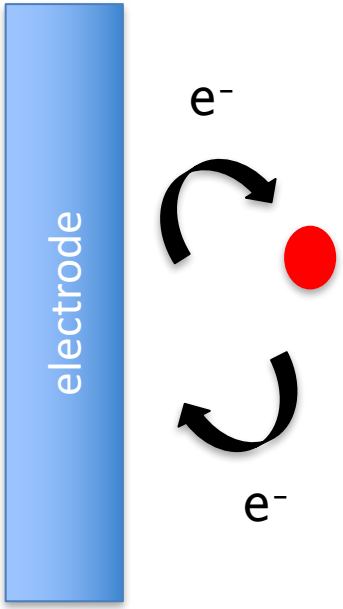
Ox + ne ⇌ Red e.g. $Fe^{3+} + e \rightleftharpoons Fe^{2+}$

Reactions occurring on electrode surfaces

$$\text{Rate}\,(\text{mol/s}) = \frac{dN}{dt} = \frac{I}{nF}$$

[A/cm²] current density
[mol/cm²s]

F = 96485 C/mol = 96485 As/mol



Cathodic current: current in which electrons cross the interface from the electrode to a species in solution

$$I_c = nF\frac{dN_{Ox}}{dt}$$

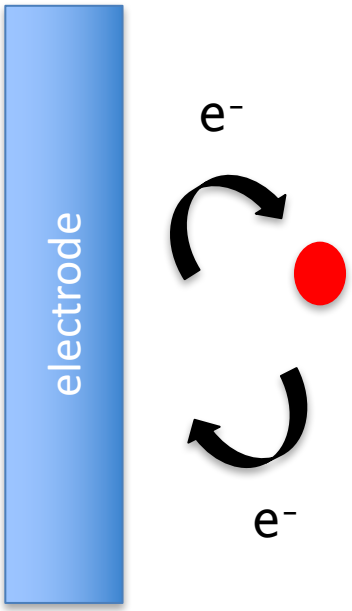
Anodic current: current in which electrons flow from a solution species into the electrode

$$I_a = nF\frac{dN_{Red}}{dt}$$

At equilibrium, the net current is zero

Factors affecting electrode reaction rates and current?

$Ox + ne \rightleftharpoons Red$ e.g. $Fe^{3+} + e \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Fe^{2+}$

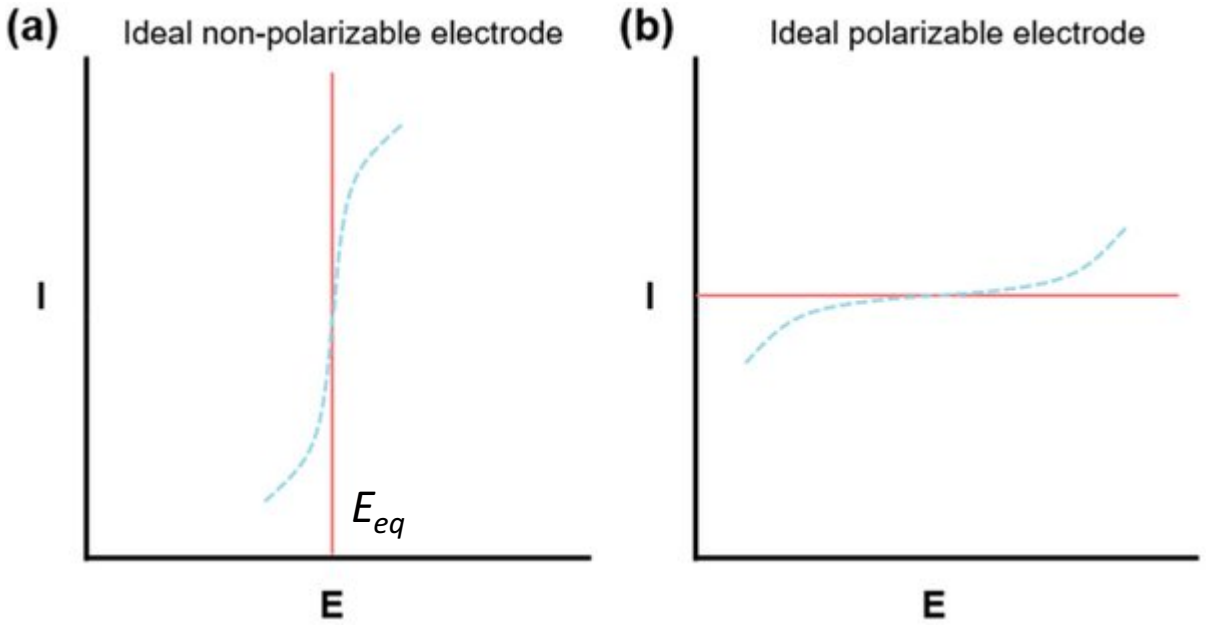


- **Mass transfer** of species from the bulk to the electrode surface (k_m)
- **Electron transfer** at the electrode surface (k_0)
- Chemical reactions preceding or following the electron transfer.
- Other surface reactions e.g. adsorption, desorption, crystallization (electrodeposition).

Polarization curves, current-potential curves

- Information about an electrode reaction is often gained by determining current as a function of potential, *I-E* curves called polarization curves

$$\eta = E - E_{eq}$$



Potential of an electrode nearer to its equilibrium. Potential does not change upon passage of current
Short circuit

Large change in potential upon the passage of of an infinitesimal current
Capacitor

Current-potential characteristics (Butler-Volmer equation)

$$I = FAk^0 \left[C_{Ox}(0,t) e^{\left(\frac{-\alpha n F (E - E^{0'})}{RT} \right)} - C_{Red}(0,t) e^{\left(\frac{(1-\alpha) n F (E - E^{0'})}{RT} \right)} \right]$$

When the concentration in the bulk is the same as at the electrode surface (no mass transfer effects)

$\longrightarrow$

$C_{ox} = C^b_{ox.}$ $\quad C_{red} = C^B_{red}$

When the overpotential η is very small, and the electrochemical system is at equilibrium, $e^x \approx 1+x$,

$I = R_{ct}^{-1} \eta$

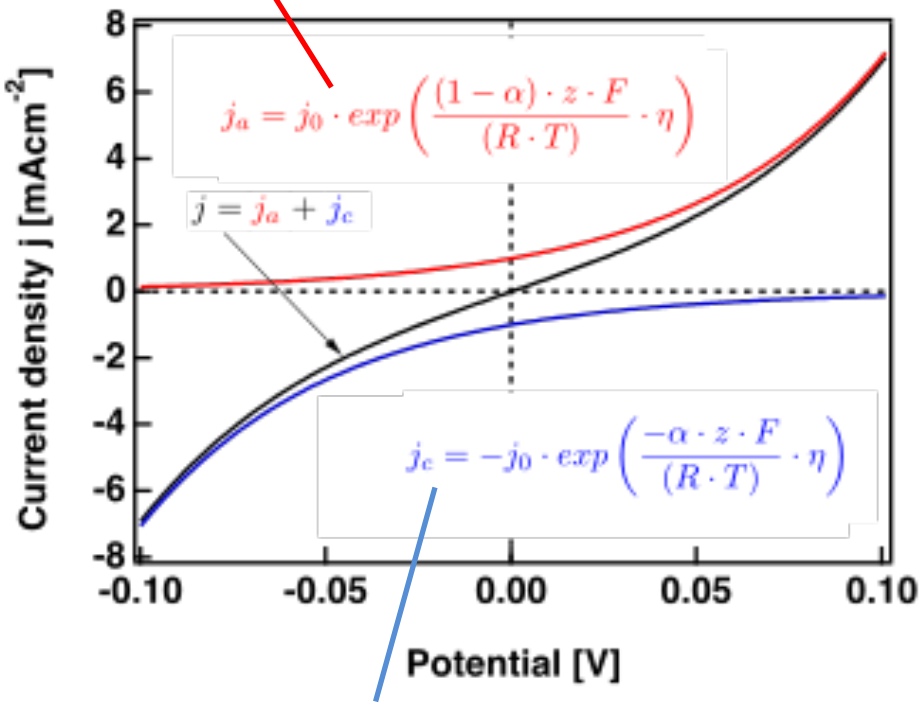
$$R_{ct} = \frac{RT}{nFI_0}$$

I_0, exchange-current

$$I_0 = FAk^0C$$

Anodic current

$\eta = E - E_{eq}$



Cathodic current

Electrode reactions at equilibrium

$$Ox + ne \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Red$$

- At equilibrium, the net conversion rate is zero:

$$v_{net} = 0 \rightarrow v_f = v_b \qquad I_{net} = 0 \rightarrow I_a = I_c$$

Rate of the forward reaction $v_f = k_f C_{Ox} = \frac{I_c}{nFA}$

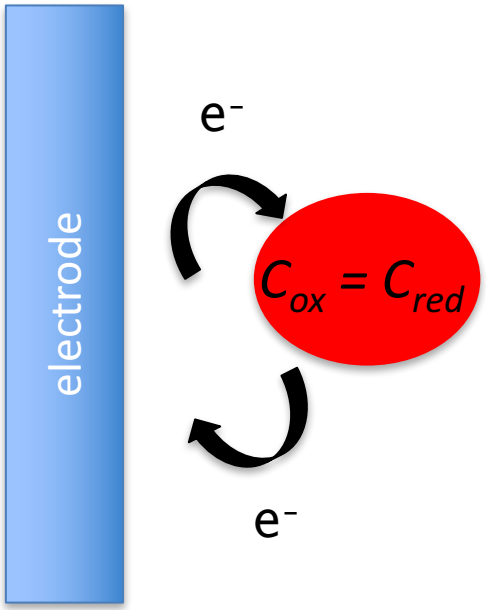
Rate of the backward reaction $v_b = k_b C_{Red} = \frac{I_a}{nFA}$

- Constant concentration ratio at equilibrium: $\frac{k_f}{k_b} = \frac{C_{Red}}{C_{Ox}}$

System at equilibrium at standard conditions

$$Ox + ne \underset{k_b}{\overset{k_f}{\rightleftharpoons}} Red$$

At *1 atm, 1M, 25°C*



$$v_{net} = 0 \rightarrow v_f = v_b$$

$$v_f = v_b \rightarrow k_f C_{Ox} = k_b C_{Red}$$

- ***When $C_{ox} = C_{red}$***

$$k_f = k_b = k_0$$

k_0 standard rate constant

k → cm/s

Rate constants follow an Arrhenius equation → $k = Ae^{\frac{-E_A}{RT}}$

Activation energy

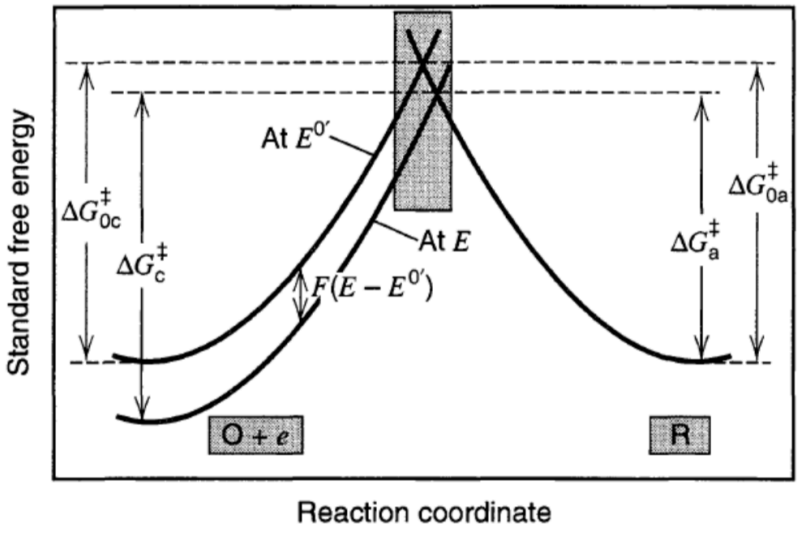
E_A → ΔG standard free energy

Frequency factor

$$k_f = A_f e^{\frac{-\Delta G_c^{\ddagger}}{RT}} \qquad k_b = A_b e^{\frac{-\Delta G_a^{\ddagger}}{RT}}$$

- *Equilibrium at $C_{ox} = C_{red}$*
  formal potential → $E^{0'}$

- *Potential different than E_{eq}*



$$\Delta G = -nF\Delta E$$

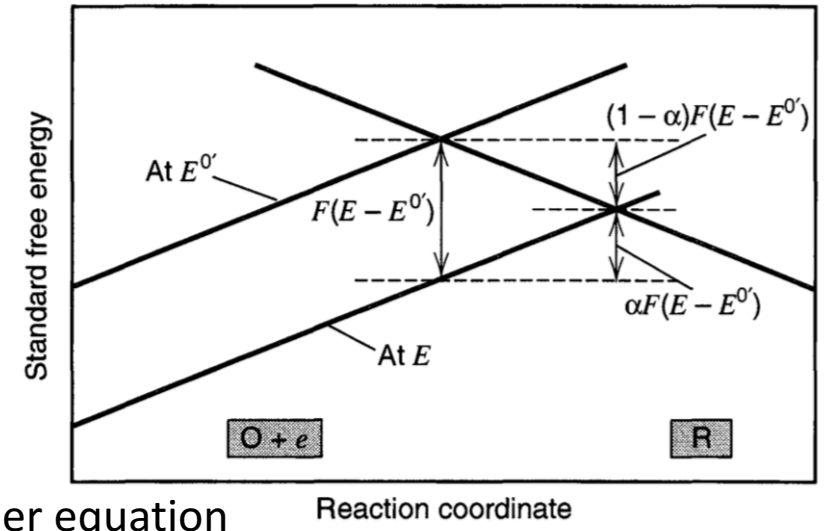
$$\Delta G_c^{\ddagger} = \Delta G_{0c}^{\ddagger} + \alpha F(E - E^{0'})$$

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

$$k_f = A_f e^{\frac{-\Delta G_c^{\ddagger}}{RT}} \qquad k_b = A_b e^{\frac{-\Delta G_a^{\ddagger}}{RT}}$$

$$k_f = k^0 e^{\frac{-nF\alpha(E-E^{0'})}{RT}}$$

$$k_b = k^0 e^{\frac{nF(1-\alpha)(E-E^{0'})}{RT}}$$



Butler-Volmer equation

$$I = FAk^0\left[C_{Ox}(0,t)e^{\left(\frac{-\alpha nF(E-E^{0'})}{RT}\right)} - C_{Red}(0,t)e^{\left(\frac{(1-\alpha)nF(E-E^{0'})}{RT}\right)}\right]$$

α – transfer coefficient

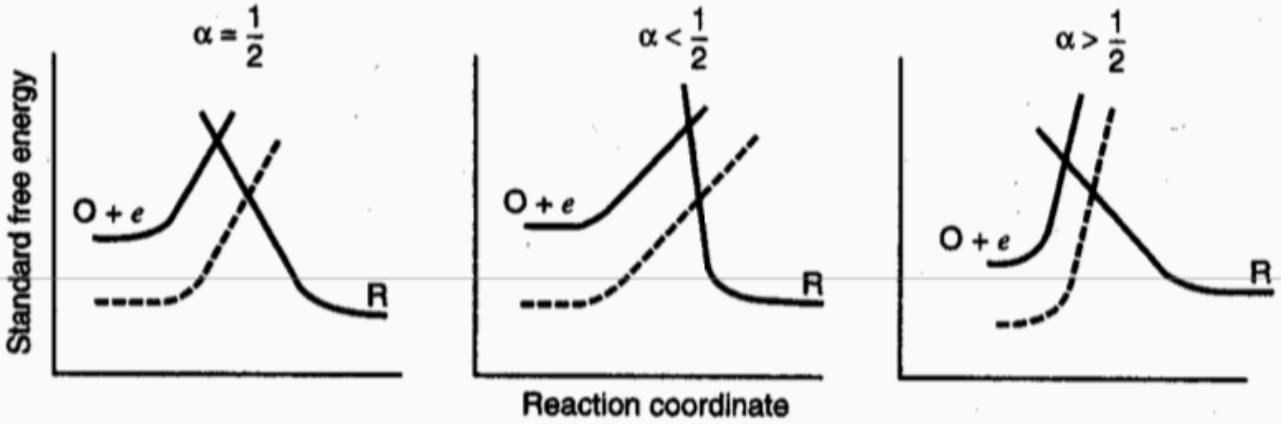
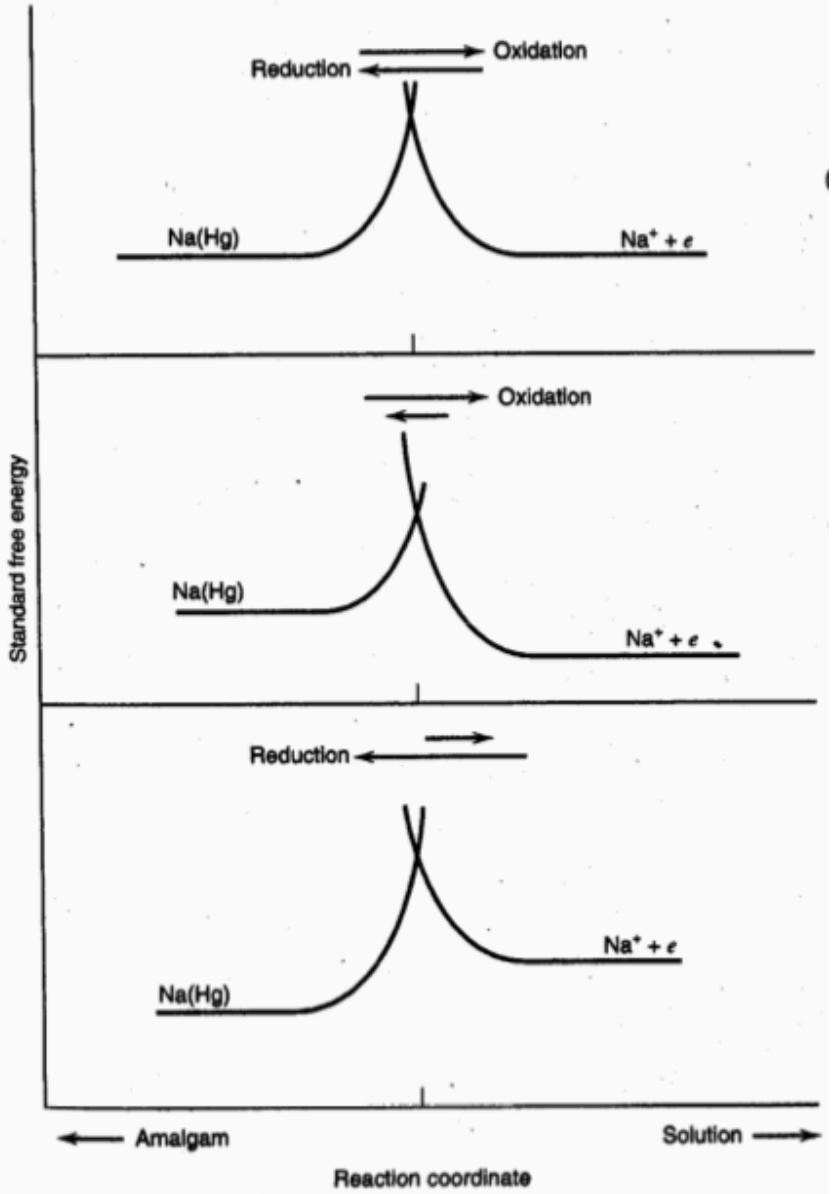


Figure 3.3.4 The transfer coefficient as an indicator of the symmetry of the barrier to reaction. The dashed lines show the shift in the curve for O + *e* as the potential is made more positive.



Potential corresponding to the equilibrium

At a more positive potential than the equilibrium value

At a more negative potential than the equilibrium value

At equilibrium

Butler-Volmer equation:

$$I = FAk^0 \left[C_{Ox}(0,t) e^{\left(\frac{-\alpha n F (E - E^{0'})}{RT} \right)} - C_{Red}(0,t) e^{\left(\frac{(1-\alpha) n F (E - E^{0'})}{RT} \right)} \right]$$

$I = 0 \rightarrow E = E_{eq}$

$$FAk^0 C_{Ox}(0,t) exp\left(\frac{-\alpha n F (E_{eq} - E^{0'})}{RT} \right) = FAk^0 C_{Red}(0,t) exp\left(\frac{(1-\alpha) n F (E_{eq} - E^{0'})}{RT} \right)$$

Since equilibrium applies,
the bulk concentrations of O and R are found also at the surface

$$E_{eq} = E^{0'} + \frac{RT}{nF} \ln \frac{C_{Ox}}{C_{Red}}$$ Nernst equation

$I = 0 = I_a - I_c \rightarrow I_a = I_c = I_0$

When $\alpha = 0.5$,
$C_{red} = C_{ox}$

$$I_0 = FAk^0 C_{Ox}^{*(1-\alpha)} C_{Red}^{*\alpha}$$ Exchange current

$$I_0 = FAk^0 C$$

Current-potential characteristics (Butler-Volmer equation)

$$I = FAk^0 \left[C_{Ox}(0,t) e^{\left(\frac{-\alpha n F (E - E^{0'})}{RT} \right)} - C_{Red}(0,t) e^{\left(\frac{(1-\alpha) n F (E - E^{0'})}{RT} \right)} \right]$$

When the concentration in the bulk is the same as at the electrode surface (no mass transfer effects)

$C^{Surface}_{Ox} = C^{Bulk}_{ox.}$ $C^{Surface}_{Red} = C^{Bulk}_{red}$

When the overpotential η is very small, and the electrochemical system is at equilibrium, $e^x \approx 1+x$,

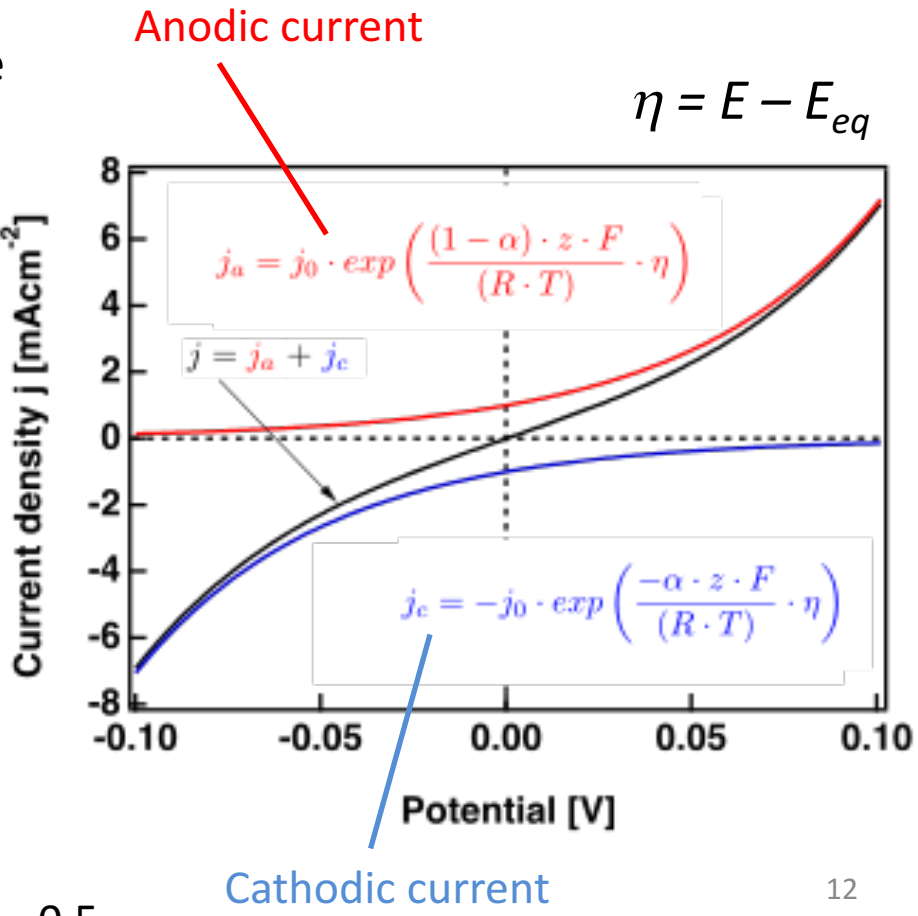
$I = R_{ct}^{-1} \eta$

$$R_{ct} = \frac{RT}{nFI_0}$$

I_0, exchange-current

$$I_0 = FAk^0C$$

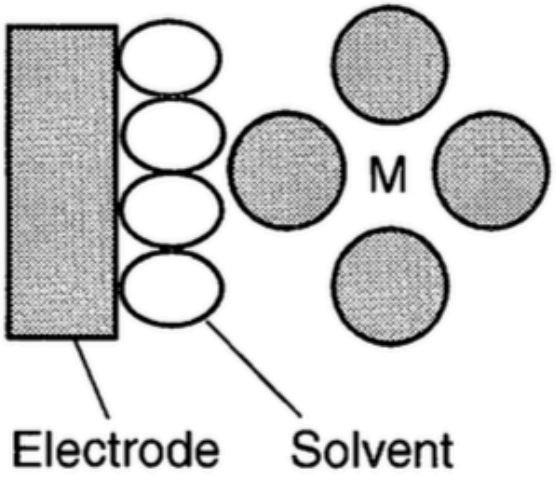
$\alpha = 0.5$



Microscopic theories of charge-transfer

- electron transfer reactions of coordination compounds (Marcus theory)

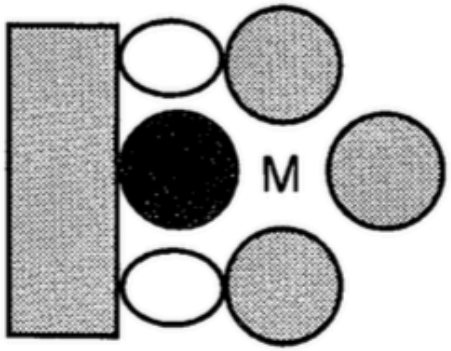
Outer-sphere



Reactant and product do not interact strongly with the electrode surface.

Reactant at the electrode surface is essentially the same as in the bulk

Inner-sphere



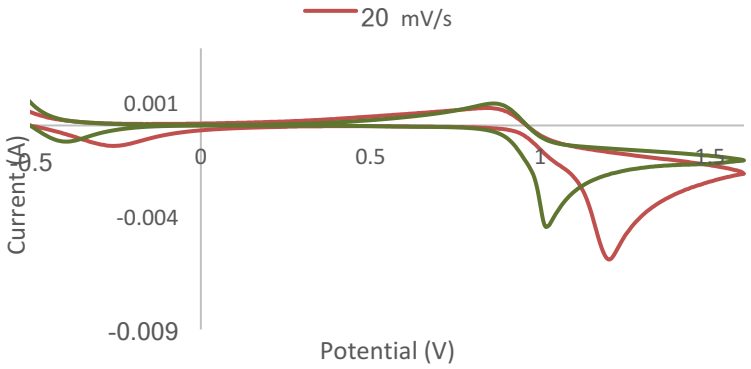
The ligand adsorbs on the electrode and bridges to the metal, stronger interaction with the electrode surface.

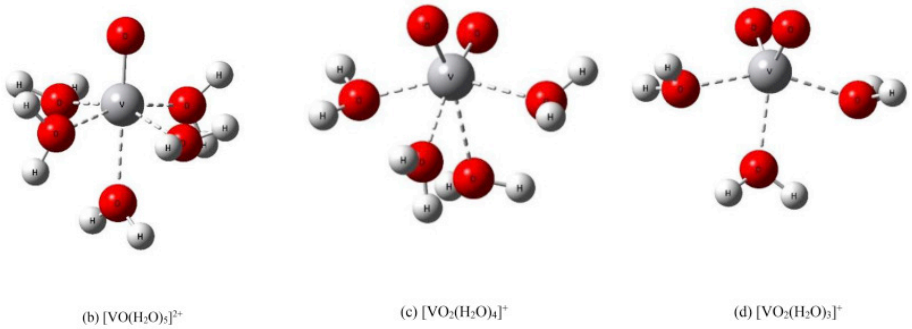
Vanadium electrolytes – affected by oxides

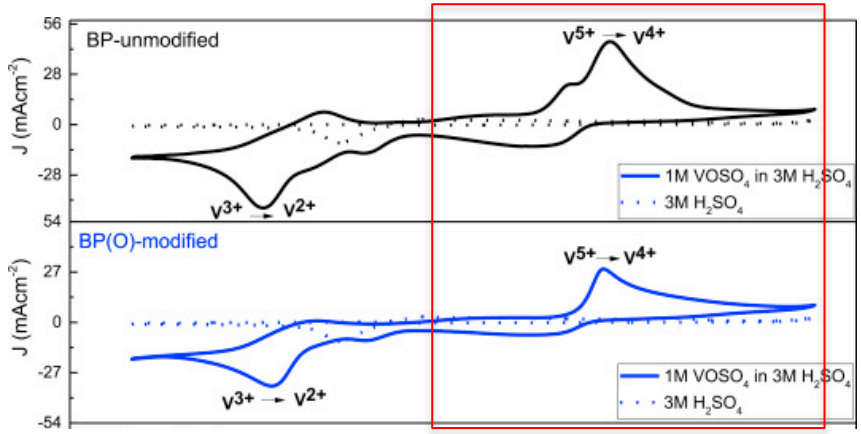
Vanadium electrolyte – sensitive to carbon surface chemistry

pre-oxidized carbon – more reversible

Toni's work: $VO^{2+}(IV) / VO_2^{+}(V)$

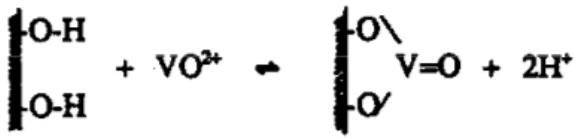


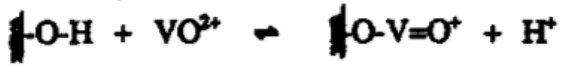




https://doi.org/10.1016/j.jpowsour.2019.02.083.

$$VO_2^+ + 2H^+ + e^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} VO^{2+} + H_2O$$

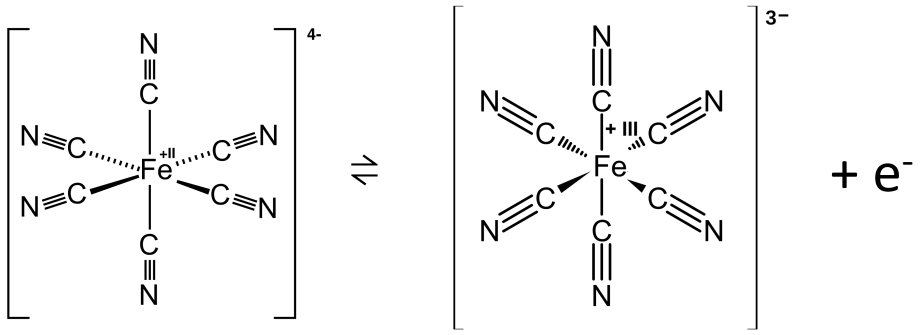


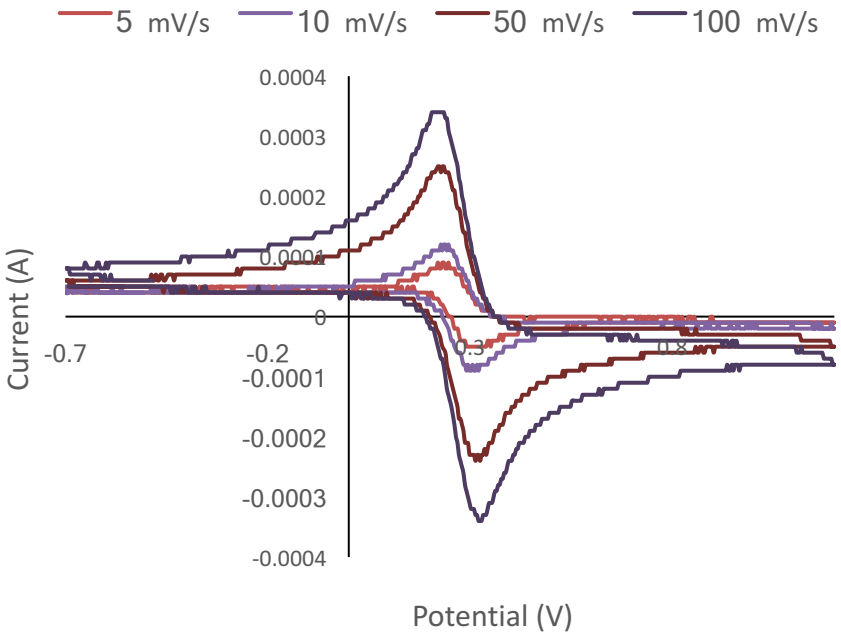


https://doi.org/10.1016/0013-4686(92)85064-R.

Ferro/ferricyanide complex – not affected by oxides

$[Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6]^{3-} + e^-$





Mass-transfer effects

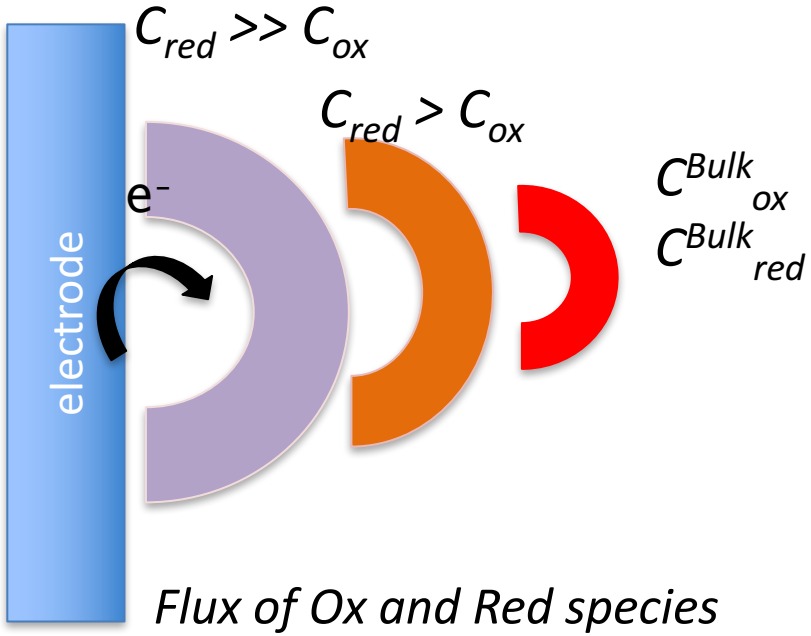
Ox + ne ⇌ Red

$C^{Surface}_{Ox} \neq C^{Bulk}_{ox.}$

$C^{Surface}_{Red} \neq C^{Bulk}_{red}$

diffusion migration Convection/ advection

$$\vec{J}_j = -D_j \vec{\nabla} C_J + \frac{z_j F}{RT} D_j C_j \vec{\nabla}\phi + C_j \vec{v}$$



Flux of Ox and Red species

J_{red}, J_{ox} (mol / cm² s)

Excess of supporting electrolyte – no migration

V = 0 → no convection, no advection

$$\frac{\partial C_j}{\partial t} = -\vec{\nabla} \vec{J}_j$$

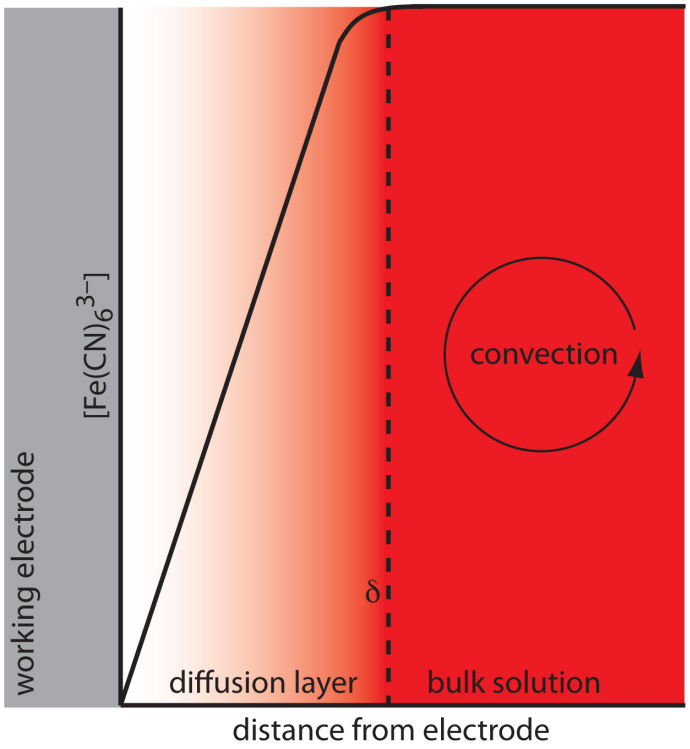
Linear diffusion, planar electrode:

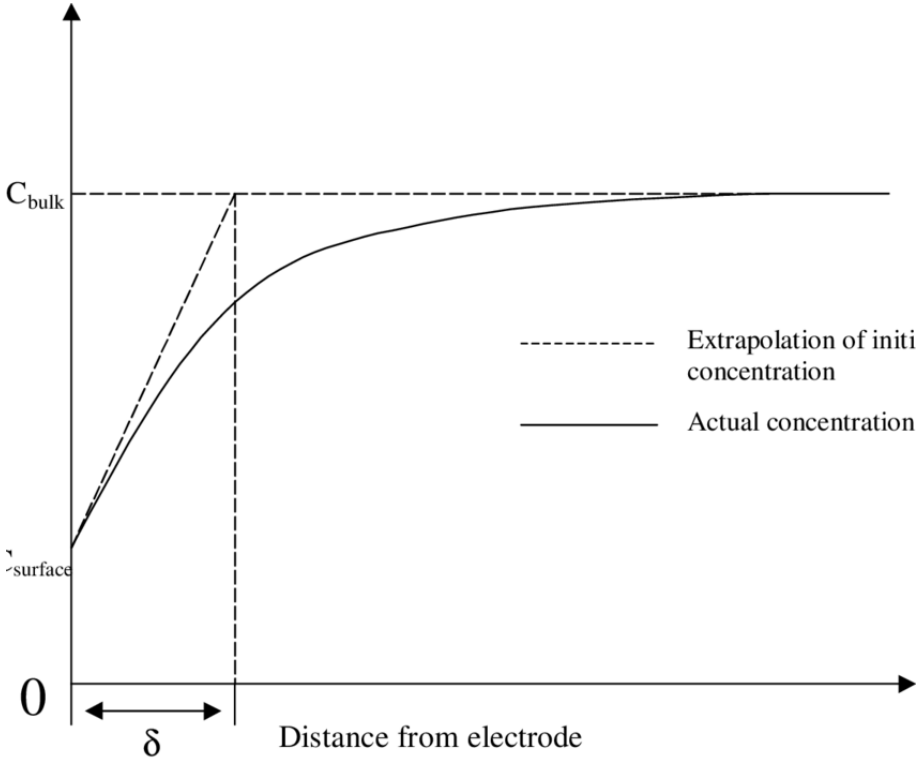
$$\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2} \qquad \frac{\partial C_R(x,t)}{\partial t} = D_R \frac{\partial^2 C_R(x,t)}{\partial x^2}$$

$$C_O(x,0) = C_O^* \qquad C_R(x,0) = 0$$

$$\lim_{x\to\infty} C_O(x,t) = C_O^* \qquad \lim_{x\to\infty} C_R(x,t) = 0$$

Mass-transfer controlled reactions





Nernst diffusion layer

$$I = \frac{nFAD(C_{bulk} - C_{surface})}{\delta}$$

$C_{surface} = 0$

$$I_L = \frac{nFADC_{bulk}}{\delta}$$

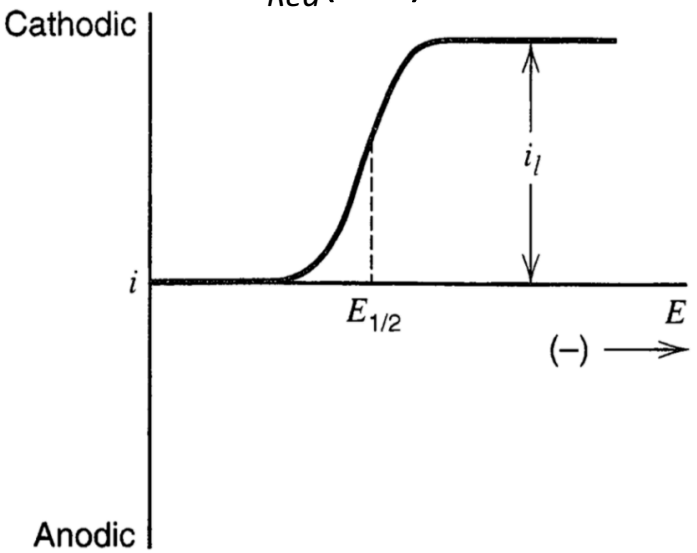
k_m: mass transfer coefficient (cm/s)

Mass-transfer controlled reactions

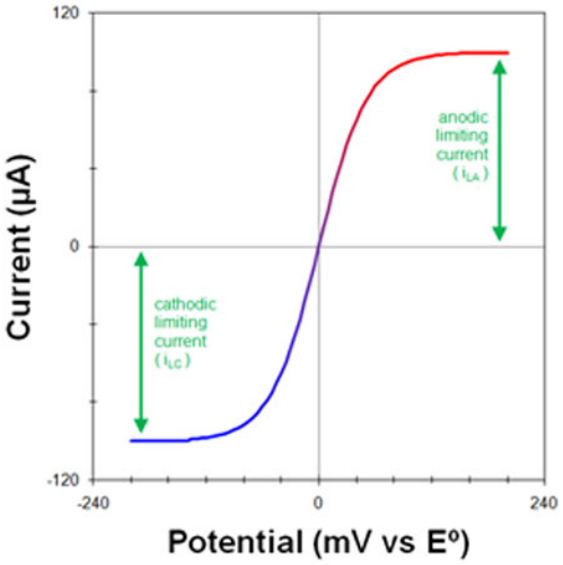
Ox + ne ⇌ Red

I – E curves

$C_{Red}(t=0) = 0$



$C_{Red}(t=0) = C_{Ox}$ (t=0)



$I_{l,c} = nFA\ k_{m,Ox}\ C^{Bulk}_{Ox}$ $\quad C^{Surface}_{Ox} = 0$

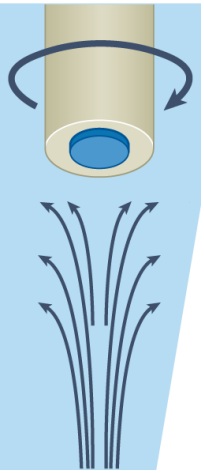
$I_{l,a} = nFA\ k_{m,Red}\ C^{Bulk}_{Red.}$ $\quad C^{Surface}_{Red} = 0$

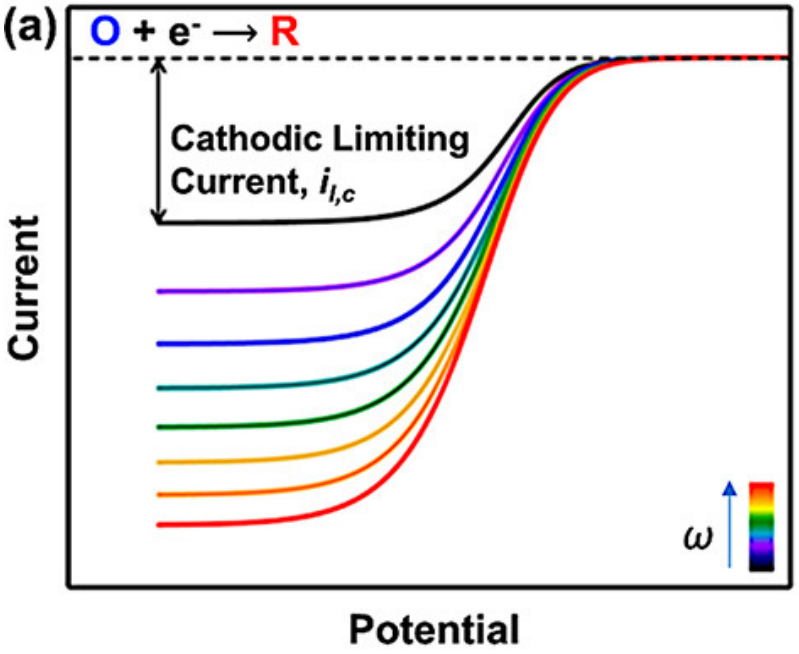
k_m mass transfer coefficient $\propto v^b$

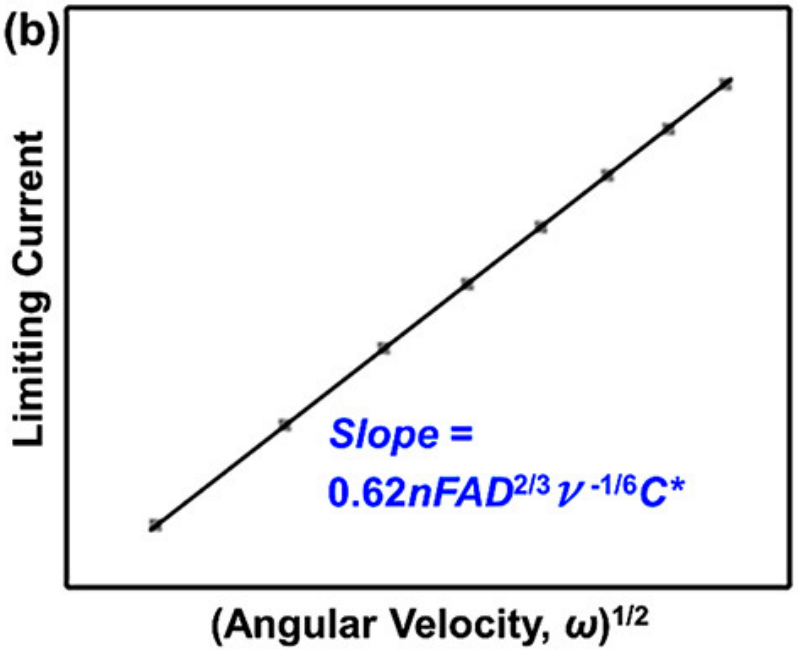
In RDE $\propto \omega^{0.5}$

Rotating disc electrode (RDE)

Rotating disk electrode (RDE) to determine the diffusion coefficient, D, for reversible, quasireversible, and irreversible redox systems



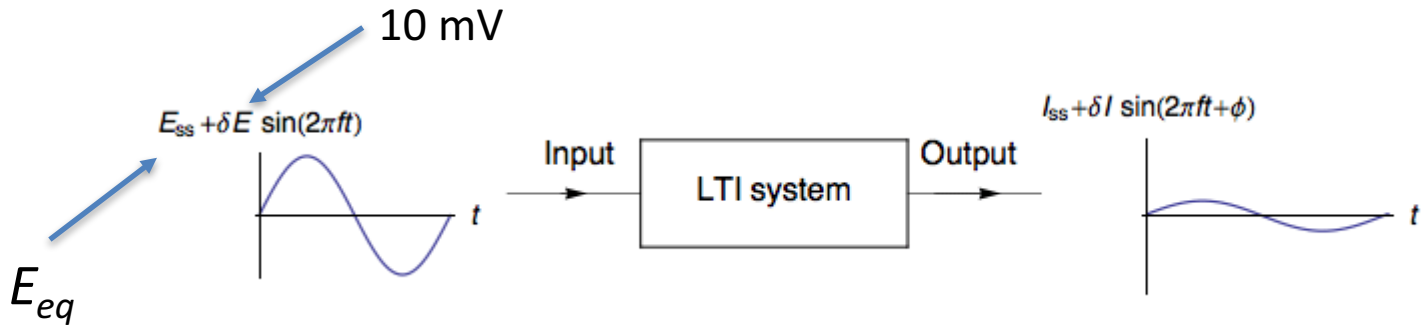




Levich-equation: Cathodic limiting current, $i_{l,c} = 0.62nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C^*$, where ν is the kinematic viscosity of the fluid (measured in cm^2/s).

$$\delta = \frac{1.61\, D_i^{1/3} \nu^{1/6}}{\omega^{1/2}}$$

Electrochemical impedance spectroscopy (EIS)



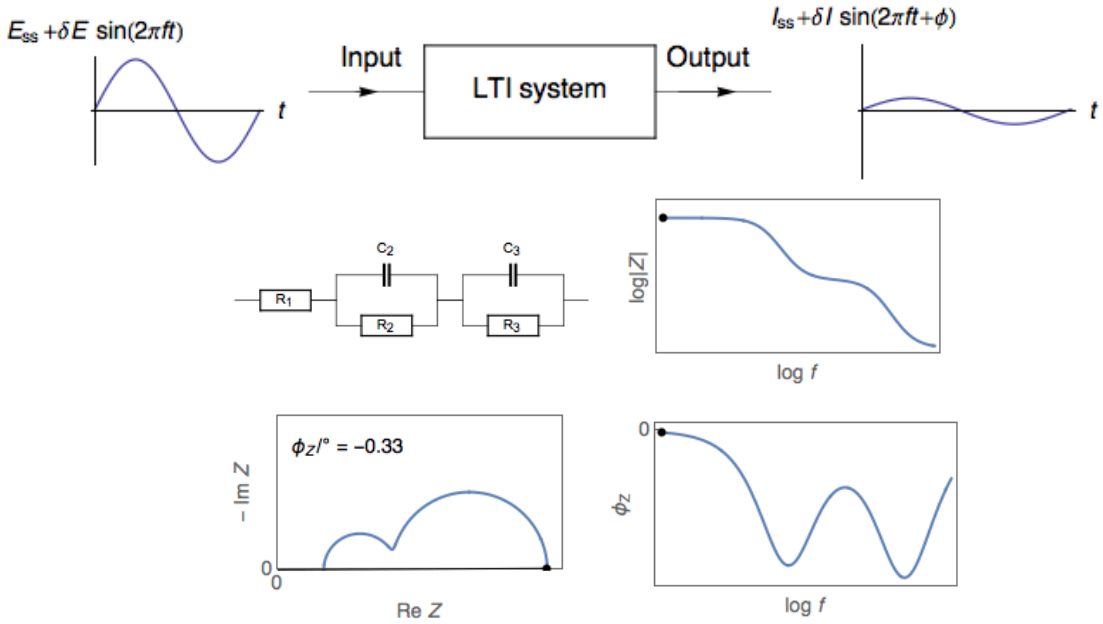
- When the overpotential η is very small (small perturbation), electrochemical system is at equilibrium, and relevant mathematical equations are transformed in linear forms:

$e^x \approx 1+x,$

$I(t) = R^{-1}\,\eta\,(t)$

- Capable of characterizing processes with different time constants.

Electrochemical impedance spectroscopy (EIS)



- Very fast process: > kHz: *ohmic drop* R_{hf}
- Fast process: From kHz to Hz frequencies: *charge-transfer controlled reactions*

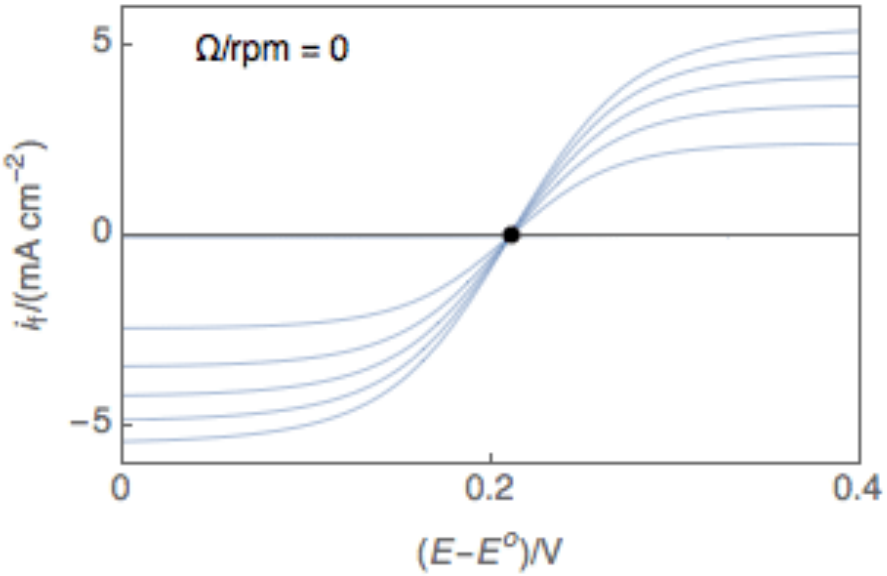
$$R_{ct} = \frac{RT}{nFI_0} = \frac{RT}{n^2F^2CAk_0}$$ → charge-transfer rate constant k_0

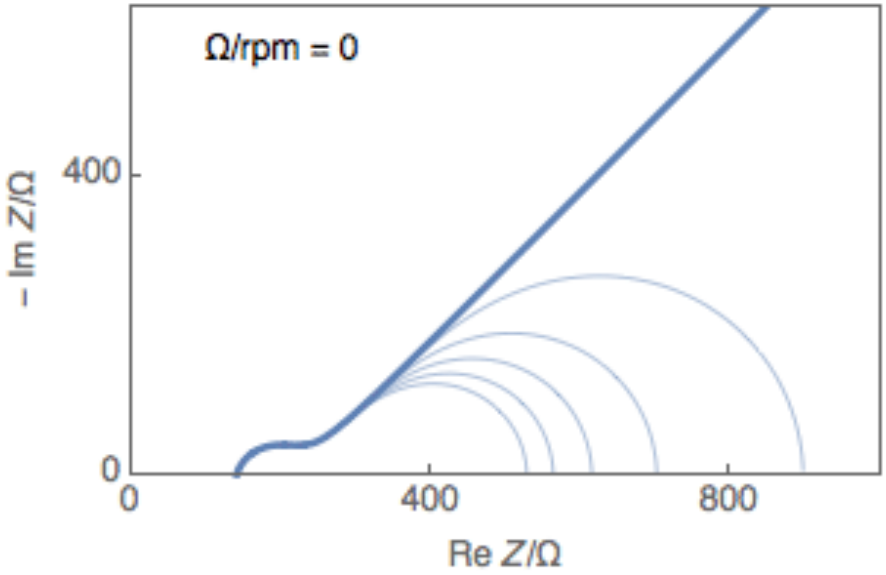
- Low process: At low frequencies < mHz : *mass-transfer controlled reactions*

$$R_m = \frac{RT}{nFI_l} = \frac{RT}{n^2F^2CAk_m}$$ → mass-transfer coefficient k_m

Electrochemical impedance spectroscopy (EIS)

- Rotating disc electrode





https://www.biologic.net/topics/the-easy-way-to-d-the-diffusion-coefficient/

Thank you for your attention!