

High Resolution Electronic Measurements in Nano-Bio Science

Mass transport in liquids A closer approach

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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: $\mathbf{O} + \mathbf{ne}^{-} \leftrightarrow \mathbf{R}$ 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)



Standard electrochemical setup

PO



For practical reasons the distance between the electrodes is \approx cm

$$\mu \approx 5 \cdot 10^{-4} \frac{cm^2}{Vs} \qquad D \approx 10^{-5} \frac{cm^2}{s} \qquad \text{Silicon:} \\ \mu \approx 1000 \text{ cm}^2/\text{Vs} \\ \text{D} \approx 20 \text{ cm}^2/\text{S} \end{aligned}$$
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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:

L=1cm:

 $L = 10 \mu m$:

(space $\cong \sqrt{2Dt}$)

- \rightarrow transit time = 7h !!!
 - \rightarrow transit time = 25ms
- [Silicon: ≈ 25ms] [Silicon: ≈ 25ns]

Drift limited:

1V applied \rightarrow electric field \approx 1V/L \rightarrow *velocity* $\cong \mu \ 1V/L$

L= 1cm: \rightarrow transit time = 20 min !!! [Silicon: $\approx 1 \mu s$]L= 10 μ m: \rightarrow transit time = 1ms[Silicon: $\approx 1 ns$]

The importance of the mass transfer



Arrival rate of species R lower than the kinetics at the electrode $\rightarrow C_R$ at the surface will decrease

Current: Mass-Transfer Effects

Pure electron transfer Mass-transport control $C_R(0)$ decreases V_{eq} $C_{\Omega}(0)$ decreases e Mass-transport control **Butler-Volmer:**

 $i = q N_{Av} A k_0 \left[\frac{C_R(0)}{C_R(0)} e^{(1-\alpha)q \left(V - V^{0'} \right)/kT} - \frac{C_O(0)}{C_O(0)} e^{-\alpha q \left(V - V^{0'} \right)/kT} \right]$

Mass transfer mechanism

- Diffusion: concentration gradient
- Migration: electric field + charged particle

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, experim. setup) or for necessity, the mass transfer of the <u>electroactive</u> <u>species</u> is very often controlled by diffusion



Necessity: example 1

Neutral redox species, no drift!

Dominant mass transfer mechanism

Diffusion or drift?

For simplicity (interpretation, experim. setup) or for necessity, the mass transfer of the <u>electroactive</u> <u>species</u> 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, experim. setup) and/or for necessity, the mass transfer of the <u>electroactive</u> <u>species</u> 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:

- 3.10²² water molecules
- ≈ 10²⁰ Na⁺, Cl⁻ ions
- ≈ 10¹⁸ K⁺ ions
- 6.10¹³ H⁺ ions (pH=7)



...and maybe the target is ...

- 1μ M= 6 10^{14} redox species 1nM= 6 10^{11} redox species
- $1pM = 6 \ 10^8$ redox species

10⁸ specific antibodies
10⁶ DNA sequences
<1 Food Poisoning Pathogens
(Salmonella, E. coli,...)

(assuming charge transfer is related to the target concentration)

Example

Electrolyte: KCI , $C_{KCI}=1M$ $\mu_{K+} \approx \mu_{CI-} \approx 7.10^{-4} \text{ cm}^2/\text{Vs}$

Redox species: $K_3[Fe(CN)_6]$, $C_{Fe(CN)}=1mM$ $\mu_{Fe(CN)} \approx 10^{-3} \text{ cm}^2/\text{Vs}$

Electrodes: Ag/AgCl and gold

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

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

Balance sheet - supporting electrolyte v_{ext} Ions in solution: K⁺, Cl⁻, [Fe(CN)₆]³⁻ $C_{Fe(CN)} = 0.001C_{CI}$ $\mu_{K+} \approx \mu_{CI-} \approx 0.7 \ \mu_{Fe(CN)}$ 10·e 0·e Let us assume a current of 10.e/s Ag/AgCl Au electric field E $10 e \leftarrow 4g_{(s)} + CI_{(aq)} \leftarrow 10CI^{-}$ 10 $[Fe(CN)_6]^3$ $[Fe(CN)_6]^3$ $+e \rightarrow [Fe(CN)_6]^4$ $\frac{4.99K^{+}}{4.99Cl^{-}} >$ 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



The drift alone CANNOT sustain the charge transport The electrolyte ions shield the redox species \rightarrow limited effect of E

Balance sheet - supporting electrolyte v_{ext} Ions in solution: K⁺, Cl⁻, [Fe(CN)₆]³⁻ $C_{Fe(CN)} = 0.001C_{CI}$ $\mu_{K+} \approx \mu_{CI-} \approx 0.7 \ \mu_{Fe(CN)}$ 10·e 10·e Let us assume a current of 10.e/s Ag/AgCl Au electric field 10 e ← 10 e 10 [Fe(CN)₆]³⁻ AgCI+e \leftarrow Ag_(s)+Cl⁻_(aq) 10Cl⁻ $[Fe(CN)_{e}]^{3-}+e \rightarrow [Fe(CN)_{e}]^{4-}$ ≈5K+ ≈5Cl⁻ 10 charges per second everywhere C_{CI-}

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Balance sheet - supporting electrolyte V_{ext} Ions in solution: K⁺, Cl⁻, [Fe(CN)₆]³⁻ $C_{Fe(CN)} = 0.001C_{CI}$ $\mu_{K+} \approx \mu_{CI-} \approx 0.7 \ \mu_{Fe(CN)}$ 10·e 10·e Let us assume a current of 10.e/s Ag/AgCl Au electric field 10 e ← - 10 e 10 [Fe(CN)₆]³⁻ 10Cl⁻ AgCI+e \leftarrow Ag_(s)+Cl⁻_(aq) $[Fe(CN)_{e}]^{3-}+e \rightarrow [Fe(CN)_{e}]^{4-}$ ≈5K+ ≈5Cl⁻ **Current limited** ≈5K+ ≈5K+ by diffusion of ≈5Cl ≈5Cl-10[Fe]³⁻ [Fe(CN)₆]³⁻ at this 0[Fe] interface diffusion diffusion







Potential step: concentration profile



Cottrell equation



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Limit current



why?

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

Current – planar electrode



Slow response to a step voltage (better work with a constant voltage) assuming D=2·10⁻⁵ cm²/s, $\delta_0 = 500 \mu m$ $t_L \approx \frac{\delta_0^2}{4D_p} = 31 s$

Double Layer vs. Diffusion



Double layer requires charge, no necessarily redox species!

Double layer charging



Step response of a planar electrode



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Assuming: $\Delta V = 0.5V$ C_R*=100μM D= $2 \cdot 10^{-5}$ cm²/s, $\delta_0 = 500 \mu$ m $\rho_{\text{PBS}} \approx 60 \ \Omega \cdot \text{cm}$ C_{dl} '= 0.1pF/ μ m² r=1mm (disk electrode) $R_{sol} = \rho/4r = 150\Omega$ $C_{dl} = 314 nF$ $\tau = R_{sol} \cdot C_{dl} = 47 \mu s$ $t_L \approx \frac{\delta_0^2}{4D_2} = 31 \, s$ $i(0) \approx \frac{\Delta V}{R_{sol}} = 3mA$ $i_L = nFAD_R \frac{C_R^*}{\delta_1} = 121nA$

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Concentration profile



Bockris, Reddy - Modern Electrochemistry

Peaked Current Profile



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Peaked Current Profile





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Warburg Impedance





Warburg Impedance



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



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Z_{Warburg}- geometrical effects



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

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The Randles Equivalent



Summary

- Bulk solution conductivity depends on the concentration of ions
 - Physiological solution is a good conductor up to \approx 350MHz
- Metal-liquid interface: charge redistribution, double-layer capacitance:
 - Large value (0.1-0.4pF/μm² in PBS)
 - High sensitivity to the surface and to the first few nm of liquid (in PBS)
- Electron transfer at the interface is possible:
 - Exponential current-voltage characteristic controlled by V-V⁰ 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 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