I^3N Innovative Integrated Instrumentation for Nanoscience

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High Resolution Electronic Measurements in Nano-Bio Science

Mass transport in liquids

A closer approach

Giorgio Ferrari

Milano, June 2025

Outline

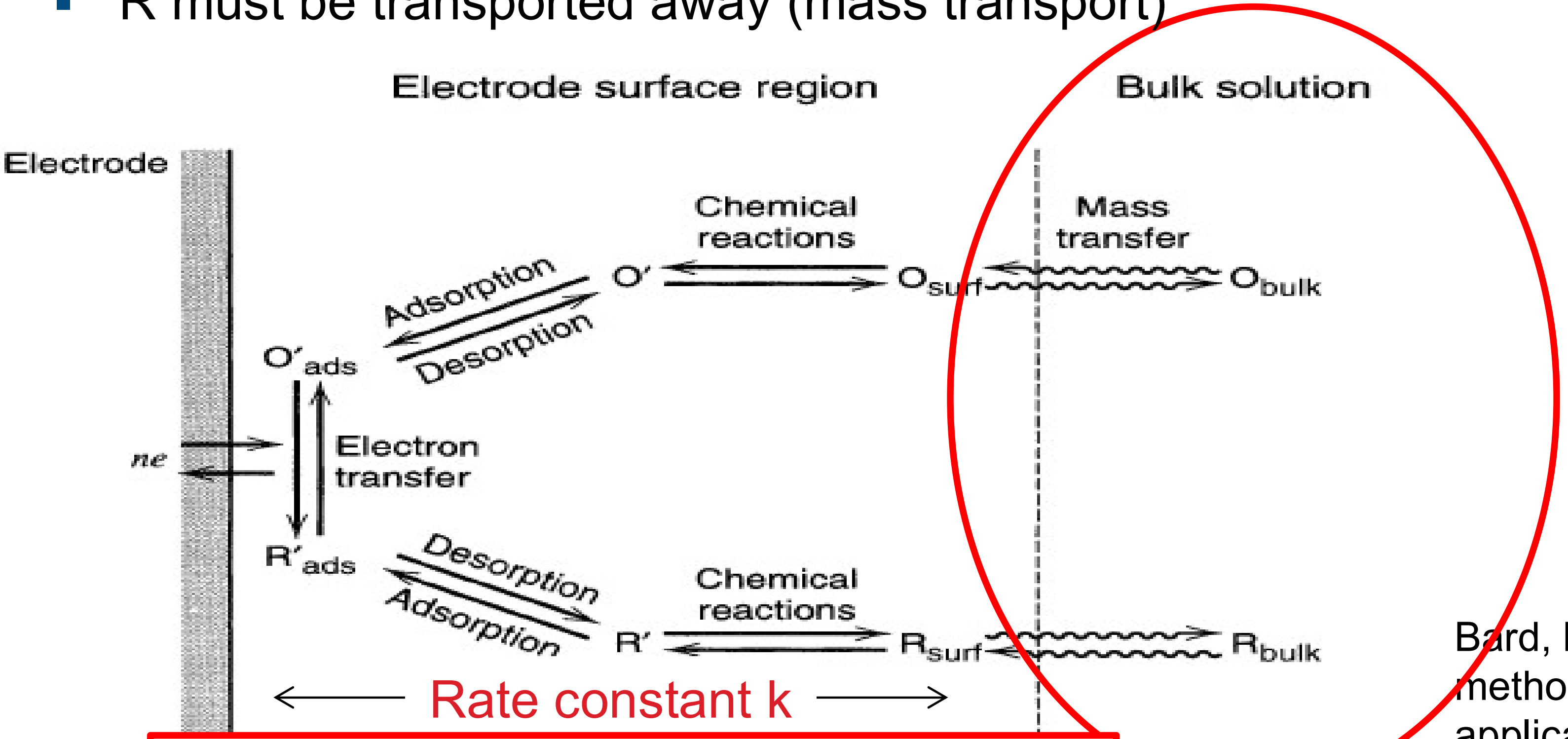
- The electrical behavior of the bulk liquid
- Metal – liquid interface: double-layer capacitance
- Potential drop across the electrode-liquid interface
- Charge transfer at the interface
- Current-Voltage relation

- Mass transfer
- Response to a potential step (amperometry)
- Response to a potential sweep (voltammetry)
- Small signal equivalent circuit (impedance spectroscopy)

An Interfacial Process

For: **O + ne$^-$ ↔ R** 5 separate events must occur:

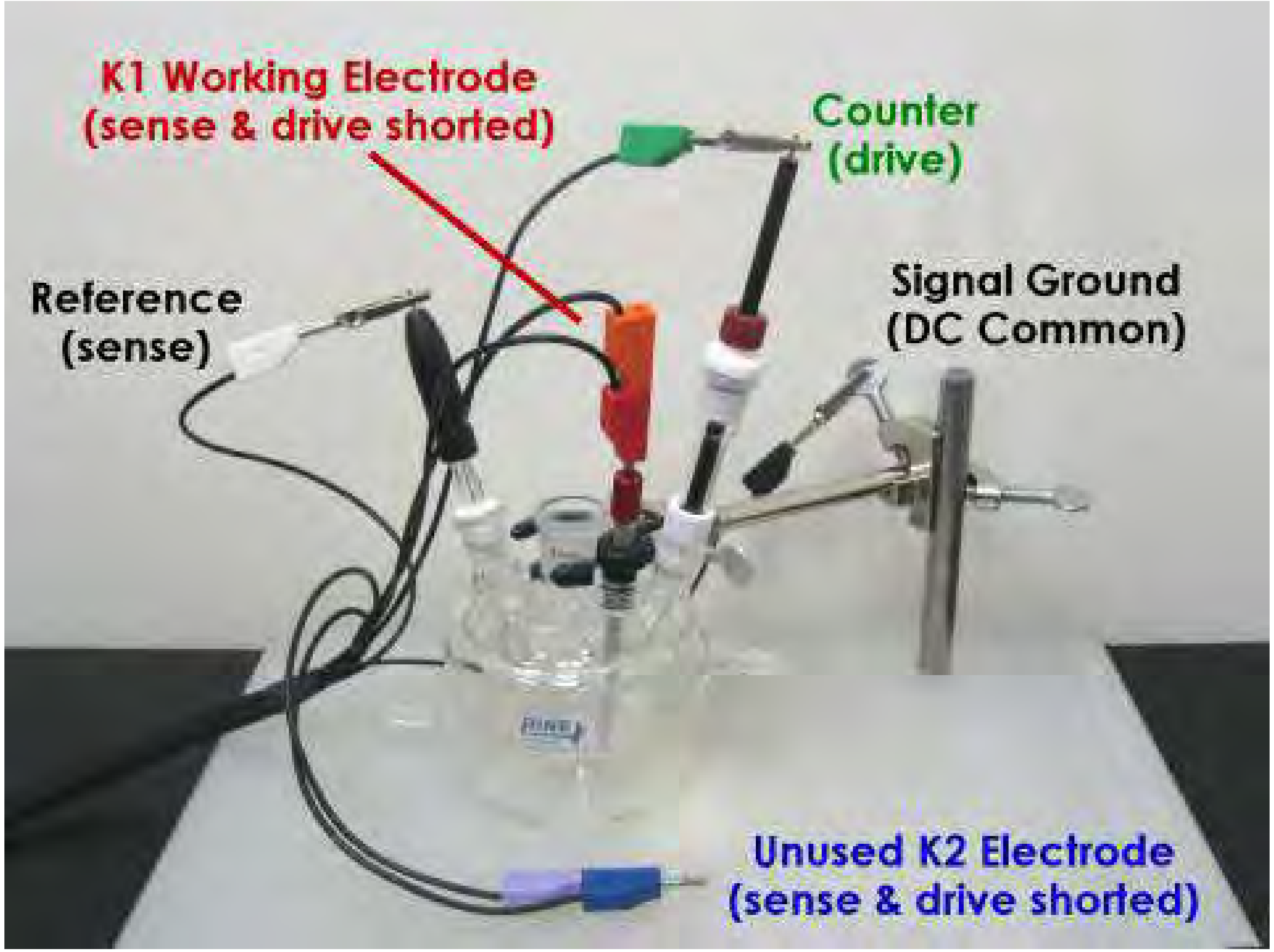
- O must be successfully transported from bulk solution (mass transport)
- O must adsorb transiently onto electrode surface (non-faradaic); Chemical reactions preceding or following the electron transfer (e.g., protonation or dimerization or catalytic decomposition) on the electrode surface.
- CT must occur between electrode and O (faradaic)
- R must desorb from electrode surface (non-faradaic)
- R must be transported away (mass transport)



$$i = nq\left[k_b N_{Av}\, A C_R(0) - k_f N_{Av}\, A C_O(0)\right]$$

Bard, Electrochemical methods. Fundamentals and applications

Standard electrochemical setup



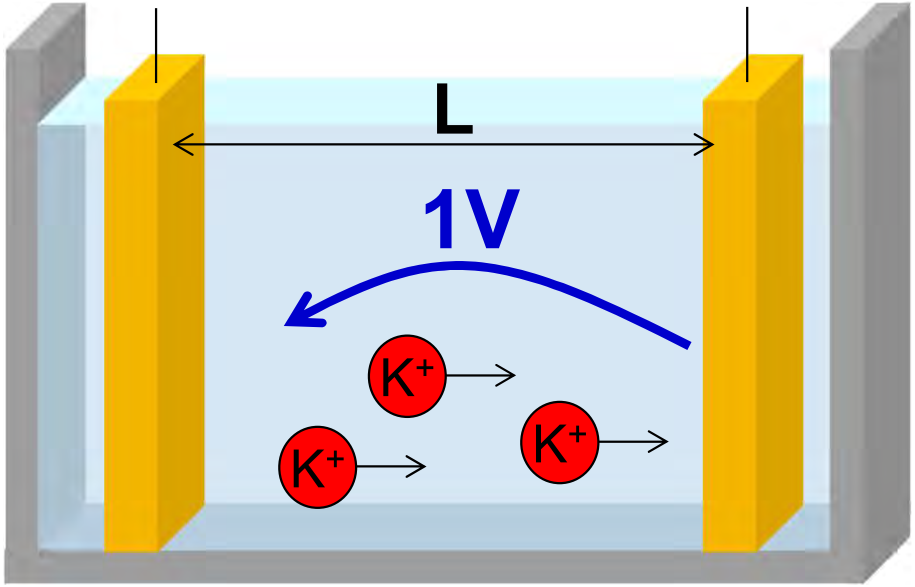
For practical reasons the distance between the electrodes is ≈ cm

$$\mu \approx 5 \cdot 10^{-4} \frac{cm^2}{Vs}$$

$$D \approx 10^{-5} \frac{cm^2}{s}$$

Silicon: (μm, nm)
$\mu \approx 1000\ \mathrm{cm^2/Vs}$
$D \approx 20\ \mathrm{cm^2/s}$

Time to pass through the cell



Example: K+

μ= 7.6 10-4 cm²/s, D=2 10-5 cm²/s

Particles move slowly,
a non-stationary condition
is common!

Diffusion limited: $(space \cong \sqrt{2Dt}\ )$

L= 1cm: → transit time = 7h !!!

L= 10μm: → transit time = 25ms [Silicon: ≈ 25ns]

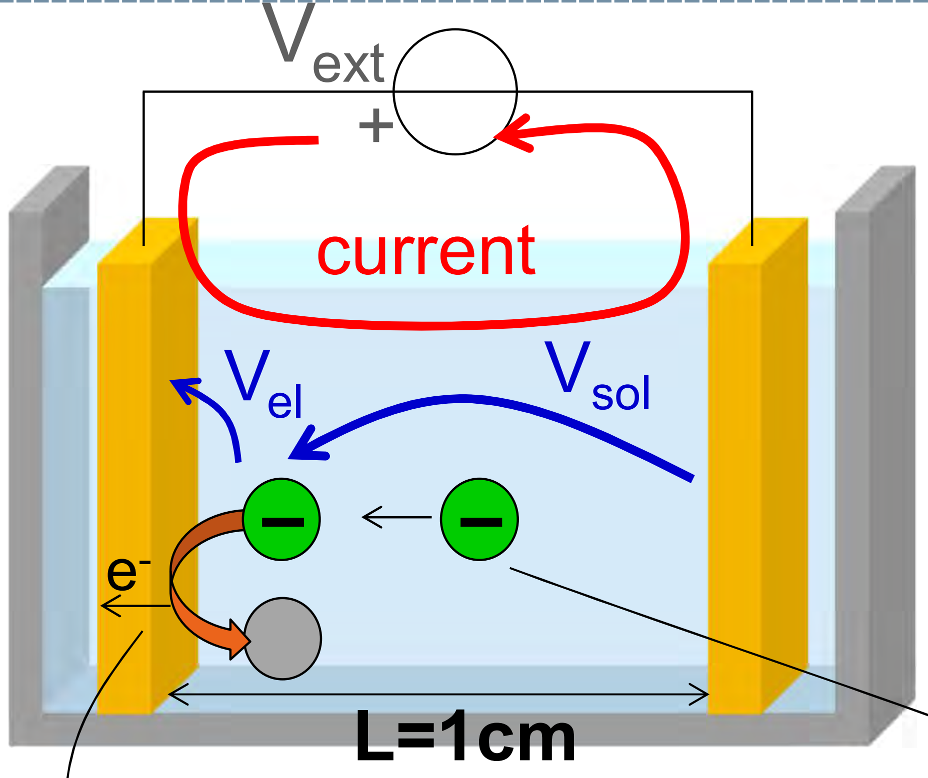
Drift limited:

1V applied → electric field ≈ 1V/L → $velocity \cong \mu\, 1V/L$

L= 1cm: → transit time = 20 min !!!

L= 10μm: → transit time = 1ms [Silicon: ≈ 1ns]

The importance of the mass transfer



Assuming:

- current controlled by the reaction at the left planar electrode (area A)
- R → O + e^- ⊖ → ●
- $V_{el}-V_0 = +100\text{mV}$
- $C_R = 1\text{mM}$, $C_O=0$ uniform at t=0s
- $k_0 = 1\text{cm/s}$, $\alpha=0.5$, $\mu_R=5\cdot10^{-4}\ \text{cm}^2/\text{Vs}$

$$i_{electrode} \cong A\, qN_{Av}\, C_R\, k_0 e^{\frac{(1-\alpha)q(V_{el}-V_0)}{kT}} \qquad i_{R,solution} \cong A\, qN_{Av} C_R\, \mu \frac{V_{sol}}{L}$$

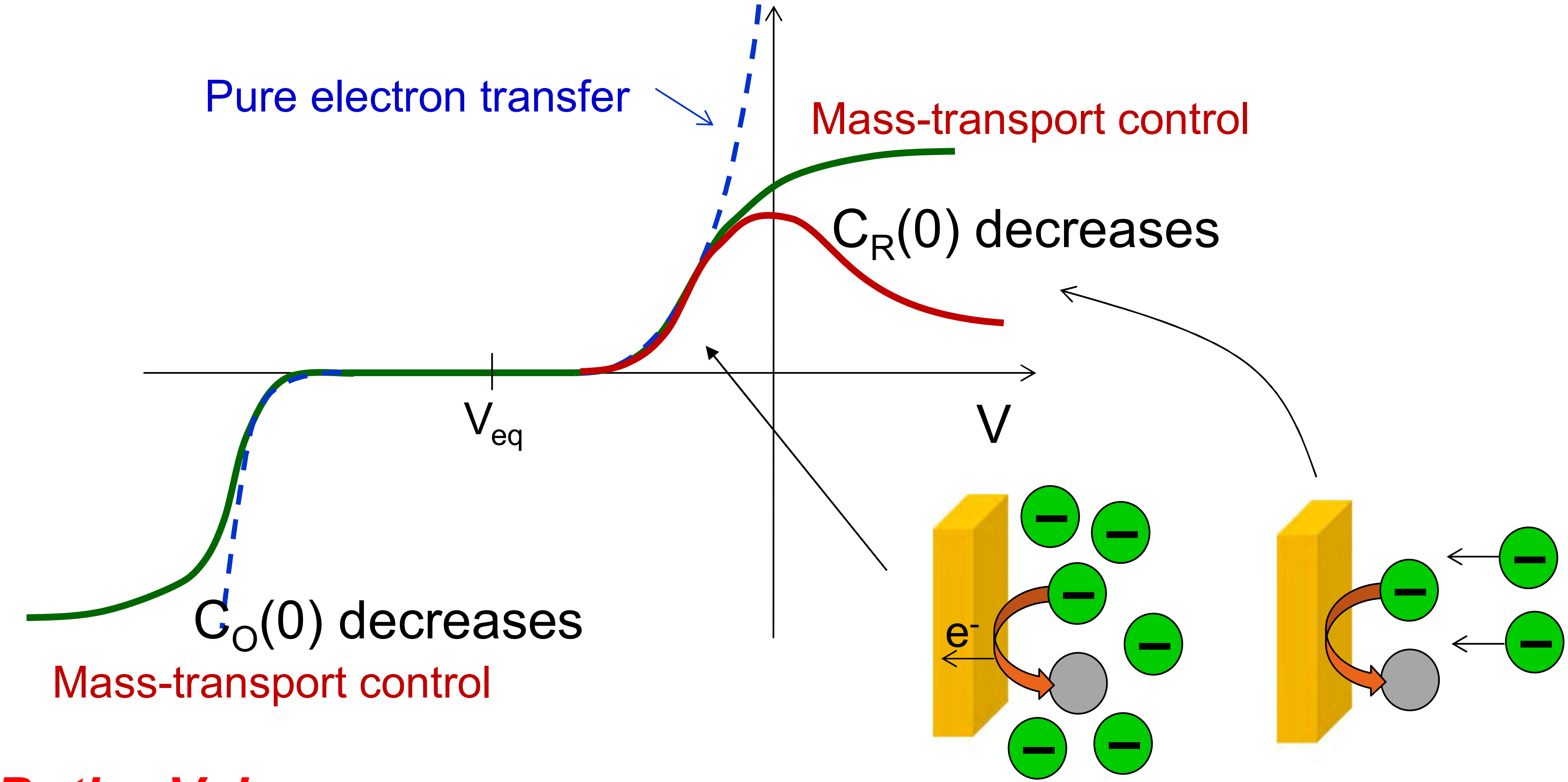
$$i_{electrode} = i_{R,solution} \Rightarrow k_0 e^{\frac{(1-\alpha)q(V_{el}-V_0)}{kT}} = \mu \frac{V_{sol}}{L} \Rightarrow$$

V_{sol} should be **≈ 138kV!!!**

Arrival rate of species R is lower than the kinetics at the electrode

→ C_R at the surface will decrease

Current: Mass-Transfer Effects

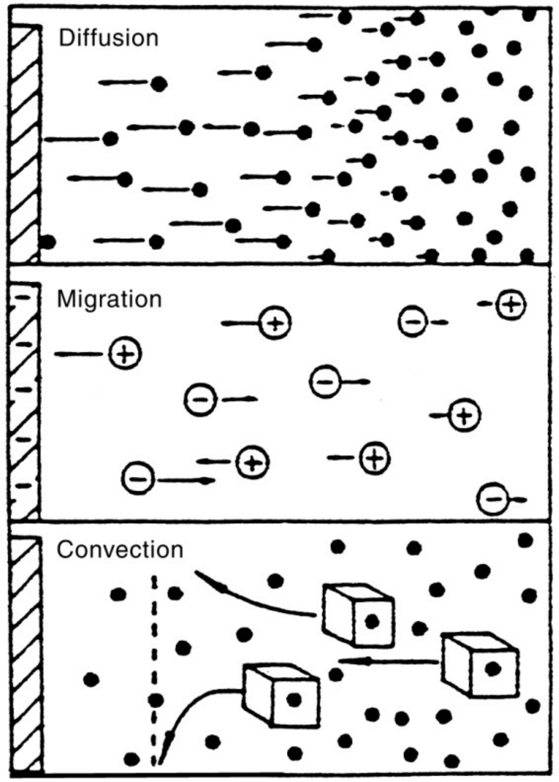


Butler-Volmer:

$$i = qN_{Av}Ak_0\left[C_R(0)e^{(1-\alpha)q\left(V-V^{0'}\right)/kT} - C_O(0)e^{-\alpha q\left(V-V^{0'}\right)/kT}\right]$$

Mass transfer mechanism

- **Diffusion**: concentration gradient
- **Drift:** electric field + charged particle (migration)
- **Convection**
  - Natural
  - Mechanical



Wang, Analytical Electrochemistry

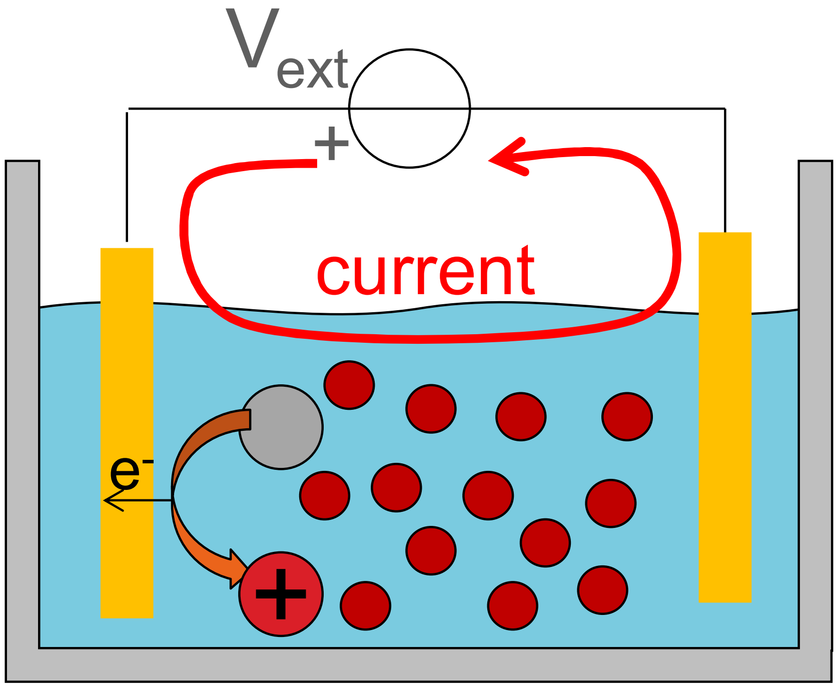
What is the most important factor?

The natural convection is negligible near the interface (stagnant layer)

Dominant mass transfer mechanism

Diffusion or drift?

For simplicity (interpretation, experimental setup) or for necessity, the mass transfer of the electroactive species is very often controlled by diffusion



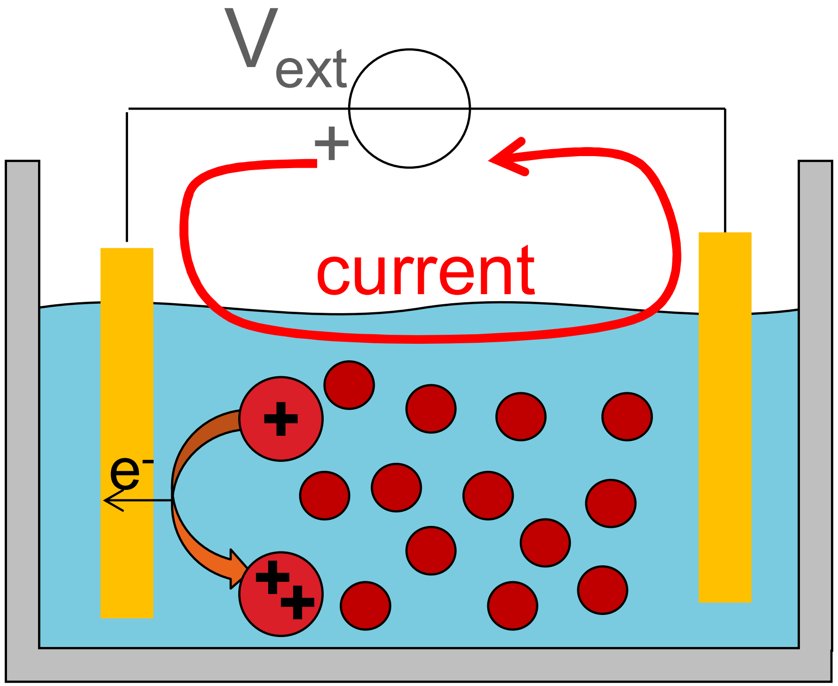
Necessity: example 1

Neutral redox species, no drift!

Dominant mass transfer mechanism

Diffusion or drift?

For simplicity (interpretation, experimental setup) or for necessity, the mass transfer of the electroactive species is very often controlled by diffusion



Necessity: example 1

Neutral redox species, no drift!

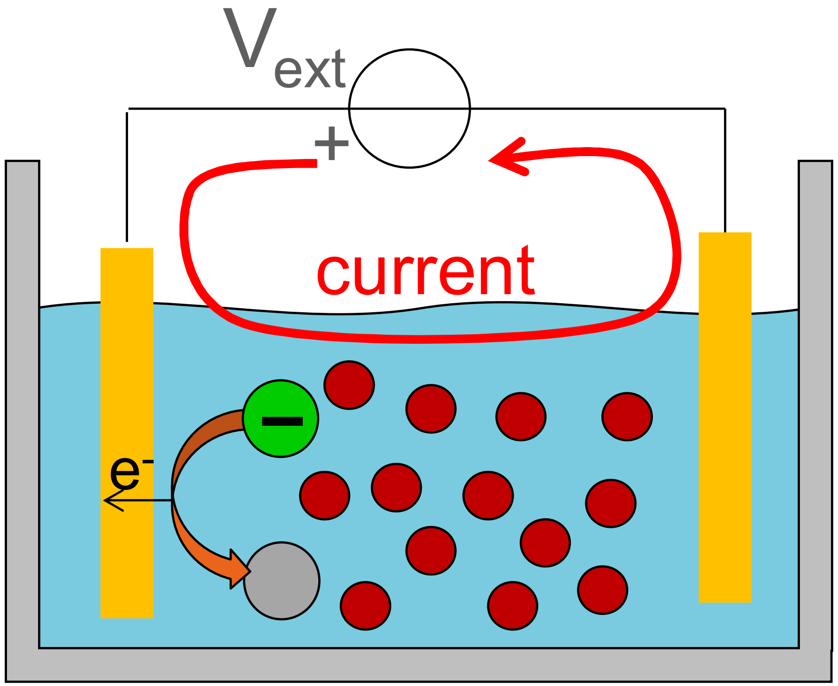
or

“wrong” charge of redox species!

Mass transfer mechanism

Diffusion or drift?

For simplicity (interpretation, experimental setup) or for necessity, the mass transfer of the electroactive species is very often controlled by diffusion



Example 2

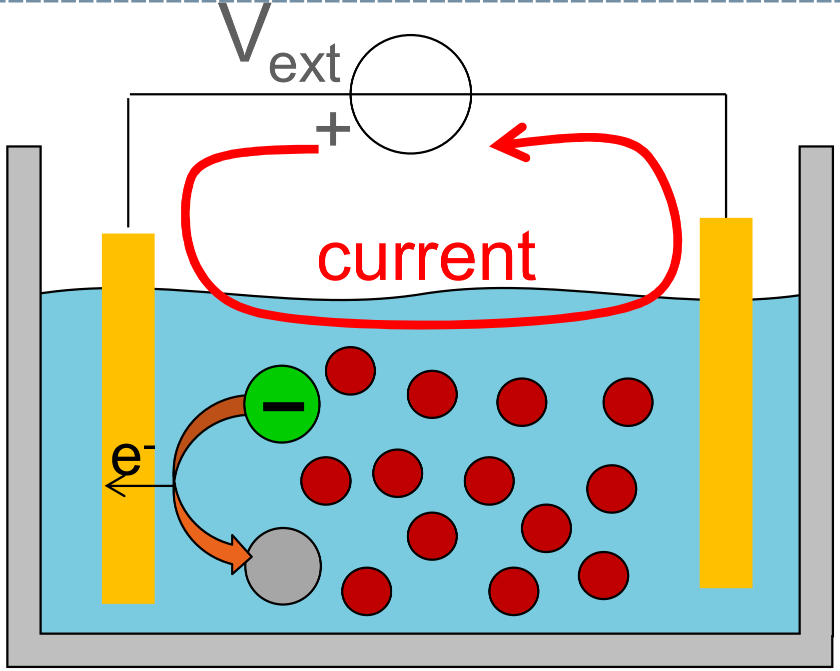
Common condition in biosensing and analytical chemistry:

Electrolyte + redox species

Target: redox species
Electrolyte: PBS, ion-rich solvent

Claim: we are limited by diffusion

What are we measuring?



1 ml of PBS contains:

$3 \cdot 10^{22}$ water molecules

$\approx 10^{20}$ Na^+, Cl^- ions

$\approx 10^{18}$ K^+ ions

$6 \cdot 10^{13}$ H^+ ions (pH=7)

…and maybe the target is …

1μM= $6 \; 10^{14}$ redox species

1nM= $6 \; 10^{11}$ redox species

1pM= $6 \; 10^{8}$ redox species

10^{8} specific antibodies

10^{6} DNA sequences

<1 Food Poisoning Pathogens (Salmonella, E. coli,…)

(assuming charge transfer is related to the target concentration)

Example

Electrolyte: KCl , C_{KCl}=1M

$\mu_{K+} \approx \mu_{Cl-} \approx 7 \cdot 10^{-4}$ cm²/Vs

Redox species: $K_3[Fe(CN)_6]$, $C_{Fe(CN)}$=1mM

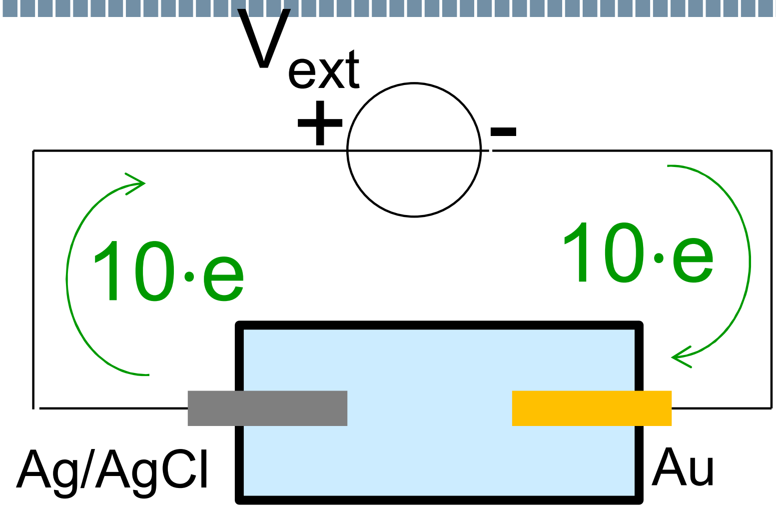
$\mu_{Fe(CN)} \approx 10^{-3}$ cm²/Vs

Electrodes: Ag/AgCl and gold

Reactions: gold electrode: $[Fe(CN)_6]^{3-} + e \leftrightarrows [Fe(CN)_6]^{4-}$

AgCl electrode: $AgCl + e \leftrightarrows Ag + Cl^-$

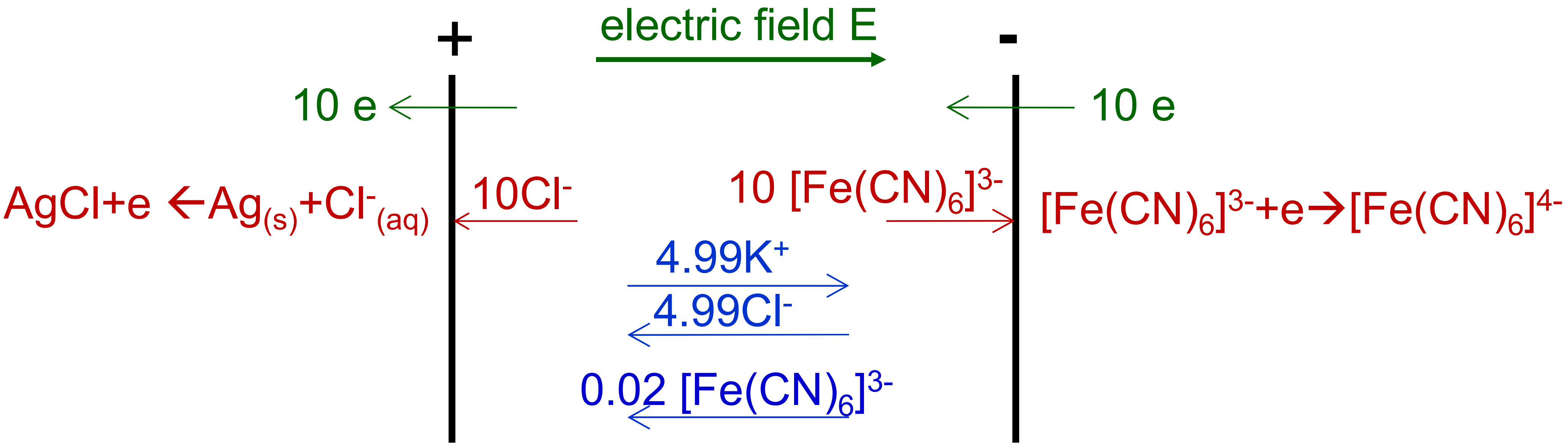
Balance sheet - supporting electrolyte



Ions in solution: K^+, Cl^-, $[Fe(CN)_6]^{3-}$

$C_{Fe(CN)}=0.001C_{Cl-}$ $\mu_{K+}\approx\mu_{Cl-}\approx 0.7\ \mu_{Fe(CN)}$

Let us assume a current of 10·e/s



$AgCl + e \leftarrow Ag_{(s)} + Cl^-_{(aq)}$

$10Cl^-$

$10\ [Fe(CN)_6]^{3-}$

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

$4.99K^+$

$4.99Cl^-$

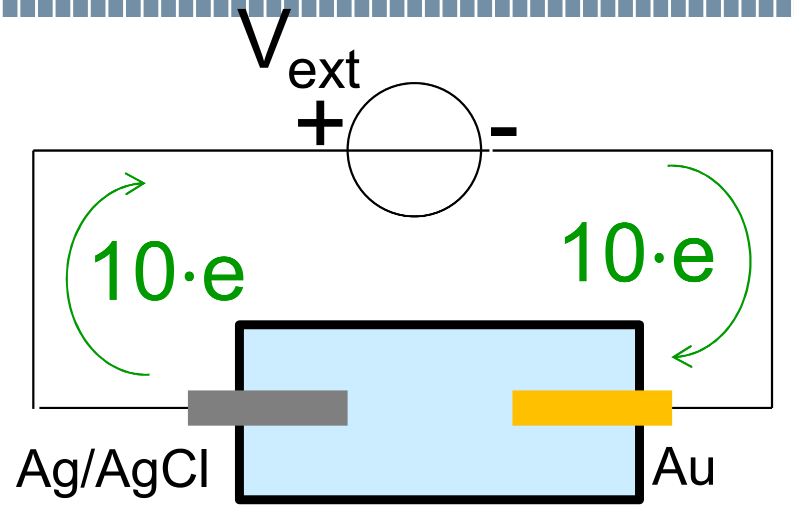
$0.02\ [Fe(CN)_6]^{3-}$

10 charges per second everywhere

$$I_K + I_{Cl} + I_{Fe(CN)_6} = 10\ e/s$$

$$qN_{av}C_K\mu_K E + qN_{av}C_{Cl}\mu_{Cl}E + 3qN_{av}C_{Fe(CN)_6}\mu_{Fe(CN)_6}E = 10\ e/s$$

Balance sheet - supporting electrolyte



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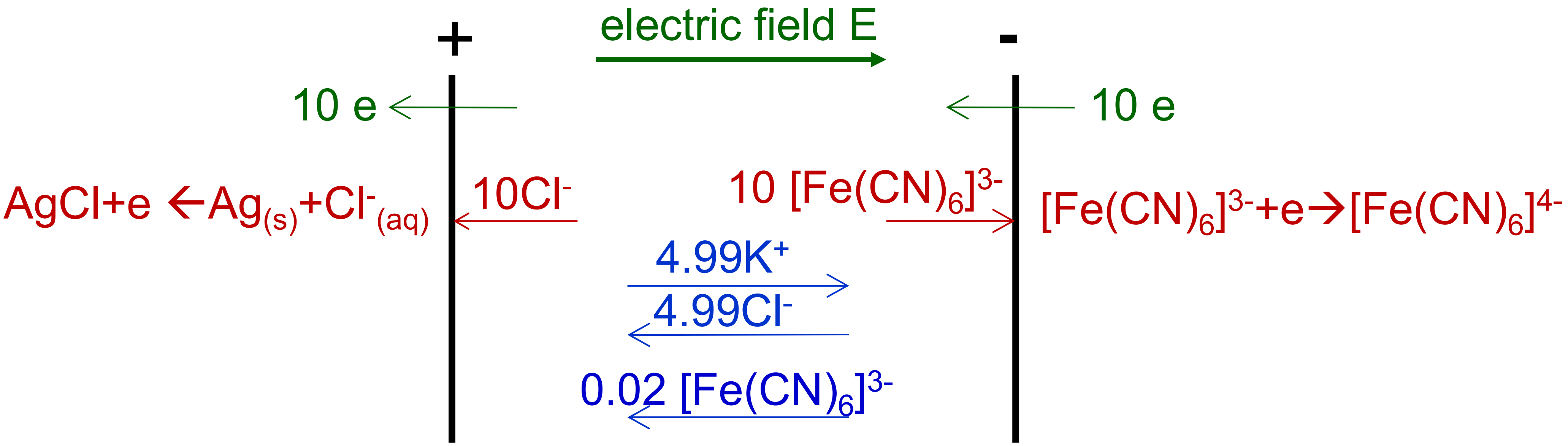


electric field E

+ -

10 e 10 e

$AgCl+e \leftarrow Ag_{(s)}+Cl^-_{(aq)}$

$10Cl^-$

$10\ [Fe(CN)_6]^{3-}$

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

$4.99K^+$

$4.99Cl^-$

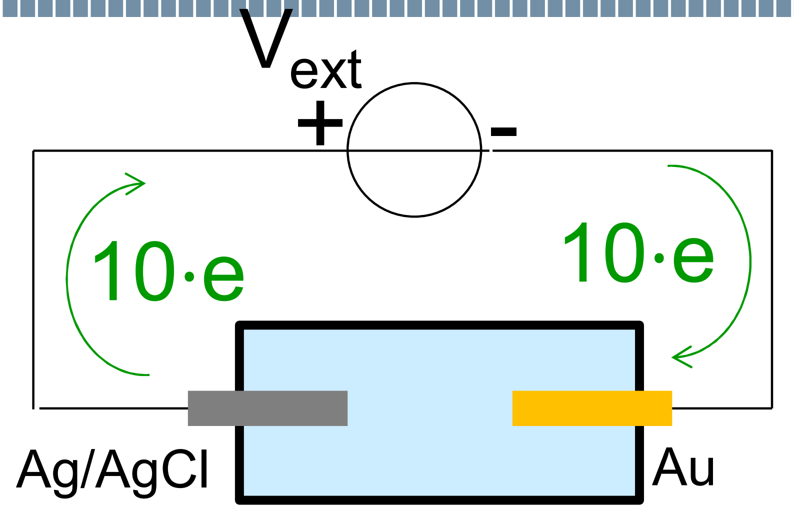
$0.02\ [Fe(CN)_6]^{3-}$

10 charges per second everywhere

The drift alone CANNOT sustain the charge transport

The electrolyte ions shield the redox species → limited effect of E

Balance sheet - supporting electrolyte



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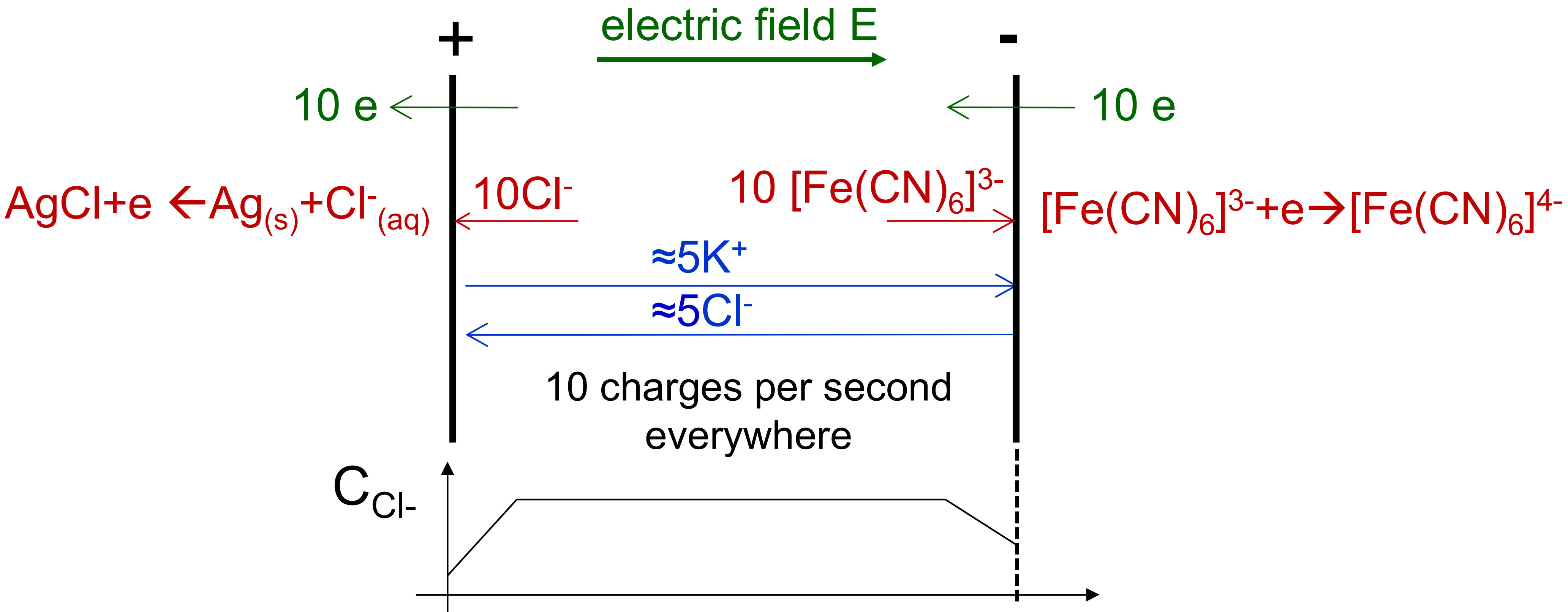
$C_{Fe(CN)} = 0.001 C_{Cl-}$ $\mu_{K+} \approx \mu_{Cl-} \approx 0.7\ \mu_{Fe(CN)}$

Let us assume a current of 10·e/s



$AgCl + e \leftarrow Ag_{(s)} + Cl^-_{(aq)}$

$10Cl^-$

$10\ [Fe(CN)_6]^{3-}$

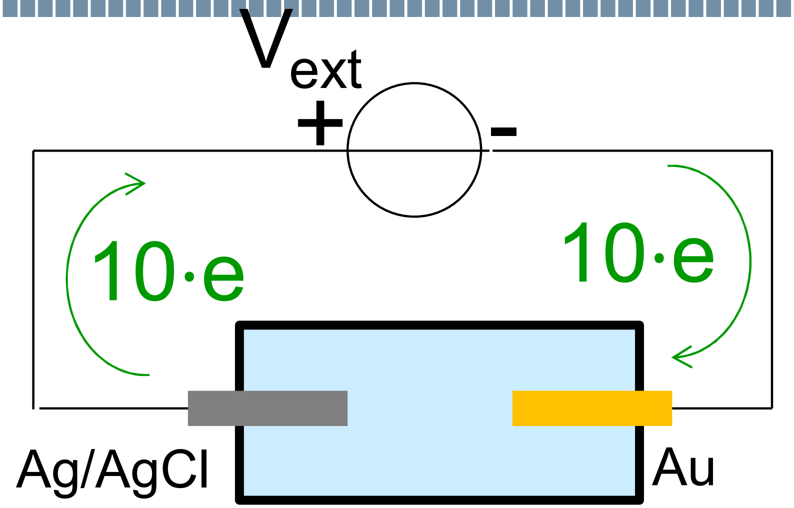
$[Fe(CN)_6]^{3-} + e \rightarrow [Fe(CN)_6]^{4-}$

$\approx 5K^+$

$\approx 5Cl^-$

10 charges per second everywhere

Balance sheet - supporting electrolyte



V_{ext}

+ -

10·e

10·e

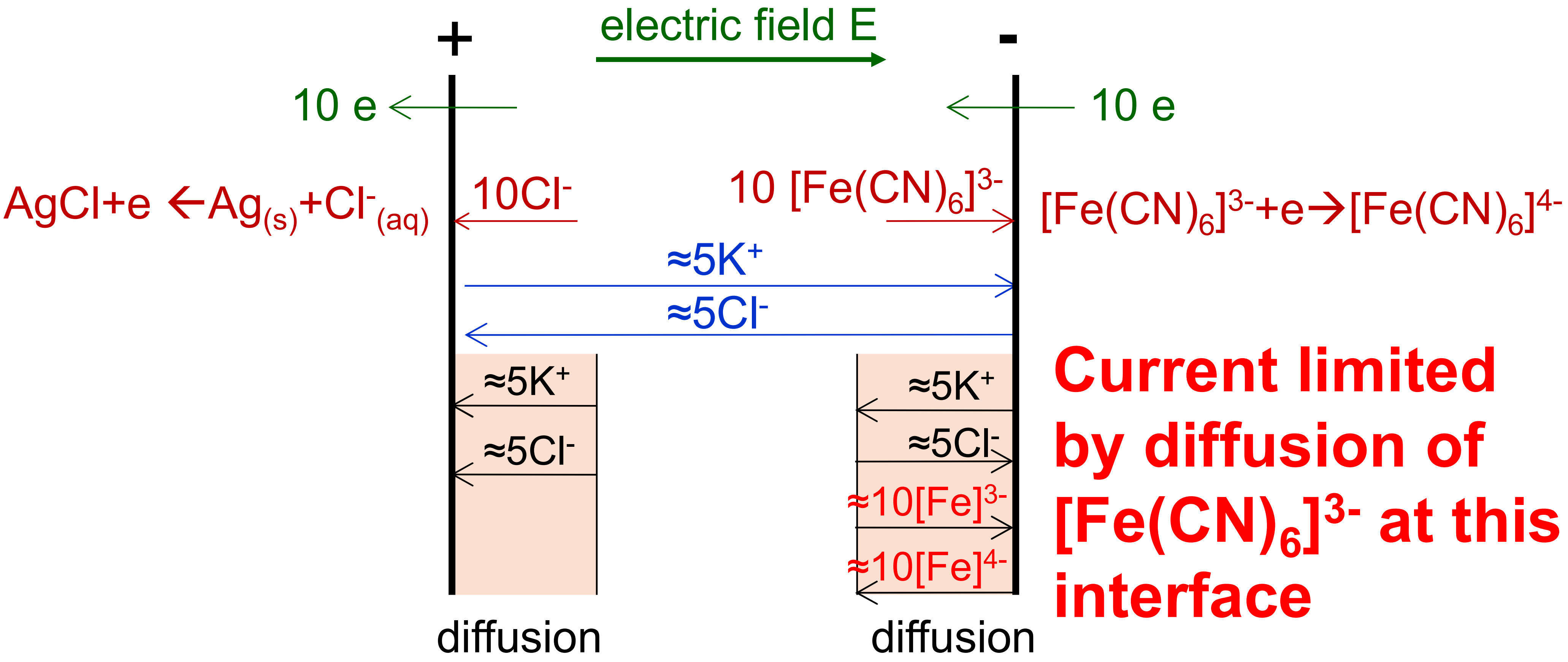
Ag/AgCl

Au

Ions in solution: K^+, Cl^-, $[Fe(CN)_6]^{3-}$

$C_{Fe(CN)} = 0.001 C_{Cl-}$ $\mu_{K+} \approx \mu_{Cl-} \approx 0.7\ \mu_{Fe(CN)}$

Let us assume a current of 10·e/s



electric field E

+

-

10 e

10 e

$AgCl + e \leftarrow Ag_{(s)} + Cl^-_{(aq)}$

$10Cl^-$

$10\ [Fe(CN)_6]^{3-}$

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

$\approx 5K^+$

$\approx 5Cl^-$

$\approx 5K^+$

$\approx 5Cl^-$

$\approx 5K^+$

$\approx 5Cl^-$

$\approx 10[Fe]^{3-}$

$\approx 10[Fe]^{4-}$

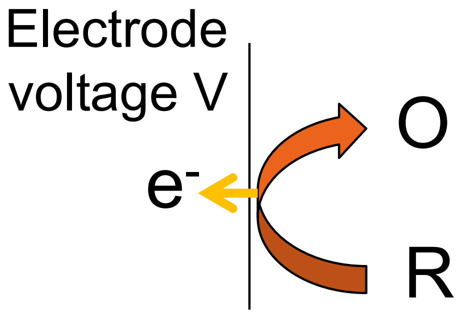
diffusion

diffusion

Current limited by diffusion of $[Fe(CN)_6]^{3-}$ at this interface

Response to a potential step

Consider: $O + e^- \leftrightarrows R$

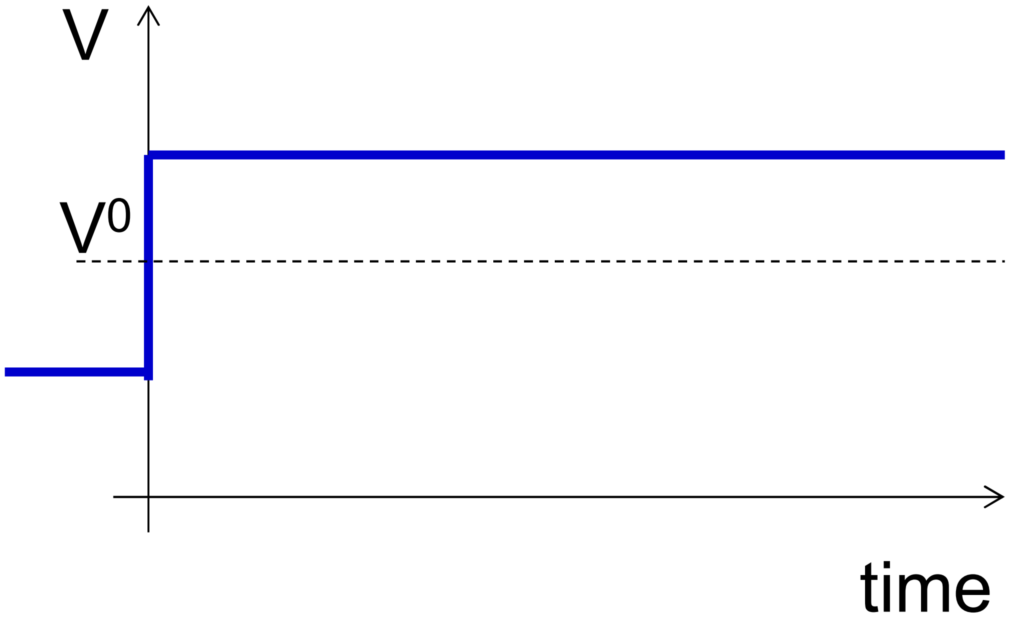


Assume:

$C_O=0$, $C_R= C_R^*$ for $t<0$

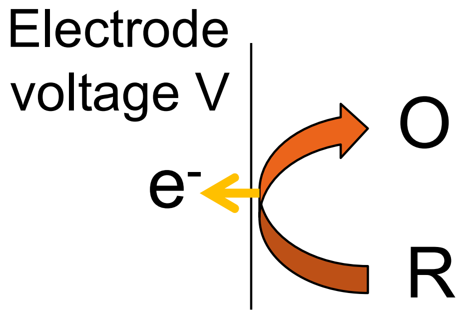
$V(t<0) \ll V^{0'}$; $V(t>0) \gg V^{0'}$ i.e. negligible reduction

Nernstian reaction: $C_O(x=0)$, $C_R(x=0)$ determined by Nernst eq.



Response to a potential step

Consider: O + e$^-$ ⇆ R

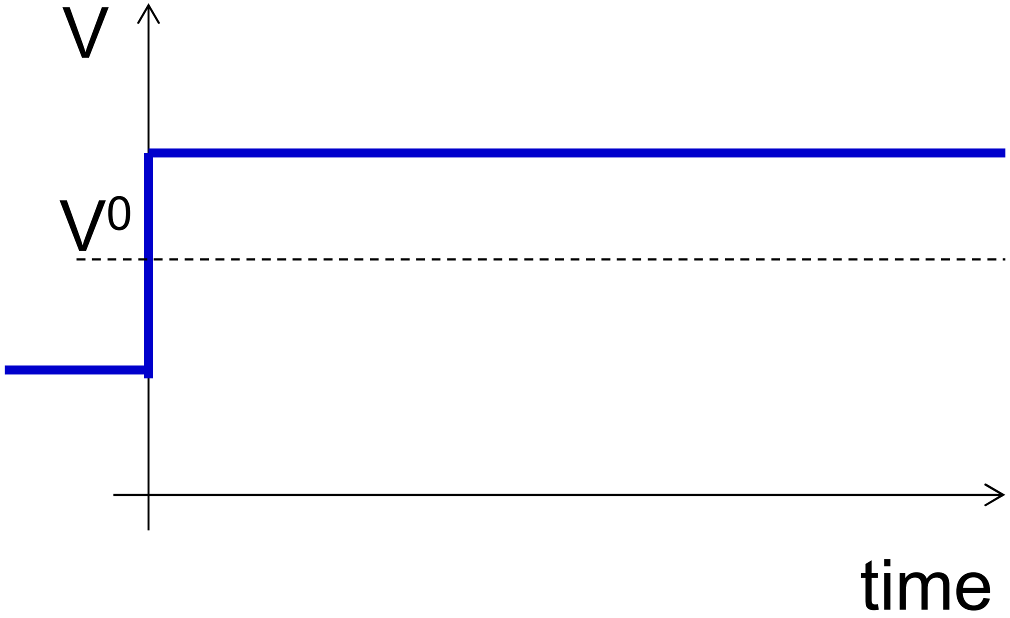


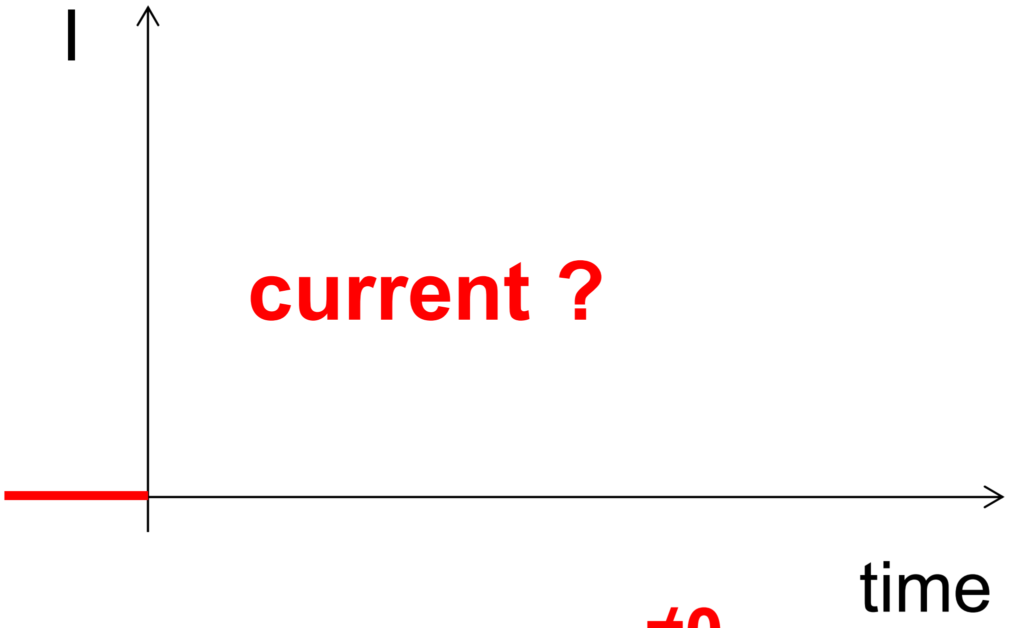
Assume:

$C_O=0$, $C_R= C_R^*$ for $t<0$

$V(t<0)<<V^{0'}$; $V(t>0) >>V^{0'}$ i.e. negligible reduction

Nernstian reaction: $C_O(x=0)$, $C_R(x=0)$ determined by Nernst eq.





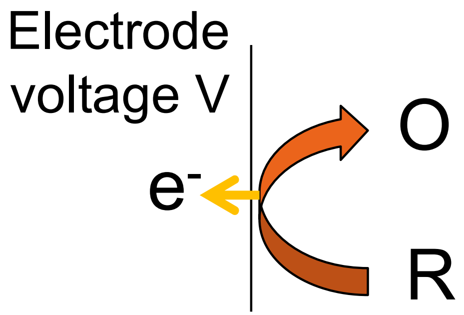
current ?

t<0

$$i = qN_{Av}Ak_0\left[\overset{\neq 0}{C_R(0)}e^{\overbrace{(1-\alpha)q\left(V-V^{0'}\right)/kT}^{\approx 0}} - \overset{0}{C_O(0)}e^{\overbrace{-\alpha q\left(V-V^{0'}\right)/kT}^{\neq 0}}\right]$$

Response to a potential step

Consider: O + e⁻ ⇆ R



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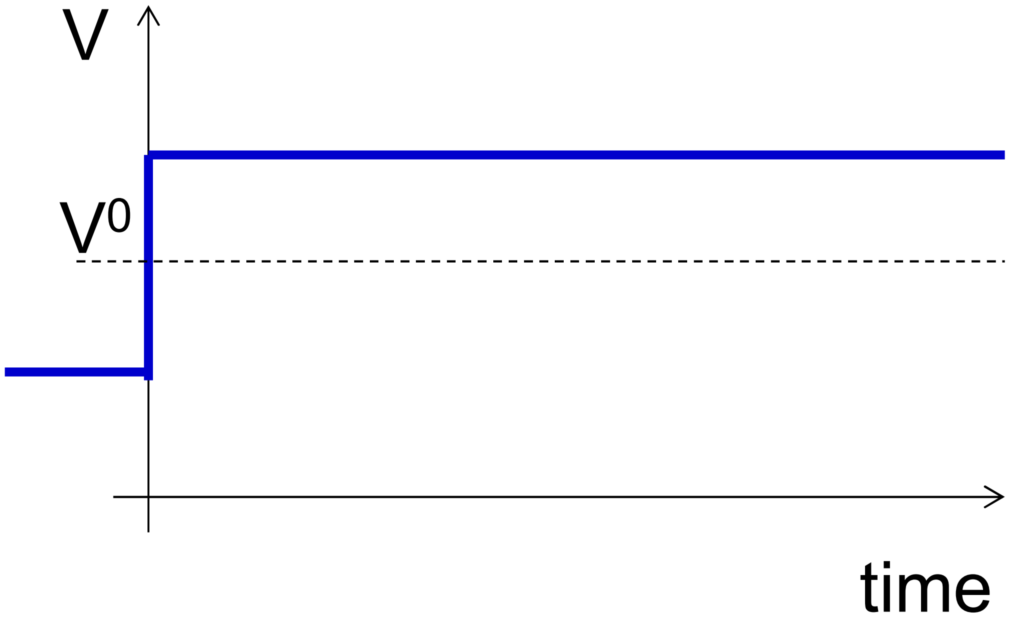
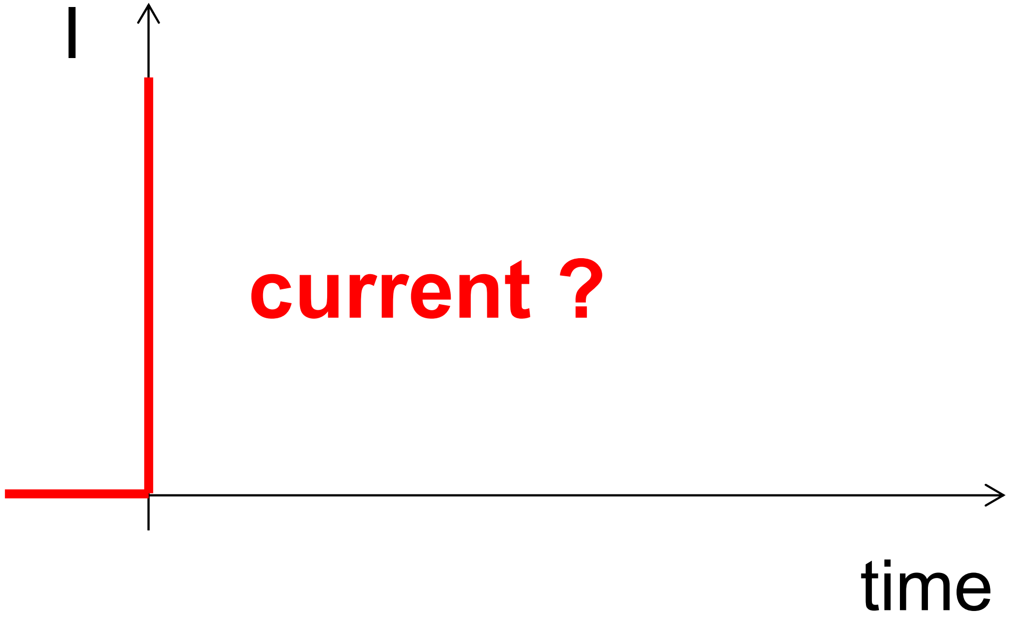
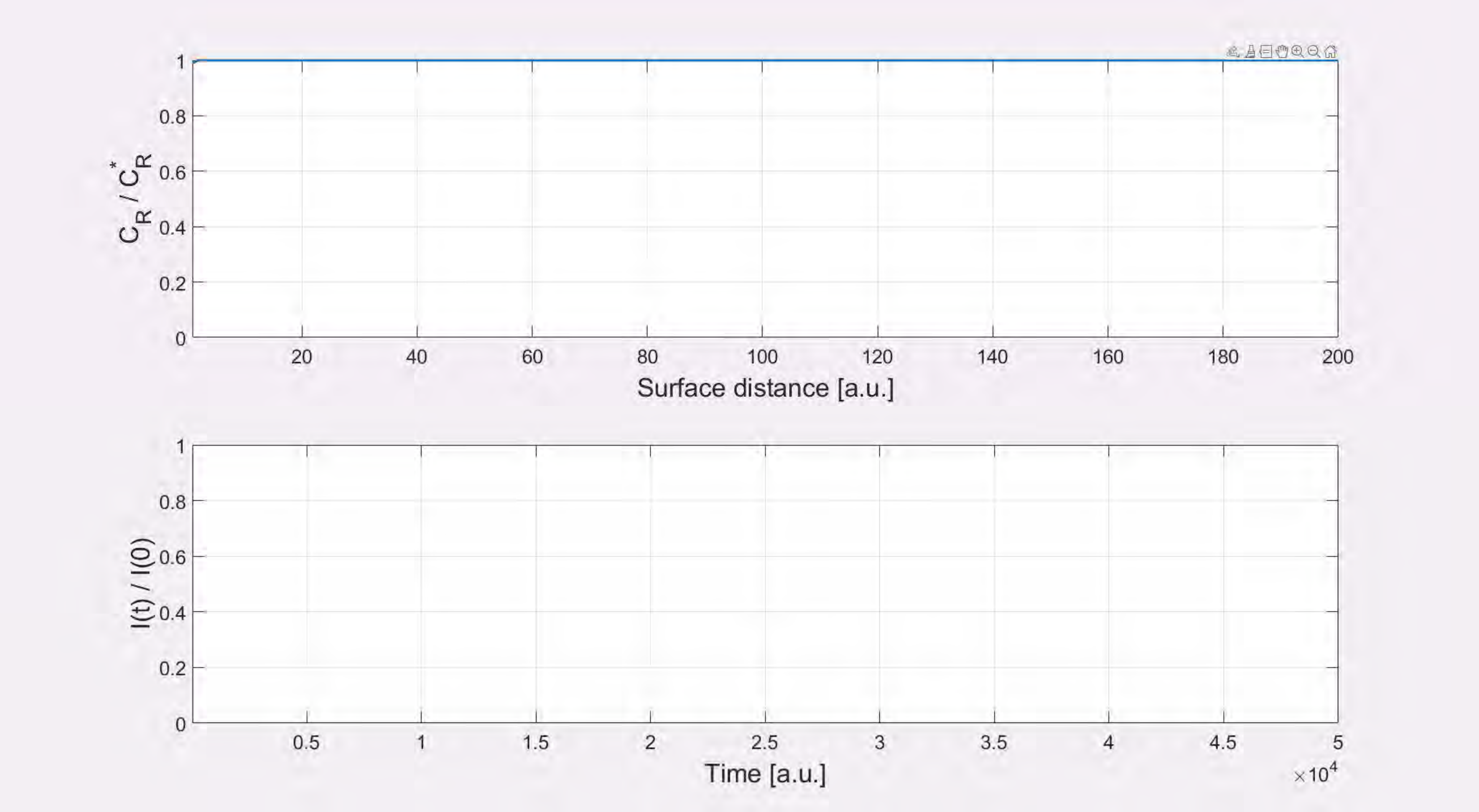




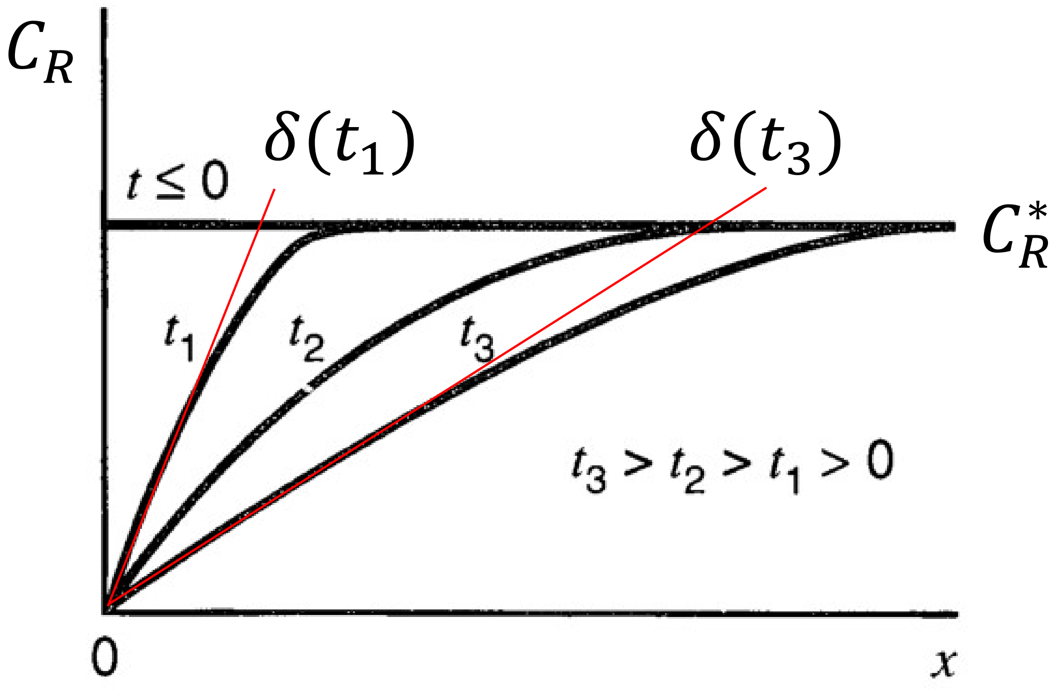
t=0

$$i = qN_{Av}Ak_0\left[\overset{C_R\text{ bulk}}{C_R(0)}\,e^{\overbrace{(1-\alpha)q\left(V-V^{0'}\right)/kT}^{>0}} - \overset{0}{C_O(0)}\,e^{\overbrace{-\alpha q\left(V-V^{0'}\right)/kT}^{\approx 0}}\right]$$

Potential step: concentration profile



Cottrell equation



reaction (current flow) causes a depletion (thickness δ) of R that increases with time

Current limited by diffusion:

$$i(t) = nFAD_R \frac{\partial C_R}{\partial x}$$

$$i(t) = nFAD_R \frac{C_R^* - C_R(x=0)}{\delta(t)}$$

$$i(t) \approx nFAD_R \frac{C_R^*}{\delta(t)}$$

F=qN$_{Av}$=Faraday constant

Depletion of R = total charge: $\int_0^t i\, dt \approx nFAC_R^* \frac{\delta(t)}{2}$

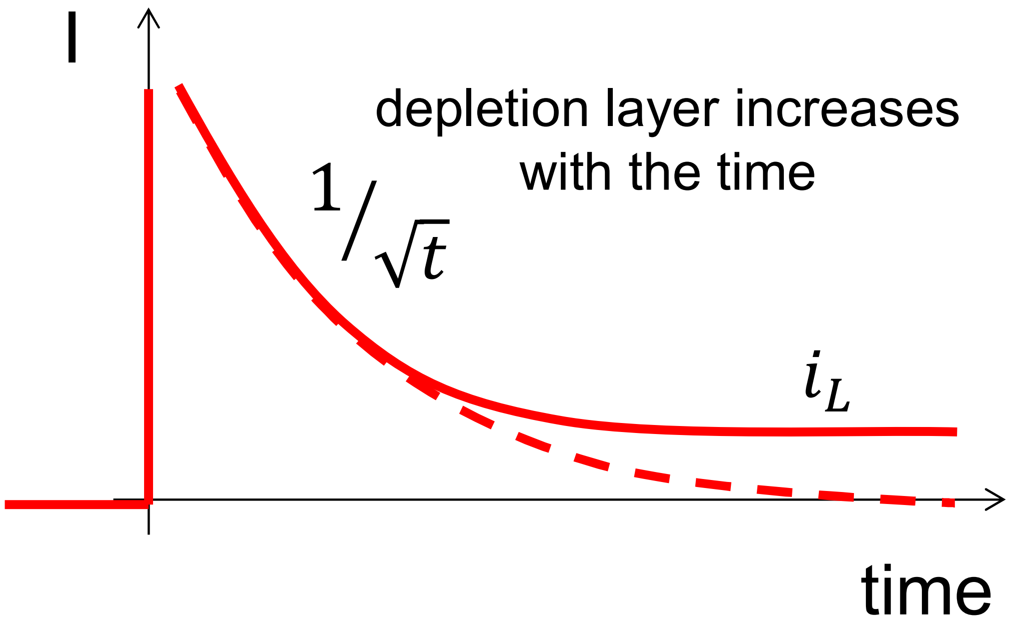
Differentianting: $i(t) \approx nFAC_R^* \frac{1}{2}\frac{d\delta(t)}{dt}$

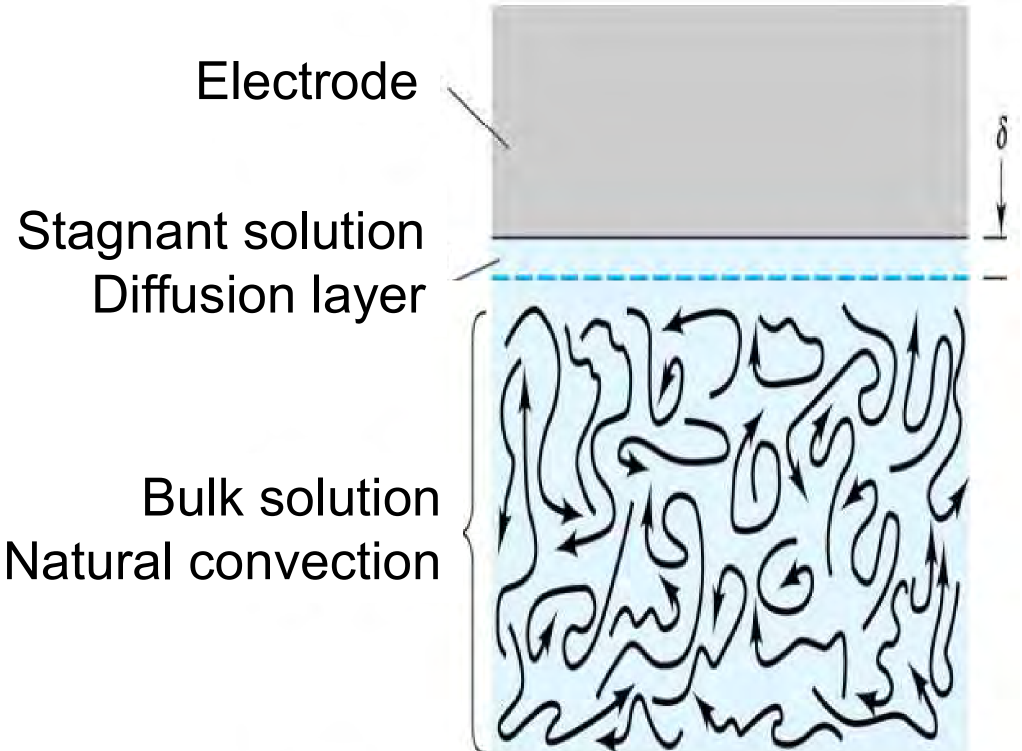
$$\frac{d\delta(t)}{dt} \approx \frac{2D_R}{\delta(t)} \quad \Rightarrow \delta(t) = 2\sqrt{D_R t}$$

$$\Rightarrow \quad i(t) = nFA\sqrt{\frac{D_R}{4t}}C_R^*$$

Cottrell equation

Limit current





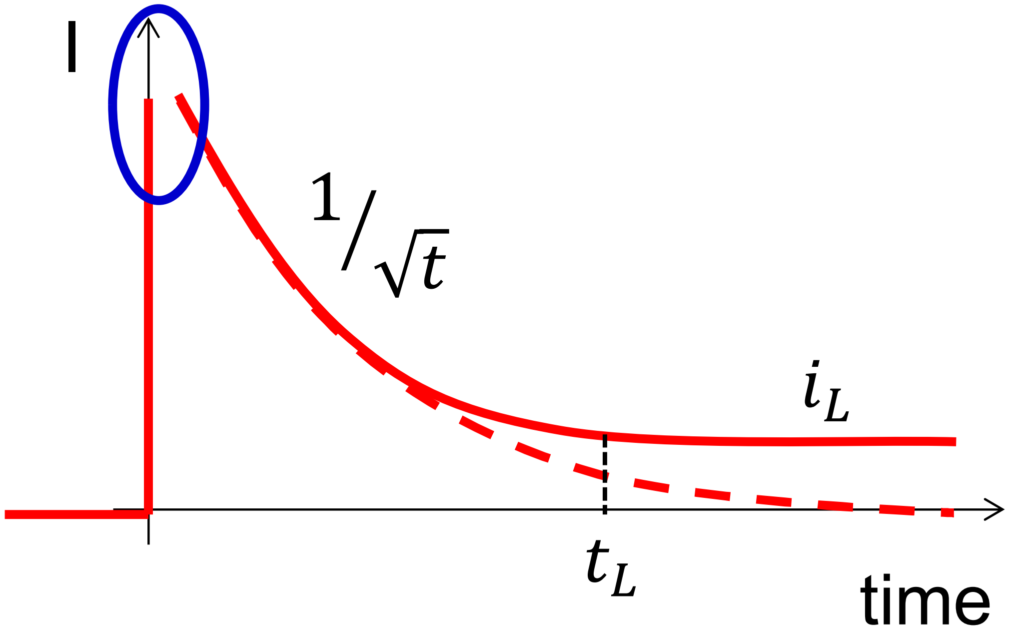
© 2004 Thomson - Brooks/Cole

The final current is not zero in real exper

why?

- geometrical effects (see lesson on nanoelectrochemistry)
- natural convection limits the layer thickness at about δ_0=100-500μm (not well controlled! mechanical vibrations, temperature gradient,…)

Current – planar electrode

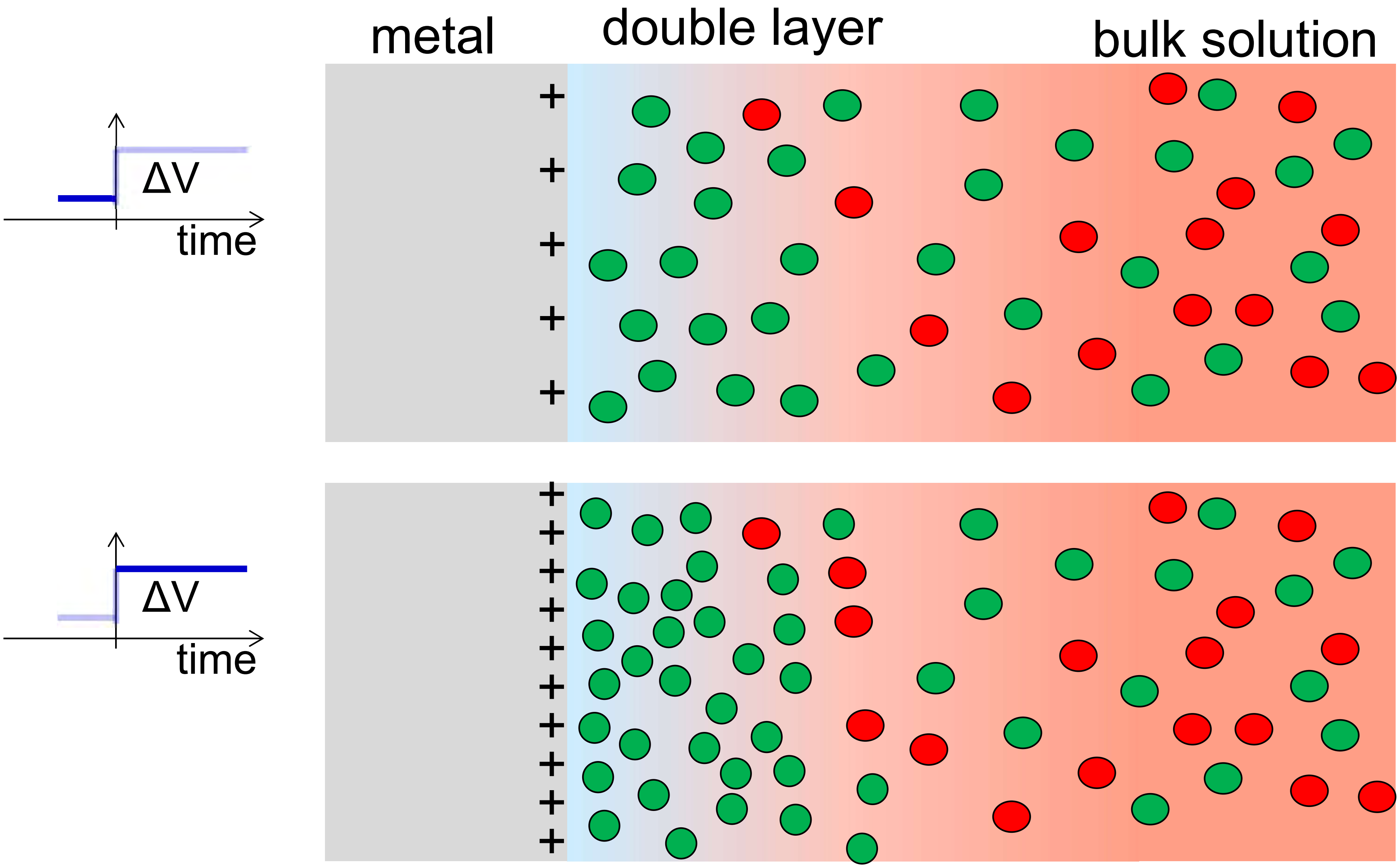


Limiting current: $i_L = nFAD_R \frac{C_R^*}{\delta_0}$ ⇨ meas. of C_R^* (amperometry)

Slow response to a step voltage (better work with a constant voltage)

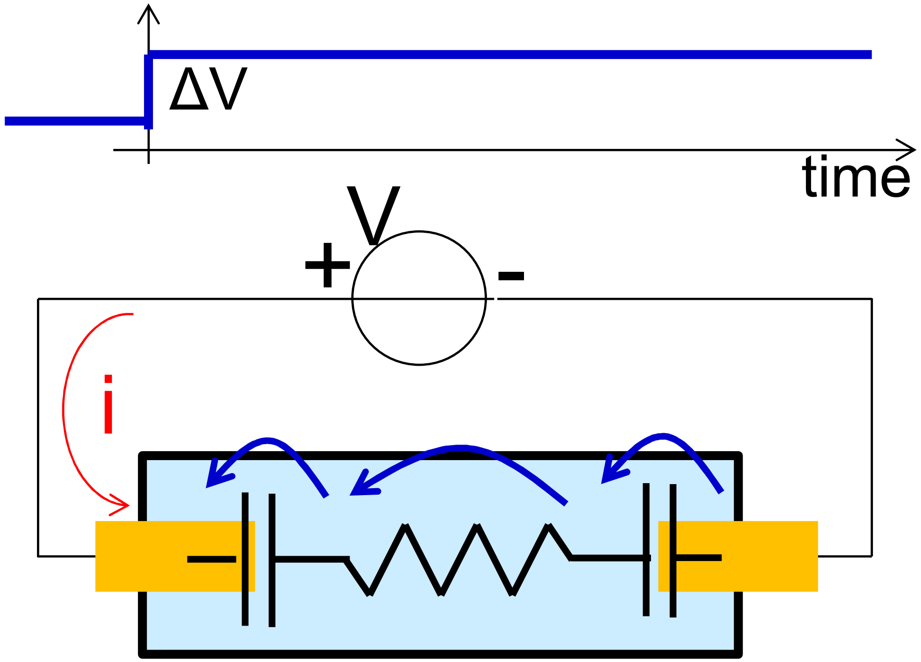
assuming $D=2\cdot10^{-5}$ cm^2/s, δ_0 =500μm ⇨ $t_L \approx \frac{\delta_0^2}{4D_R} = 31\ s$

Double Layer vs. Diffusion



The double layer requires charge, not necessarily redox species!

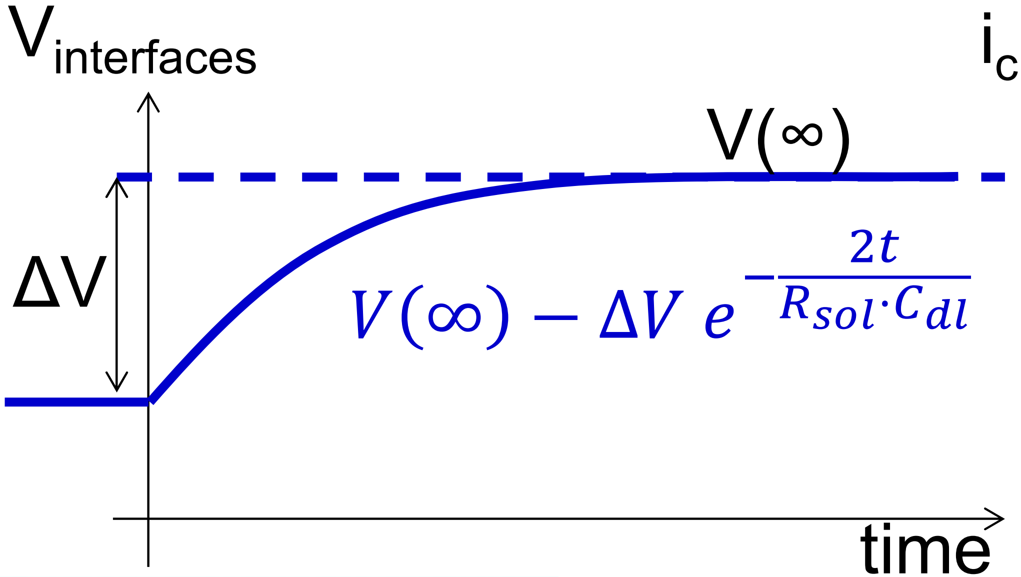
Double layer charging



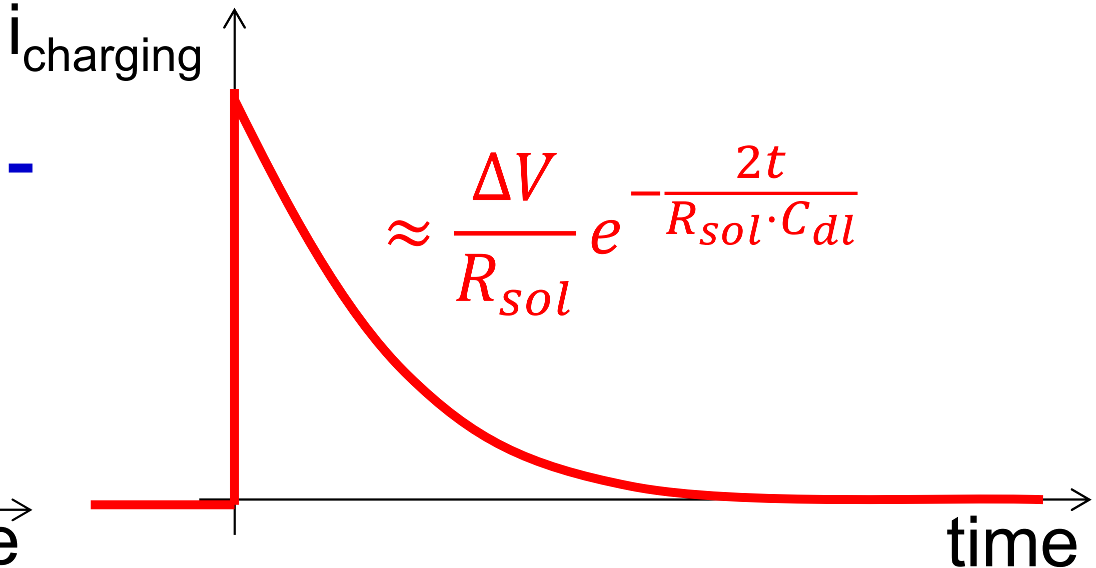
charging of C_{dl} through the ions of the supporting electrolyte (drift)

↓

"fast" exponential transient

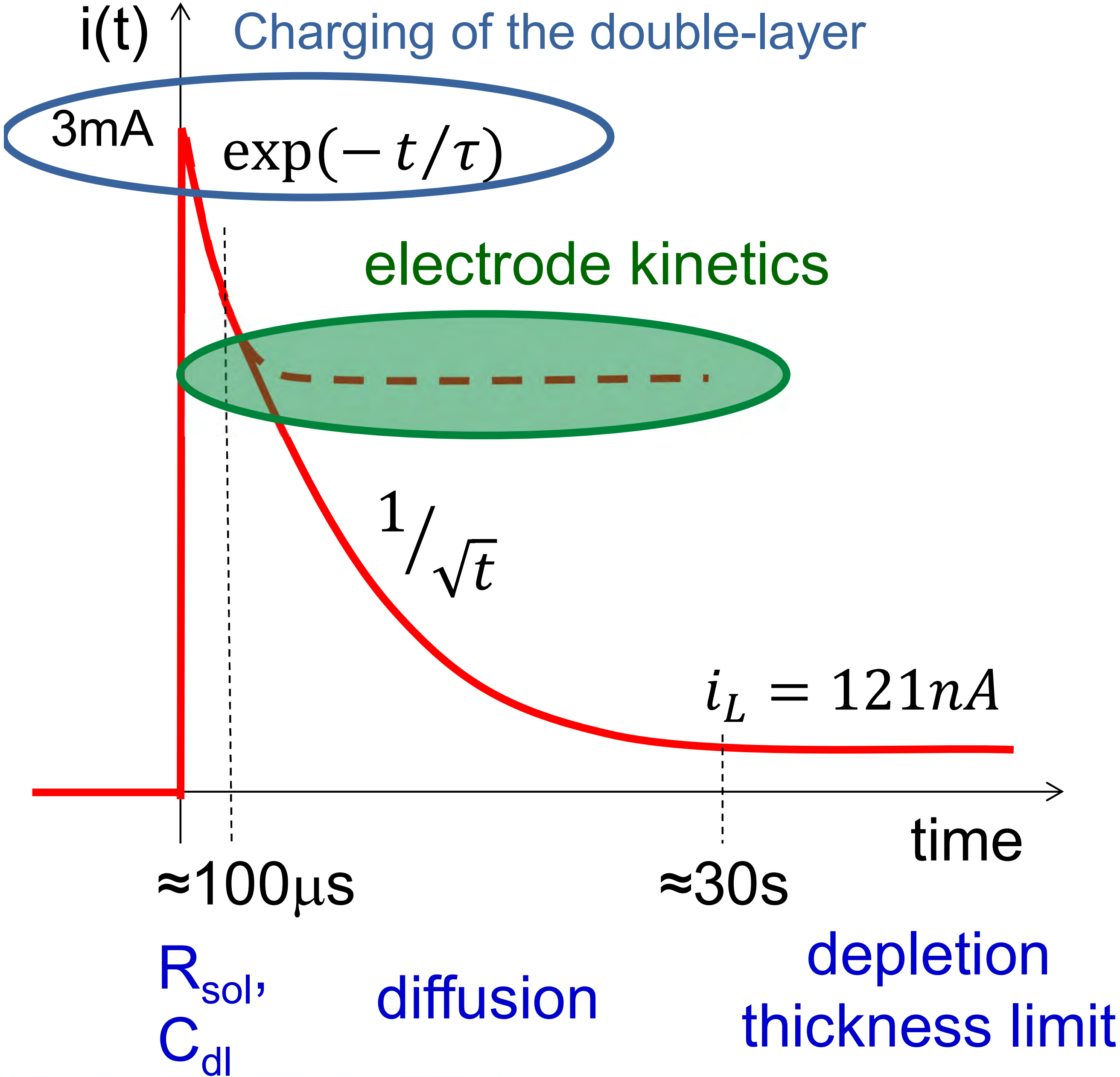


$$V(\infty) - \Delta V\, e^{-\frac{2t}{R_{sol} \cdot C_{dl}}}$$



$$\approx \frac{\Delta V}{R_{sol}} e^{-\frac{2t}{R_{sol} \cdot C_{dl}}}$$

Step response of a planar electrode



Assuming:

$\Delta V = 0.5V$

$C_R^* = 100\mu M$

$D = 2\cdot 10^{-5}\ cm^2/s$, $\delta_0 = 500\mu m$

$\rho_{PBS} \approx 60\ \Omega\cdot cm$

$C_{dl}' = 0.1pF/\mu m^2$

r=1mm (disk electrode)

⇩

$R_{sol} = \rho/4r = 150\Omega$

$C_{dl} = 314nF$

⇩

$\tau = R_{sol}\cdot C_{dl} = 47\mu s$

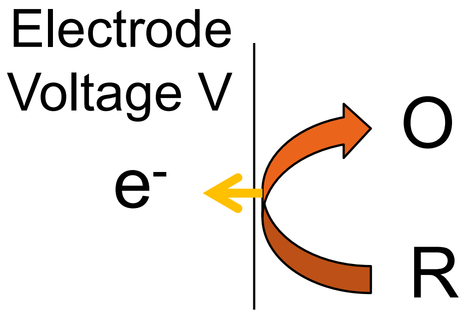
$$t_L \approx \frac{\delta_0^2}{4D_R} = 31\ s$$

$$i(0) \approx \frac{\Delta V}{R_{sol}} = 3mA$$

$$i_L = nFAD_R\frac{C_R^*}{\delta_0} = 121nA$$

Response to a potential sweep

Consider: $O + e^- \leftrightarrows R$

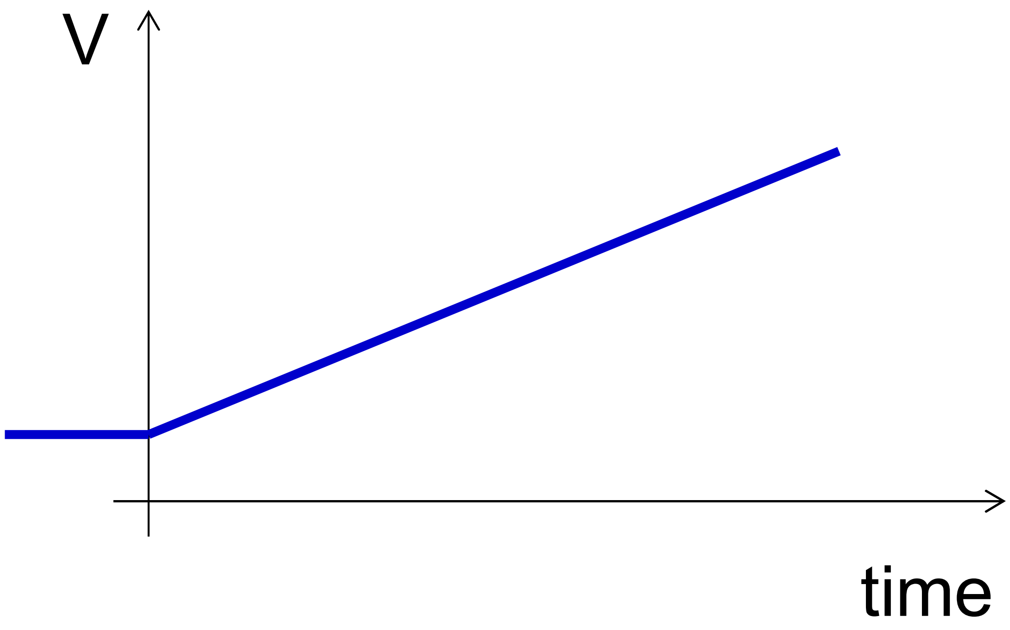


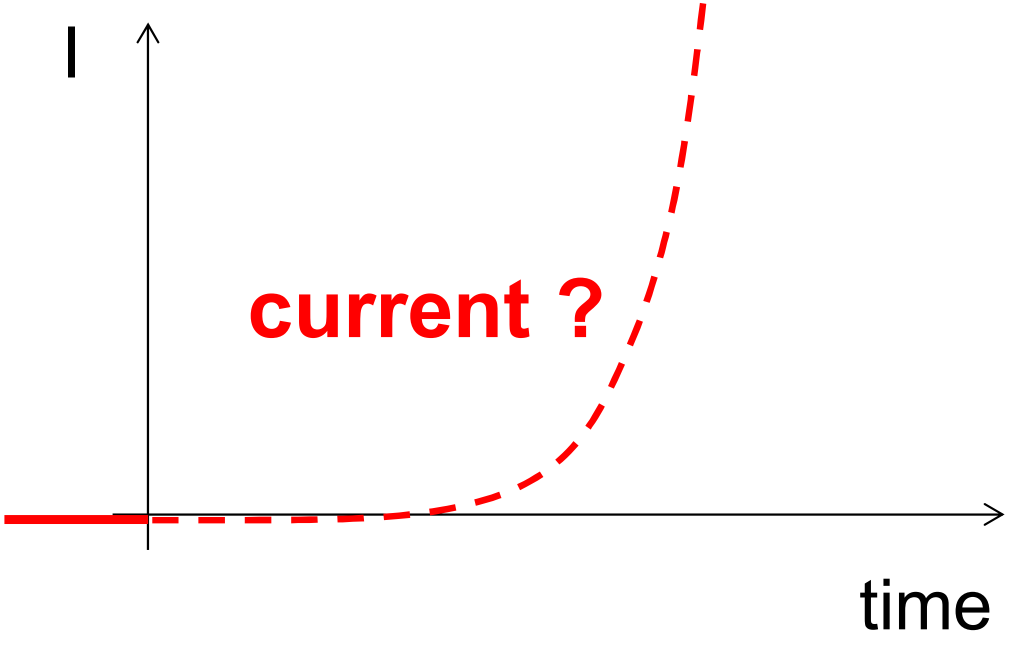
Assume:

$C_O=0$, $C_R= C_R^*$ for $t<0$

$V(t<0) \ll V^{0'}$

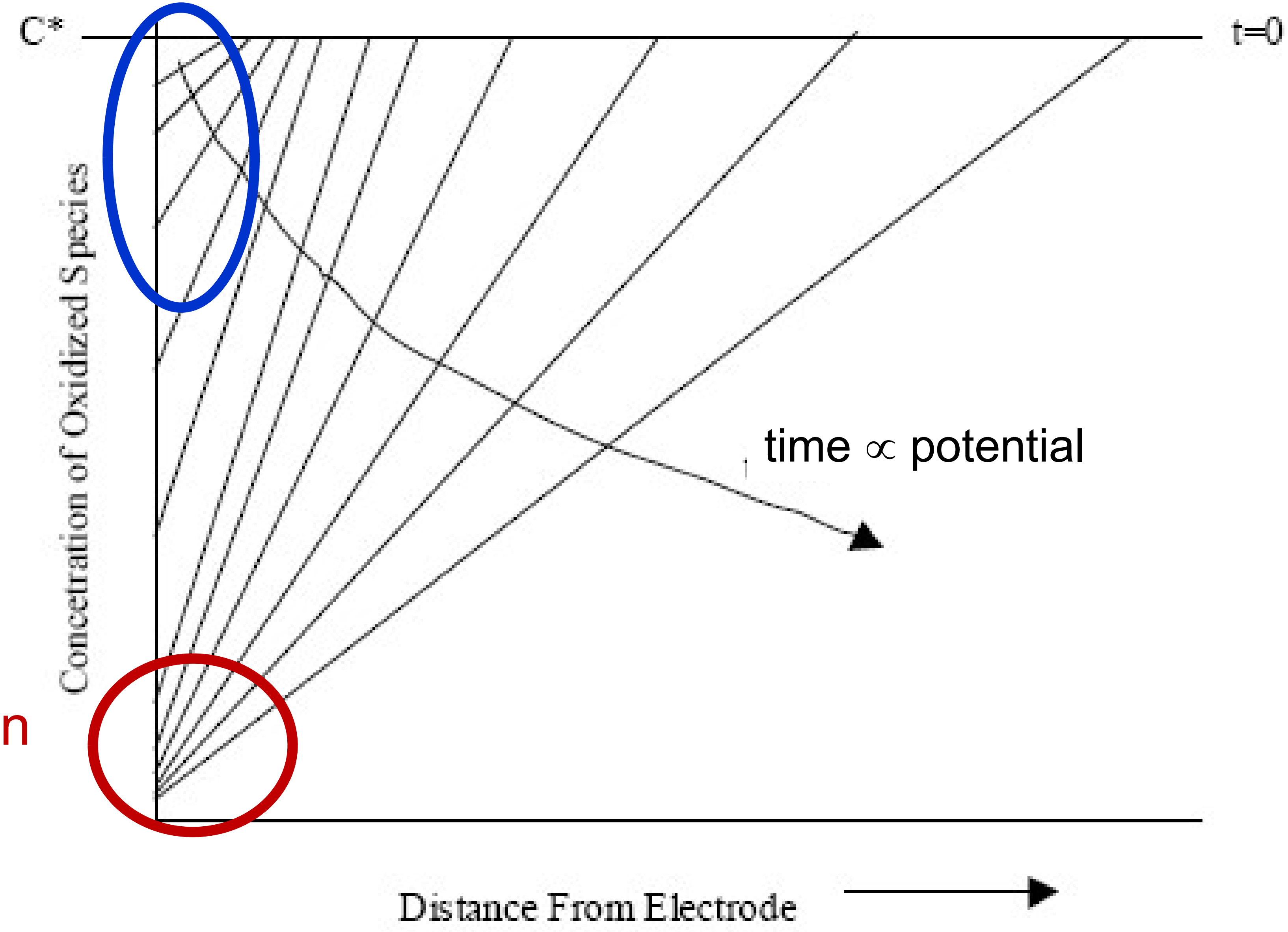
Nernstian reaction: $C_O(x=0)$, $C_R(x=0)$ determined by Nernst eq.





$$i = qN_{Av}Ak_0\left[C_R(0)e^{(1-\alpha)q\left(V-V^{0'}\right)/kT} - C_O(0)e^{-\alpha q\left(V-V^{0'}\right)/kT}\right]$$

Concentration profile



Electron transfer limited

Diffusion limited

time ∝ potential

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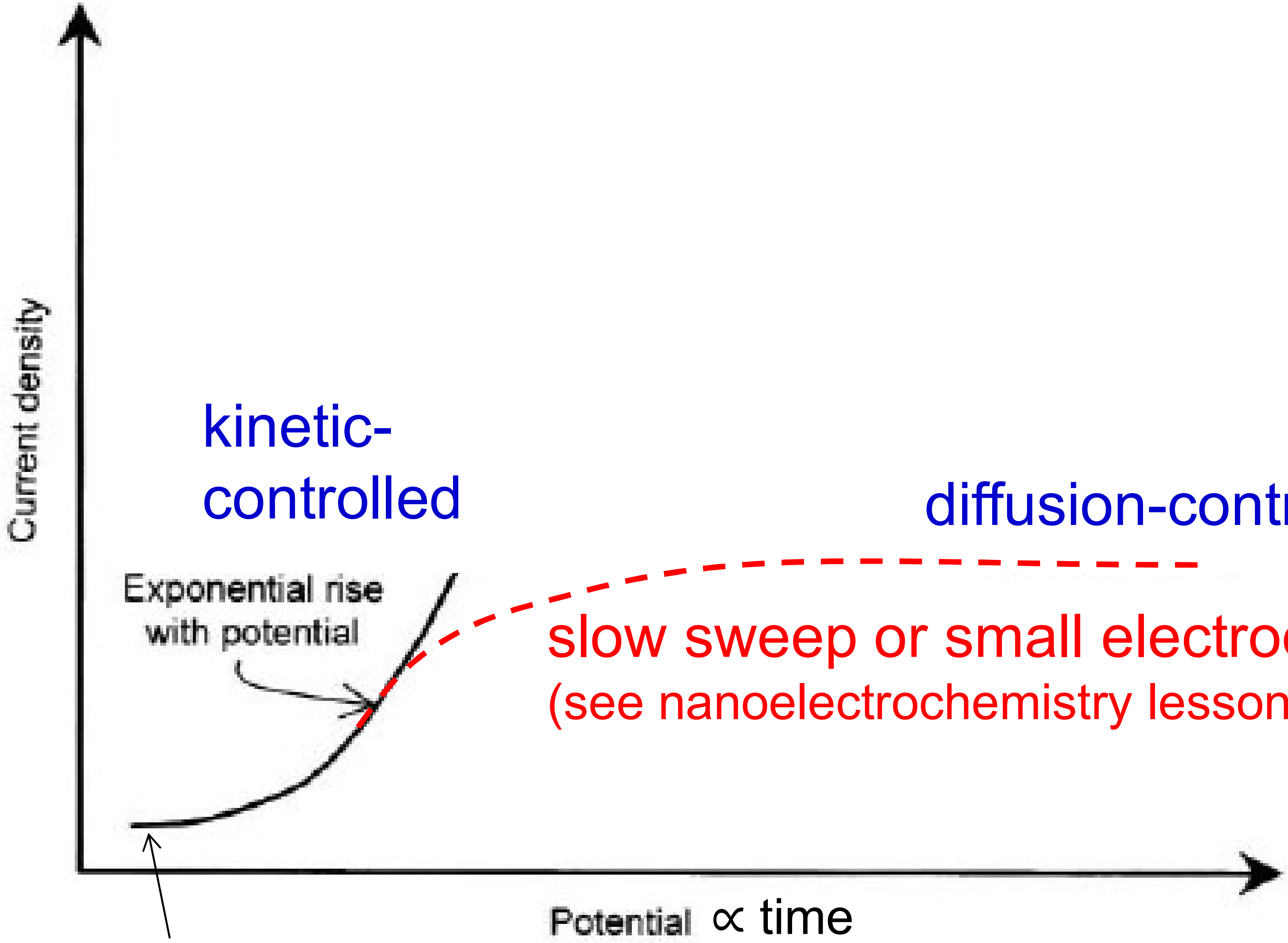
Slow sweep: Stationary Current Profile



kinetic-
controlled

diffusion-controlled

slow sweep or small electrodes
(see nanoelectrochemistry lesson)

∝ time

C_{dl} charging: $i=C_{dl} \cdot dV/dt \approx$ constant

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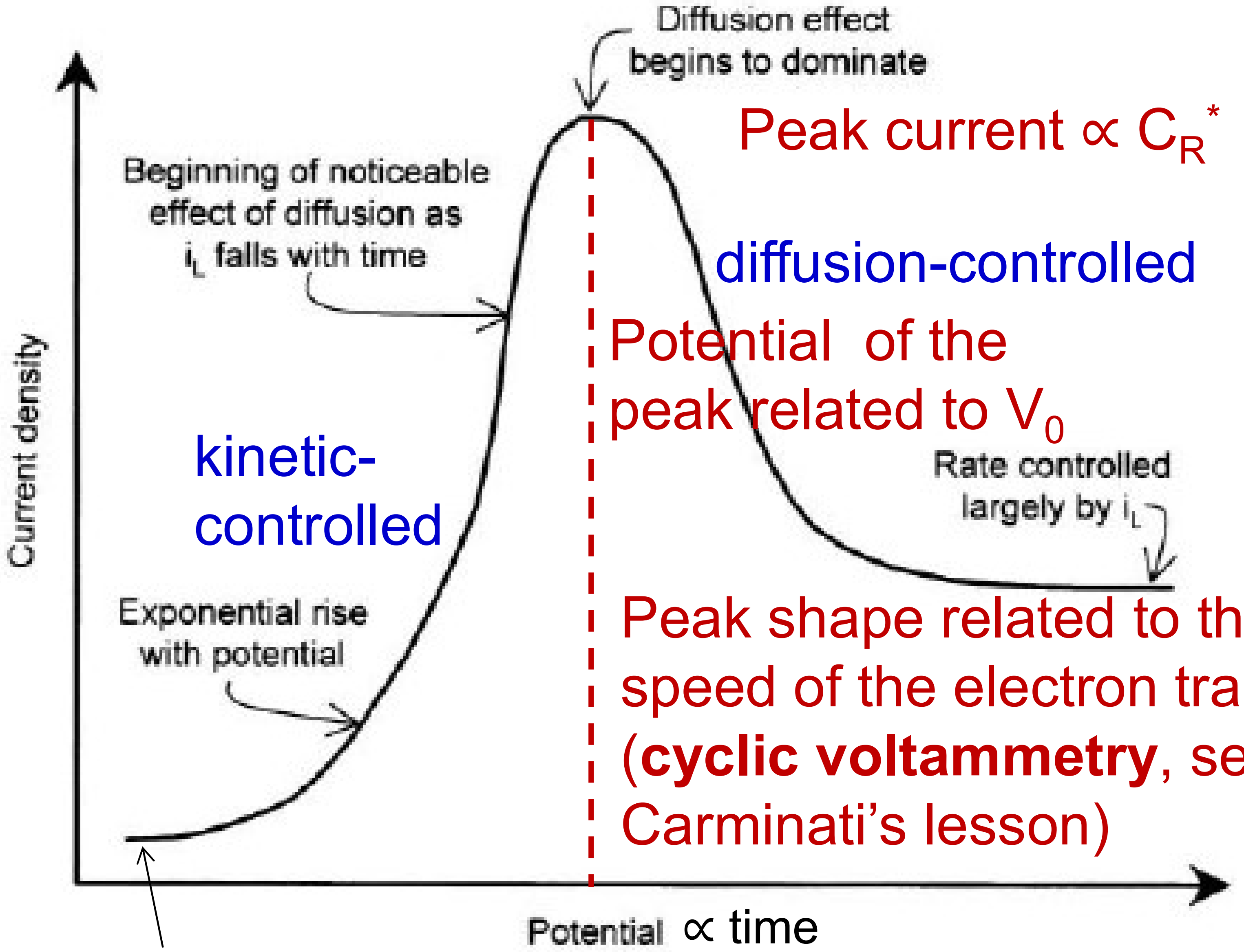
Fast sweep: Peaked Current Profile



Peak current $\propto C_R^*$

diffusion-controlled

Potential of the peak related to V_0

kinetic-controlled

Peak shape related to the speed of the electron transfer (**cyclic voltammetry**, see Carminati’s lesson)

$\propto$ time

C_{dl} charging: $i=C_{dl} \cdot dV/dt \approx$ constant

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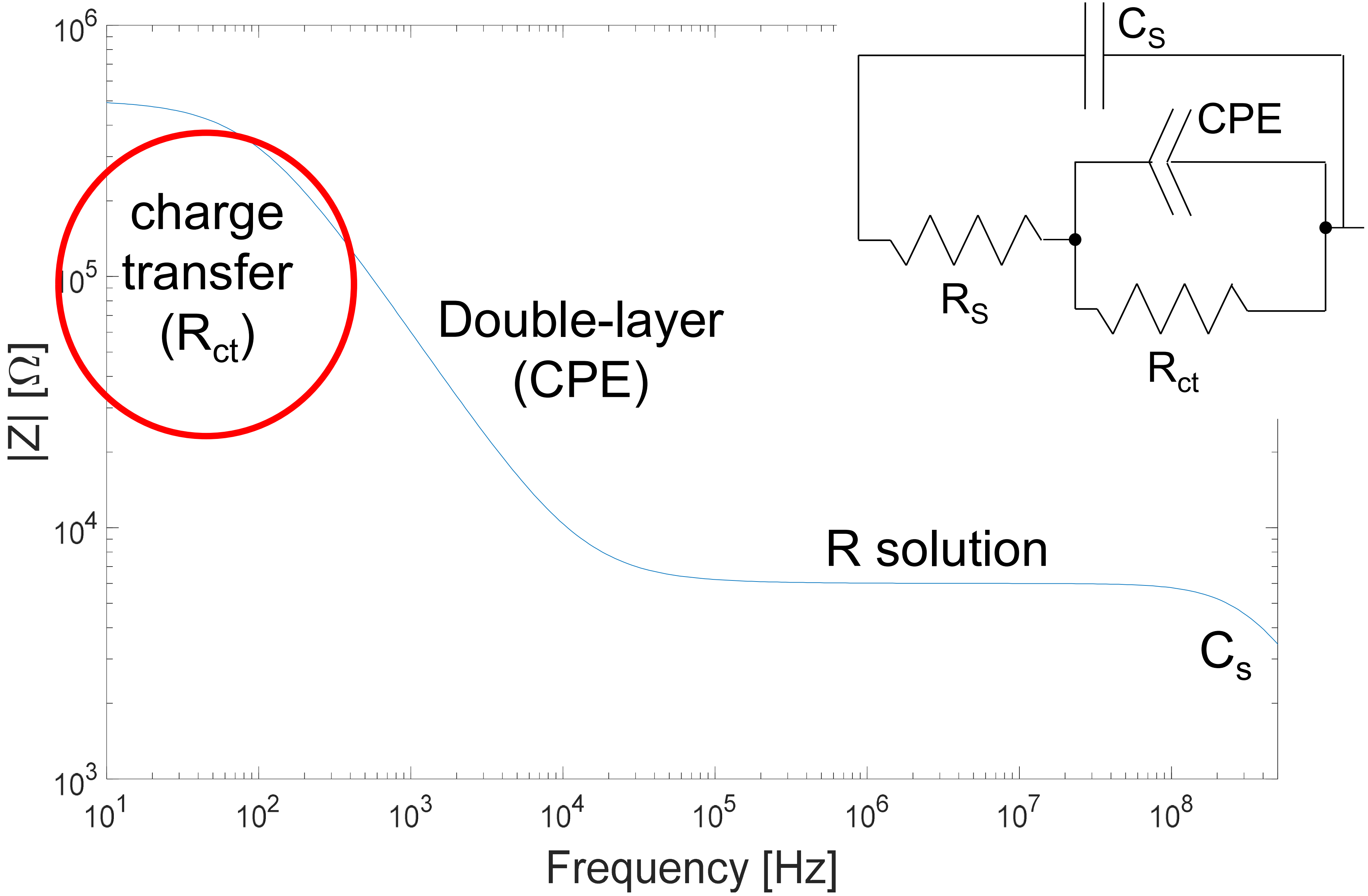
What about impedance spectra?

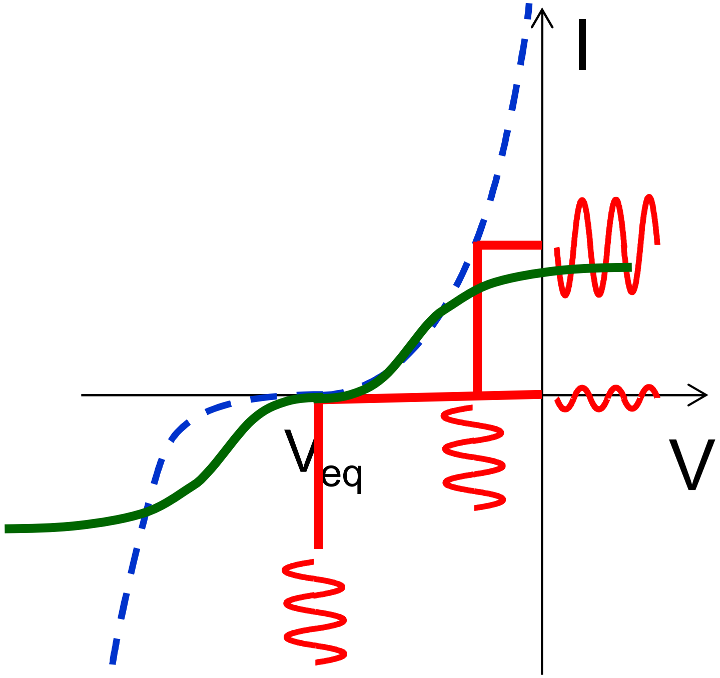
From the previous lesson WITHOUT mass transfer



Equivalent Circuit: Charge Transfer

The impedance concept requires a linear system
Electrode kinetics gives a non-linear behavior

Small signal
↓
linearization



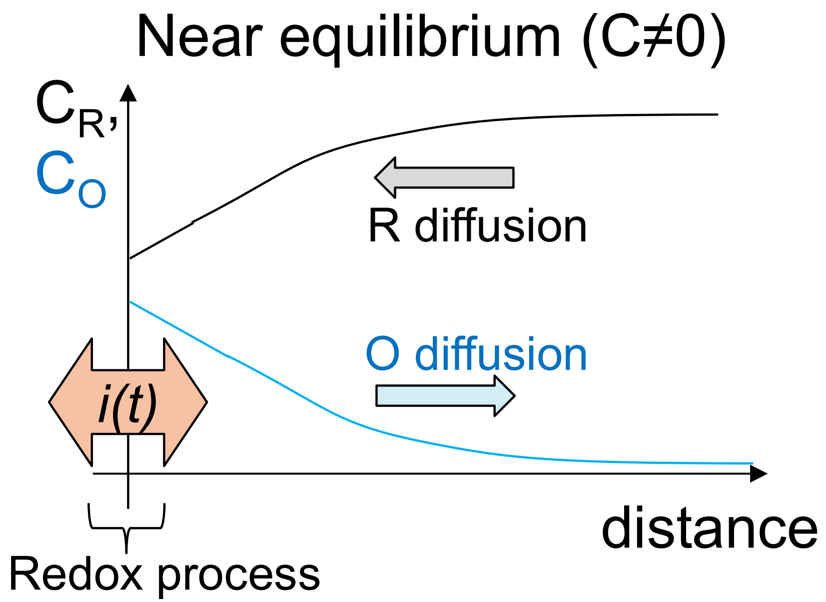
$$R_{ct} = \left.\frac{\partial V}{\partial i}\right|_{working\ point}$$

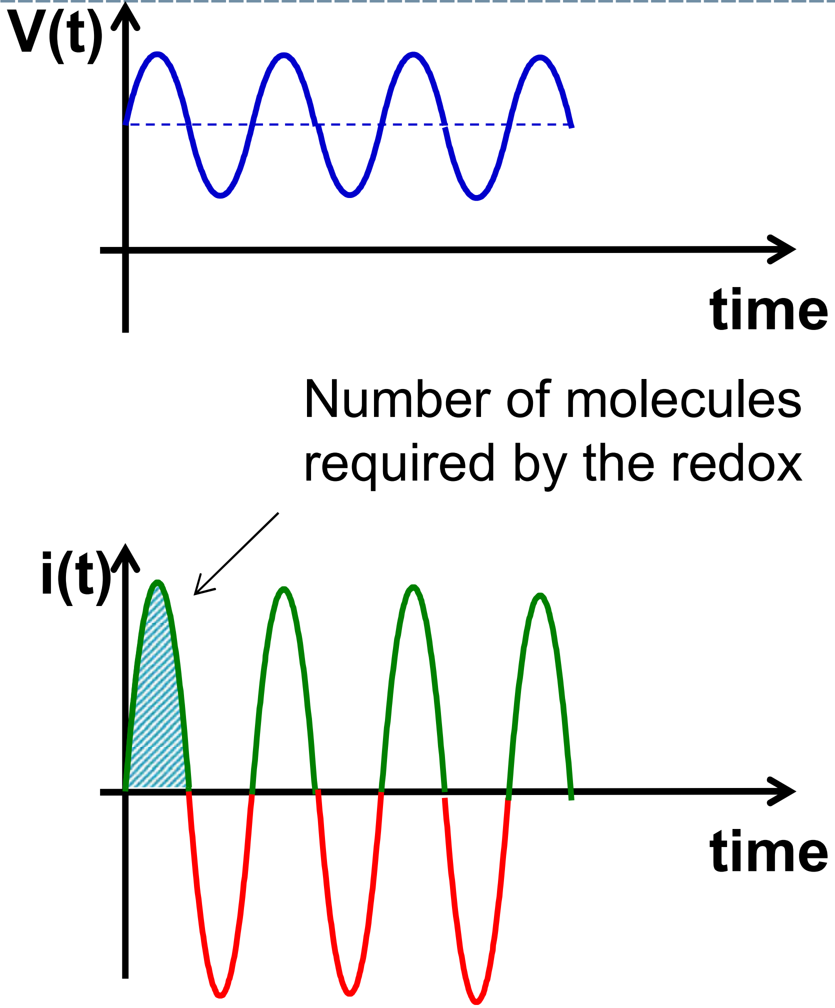
$$i = i_0\left(e^{-\alpha nq(V-V_{eq})/kT} - e^{-(1-\alpha)nq(V-V_{eq})/kT}\right)$$

$$i_0 = qN_{Av}Ak_0C_O^{1-\alpha}C_R^{\alpha}$$

A stationary condition is more easily obtained with $V \approx V_{eq}$ → $R_{ct} \approx \frac{kT}{nq}\frac{1}{i_0}$

Warburg Impedance





“high frequency”:

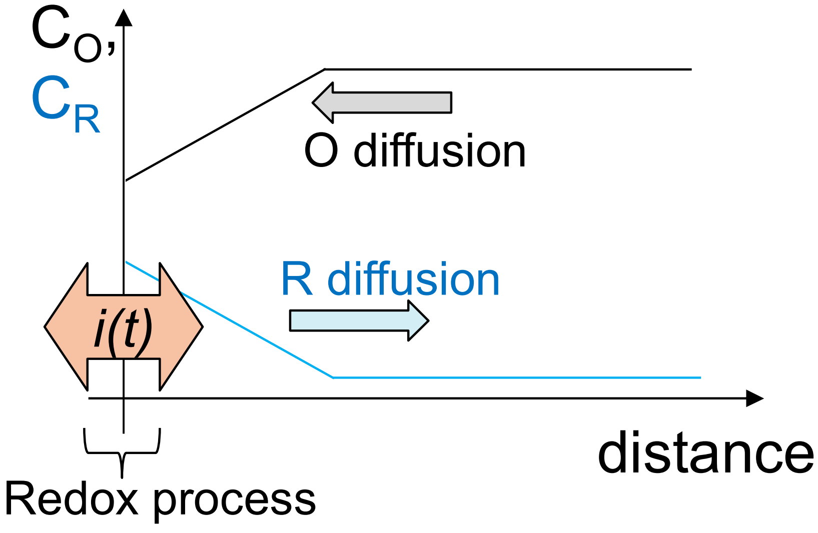
Few molecules are required at the interface

→ kinetic-limited current

→ R_{ct}

Warburg Impedance

Near equilibrium (C≠0)



“high frequency”:

Few molecules are required at the interface

→ kinetic-limited current

→ R_{ct}

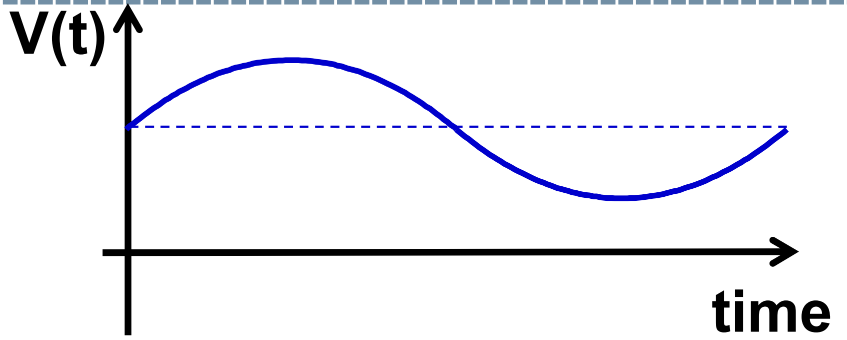
“low frequency”:

Many more molecules are required

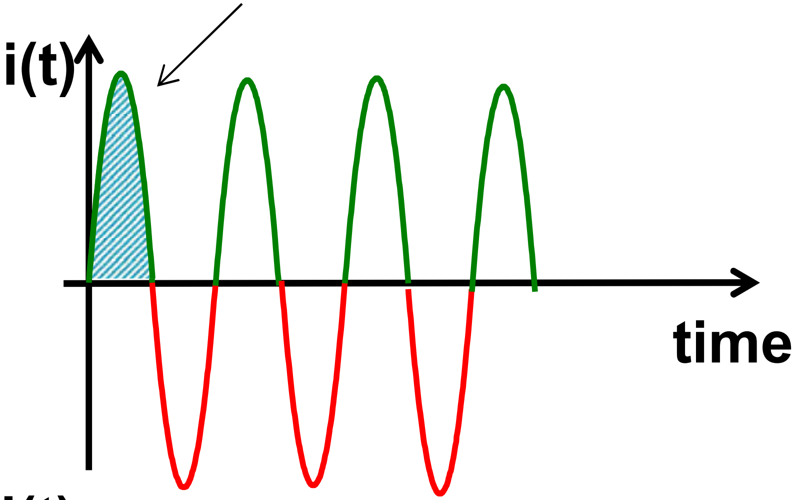
→ diffusion-limited current

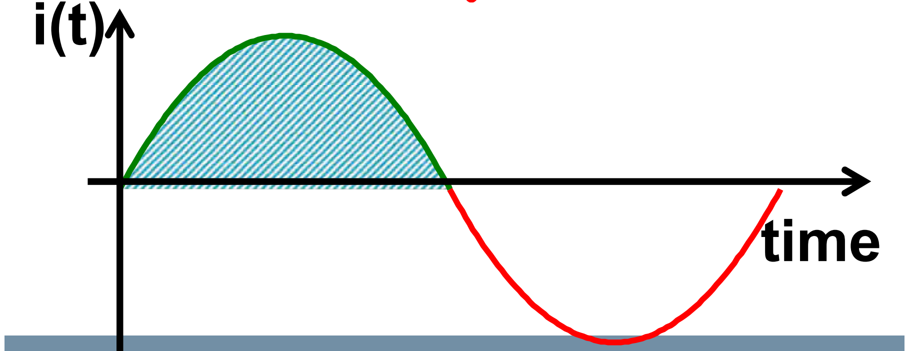
→ higher impedance: Z_W

f↓ → Z_W ↑

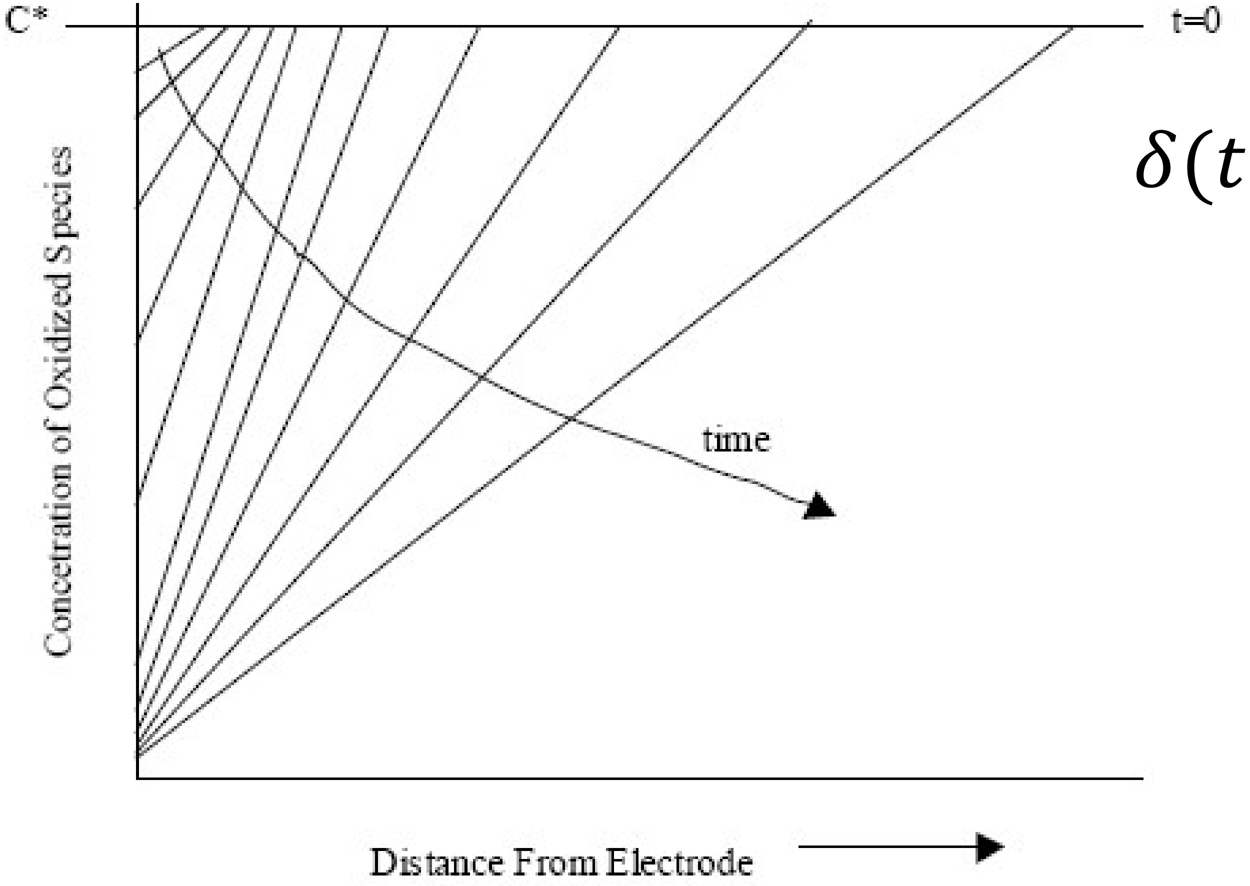


Number of molecules required by the redox





Warburg Impedance



$$\delta(t) \propto \frac{1}{\sqrt{t}} \quad \Rightarrow \quad I \propto \frac{1}{\sqrt{t}}$$

$\delta_{max} \approx 500\mu m$ (convection in an undisturbed solution)

$\Downarrow$

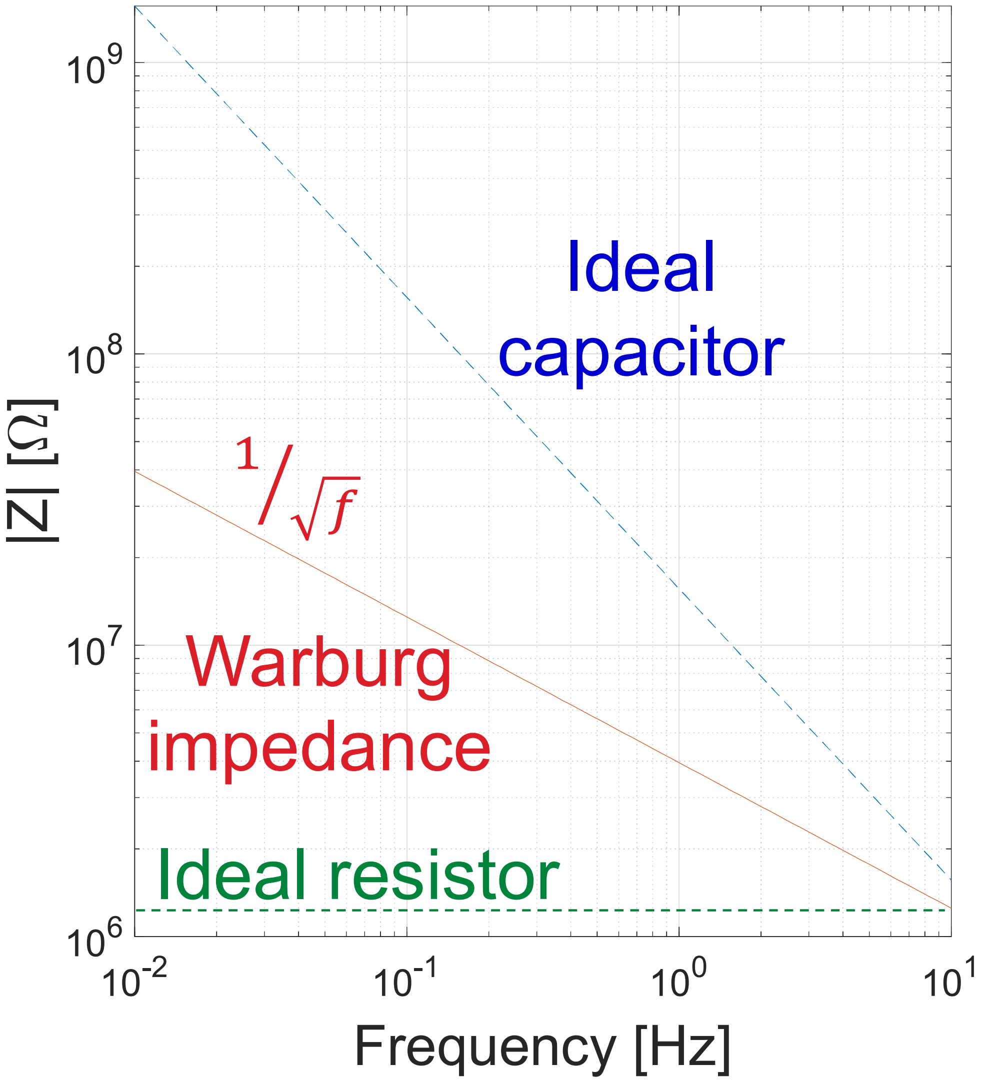
$f_{min} \approx$ 1/30s ≈ 10mHz

$$Z_W = \frac{\sigma}{\sqrt{\omega}} - j\frac{\sigma}{\sqrt{\omega}}$$

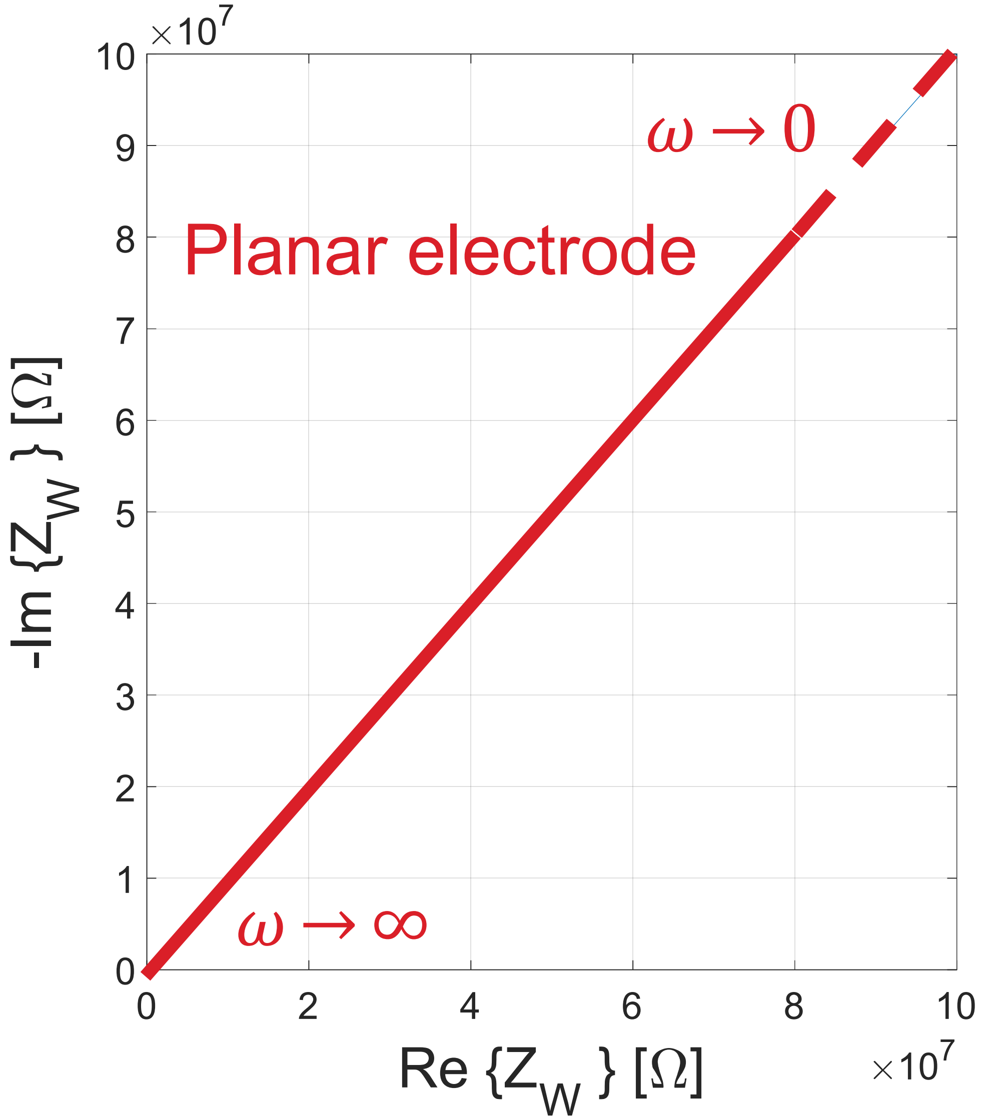
$$\sigma = \frac{RT}{F^2 A\sqrt{2}}\left(\frac{1}{D_O^{1/2} C_O^*} + \frac{1}{D_R^{1/2} C_R^*}\right)$$

Z_{Warburg} – Bode plot and Cole-Cole plot

$$Z_W = \frac{\sigma}{\sqrt{\omega}} - j\frac{\sigma}{\sqrt{\omega}}$$



Cole-Cole plot:



$Z_{Warburg}$ – geometrical effects

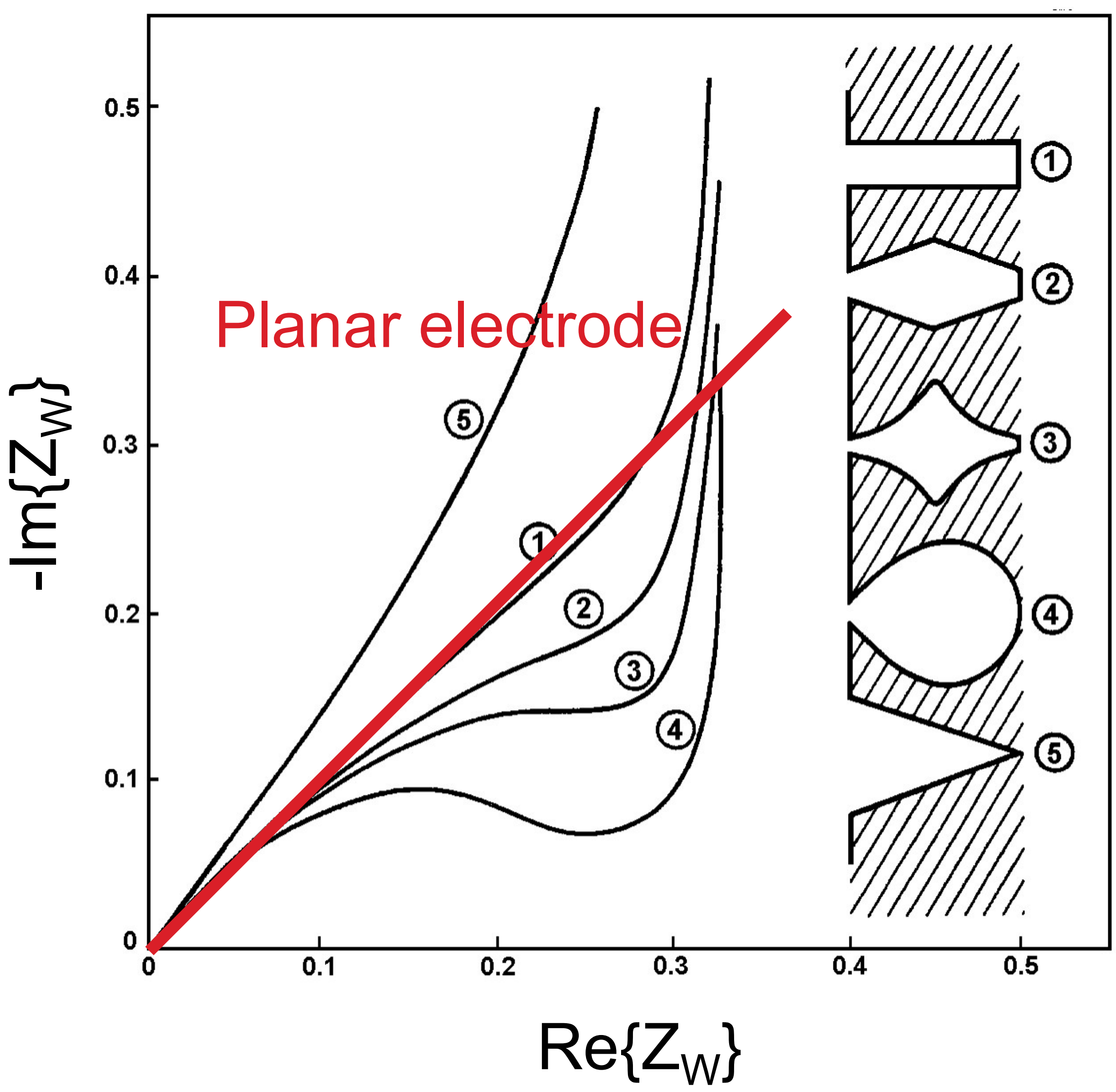
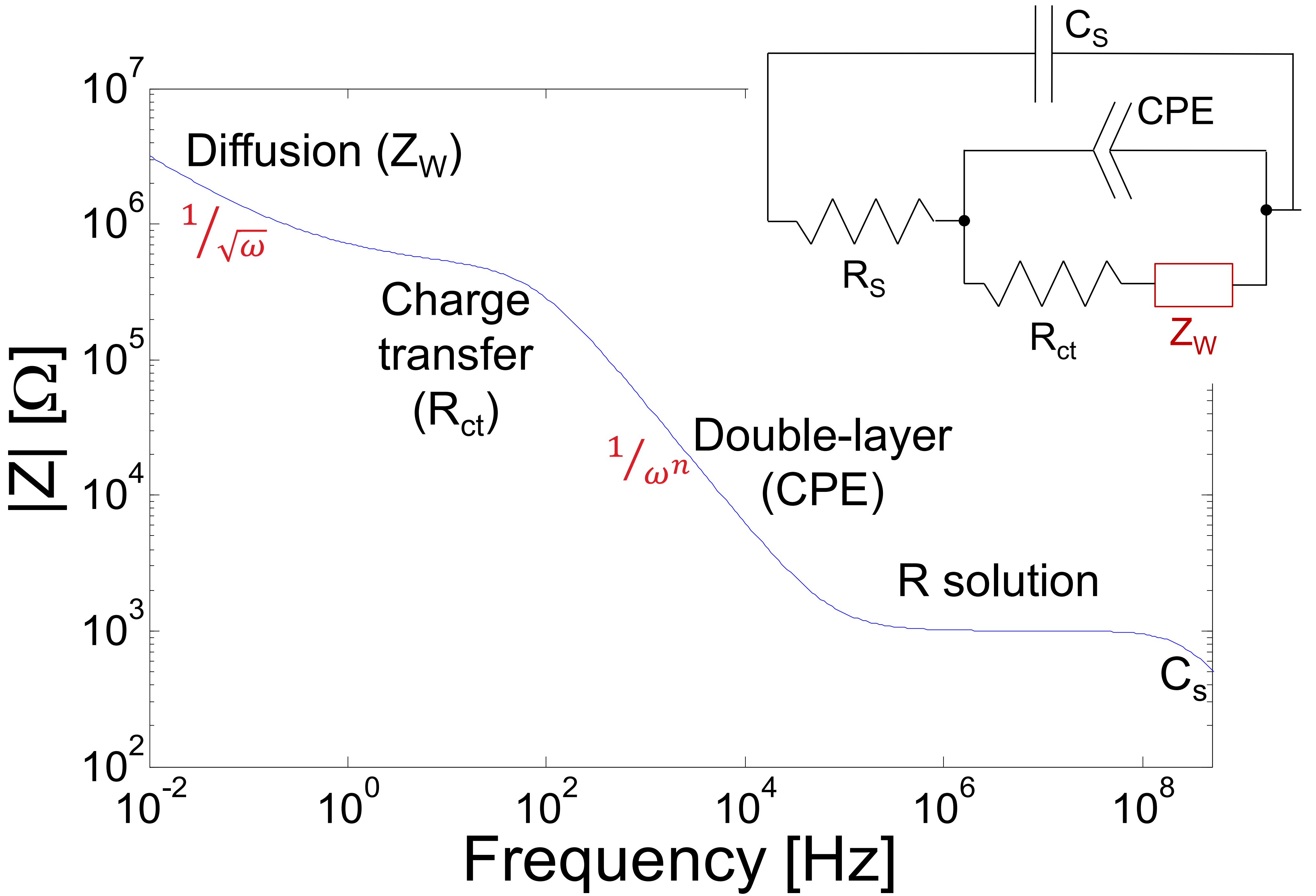


Fig 3.4 Calculated impedance for various shapes of a single pore (from [15])

Kaiser et al., Electrochim. Acta 21, 539 (1976)

The Randles Equivalent



Summary

- Bulk solution conductivity depends on the concentration of ions
    - Physiological solution is a good conductor up to ≈350MHz
- Metal-liquid interface: charge redistribution, double-layer capacitance:
    - Large value (0.1-0.4pF/μm^2 in PBS)
    - High sensitivity to the surface and the first few nm of liquid (in PBS)
- Electron transfer at the interface is possible:
    - Exponential current-voltage characteristic controlled by $V-V^0$ and conc.
    - Easily limited by the mass transfer
    - Equilibrium does not mean external voltage = 0V
- For high ionic concentration (supporting electrolyte; PBS)
    - Mass transfer of redox species is limited by diffusion
- Potential step and potential sweep to study redox processes
    - Non-stationary condition is usual (macroelectrodes)
- Impedance described by the Randles equivalent model