Electrochemistry for materials technology

Chapter 5

Experimental techniques

Measurement techniques

1. Polarisation measurements
2. Double layer capacitance (galvanostatic impulsion)
3. Potentiostatic impulsion (Cottrell diffusion equation)
4. Cyclic voltammetry
5. Rotating Disk Electrodes (RDE) (Levich-(Koutecky) equation)
6. Electrochemical Impedance Spectroscopy (EIS)

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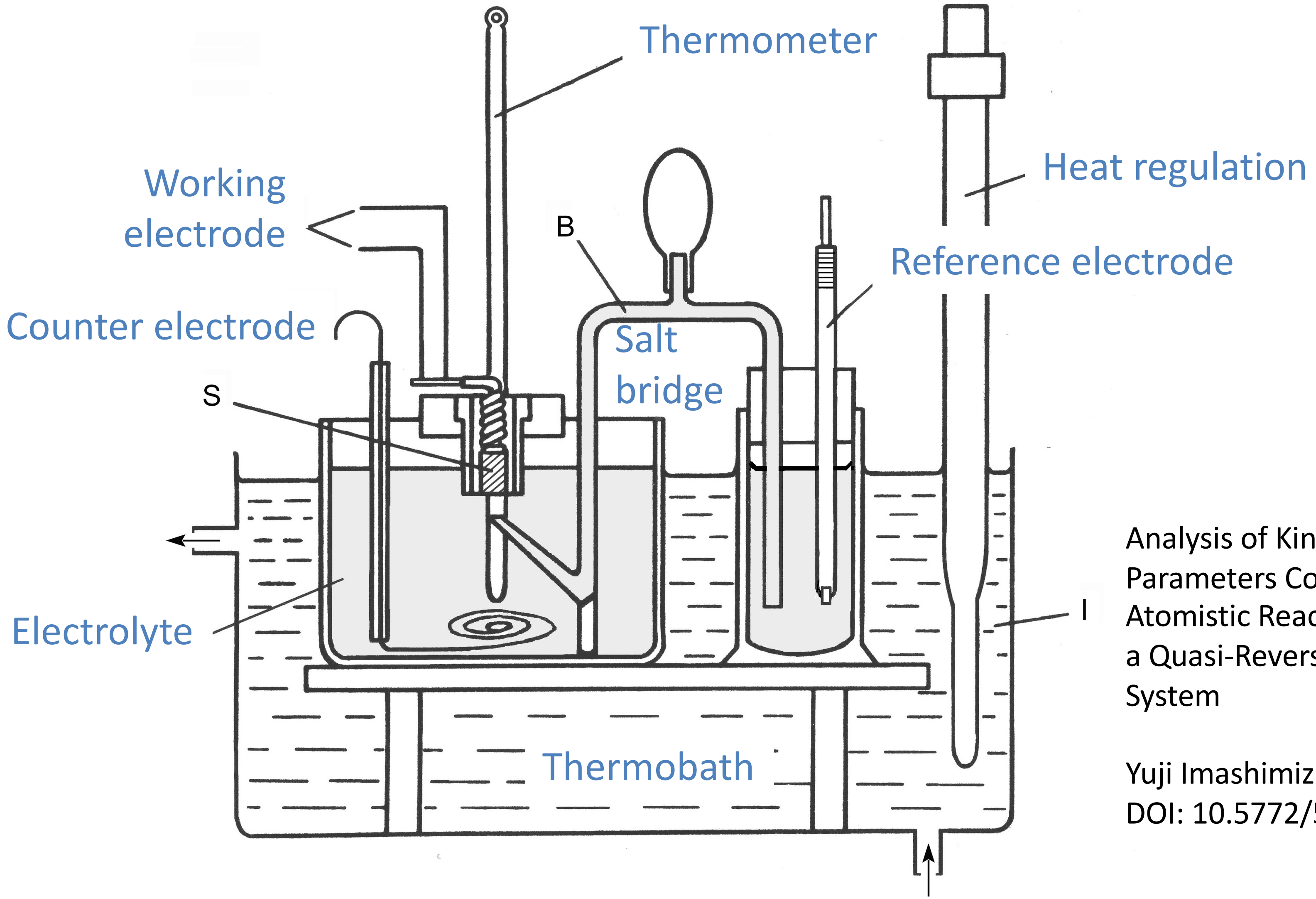
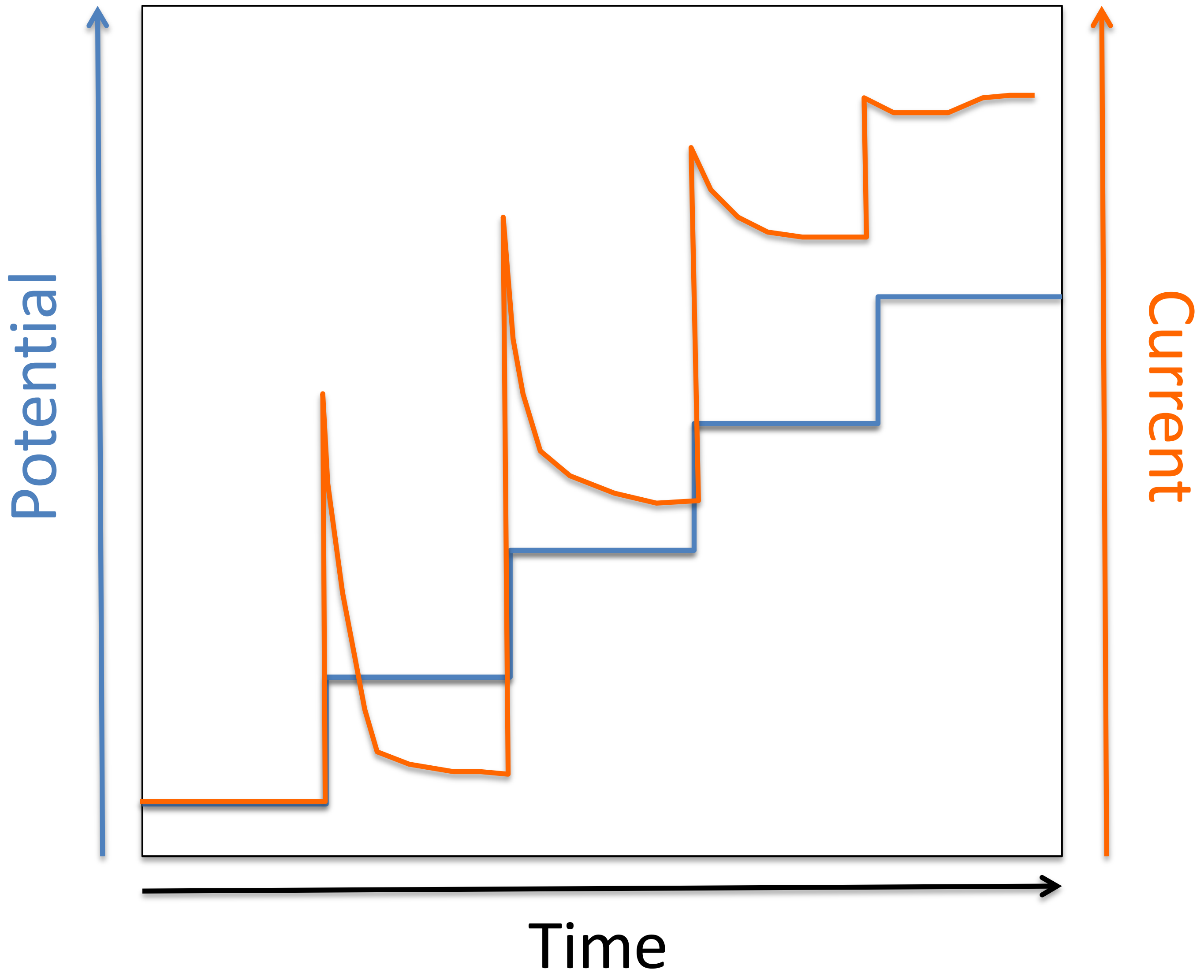
Schematic diagram of an electrolytic cell for polarisation experiments



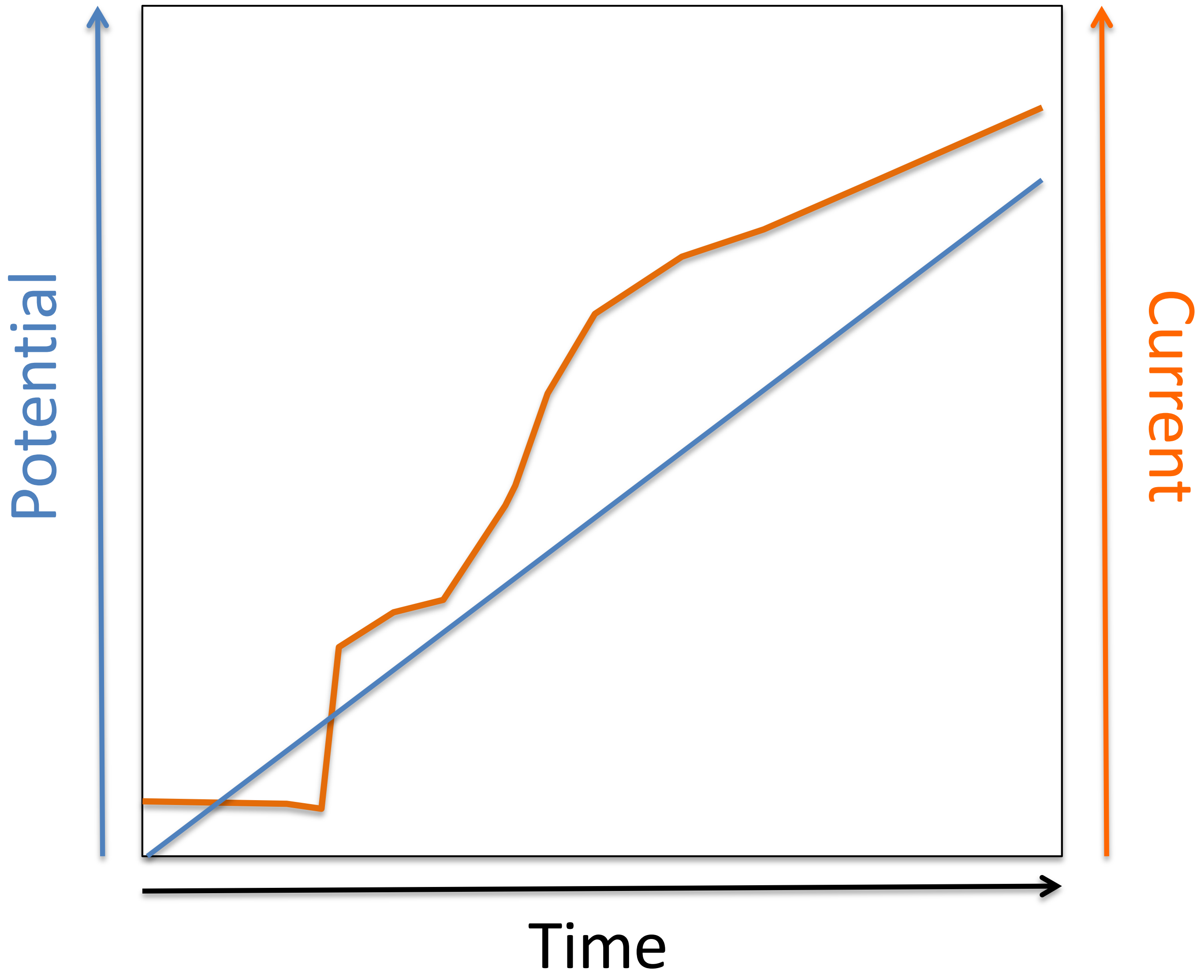
Analysis of Kinetic Parameters Controlling Atomistic Reaction Process of a Quasi-Reversible Electrode System

Yuji Imashimizu
DOI: 10.5772/51896

Principle of potentiostatic polarisation experiments

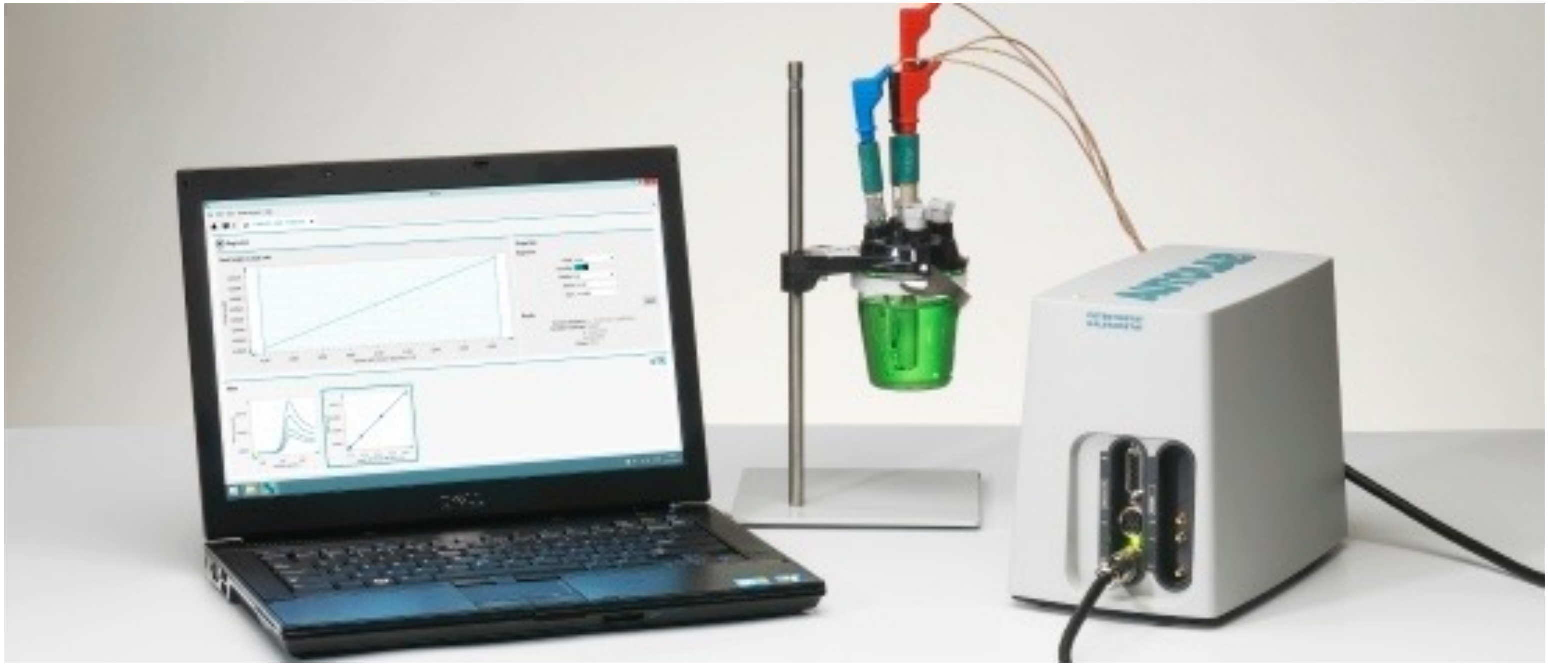


Principle of potentiodynamic polarisation experiments



Equipment

A **potentiostat (galvanostat)** is used for controlled-potential (current) experiments



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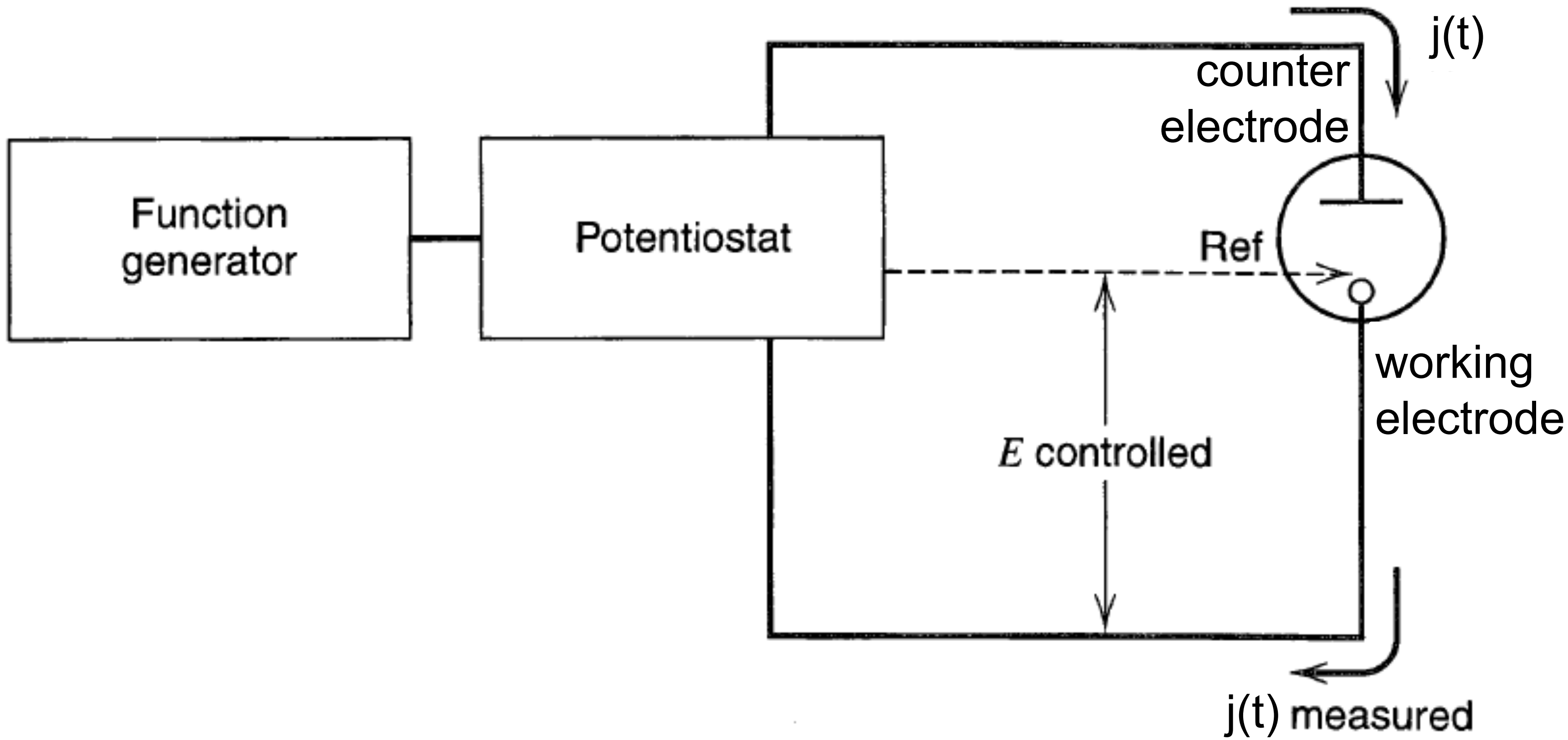
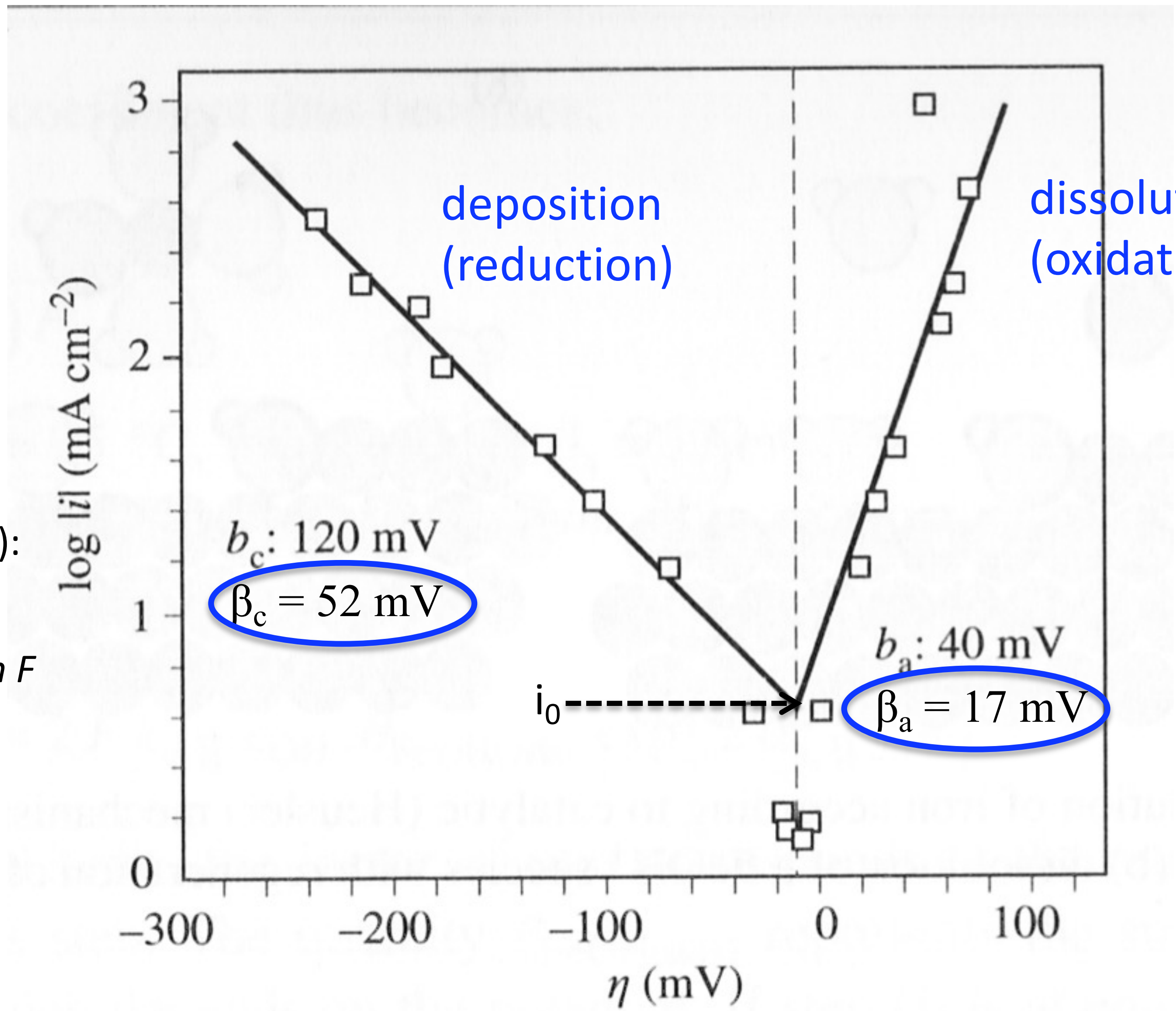


lnj – η polarisation curve of copper
(in 0.5 M H_2SO_4 + 0.075 M $CuSO_4$)

Tafel slope (log):
$b_c = 2.303\ ß_c$

$\beta_c = RT / (1-\alpha)\ n\ F$



Tafel slope (log) :
$b_a = 2.303\ ß_a$

$\beta_a = RT / \alpha\ n\ F$

<u>Rem</u>. : RT/F = 25.7 mV for T=298K

From $\ln j - \eta$ => mechanistic interpretation of copper redox reaction:

Step 1: $Cu = Cu^{+} + e^{-}$

Step 2 (rate limiting): $Cu^{+} = Cu^{2+} + e^{-}$ 1-electron transfer

Overall reaction (1+2): $Cu = Cu^{2+} + 2e^{-}$

Butler-Volmer:

$$i_1 = z\,F\,k_{a,1}\exp(F\,\alpha_{a,1}\,\eta/R\,T) - z\,F\,k_{c,1}\,a_{Cu+}\exp(-F\,\alpha_{c,1}\,\eta/R\,T)$$

$$i_2 = \boxed{z\,F\,k_{a,2}\,a_{Cu+}\exp(F\,\alpha_{a,2}\,\eta/R\,T)} - \boxed{z\,F\,k_{c,2}\,a_{Cu2+}\exp(-F\,\alpha_{c,2}\,\eta/R\,T)}$$

Step 1 is at equilibrium -> $i_1 = 0$ -> $a_{Cu+} = K_1\exp(F\eta/R\,T)$ $K_1 = k_{a,1}/k_{a,2}$

$$\boxed{i_{a,2} = z\,F\,k_{a,2}\,K_1\exp(F\,(1+\alpha_{a,2})\,\eta/R\,T)}$$

$$\boxed{i_{c,2} = z\,F\,k_{c,2}\,a_{Cu2+}\exp(-F\,\alpha_{c,2}\,\eta/R\,T)}$$

Tafel slope ($\ln$) :

$\beta_a = d\eta / d\ln i_{a,2} = RT/((1+\alpha_{a,2})F)$ = 17 mV for α=0.5

$\beta_c = d\eta / d\ln i_{c,2} = RT/(-\alpha_{c,2}F)$ = 52 mV for α=0.5

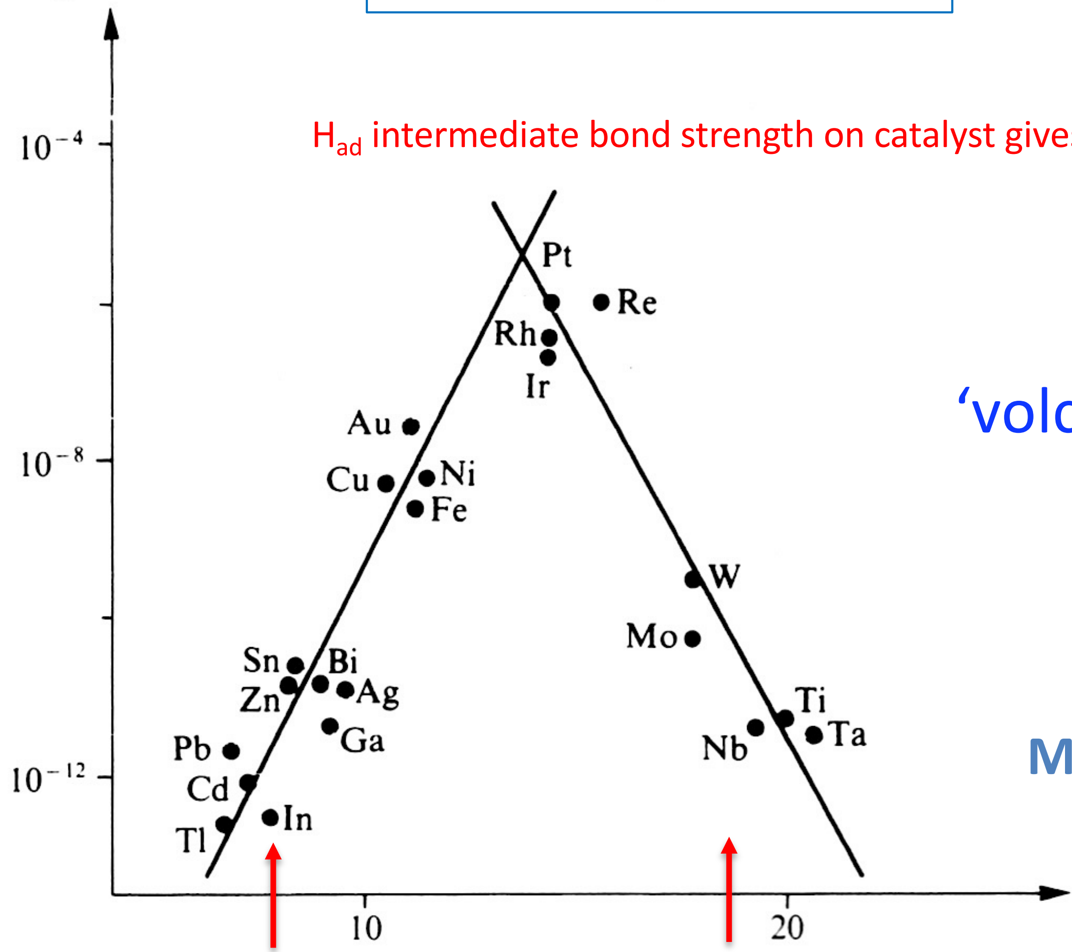
Rem. : RT/F = 25.7 mV for T=298K

Exchange current i_0 of hydrogen half-cell on different metals M

i_0 A/cm²

$$2\,H^+ + 2\,e^- = H_2$$

H_{ad} intermediate bond strength on catalyst gives highest j^0



'volcano'-curve

M-H bond energy kJ/mol

H_{ad} too weakly bound on catalyst

H_{ad} too strongly bound on catalyst

Reaction mechanisms for H^+ reduction to H_2 (acidic)

Volmer-Heyrovsky mechanism (for low coverage H_{ads}):

Step 1 (Volmer):	$H^+ + e^- \rightarrow H_{ads}$	sorption
Step 2 (Heyrovsky):	$H^+ + H_{ads} + e^- \rightarrow H_2$	charge transfer
1 + 2:	$2\,H^+ + 2\,e^- \rightarrow H_2$	**(β_c = 52 mV)**

Volmer-Tafel mechanism (at high coverage H_{ads}):

Step 1 (Volmer):	$H^+ + e^- \rightarrow H_{ads}$	sorption
Step 2 (Tafel):	$H_{ads} + H_{ads} \rightarrow H_2$	chem.reaction
1 + 2:	$2\,H^+ + 2\,e^- \rightarrow H_2$	**(β_c = 13 mV)**

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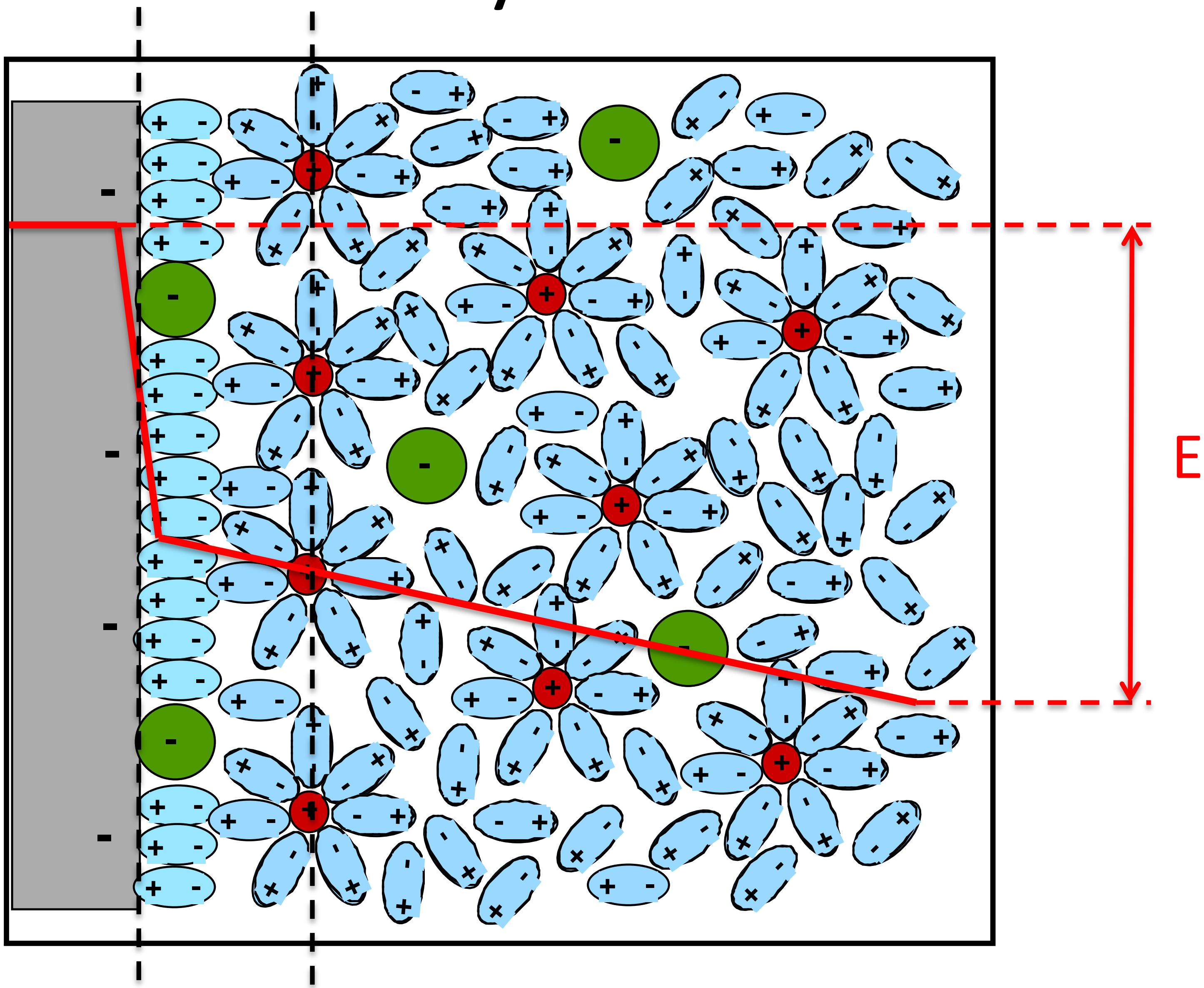
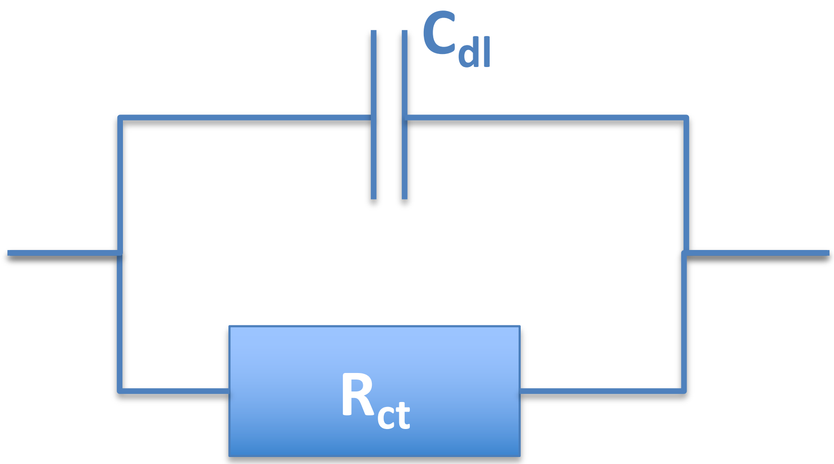
Electrical double layer at metal-electrolyte interface

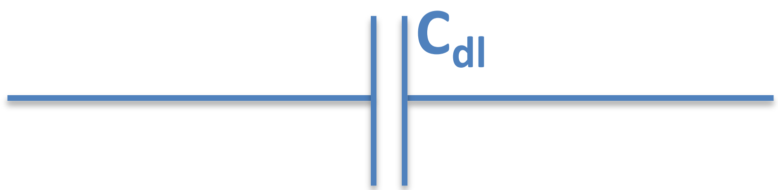


Equivalent circuit of metal-electrolyte interface

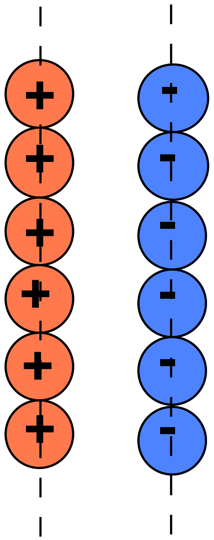
Electrode with double layer capacitance C_{dl} and charge transfer resistance R_{ct}



Ideally polarizable electrode, i.e. with infinite charge transfer resistance R_{ct}



Helmholtz model of (rigid) electrical double layer



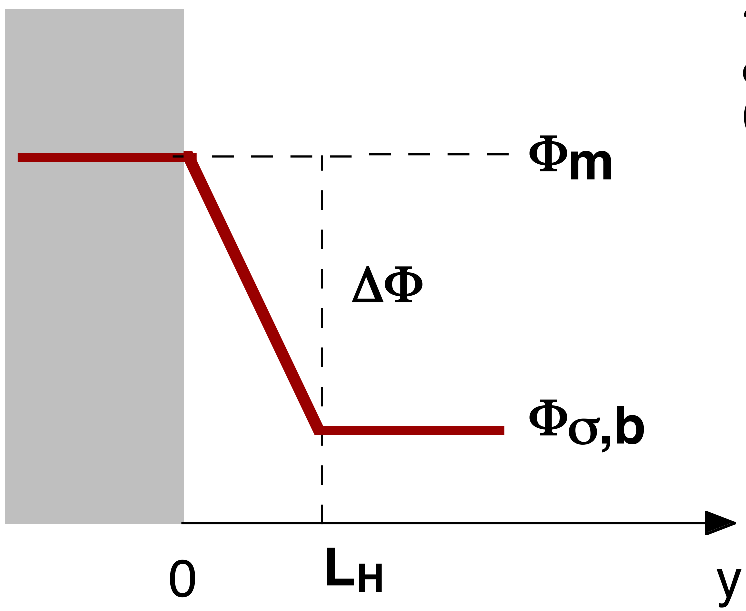
$$C_H = \frac{\varepsilon\,\varepsilon_0}{L_H}$$

C_H: double layer capacitance (F/m^2)

ε : dielectric constant of the solvent

ε_0 : permittivity in vacuum (F/m)

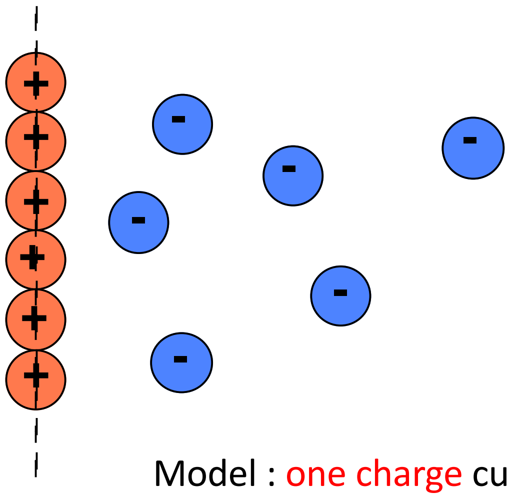
L_H : thickness of the double layer (m)



'Permittivity' (ε_0 = 8.85 10^{-12} F/m):
charge density needed to exert a force of 1 N on a charge of 1 C
(=ease with which the medium carries electrical force)

For L_H = 0.5 nm and ε_{H2O} = 78,
C_H corresponds to 70 $\mu F/cm^2$

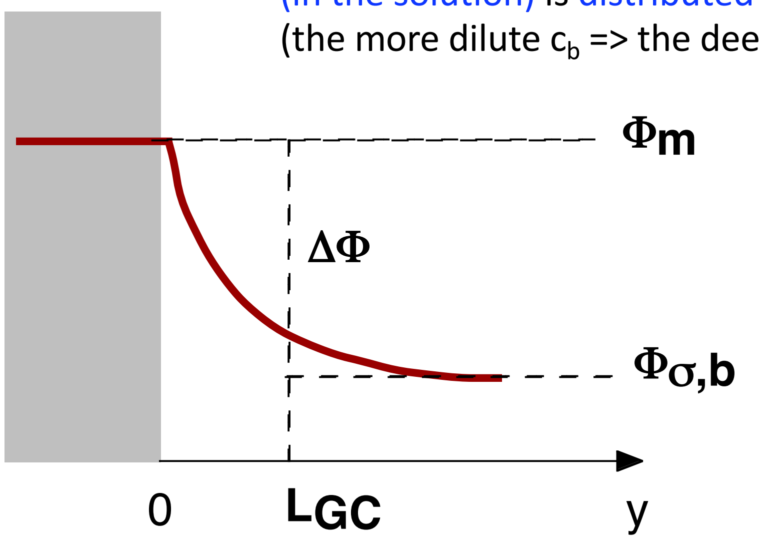
Gouy-Chapman model of (diffuse) electrical double layer (binary electrolyte, e.g. NaCl)



$$C_{GC} = \frac{\varepsilon\, \varepsilon_0}{L_{GC}} \cosh\left(\frac{zF\Delta\Phi}{2RT}\right)$$

$$L_{GC} = \left(\frac{\varepsilon\, \varepsilon_0^2\, R\, T}{2\, z^2\, F^2\, c_b}\right)^{0.5}$$

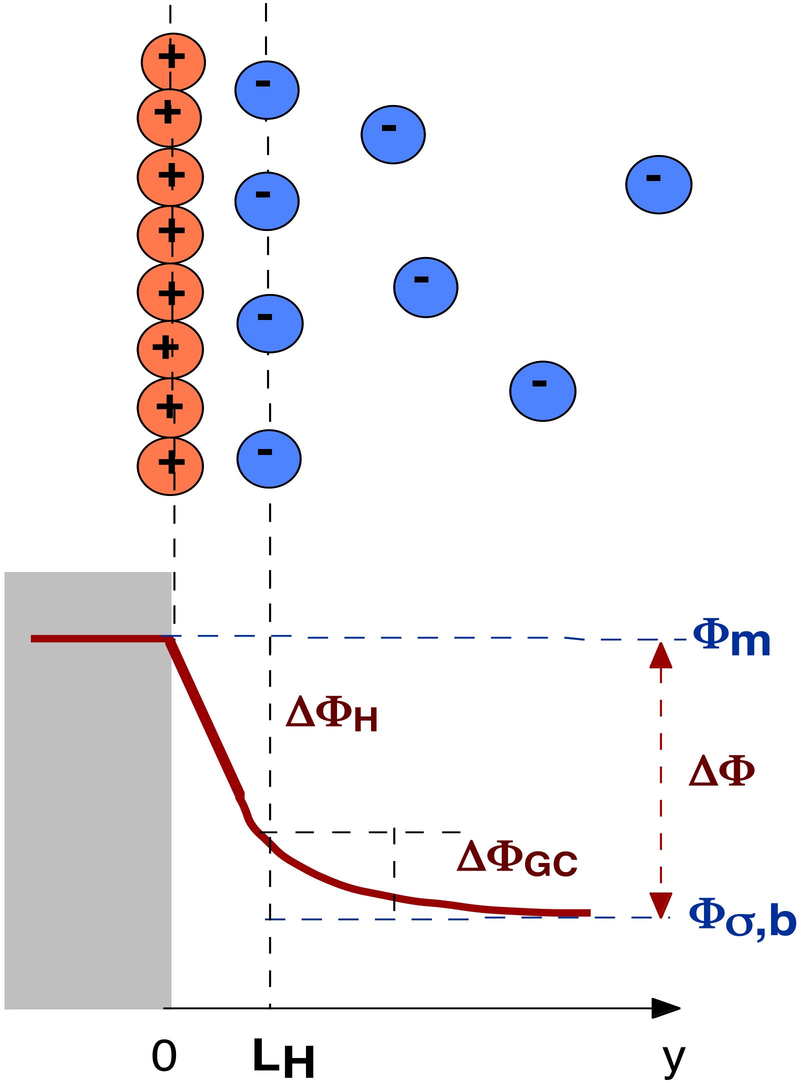
Model : one charge cumulates to the metal electrode surface; the other charge (in the solution) is distributed according to the concentration c_b of charge carriers (the more dilute c_b => the deeper the charge distribution into the solution)



c_b : salt concentration

z : ion's charge

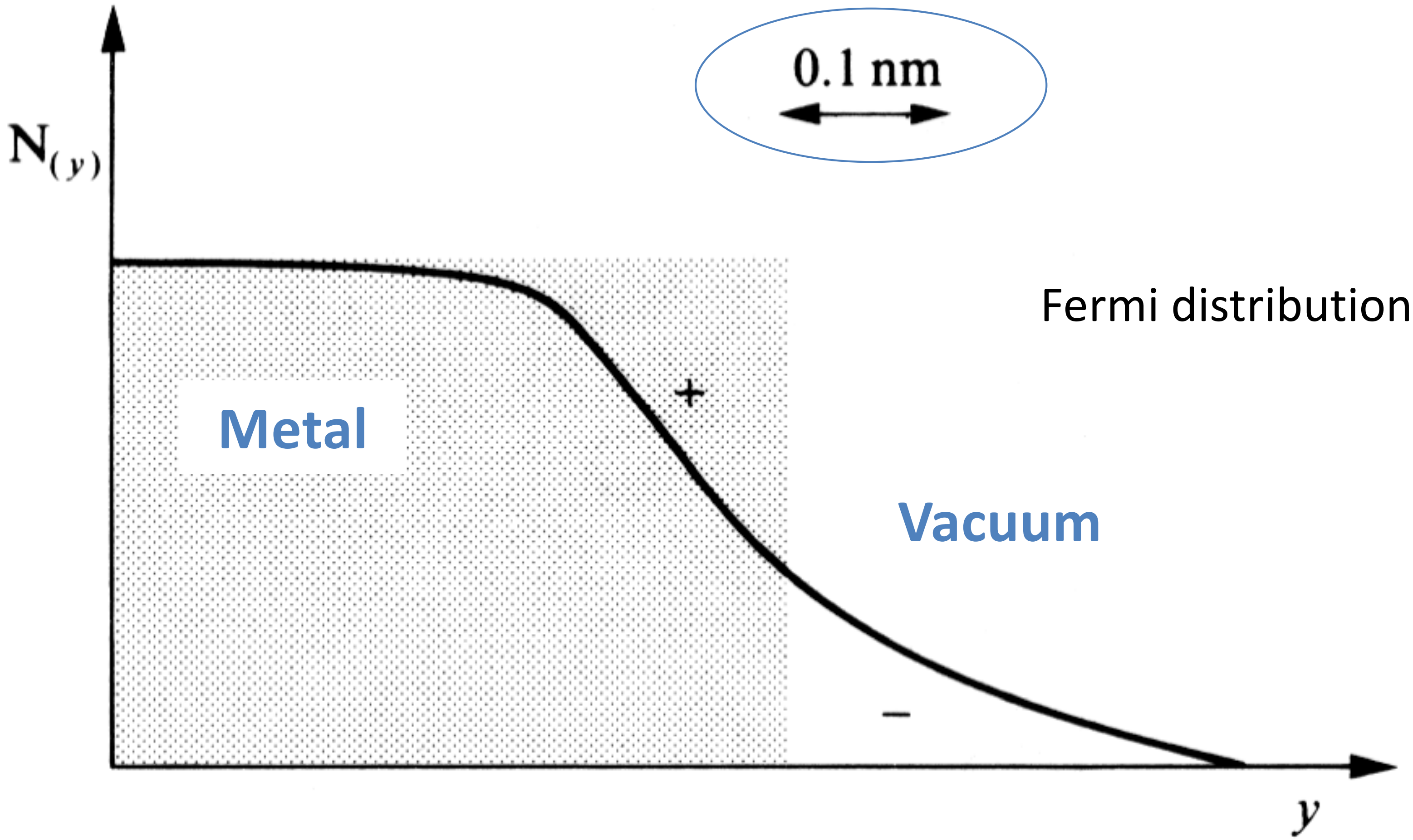
Stern model of electrical double layer



$$C^{-1} = C_H^{-1} + C_{GC}^{-1}$$

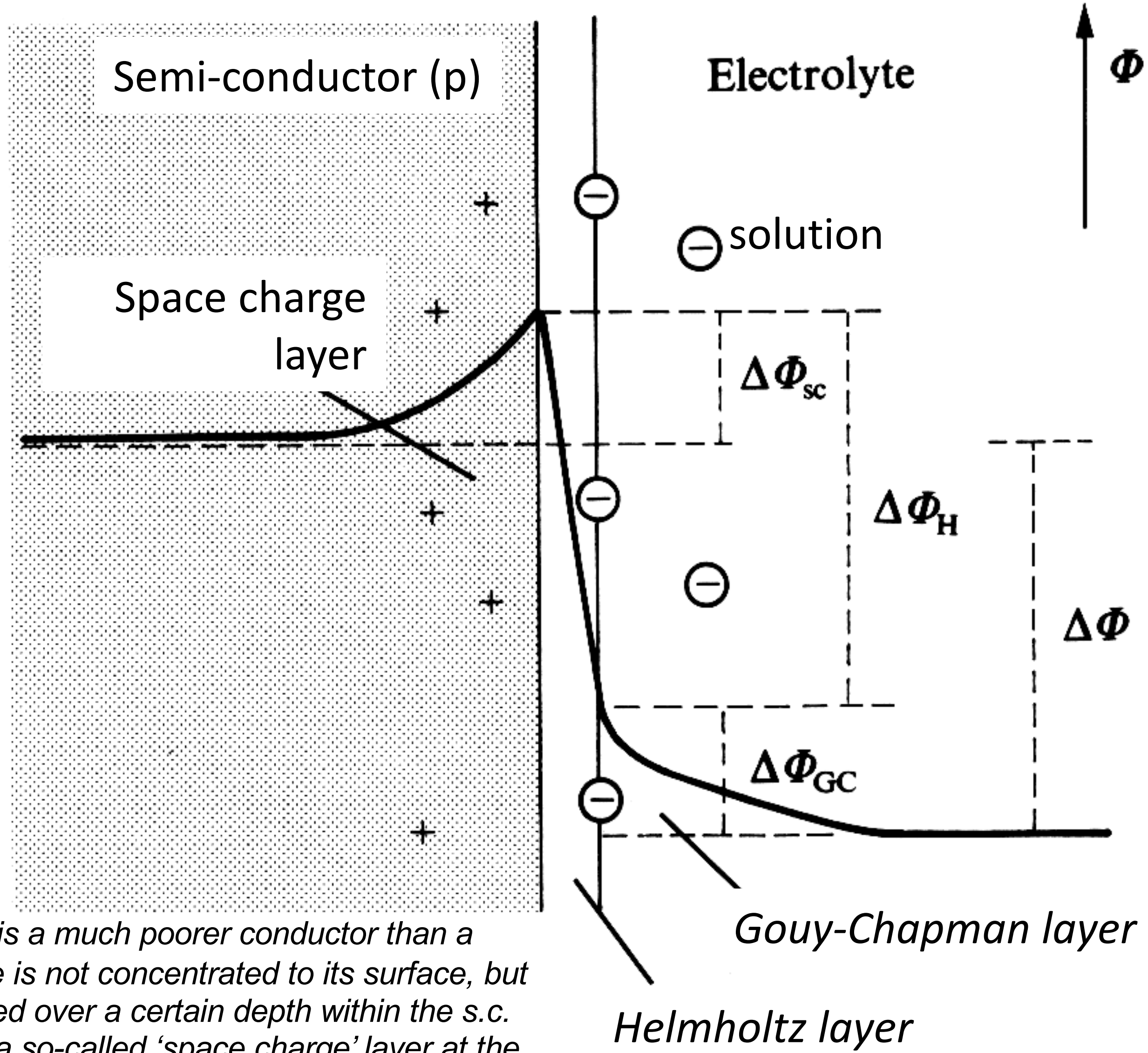
series connection of **Helmholtz** and **Gouy-Chapman** capacitances

Electron density variation with distance at metal-vacuum interface



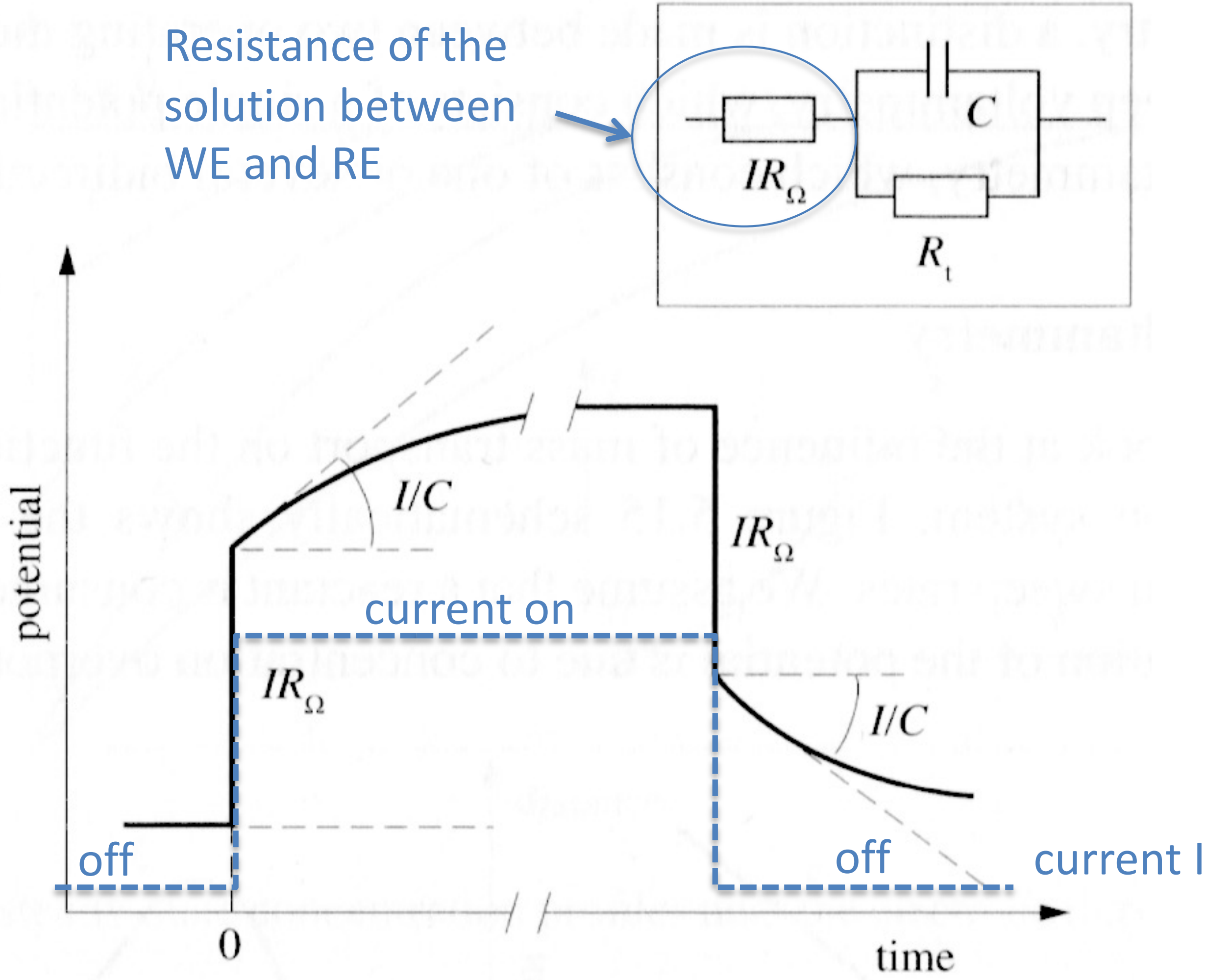
Fermi distribution

Double layer at semiconductor (s.c.)-electrolyte interface



(Since a s.c. is a much poorer conductor than a metal, charge is not concentrated to its surface, but also distributed over a certain depth within the s.c. This creates a so-called 'space charge' layer at the interface which creates an extra potential barrier.)

Measurement of double layer capacitance C_{dl} by galvanostatic transient method (switching current i on/off)



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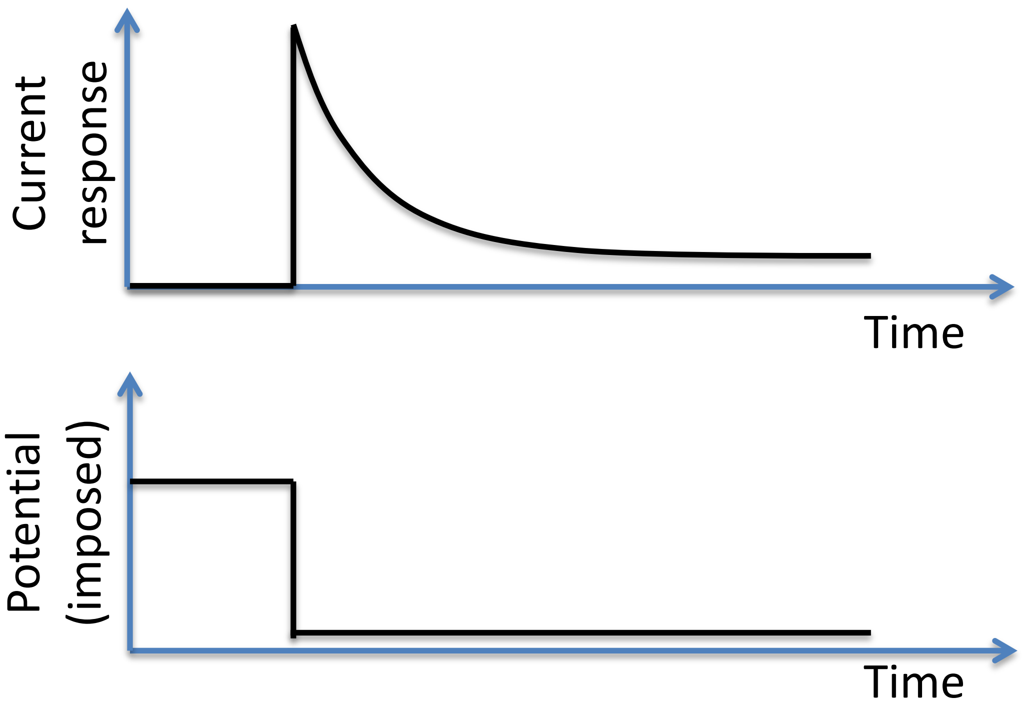
Potential step method (diffusion control)

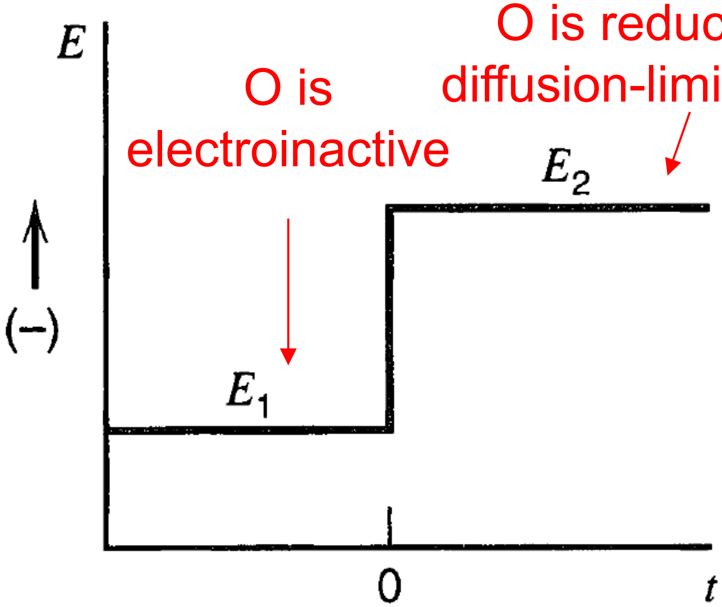
Cottrell's equation describes the evolution of current with time during a potential step in case of a **mass transport (diffusion only) limited** electrode reaction (e.g. metal deposition O + ze- → R)



Potential step method (diffusion control)

$O + ze^- \rightarrow R$

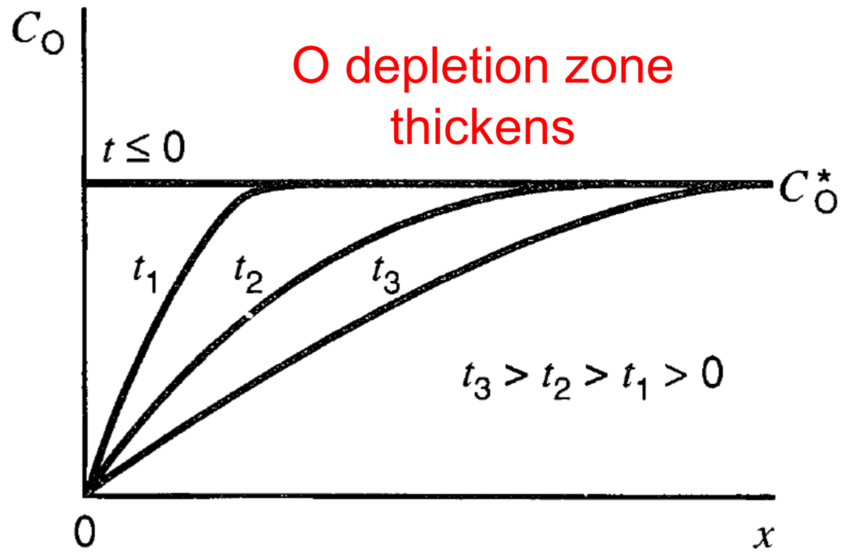
Potential change



O is electroinactive

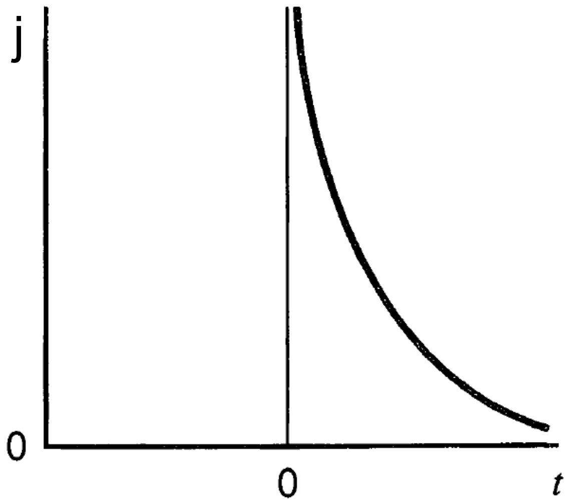
O is reduced at diffusion-limited rate

Corresponding concentration profile



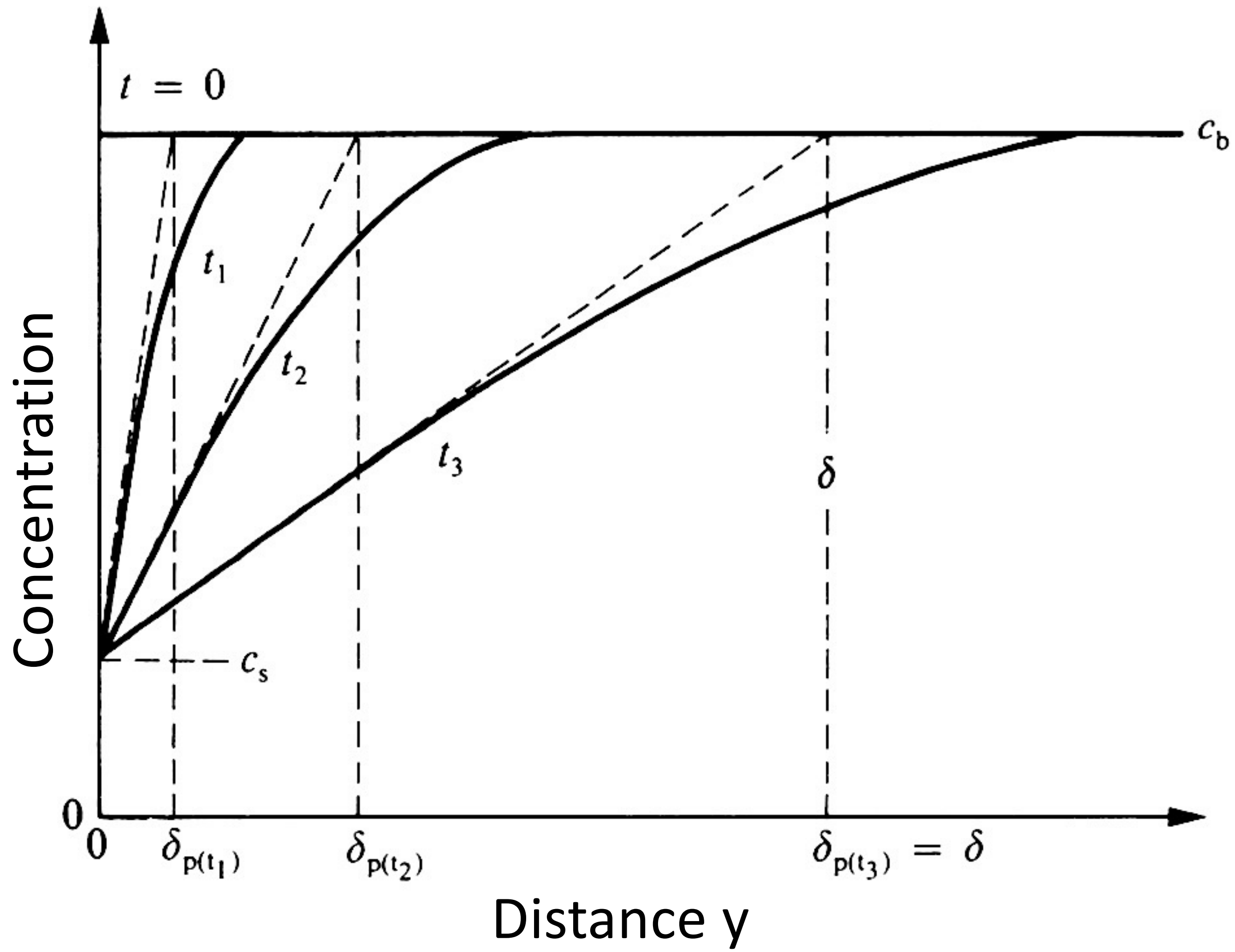
O depletion zone thickens

Current flow vs. time



Current is proportional to the concentration gradient at the surface ("chronoamperometry")

Concentration profiles near the electrode after potential step



δ: thickness of the steady state diffusion layer

δ_p : thickness of the non steady state diffusion layer

c_b, c_s: concentration of reacting species at the surface (s) and in the bulk (b).

Current density for non-steady state concentration profiles

Case of the cathodic reduction of a species at the electrode:

$$i_c = -\,n\,F \left.\frac{d\,c}{d\,x}\right|_{x=0}$$

mass transport controlled kinetics, Fick's 1st Law
(current is proportional to the **concentration gradient**)

$$\left.\frac{d\,c}{d\,t}\right|_{x} = D\,\frac{d^2c}{d\,x^2}$$

concentration evolution with time, Fick's 2nd Law
(conc. change with t, at position x, changes with the **current gradient** at that position)

Solving the above equation system yields the **Cottrell equation**:
$\mathbf{i_c = -\,z\,F\,(c_b - c_s)\,(D/(\pi\,t))^{0.5}}$

in practice : plot i vs $1/\sqrt{t}$;
when the result is linear, the reaction is diffusion-controlled,
and from the slope a diffusion coefficient D can be extracted

Cottrell equation and transition time from non-steady state to steady state diffusion layer

Cottrell equation:

$\mathbf{i_c = - z\ F\ (c_b - c_s)\ (D/(\pi\ t))^{0.5}}$ (current proportional to √D)

Introducing the non-steady state diffusion layer δ_p

$\delta_{p\ (t)} = (D\ \pi\ t)^{0.5}$

$\mathbf{i_c = - z\ F\ (c_b - c_s)\ D\ /\ \delta_{p(t)}}$

Steady state when $\delta_{p(t)} = \delta$

Transition time t_{tr} from non-steady state to steady state

$\mathbf{t_{tr} = \delta^2\ /\ D\ \pi}$

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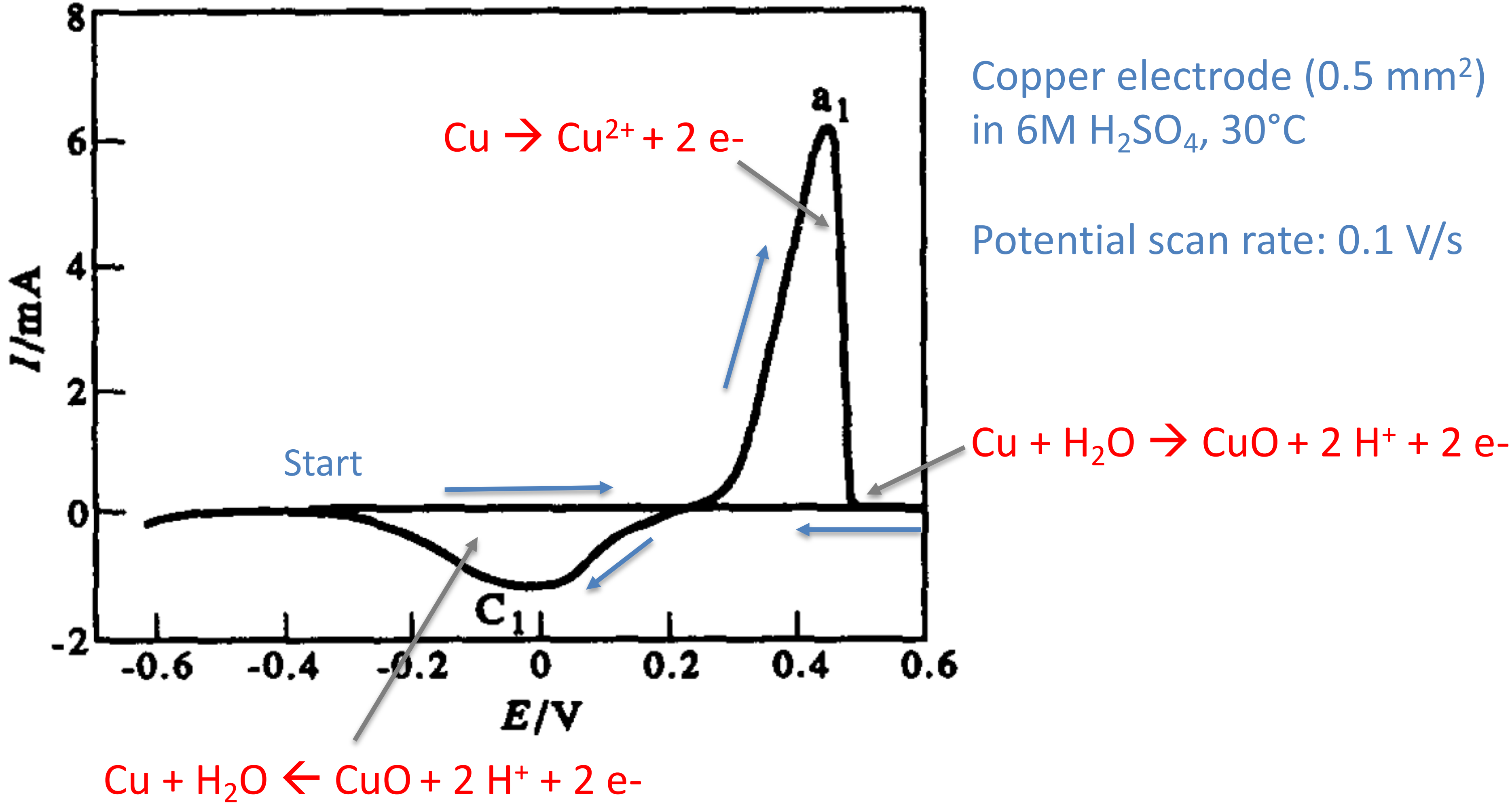
Cyclic voltammetry (CV) example
(back-and-forth potential scan at different rates)



Copper electrode (0.5 mm^2)
in 6M H_2SO_4, 30°C

Potential scan rate: 0.1 V/s

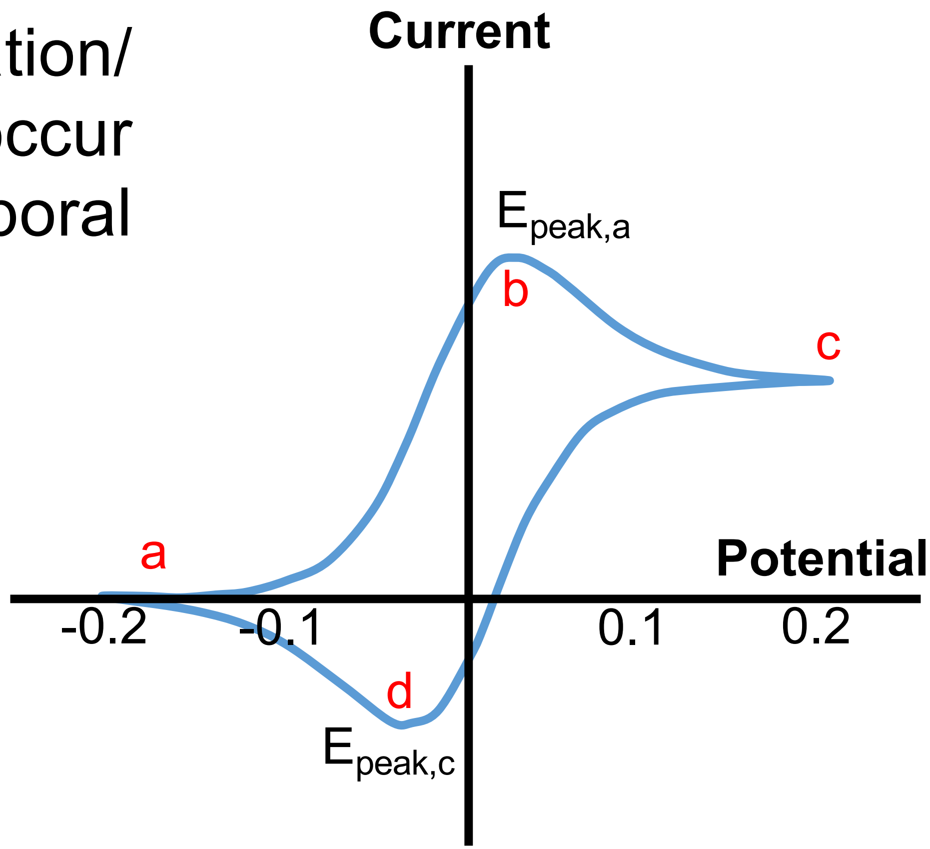
Electrochemical behaviour of copper electrode in concentrated sulfuric acid solutions
A.H. Moreira, A.V. Benedetti, P.L. Cabot, P.T.A. Sumodjo

CV curve

100% immediate species oxidation/ reduction does not occur experimentally – there is a temporal dependence (hysteresis).

The formal reduction potential, E°, of a species, is defined as

$$E° = (E_{p,a} + E_{p,c})/2$$



a : onset potential
b, d : peak potential E_p
c : switching potential

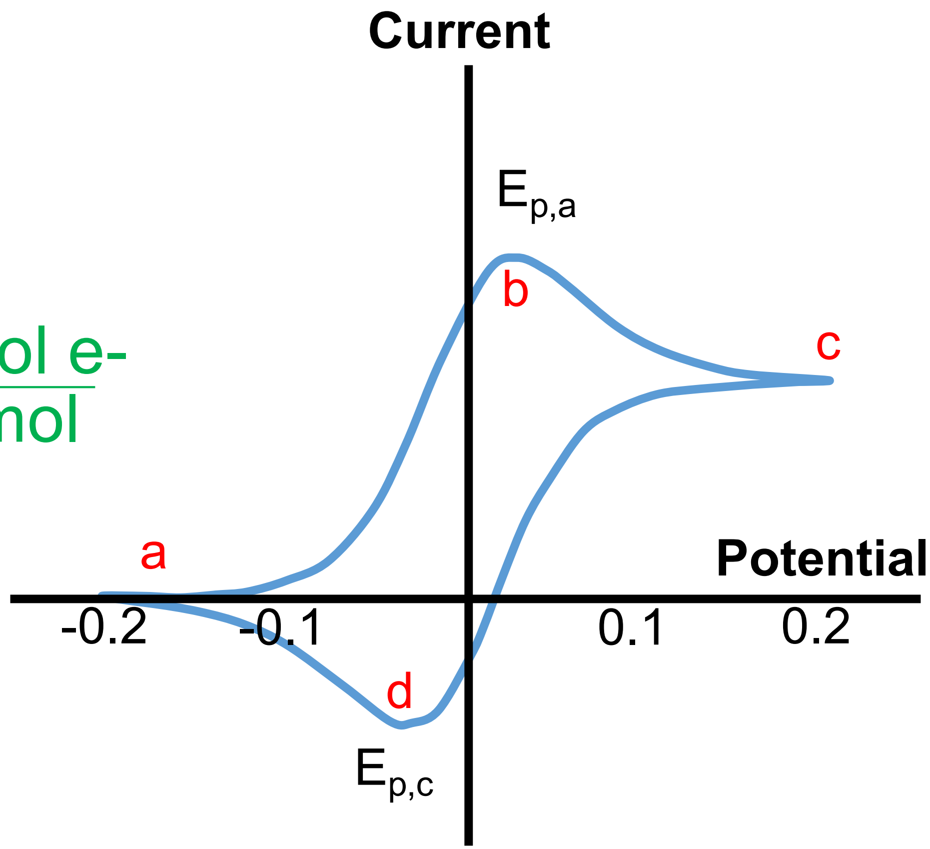
CV curve

For a reversible reaction, the separation between the two peaks is defined as

$$|E_{p,a} - E_{p,c}| = \Delta E_p = \frac{0.059\ V}{z}$$

$z \rightarrow \frac{\text{mol e-}}{\text{mol}}$

- ΔE_p is independent of the scan rate for a fast electron transfer reaction.
- Increasing values of ΔE_p as a function of increasing scan rate indicates the presence of electrochemical irreversibility.



a : onset potential
b,d : peak potential
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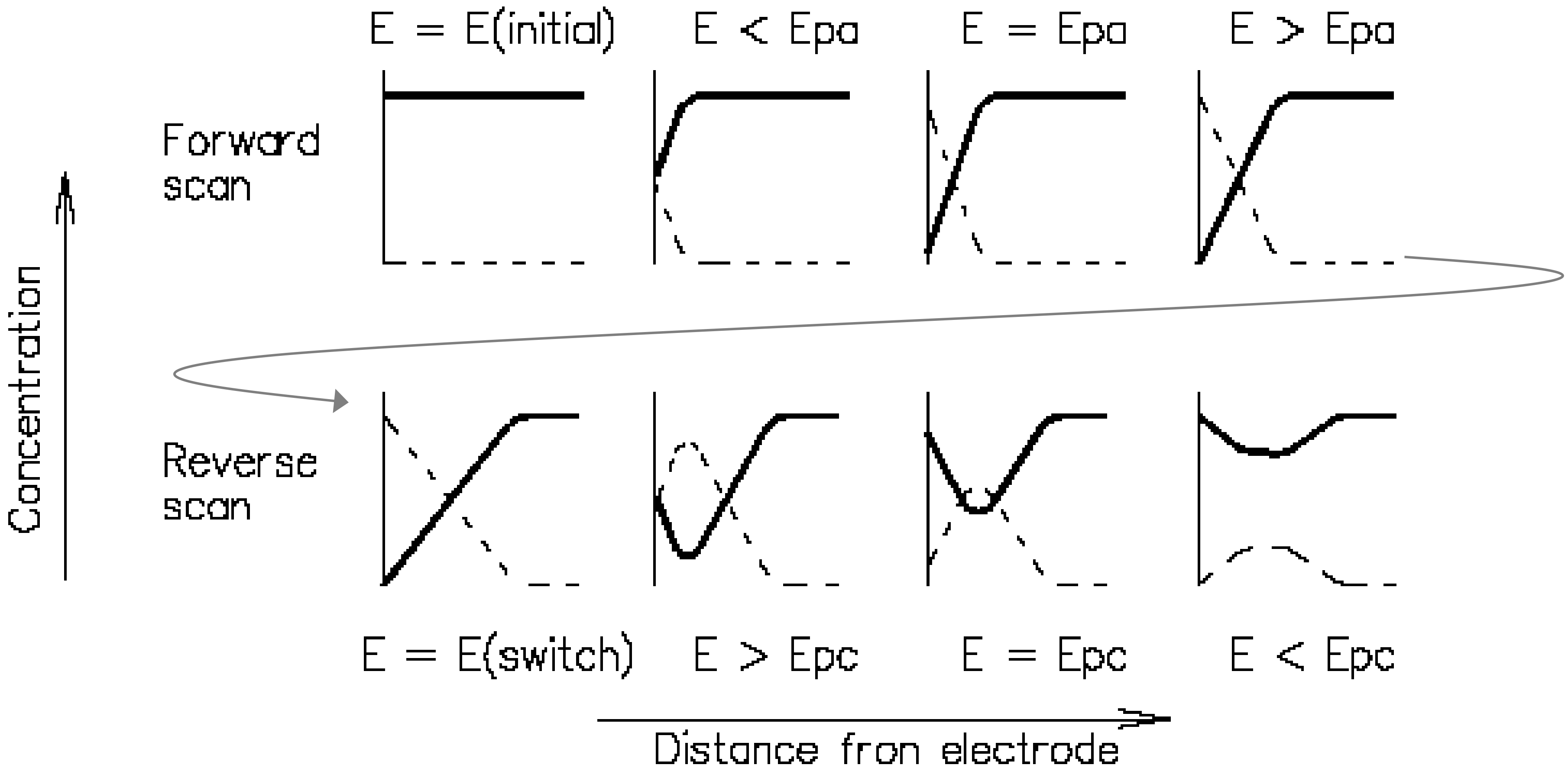
CV curve

Recall: CV peak currents arise from diffusion control



Solid lines correspond to reducing species
Dotted lines correspond to oxidizing species

CV curve

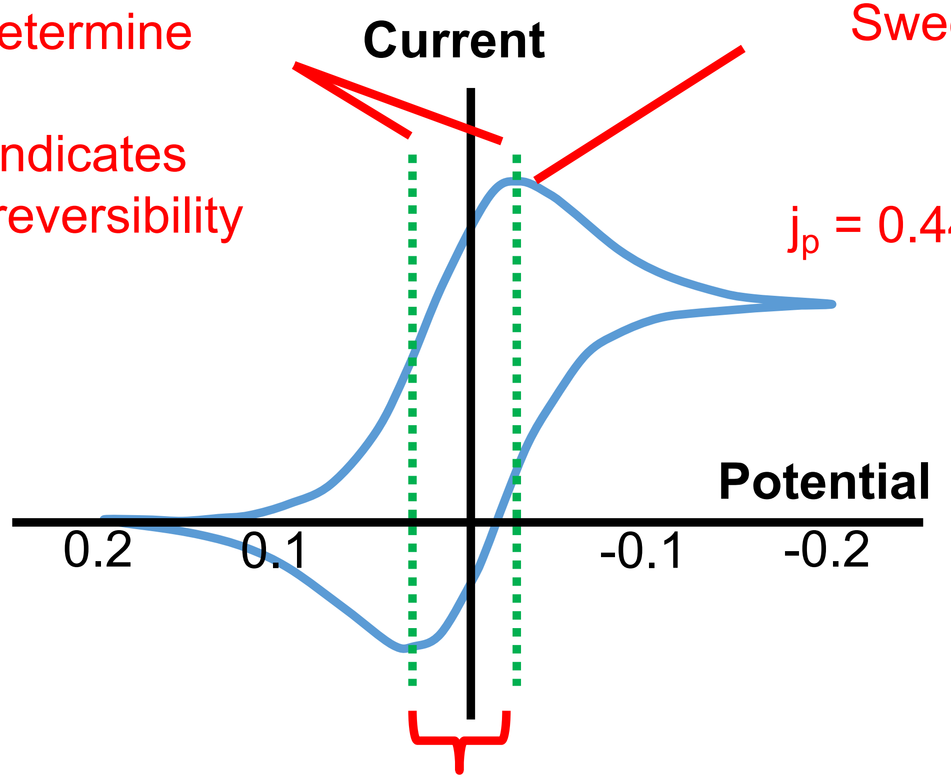
For stationary electrodes, a relation exists between the peak current density j_p and the potential scan rate [V s^{-1}] (Randles-Sevcik equation):

$$j_p = 0.4463\ zF[C^*]\left[\frac{zF\underline{v}\ D}{RT}\right]^{1/2}$$

j_p = peak current density
z = mol e-/mol reactant
[C*] = bulk density of reactant
D = diffusion coefficient
$\underline{v}$ = scan rate [V s^{-1}]

What information can we get from a CV curve?

- Peak locations determine redox potential
- Peak symmetry indicates electrochemical reversibility



Sweep rate ($\underline{v}$) can give diffusivity (D)

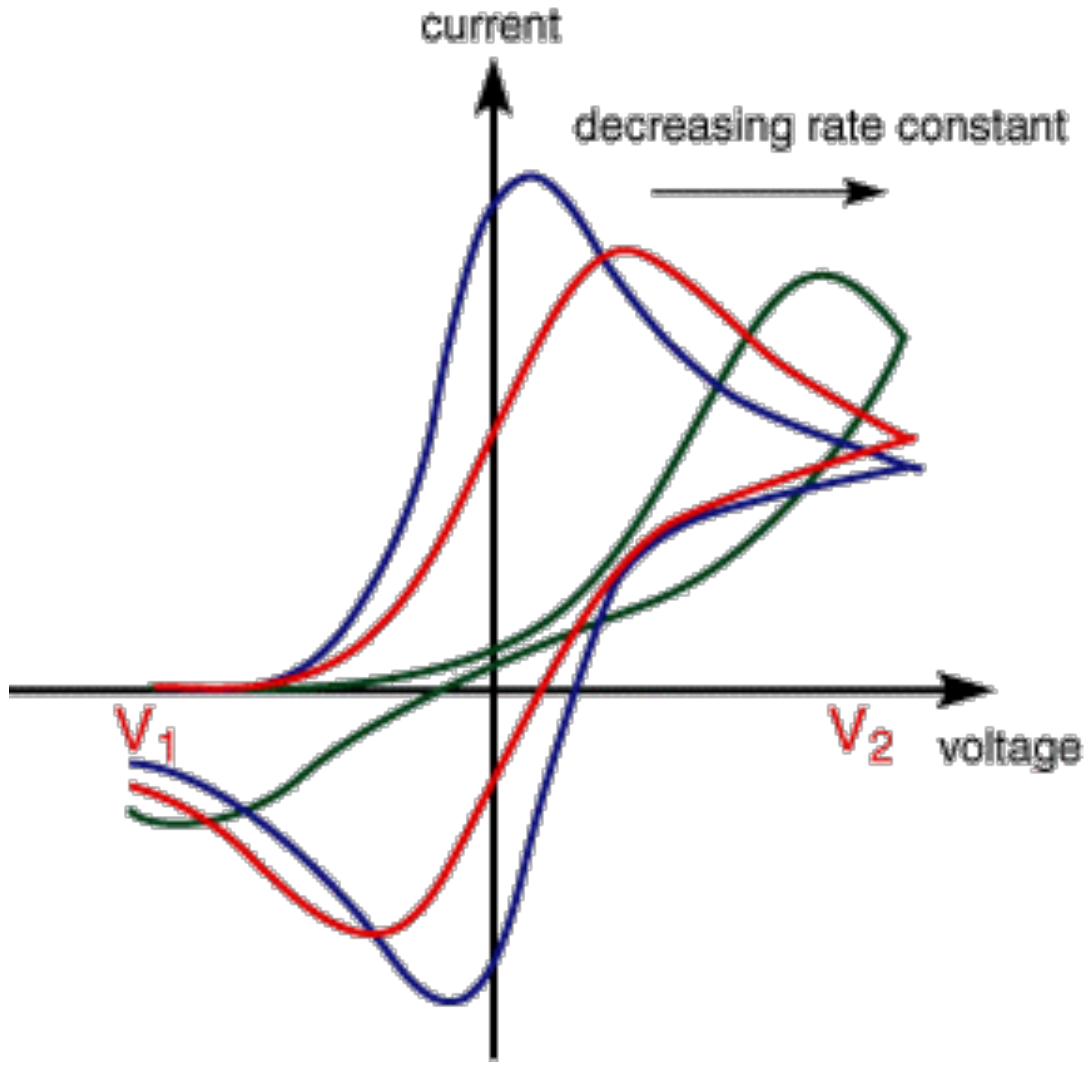
$$j_p = 0.4463\, zF[C^*]\left[\frac{zF\underline{v}\,D}{RT}\right]^{1/2}$$

- <u>Difference between 2 peaks results from diffusion effects</u>
- Distance over multiple scans used to determine reversibility
- Distance between peaks used to determine charge z (mol e-/mol)

$$|E_{p,a} - E_{p,c}| = \Delta E_p = \frac{0.059\ V}{z}$$

What information can we get from a CV curve?

When the reaction rate is slow, equilibrium concentrations (Nernst equation) at the electrode surface are not so quickly established compared to the scan rate



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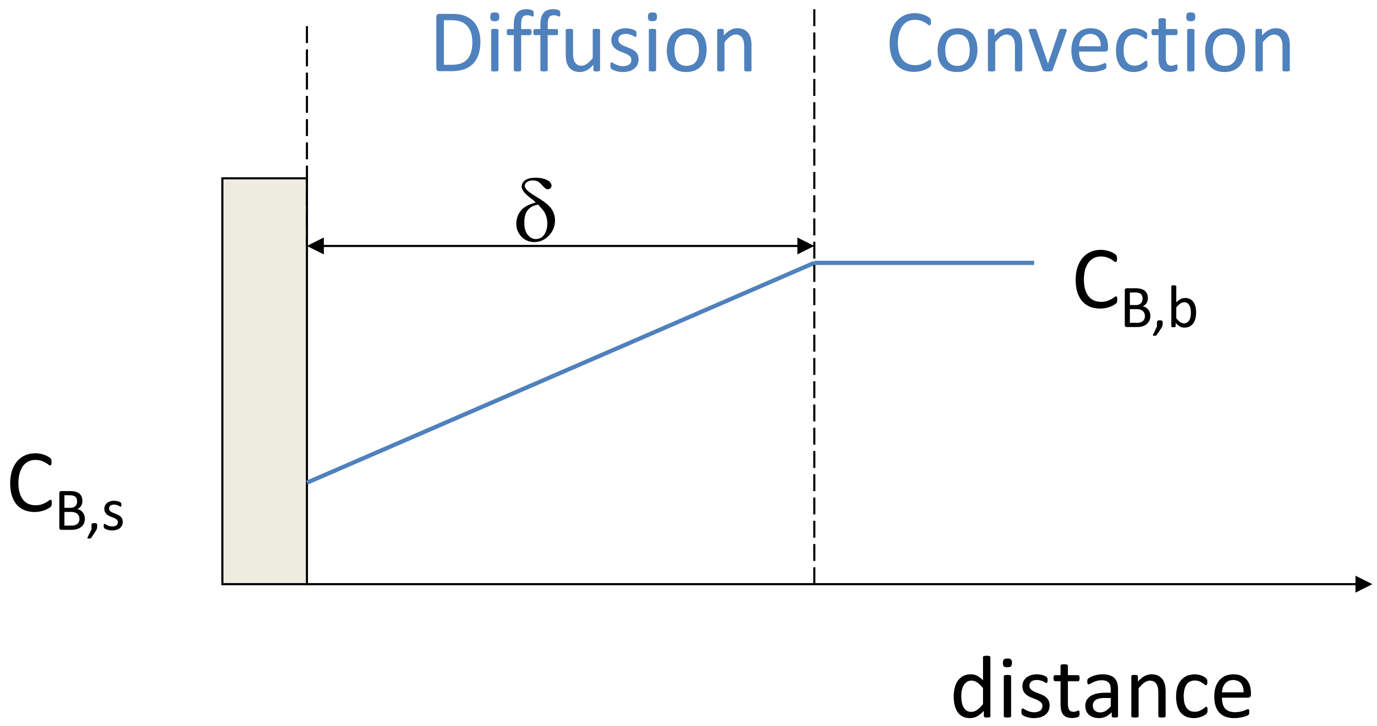
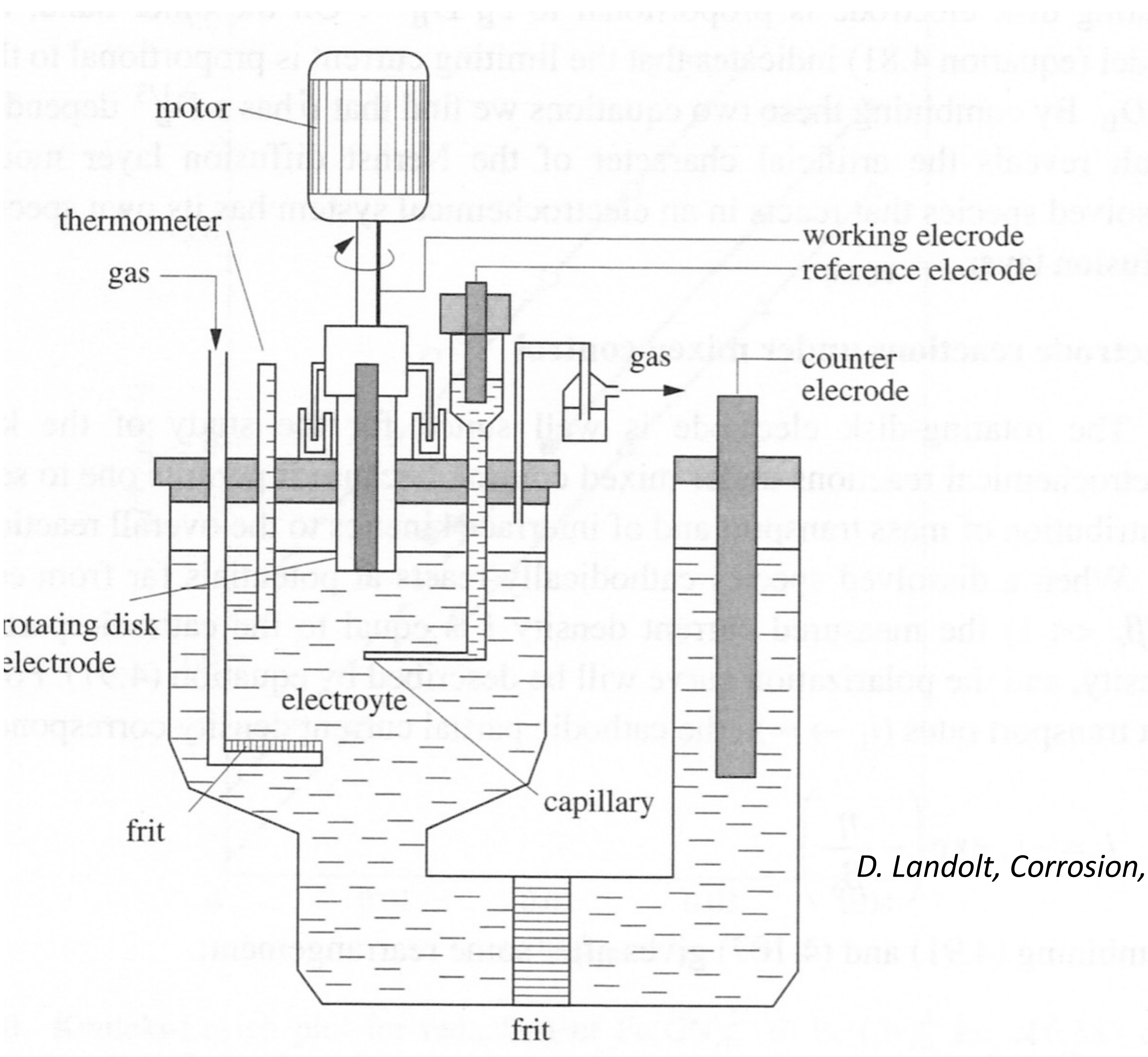


Diffusion
Convection
δ
$C_{B,b}$
$C_{B,s}$
distance

Transport correlations in <u>forced convection</u> systems

Geometry	Flow	Characteristic Length L	Sh (mean value, Sc>1000))
Pipe, smooth walls	turbulent: Re > 3000	diameter D_h	$0.0115\ Re^{7/8}Sc^{1/3}$
Pipe, smooth walls	laminar: Re < 2000 fully developed velocity profile: $D_h/L_x > 1.85$	diameter D_h	$1.85\ Re^{1/3}Sc^{1/3}(D_h/L_x)^{1/3}$ (L_x= electrode length)
Pipe, smooth walls	laminar, Re < 2000 fully developed velocity profile: D_h/L_x --> 0	diameter D_h	3.66 cf. Levich equation
Rotating disk	laminar: $Re < 2.7x10^5$	radius R	$0.62\ Re^{1/2}Sc^{1/3}$ => next slide
Rotating disk	turbulent: $8.9x10^5 < Re < 1.18x10^7$	radius	$0.0117\ Re^{0.896}Sc^{0.249}$
Rotating hemisphere	laminar: $Re < 1.5x10^4$	radius	$0.474\ Re^{1/2}Sc^{1/3}$
Rotating cylinder	turbulent: $10^3 < Re < 2.7x10^5$	radius	$0.079\ Re^{0.7}Sc^{0.35}$

Rotating disk electrode set-up



D. Landolt, Corrosion, EPFL press

Rotating disk equipment

Complete
setup

Example electrodes

Rotator controller and
electrode head

Sherwood number *Sh*

$i_{lim} = +/- \, z \, F \, D_A \, c_{A,b} \, / \, \delta$

$$Sh = \frac{|\, i_l \,|\, L}{n \, F \, D_b \, c_b} = L \, / \, \delta$$

convective
vs
diffusive
mass transfer

Nernst characteristic diffusion length

Sh = f (Re, Sc)

for fluid subjected to relative internal movement due to different fluid velocities, e.g. boundary layer at a surface

Reynolds number: $Re = u \, L \, / \, \nu$ (inertial forces (speed) vs viscous forces)

Schmidt number: $Sc = \nu \, / \, D_b$ (viscous forces vs diffusion transfer)

for fluid where viscosity and mass transfer play simultaneous roles
(mass transfer equivalent to the Prandtl number)

L: characteristic (convection) length (m)

ν: kinematic viscosity (m^2/s)

= dynamic viscosity divided by fluid density

= absolute viscosity = resistance of a fluid to flow

u: linear flow rate (m/s)

D_b: diffusion coefficient (m^2/s)

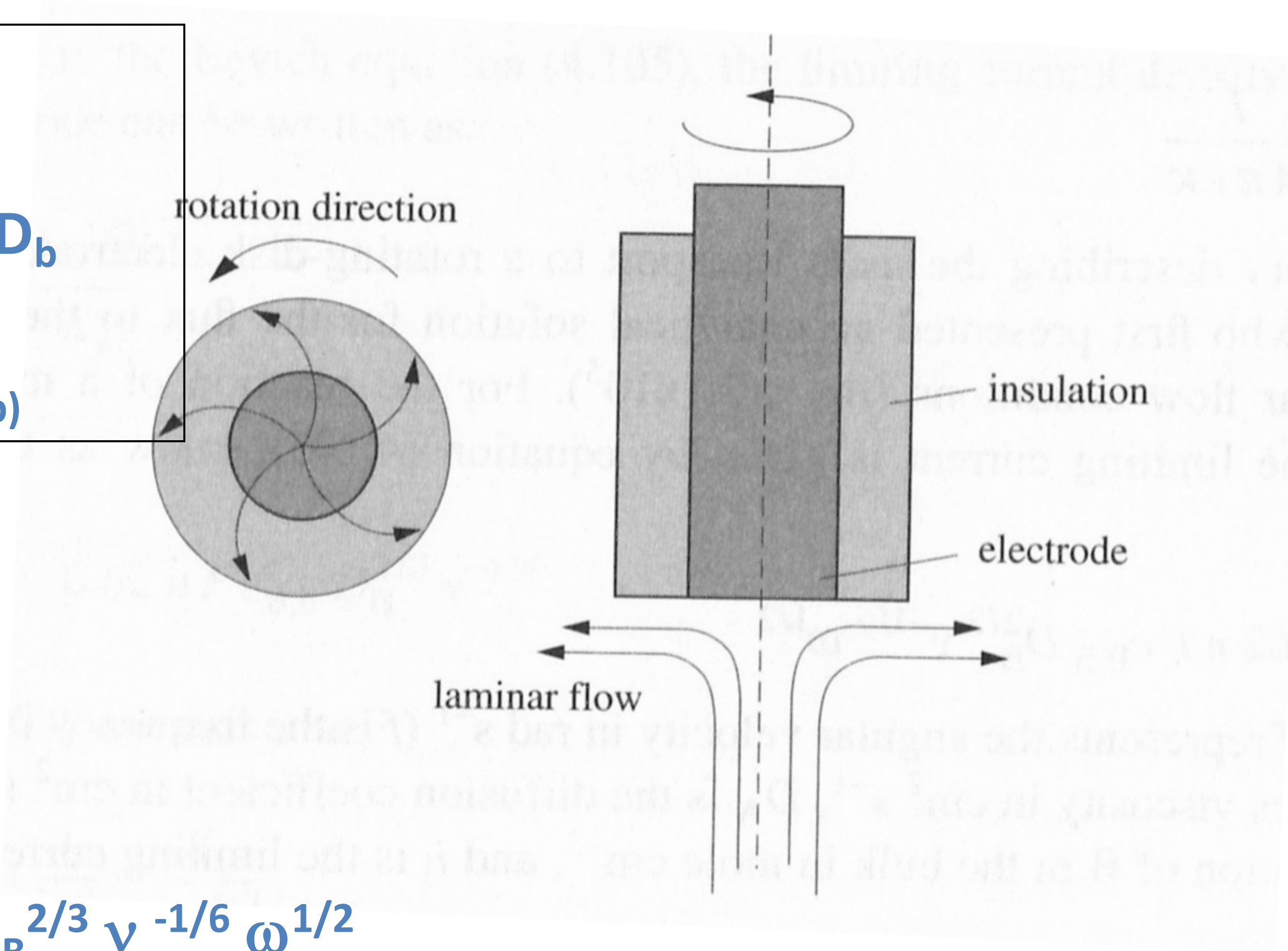
Rotating disk electrode (RDE)

$$Sh = 0.62\, Re^{0.5}\, Sc^{0.333}$$

$$Re = u\,R/\nu \qquad Sc = \nu / D_b$$

$$Sh = |i_{lim}|\, R / (n\, F\, D_b\, c_b)$$

(characteristic length
L=R for a disc)



Levich equation:

$$|\, i_{lim}\,| = 0.62\, n\, F\, C_{B,b}\, D_B^{2/3}\, \nu^{-1/6}\, \omega^{1/2}$$

plot i_{lim} vs ω

$$\Rightarrow \delta = 1.61\, D_B^{1/3}\, \nu^{1/6}\, \omega^{-1/2}$$

(with $i_{lim} = n\, F\, D_B\, c_{B,b} / \delta$)

Rotating disk electrode (RDE)

- The RDE is a method to achieve steady state conditions that allows accurate measurement of diffusion and kinetic parameters under controlled hydrodynamic conditions.
- It has the advantage over <u>stationary</u> electrodes (e.g. cyclic voltammetry - CV) that suffer from random convection caused by gravity and temperature gradients.
- CV gives accurate results at fast scan rate (>100 mV s^{-1}) but is liable to error at slower scan rates.
- Common practice: do CV on the stationary RDE and afterwards start the disc rotating and see the effect on the CV: at some point, steady state kicks in and there is no more hysteresis in the CV.
- The two methods are complimentary. Perform both to get a completer picture.
- Other forced convection methods are:
  - rotating cylinder electrode (easier to make than rotating discs and popular for corrosion experiments where multi samples might need to be studied)
  - wall-jet (impingement) : similar to RDE but easier to make as the electrode is stationary and the electrolyte is forced through a small nozzle to create the jet impingement (popular for corrosion studies)
  - thin layer cells in which the electrolyte is forced through a gap between two stationary electrodes.

Levich equation - example

Reduction of potassium ferricyanide $K_3[Fe(CN)_6]$
($Fe^{3+} \rightarrow Fe^{2+}$)

Concentration C_0 = 0.81 mM in 0.1 M KCl

$$i_L = 0.620\, nFAD^{\frac{2}{3}} \omega^{\frac{1}{2}} \nu^{-\frac{1}{6}} C_0$$

F = Faraday constant
A = area of the electrode
n = number of electrons transferred
ν = kinematic viscosity = 9.913×10^{-3} $cm^2\ s^{-1}$ for 0.1 M KCL

=> calculated diffusion coefficient from the slope
D = 7.6×10^{-6} $cm^2\ s^{-1}$

Example of experimental data

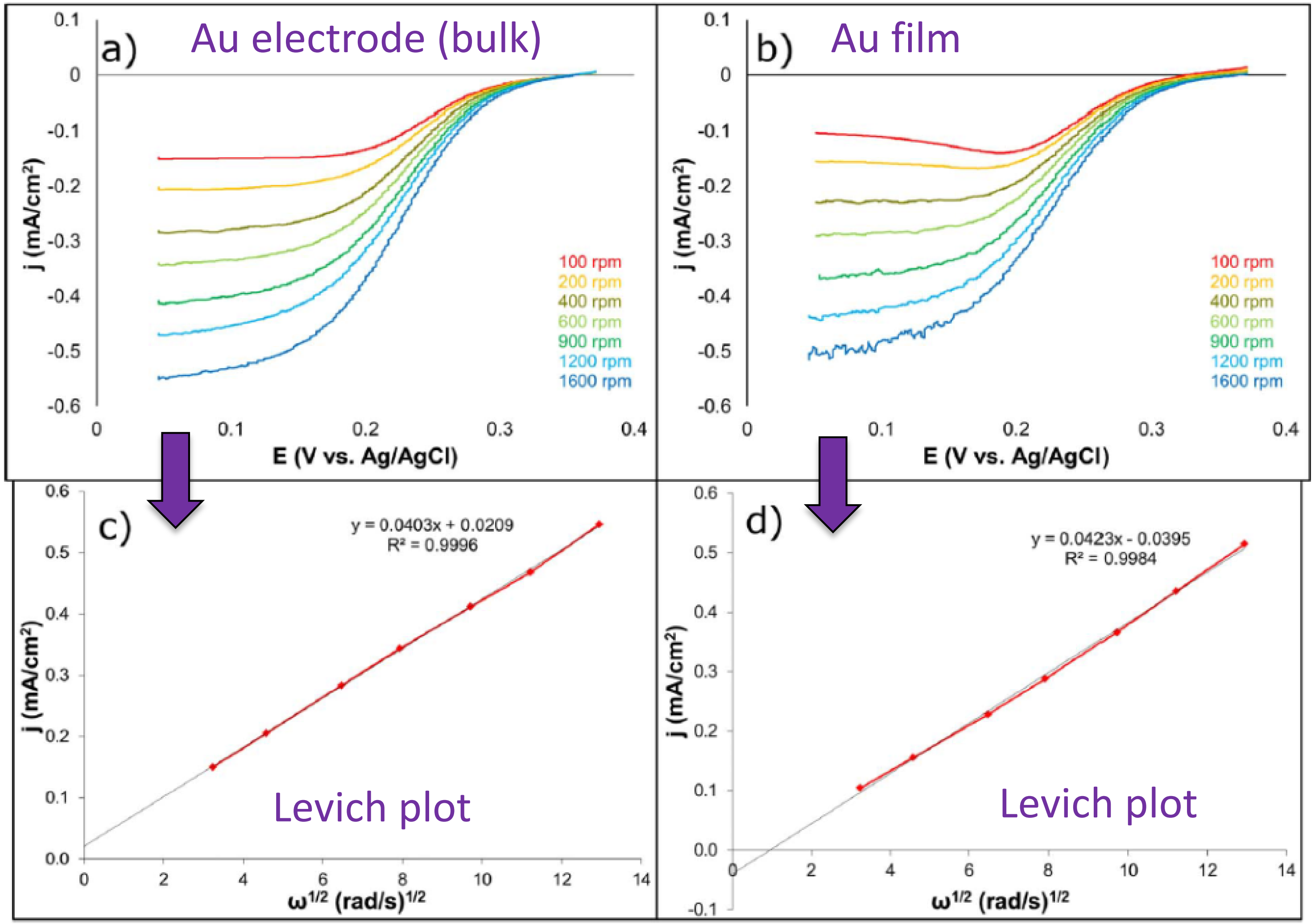


Figure 6. Rotating disk electrode voltammetery of 0.81 mM $K_3[Fe(CN)_6]$ in 0.1 M KCl on bulk Au (a) and Au film (b). (c) Levich plots at 0.06 V vs. Ag/AgCl of bulk Au and Au film (d).

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Koutecky–Levich equation

Add the kinetic term:

$$\frac{1}{i_L} = \frac{1}{i_K} + \left(\frac{1}{0.620nFAD^{2/3}\nu^{-1/6}C}\right)\omega^{-1/2}$$

kinetic term

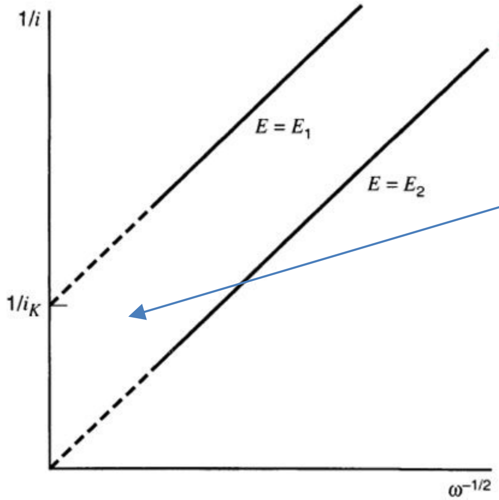
mass transport term (forced convection)

i_L = measured current
i_K = kinetic current

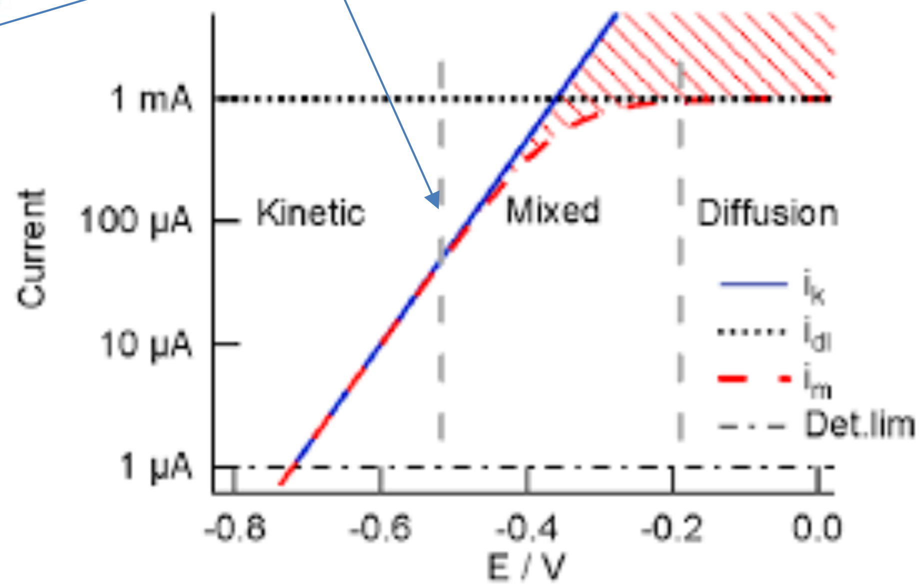
Experiment
Measure the current over a range of rotation speeds, as a function of applied electrode potential as additional parameter, to obtain a series of linear plots – the intercept determines the kinetic parameter and the slope the diffusion parameter

Koutecký-Levich Equation

As the electrode potential is increased, the control switches from kinetic to diffusion (at higher V the kinetics become fast)



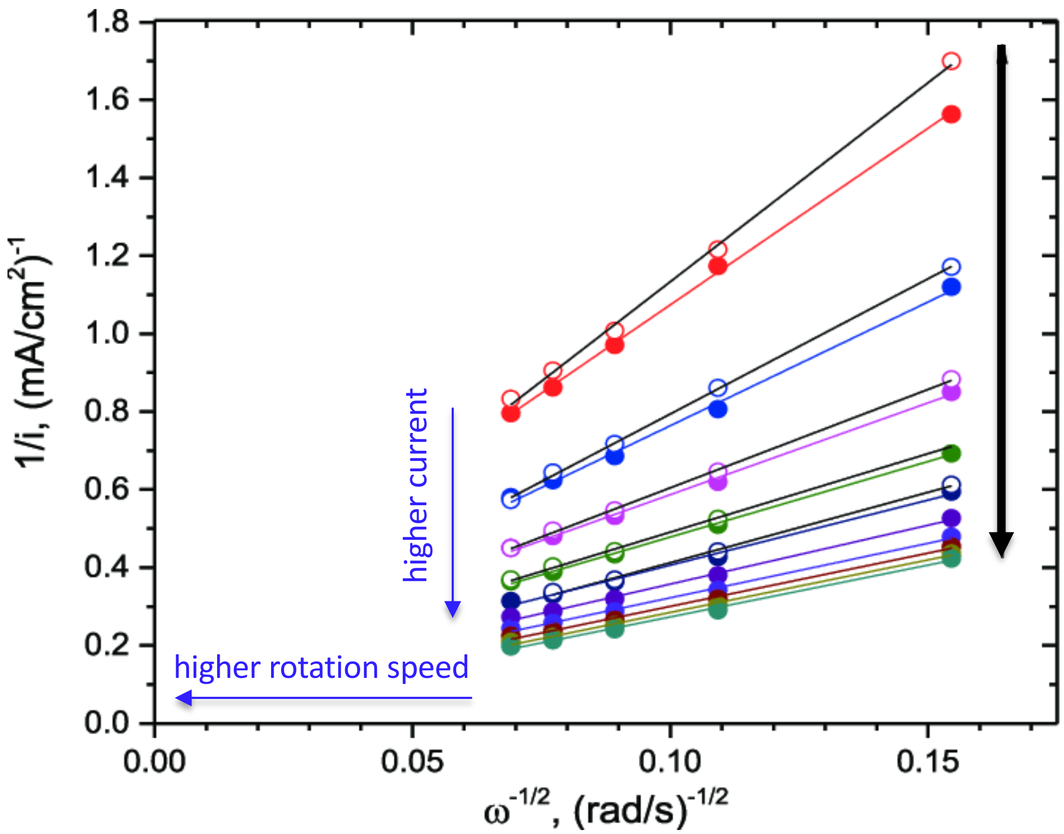
Where E2 < E1 (reduction)
E2>E1 (oxidation)



As expected, i_K grows larger ($1/i_K$ grows smaller) as the overpotentials is increased.

(The higher the rotation speed, the higher the i_{LIM}
Hence the smaller $1/\omega$, the smaller $1/i$)

Example: oxidation of bromide Br^-



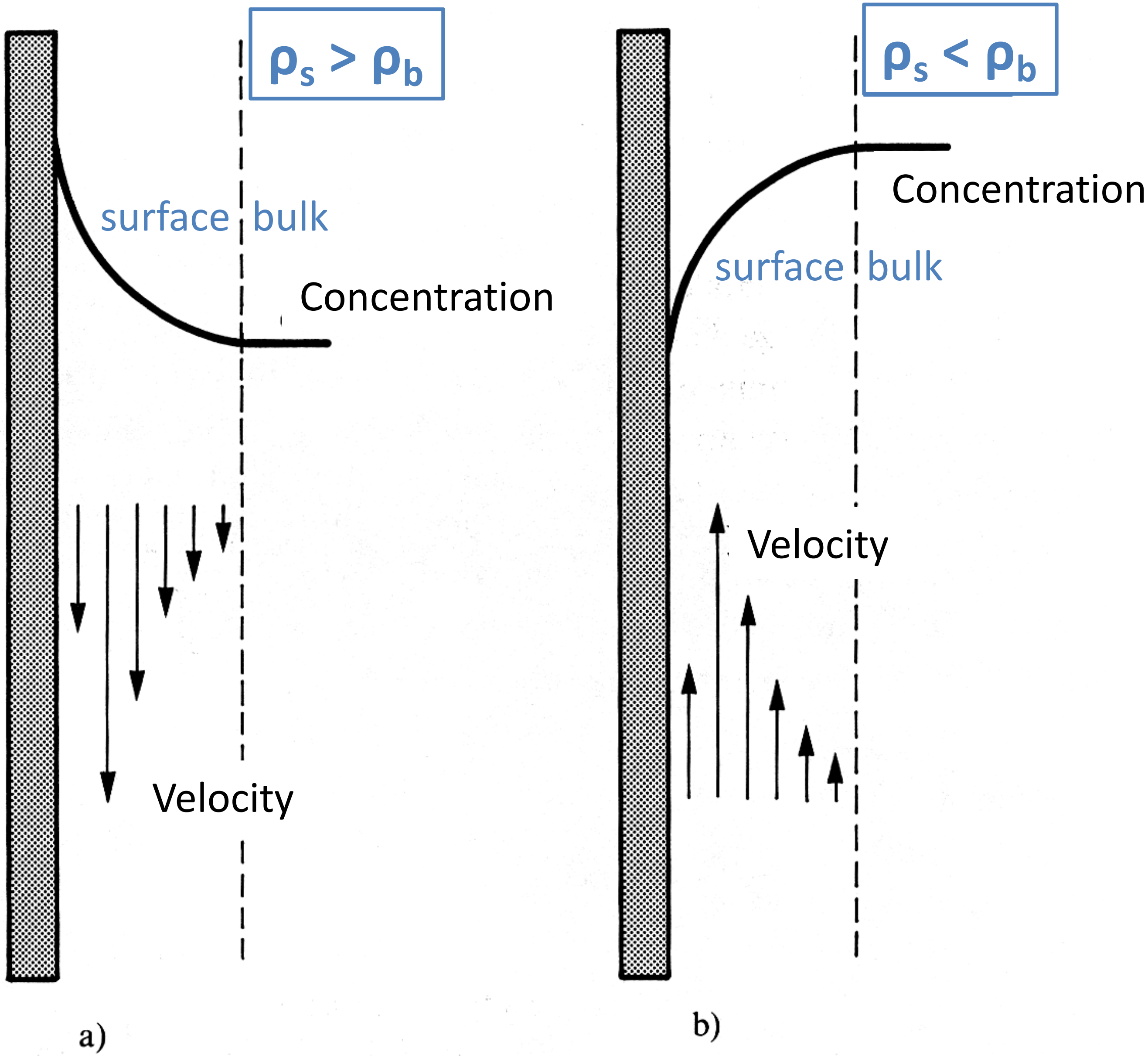
Increasing electrode potentials from 1.21 to 1.3 V in steps of 0.01 V

Oxidation: 1.3 V is more oxidizing than 1.2 V and will produce a higher current.
=>
higher V of 1.3 V is the point plotted lowest in a 1/i scale (higher current).

Koutecky-Levich plots for the oxidation of bromide Br^- at a rotating Pt disk electrode. The solid and open circles represent data collected in two fully independent runs and the arrow points in the direction of increasing potentials from 1.21 to 1.3 V in steps of 0.01 V.

The oxidation of Bromide on Platinum Electrodes in aqueous acidic solutions: electrochemical and in situ spectroscopic studies
Journal of The Electrochemical Society 161(6):H392-H398 · April 2014

Free convection at vertical electrodes



Transport correlations for free convection systems

Geometry	Flow	Characteristic length L	Sh (mean value: Sc>1000))
vertical plane electrode	laminar $Gr < 10^{12}$	height	$0.67\ (ScGr)^{1/4}$
vertical plane electrode	turbulent $Gr > 10^{13}$	height	$0.31\ (ScGr)^{0.28}$
horizontal plane electrode facing upwards	laminar $Gr < 10^{7}$	surface/perimeter	$0.54\ (ScGr)^{1/4}$
horizontal plane electrode facing downwards	turbulent $Gr > 10^{7}$	surface/perimeter	$0.15(ScGr)^{1/3}$

Grashof number $Gr = g\ \Delta\rho\ L^3 / \rho_b \nu^2$

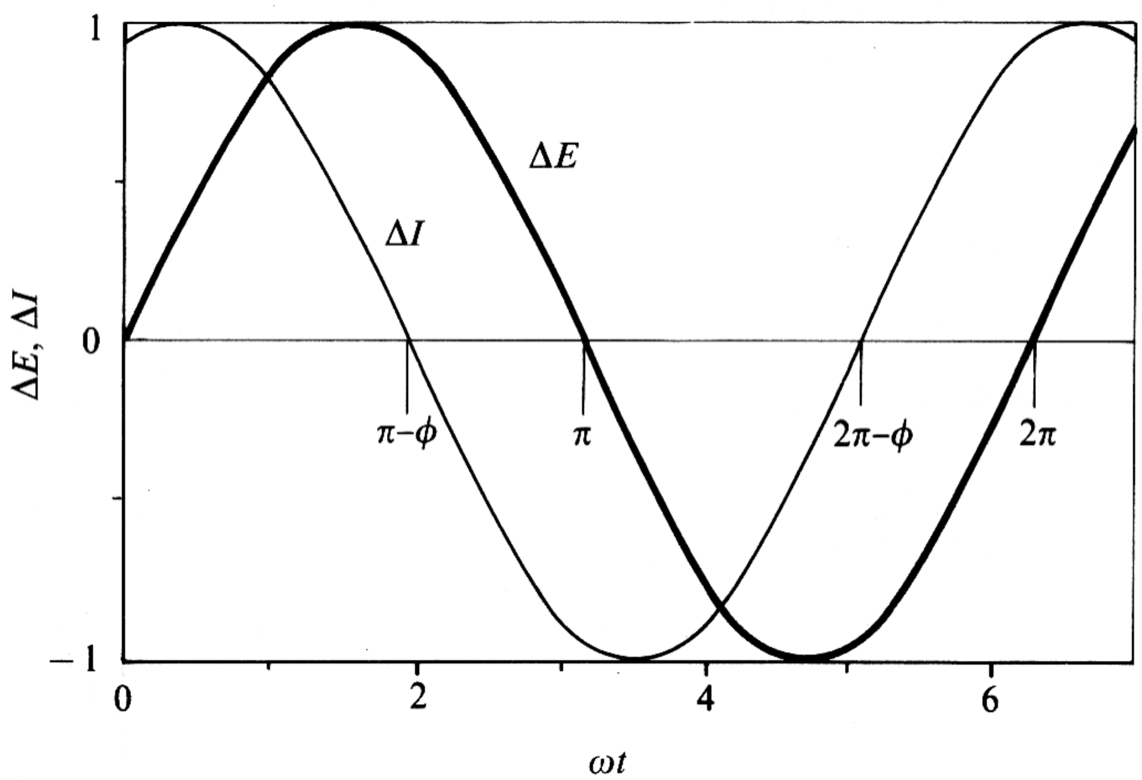
The Grashof number approximates the ratio of gravity (buoyancy) to viscous force acting on a fluid.
It arises in situations involving natural convection and is analogous to the Reynolds convection (=forced convection).

Measurement techniques

1. Polarisation measurements
2. Double layer capacitance (galvanostatic impulsion)
3. Potentiostatic impulsion (Cottrell diffusion equation)
4. Cyclic voltammetry
5. Rotating Disk Electrodes (RDE) (Levich-(Koutecky) equation)
6. Electrochemical Impedance Spectroscopy (EIS)

Principle of Electrochemical Impedance Spectroscopy (EIS)

An *ac* voltage (typically ±10 mV) with frequencies ranging from MHz to mHz is added to an imposed (*dc*) potential. The *ac* potentials and current responses are then passed to a frequency response analyzer (FRA) to calculate the impedance and phase shift.



Electrochemical Impedance

$\omega = 2\pi f$ angular frequency where f is the AC frequency

$E_t = E_0 \sin(\omega t)$ potential vs time

$I_t = I_0 \sin(\omega t + \phi)$ current vs time

Impedance Z

$$Z = E_t / I_t = Z_0 \sin(\omega t) / \sin(\omega t + \phi)$$

Impedance in the complex plane

$\exp(j\,\phi) = \cos\phi + j\sin\phi$ Euler's relationship

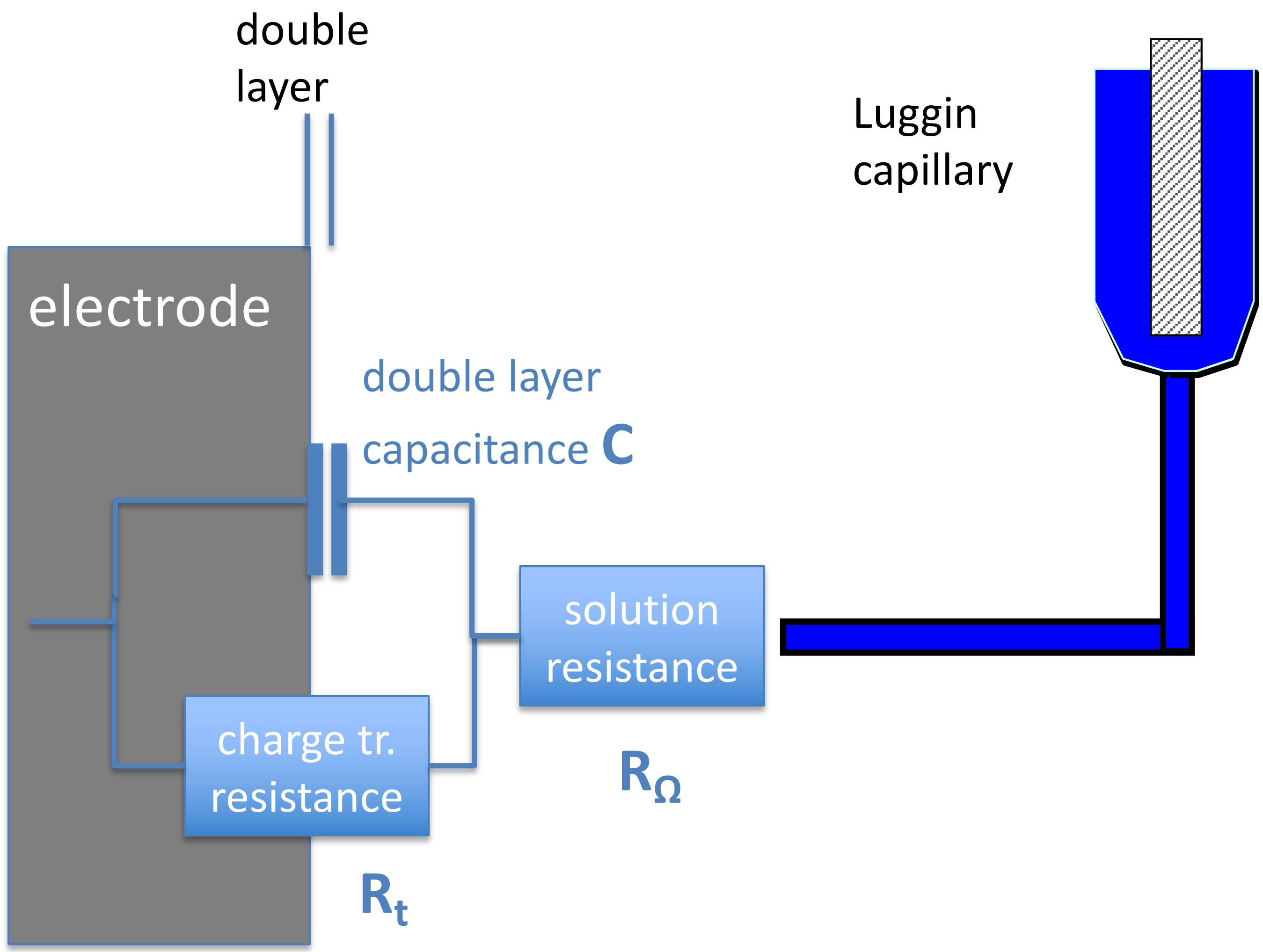
$E_t = E_0 \exp(j\omega t)$

$I_t = I_0 \exp(j\omega t - \phi)$

Impedance Z

$Z(\omega) = E_t / I_t = Z_0 \exp(j\phi) = Z_0 (\cos\phi + j\sin\phi)$

Electrochemical interfaces and equivalent circuits



Impedance of some electrical elements

Resistance:

$Z_{re} = R$ $\qquad$ $Z_{im} = 0$

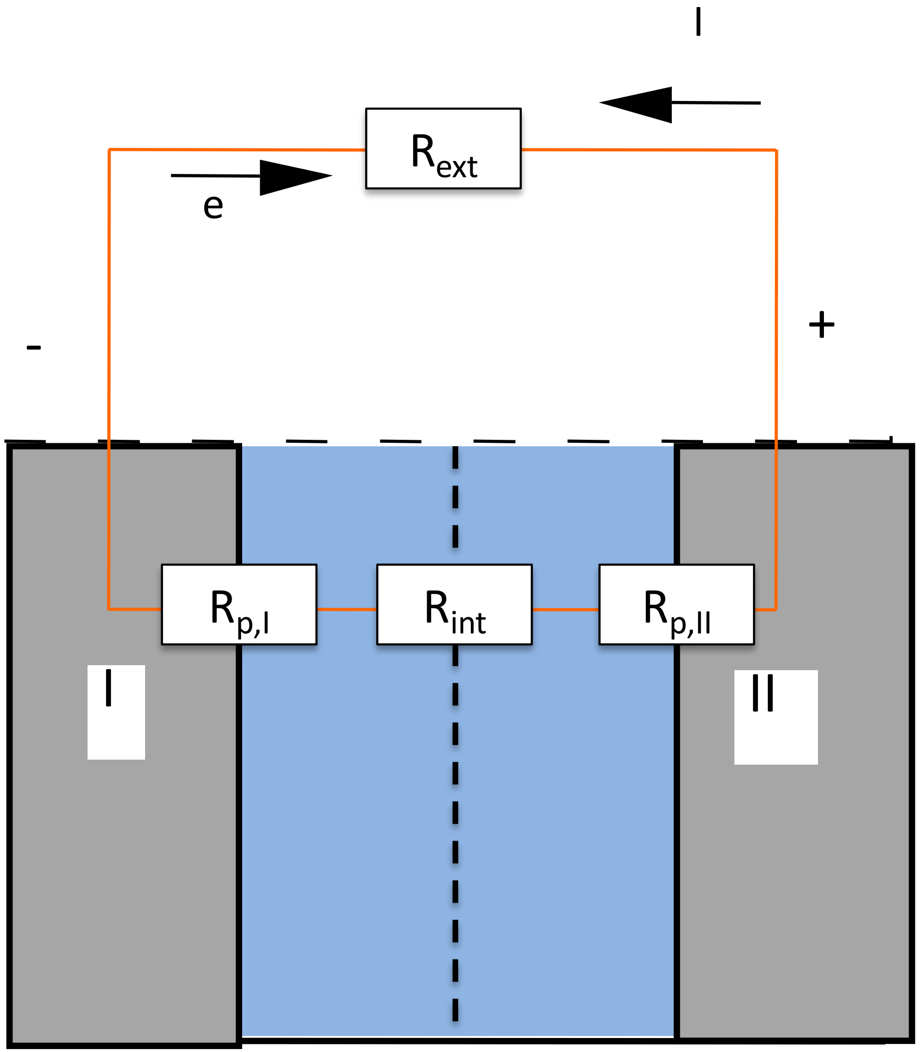
Capacitance

$Z_{re} = 0$ $\qquad$ $Z_{im} = -j/\omega C$

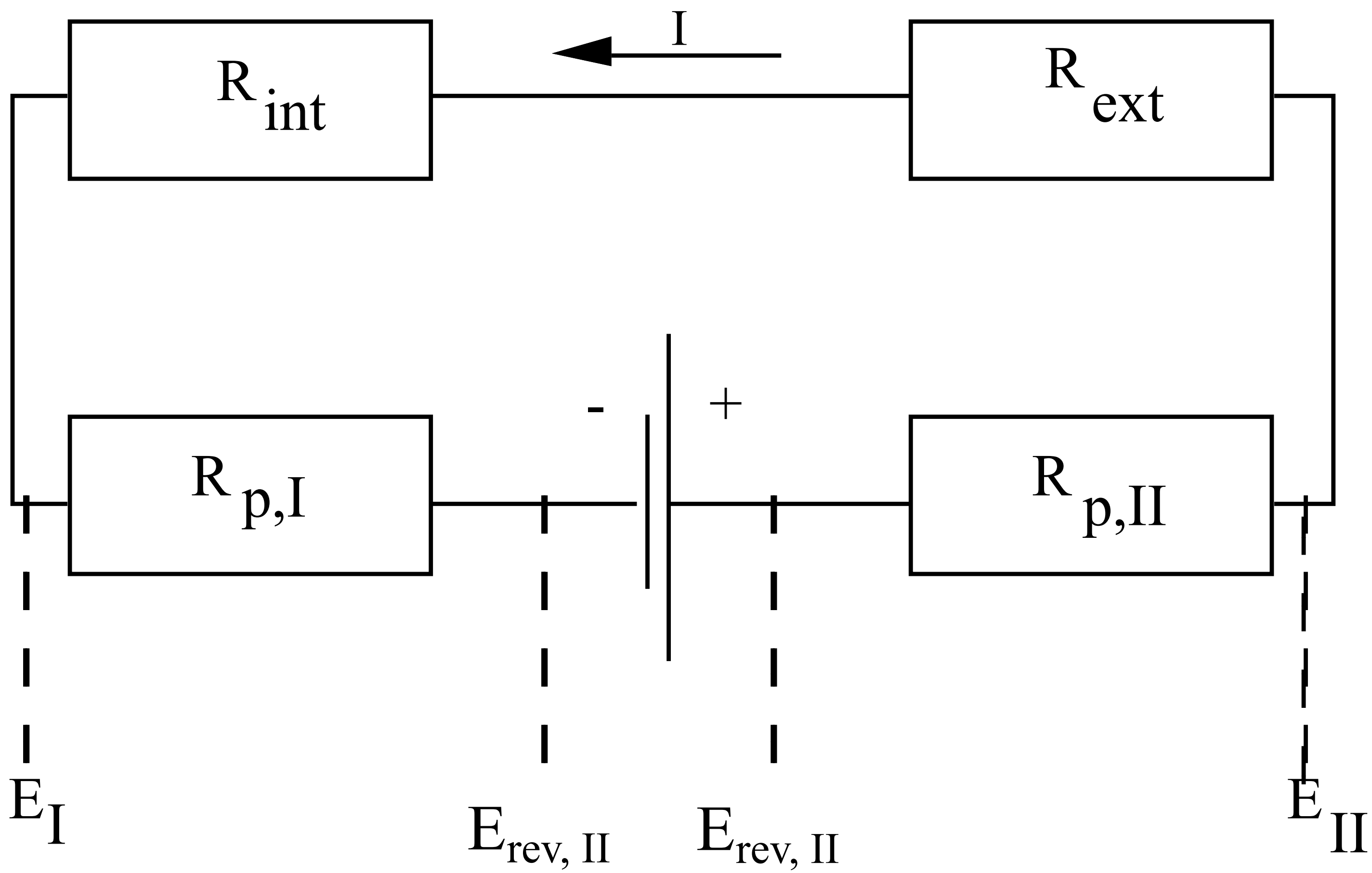
Inductance

$Z_{re} = 0$ $\qquad$ $Z_{im} = -j\,\omega\,L$

Resistances in electrochemical cells

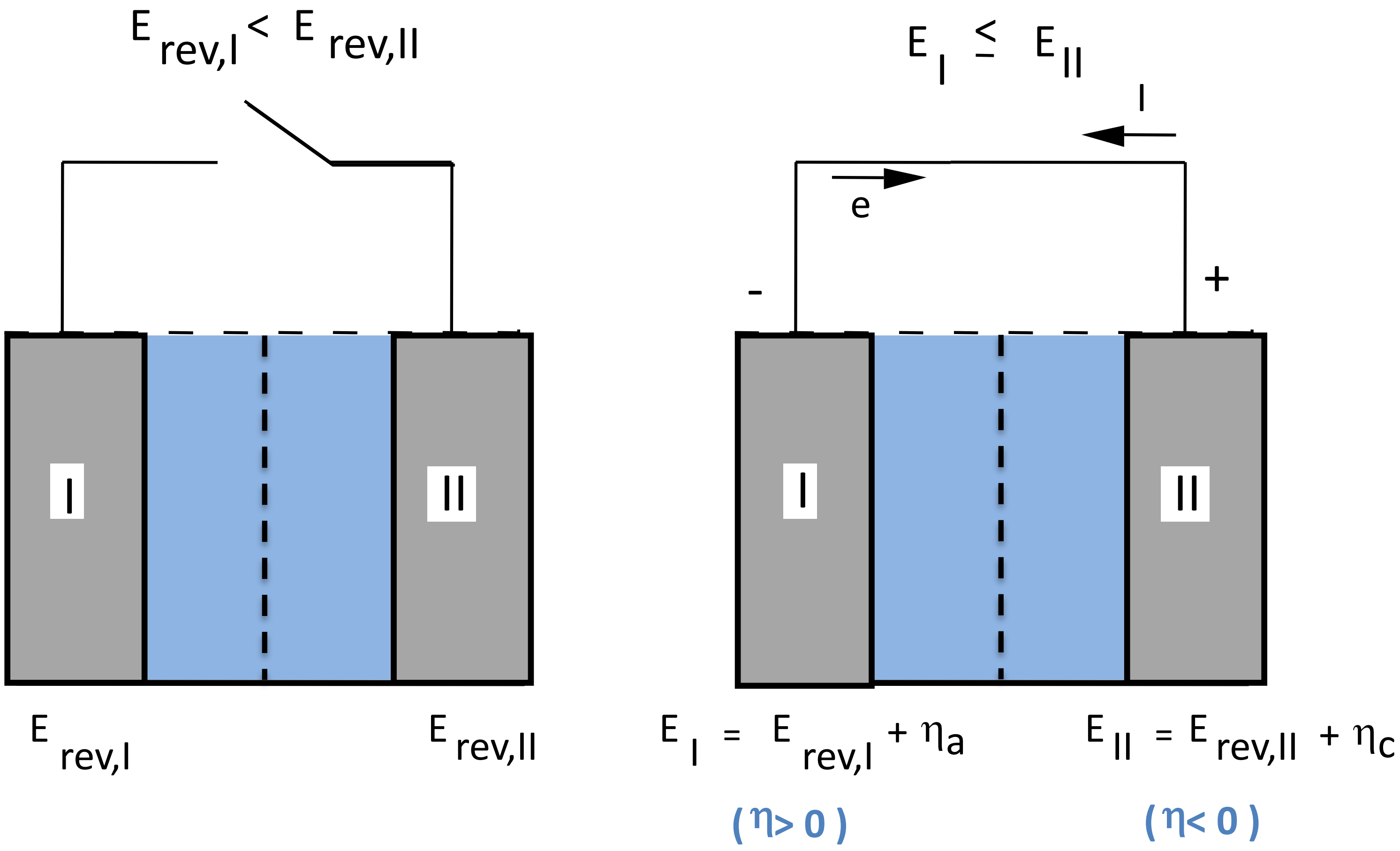


Electrical equivalent circuit



$$I = \frac{E_{rev,\,II} - E_{rev,\,I}}{R_{int} + R_{ext} + R_{p,I} + R_{p,II}}$$ (dc conditions)

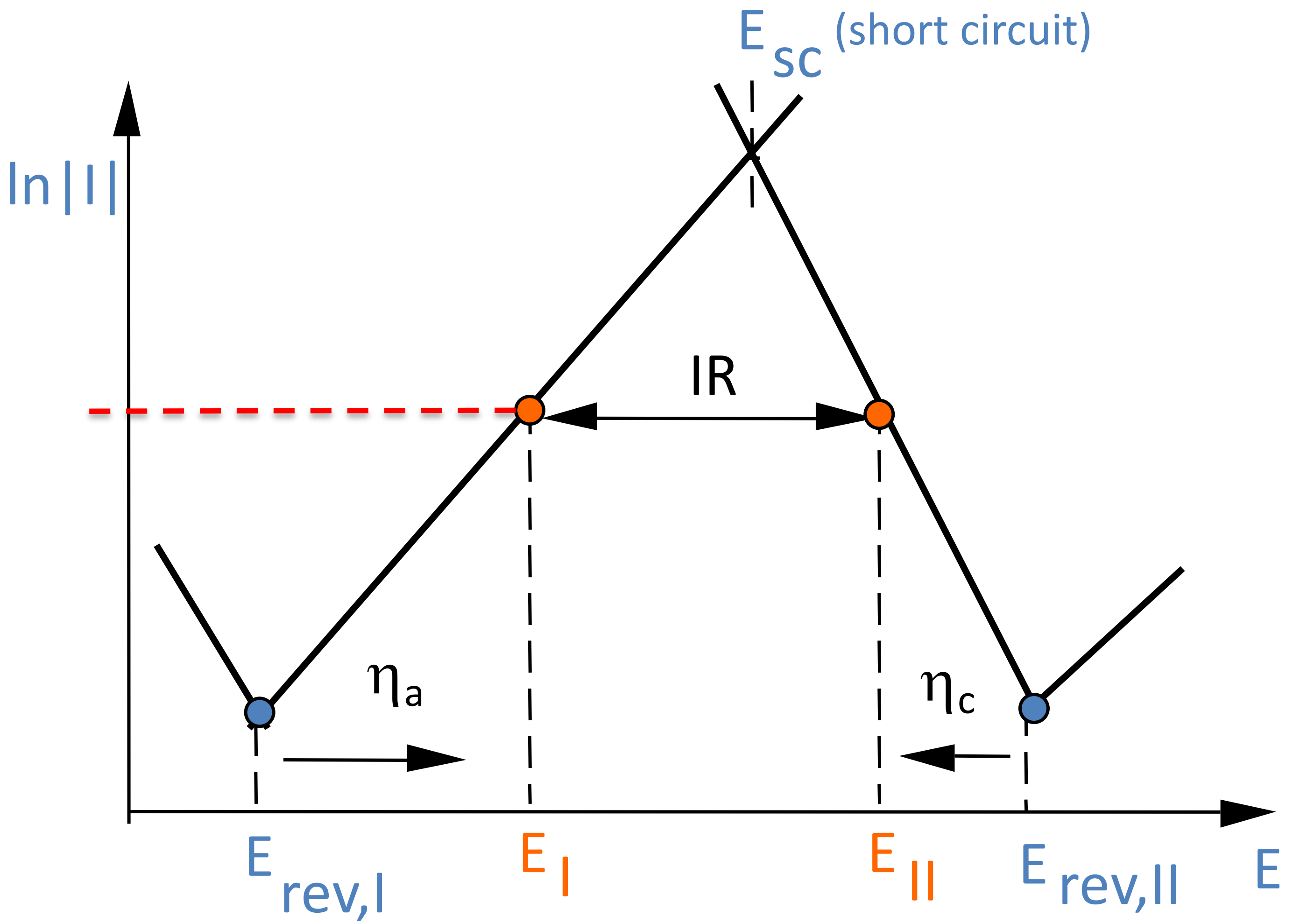
Electrochemical cell: block diagram



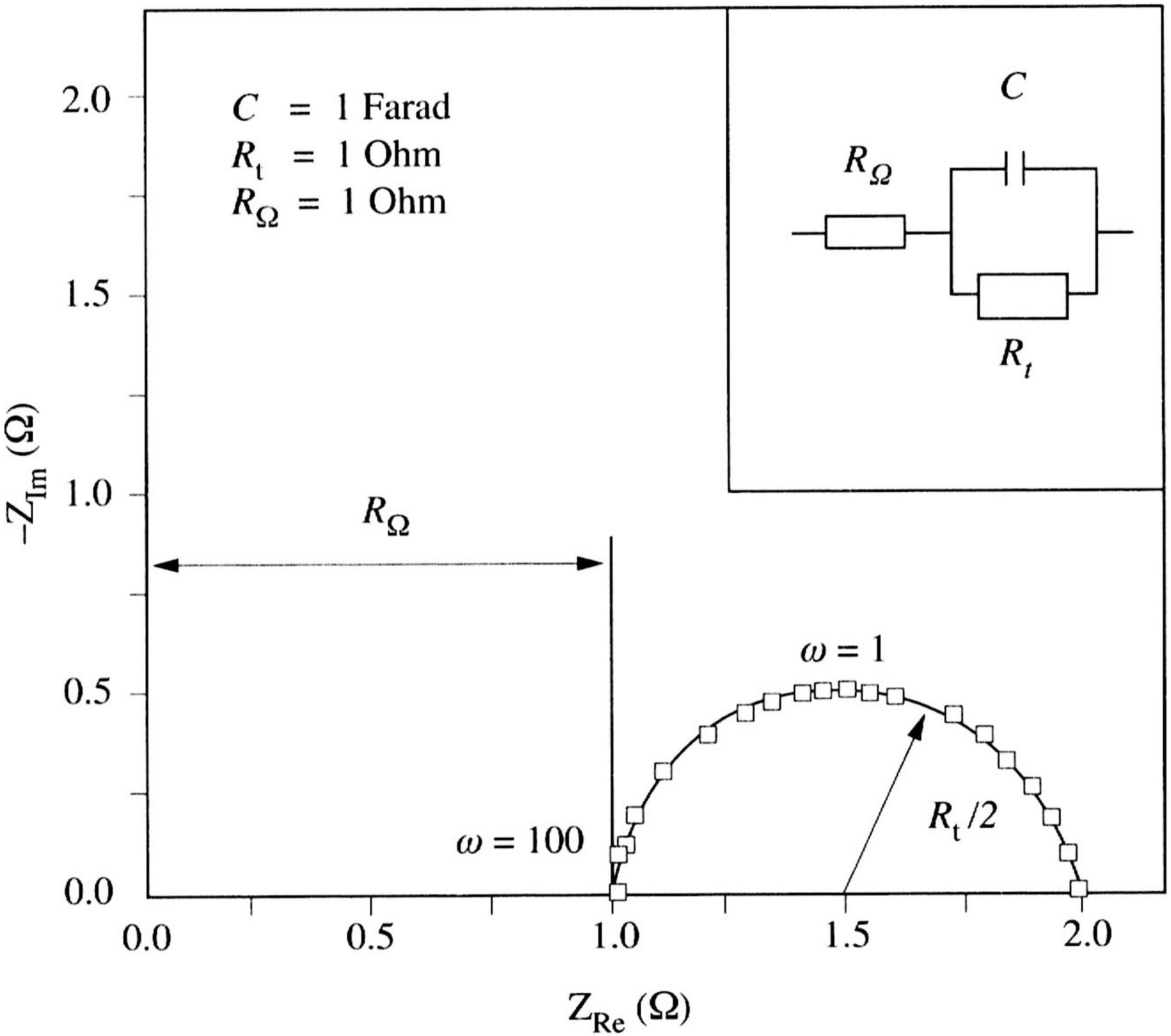
open circuit

closed circuit

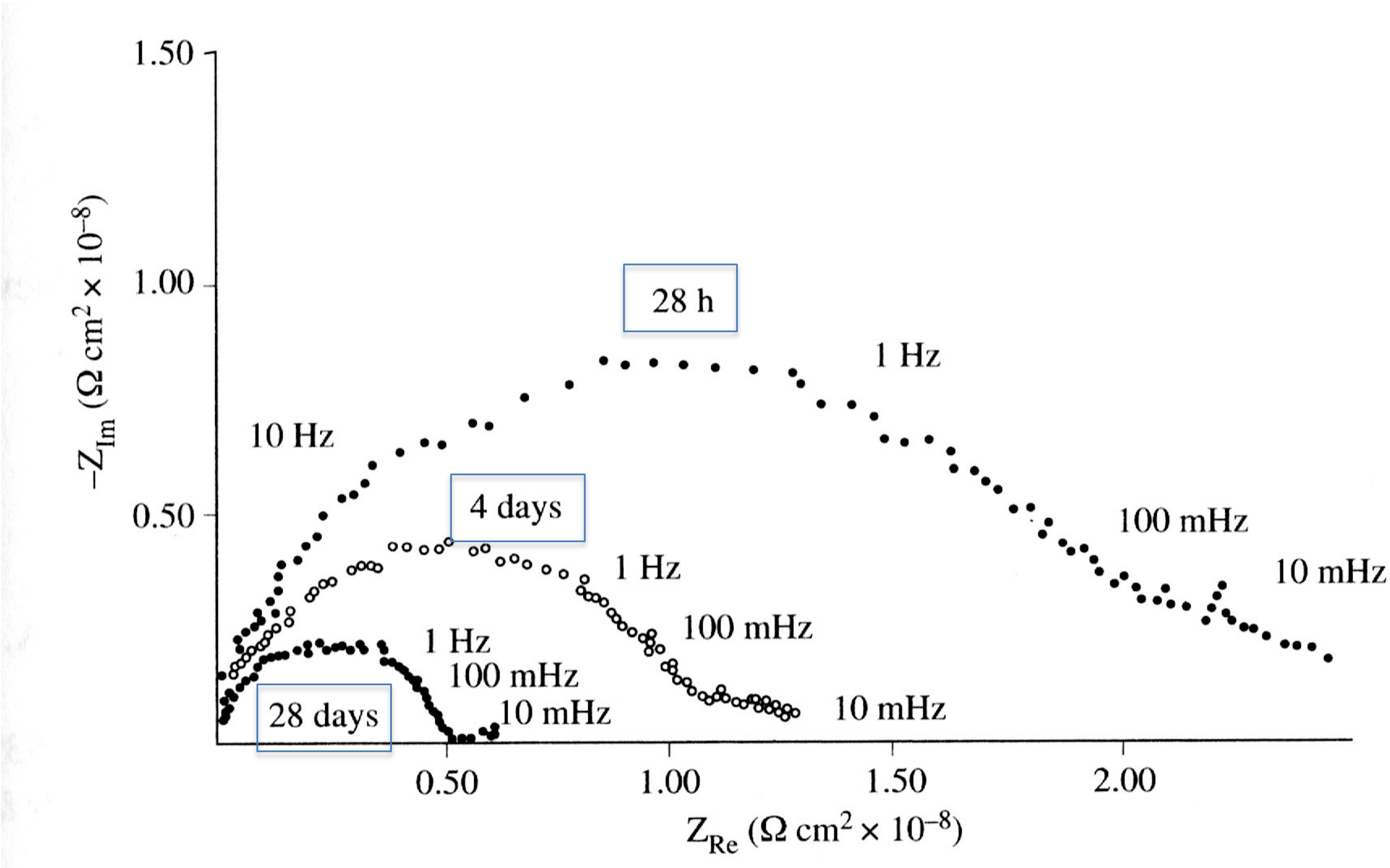
Evans diagram of an electrochemical cell



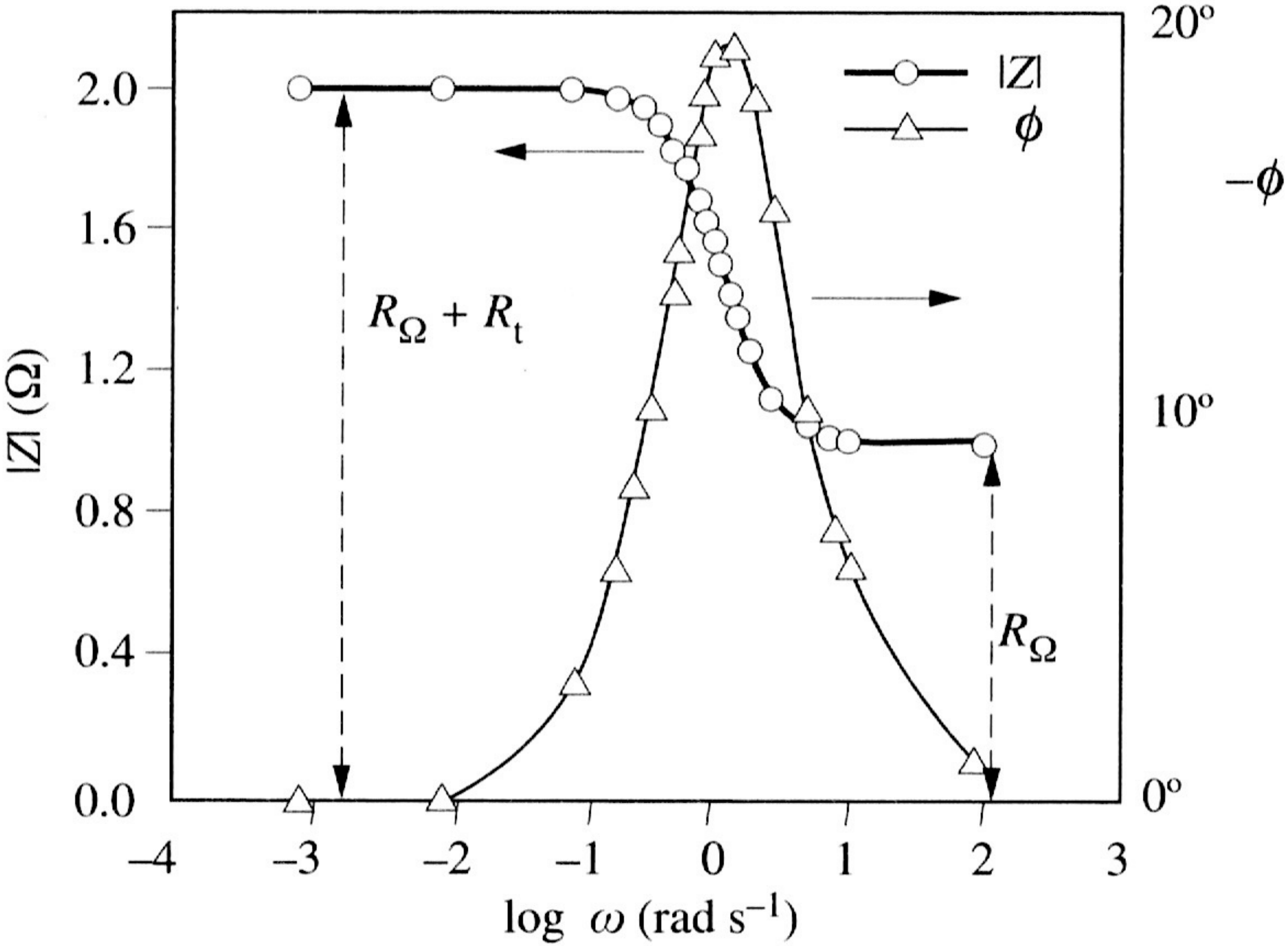
Nyquist plot



Nyquist diagram of a paint-coated steel vs exposure time to NaCl solutions



Bode plot



2.0
1.6
1.2
0.8
0.4
0.0
|Z| (Ω)
20°
10°
0°
−φ
|Z|
φ
$R_\Omega + R_t$
R_Ω
−4
−3
−2
−1
0
1
2
3
log ω (rad s⁻¹)

Bode plot for a passivating metal electrode at different immersion times

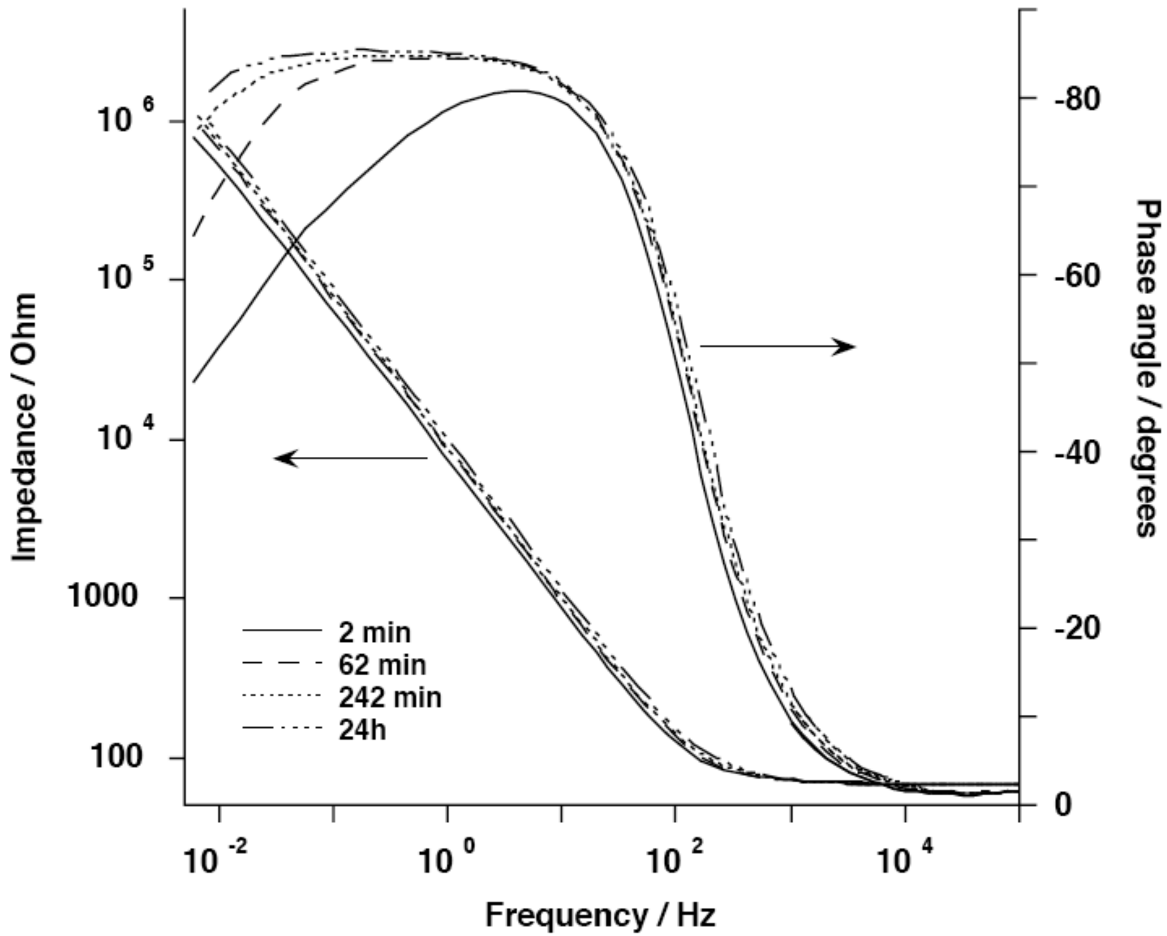
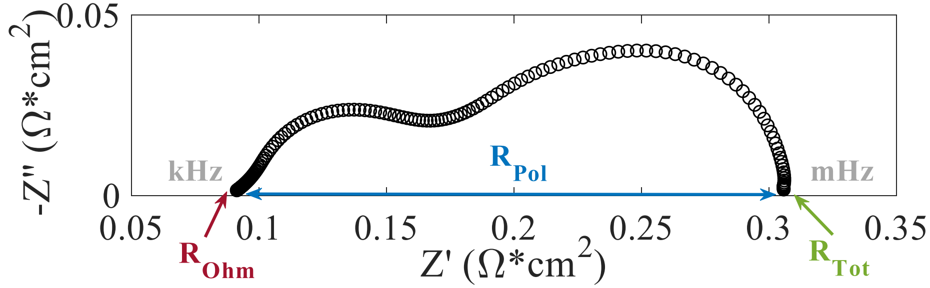


Fig. 6. EIS measurements for CoCrMo alloy during polarisation at −0.1 V after different time intervals in buffered 0.14 M NaCl (pH 7.4, 37 °C). Open-circuit potential before measurement: −610 mV.

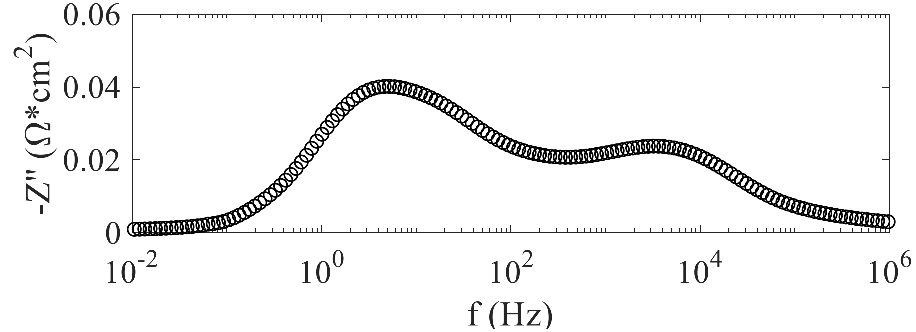
A.W.E. Hodgson et al. / Electrochimica Acta 49 (2004) 2167–2178

DRT approach & tool

Nyquist plot

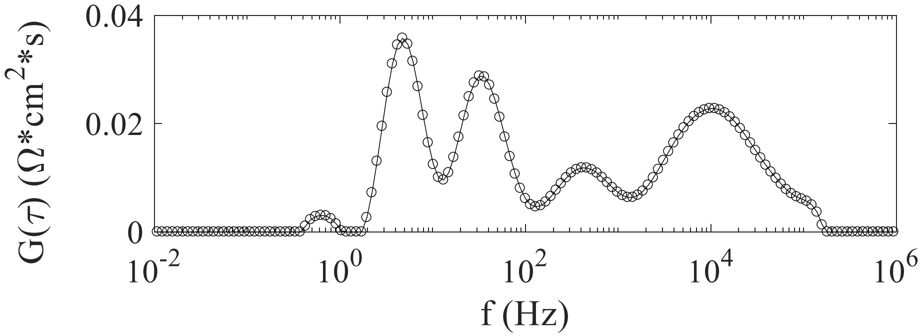


Imaginary Bode plot

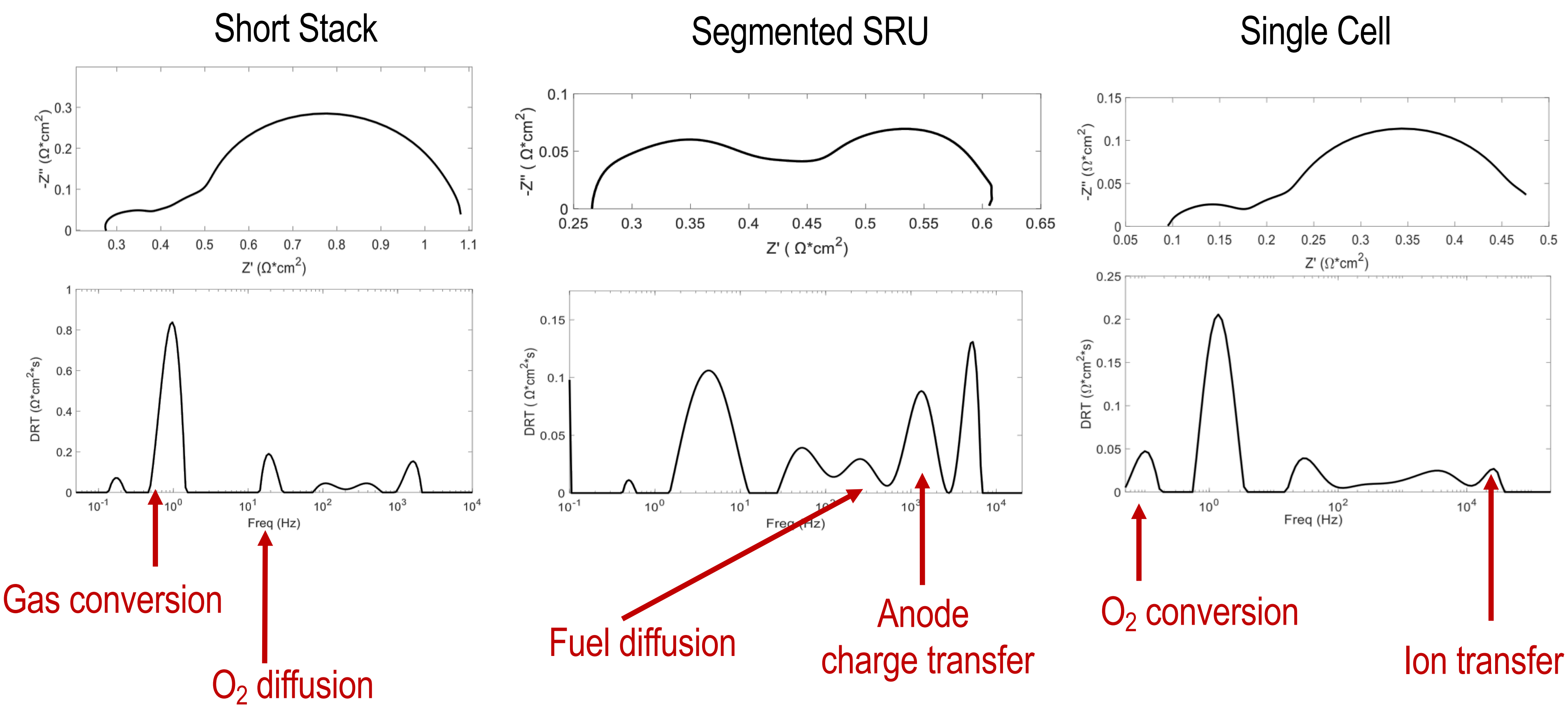


DRT plot

Distribution of Relaxation Times

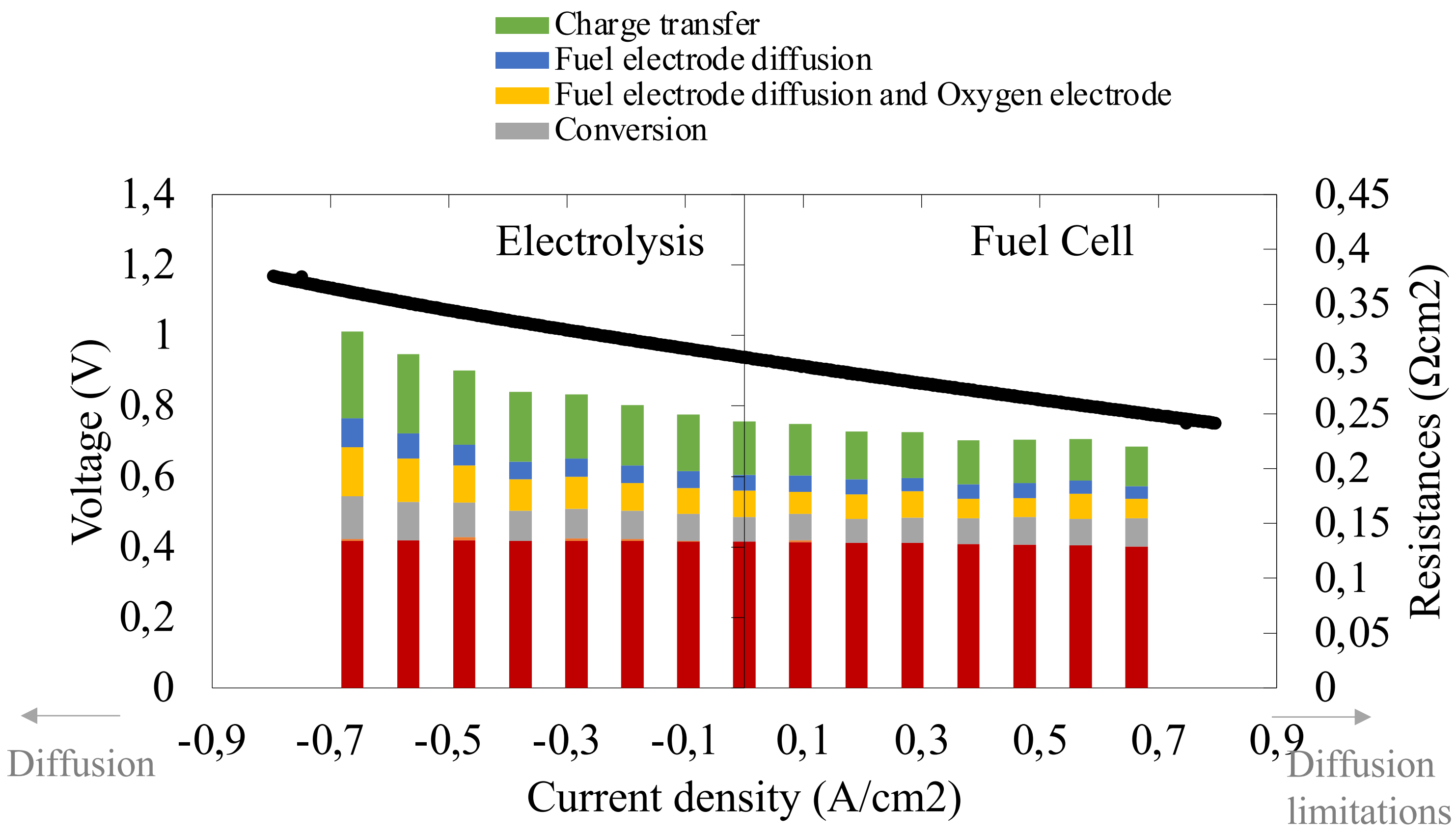


EIS-DRT consistent in different test configurations



The same 6 processes in similar frequency regimes determined in different test configurations

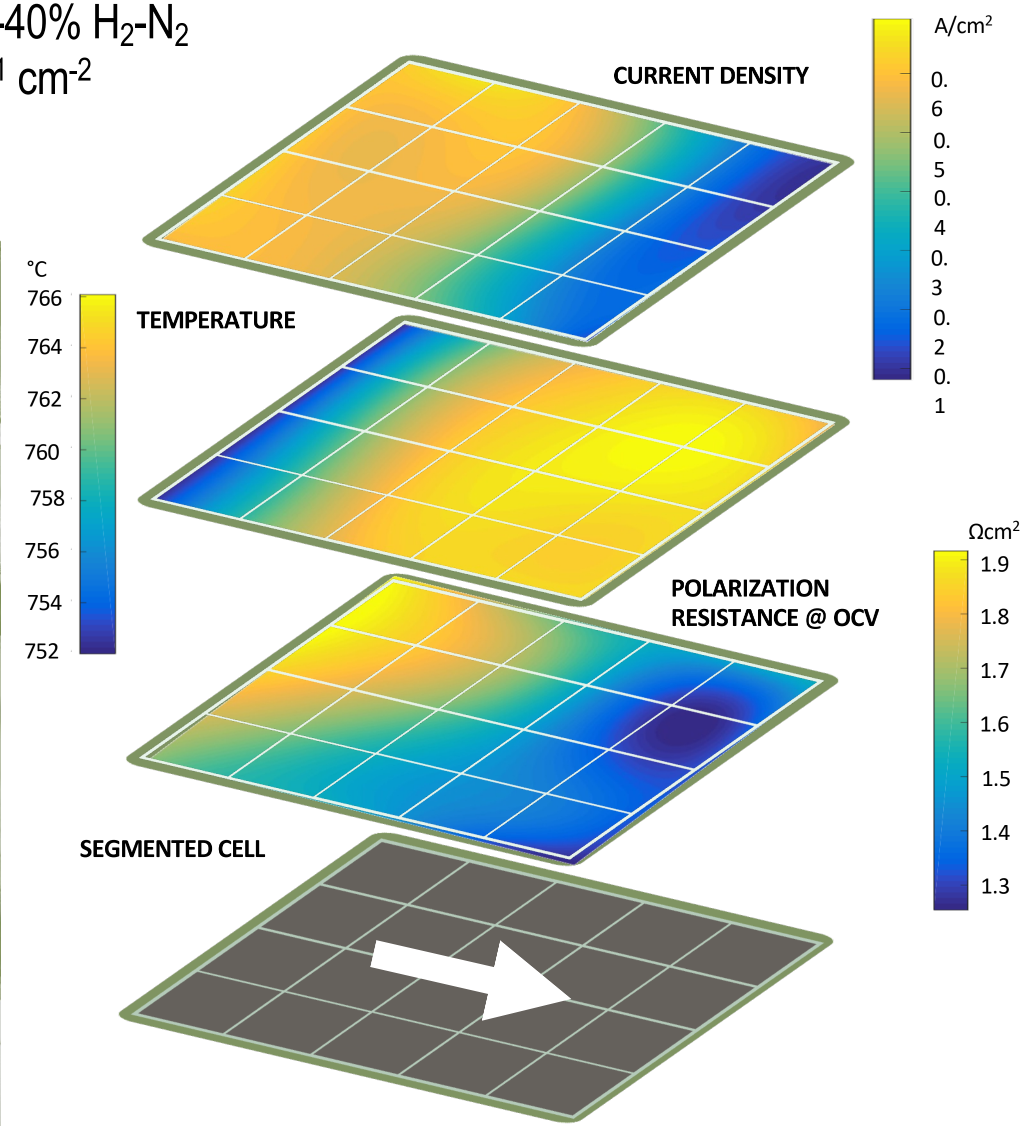
Process identification

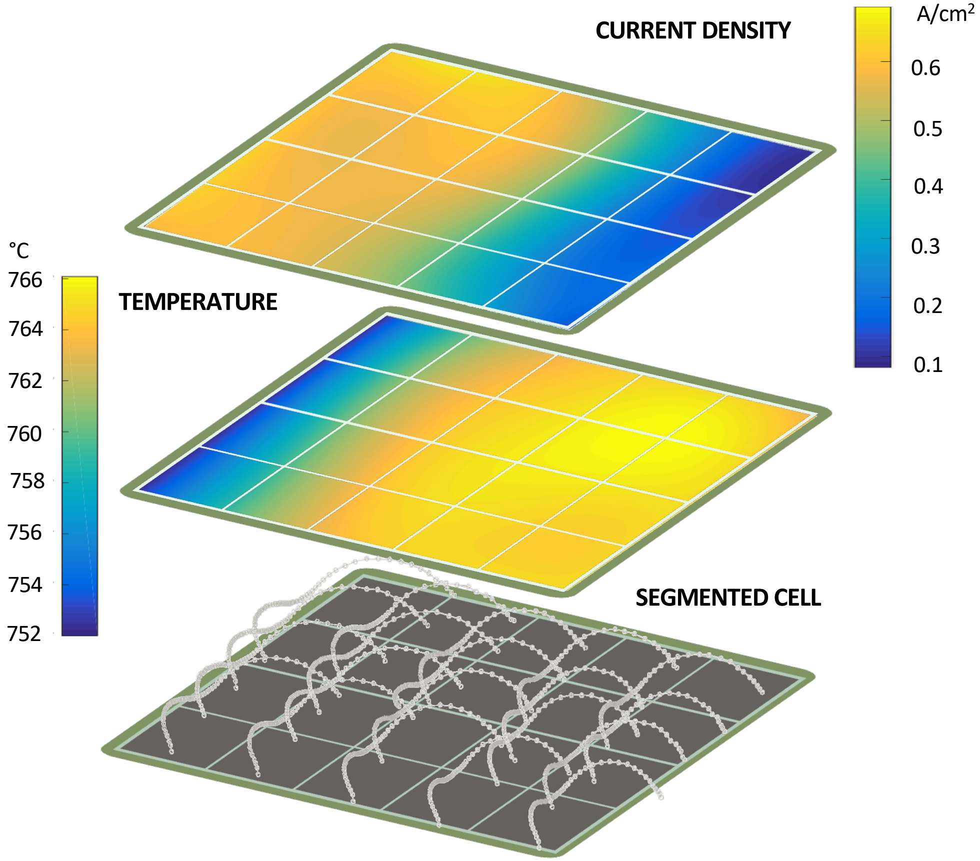


PhD Thesis EPFL Priscilla Caliandro 2018

SEGMENTED CELL OPERATION

Co-flow configuration
Fuel composition 60-40% H_2-N_2
Fuel flow 5 Nml min^{-1} cm^{-2}
Total current 33 A
Voltage 0.65 V



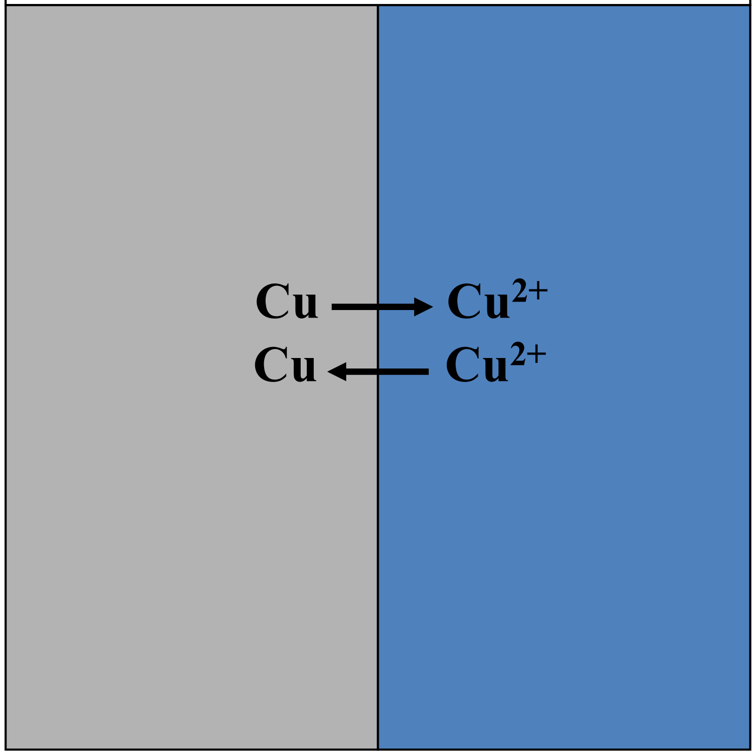


Impedance plot on each segment

Corrosion

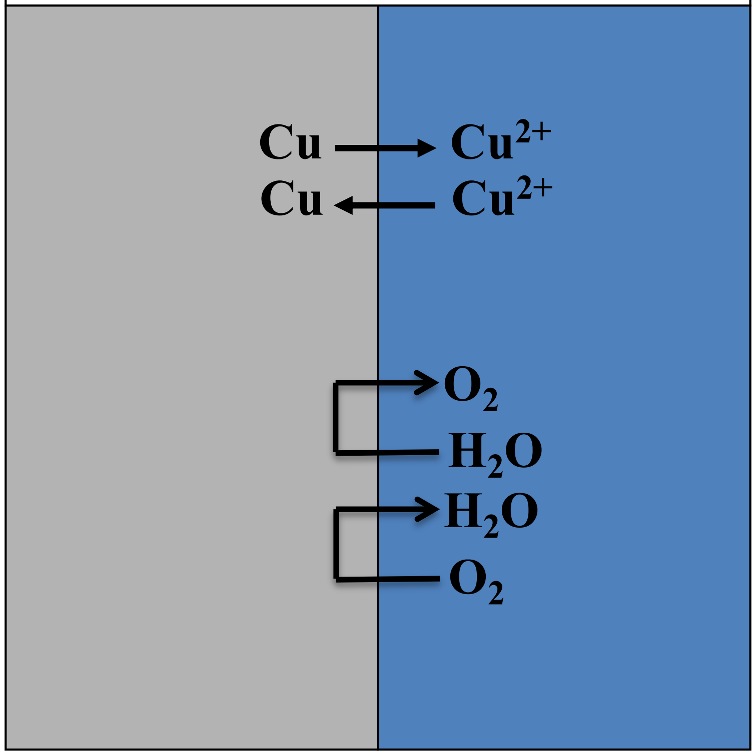
Mixed electrodes (='corrosion')

Simple electrode:
1 half cell reaction occurs
on the electrode



$Cu^{2+} + 2\ e = Cu$

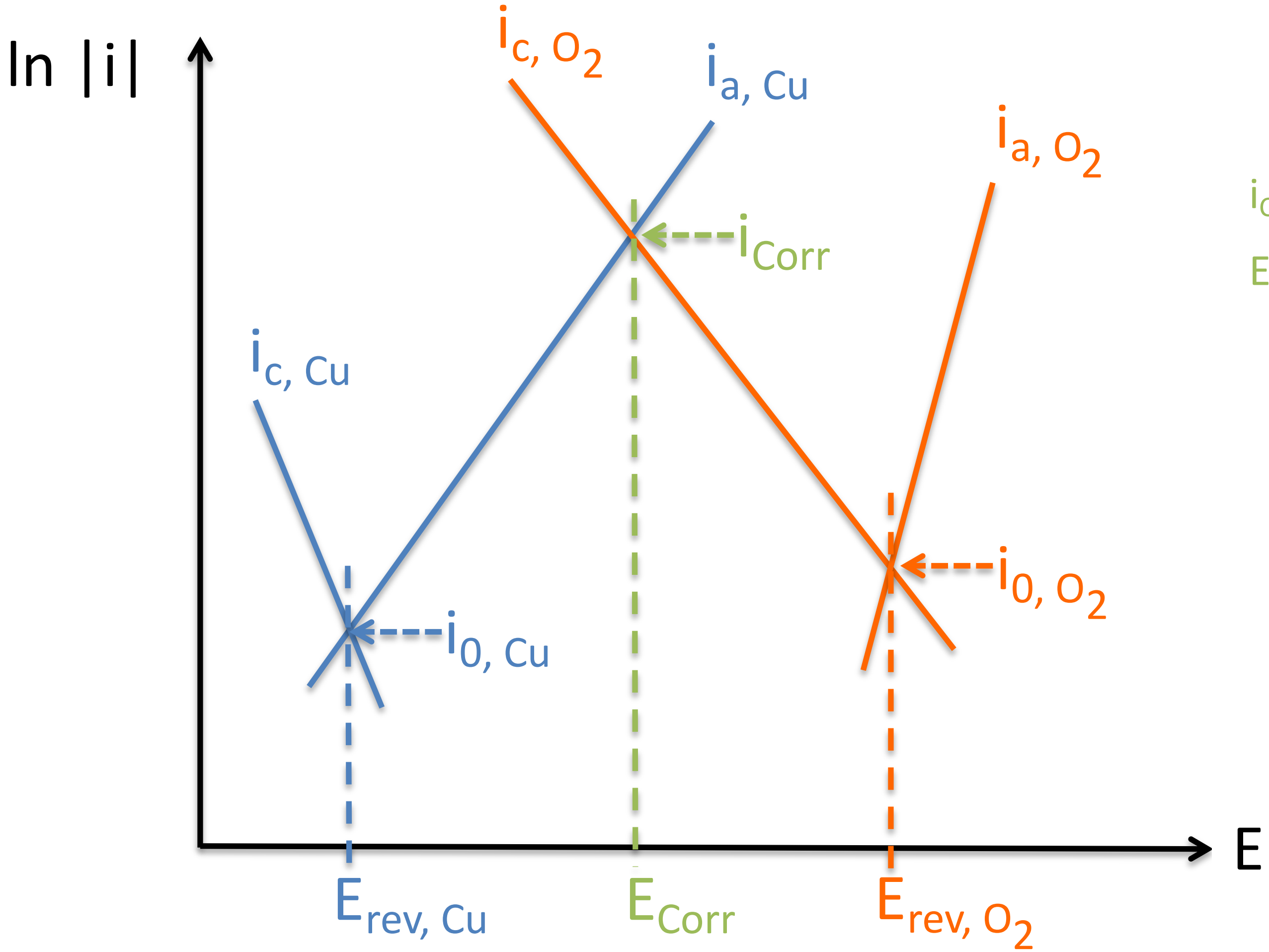
Mixed electrode:
2 or more half cell reactions
occur on the electrode



$Cu^{2+} + 2\ e = Cu$

$O_2 + 4\ H^+ + 4\ e = 2H_2O$

Evans diagram of mixed electrodes



i_{Corr}: corrosion current density

E_{corr}: corrosion potential

Corrosion current =
the anodic branch of one reaction overlaps with the cathodic branch of another, different reaction

Total and partial currents in mixed electrodes

$i = i_{a,Cu} + i_{c,Cu} + i_{a,O2} + i_{c,O2}$

At E_{corr} $\quad i \approx i_{a,Cu} + i_{c,O2} = 0$ $\quad$ (if $i_{c,Cu}$ and $i_{a,O2} \approx 0$)

$i_{corr} = i_{a,Cu} = - i_{c,O2}$

$i_{corr} = i_{a,Cu} = i_{0,Cu} \exp ((E_{corr}-E_{rev,Cu})/\beta_{a,Cu})$

$i_{corr} = - i_{c,O2} = -i_{0,O2} \exp ((E_{corr}-E_{rev,O2})/\beta_{c,O2})$

Butler-Volmer equation for a mixed electrode

$i_a = i_{corr} \exp(\xi / \beta_a)$ anodic current density

$i_c = - i_{corr} \exp(- \xi / \beta_c)$ cathodic current density

$i = i_a + i_c = i_{corr} \exp(\xi / \beta_a) - i_{corr} \exp(- \xi / \beta_c)$

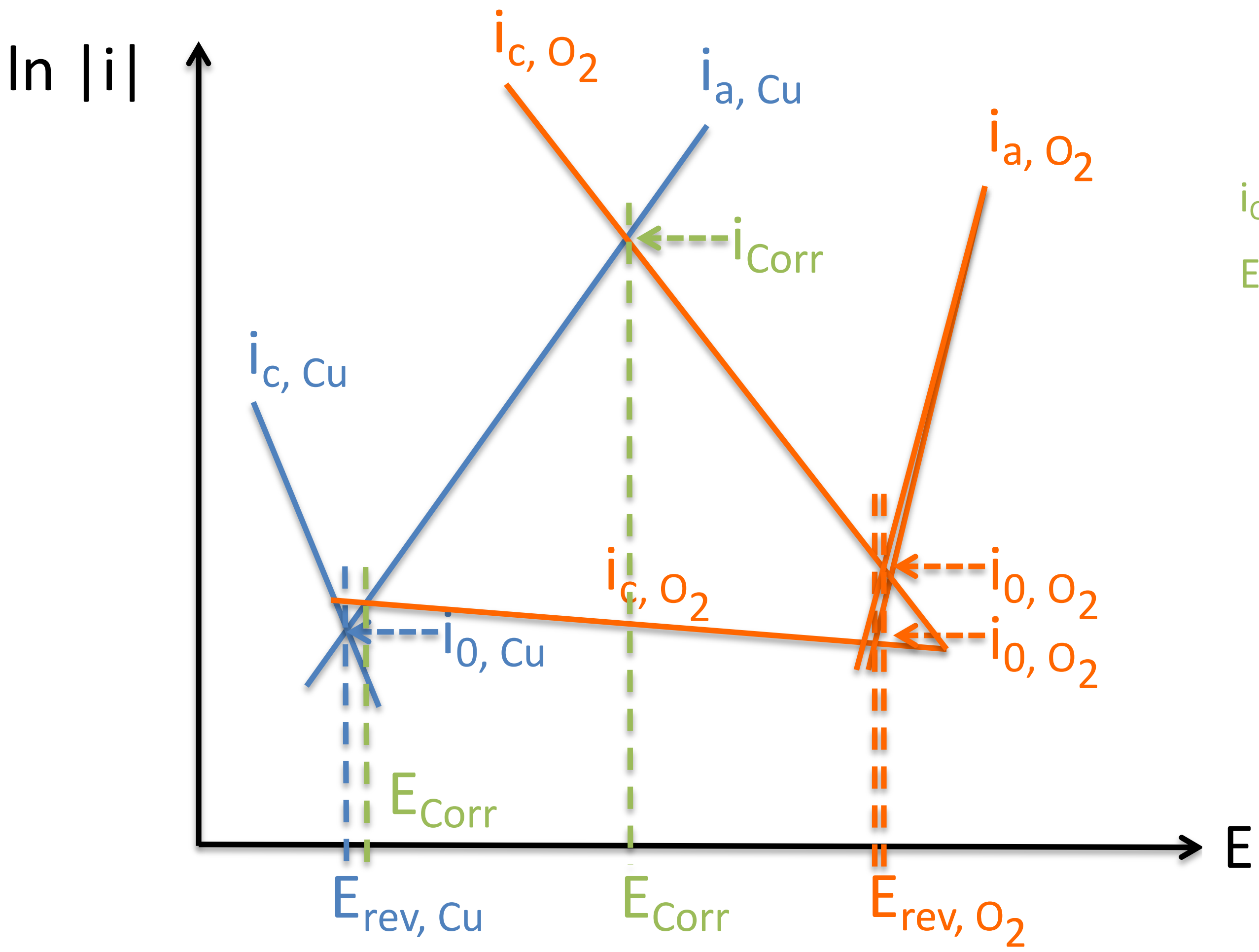
ξ : *polarisation* $= E - E_{corr}$

$\beta_a = RT / \alpha zF$

$\beta_c = RT / (1-\alpha') z F$

i_{corr} : *corrosion current density*

E_{corr} and i_{corr} depend on kinetics



i_{Corr}: corrosion current density

E_{corr}: corrosion potential