Electrochemical Methods

MCHV C5060

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Outline

- **Introduction**
- **From Potentiometry (equilibrium) to Polarography and Voltammetry (dynamics)**

  Reduction and Oxidation, Redox Potentials, Overpotential, Electrode system, Cells, Reversibility and Irreversibility)
- **Electrochemical Methods** (**potentiostatic techniques**)

  (**Voltammetry-CV**, **LSV**, **AC, NPV**, **DPV**, **SWV**, **Coulometry**)

  Fundamentals and Application Basic Equations, Double Layer, Overpotential
- **Hyphenated Methods** (**with electroanalysis**)

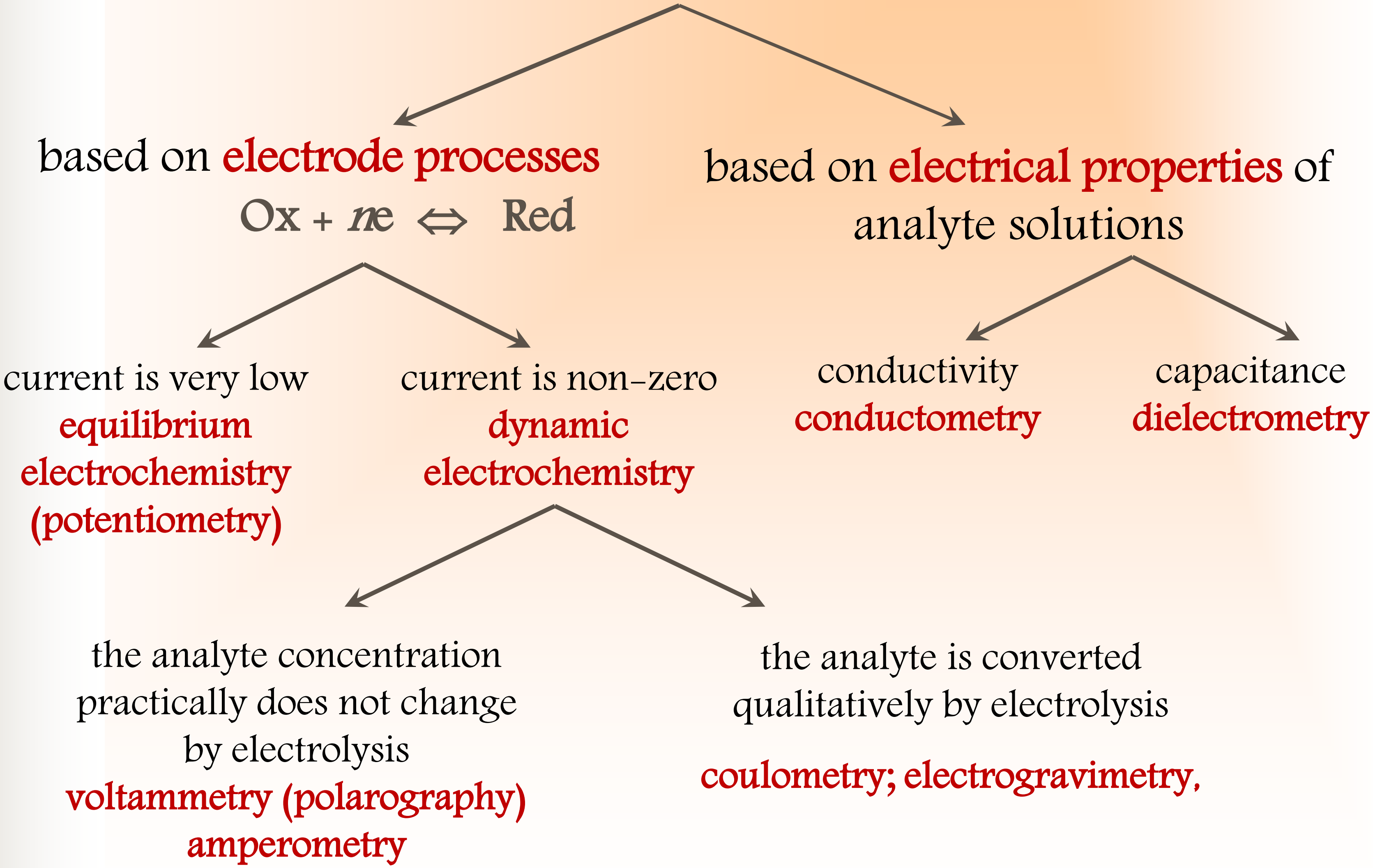
  (**EIS** - Electrochemical impedance spectra, **HPLC with ED**
  SE – Spectroelectrochemistry, **QCMB** - Quarz Crystal Microbalance, **AFM** – Atomic Force Microscopy)

Introduction

Books and Monograph Series

1. A. J. Bard, Electroanalytical Chemistry, Marcel Dekker, N.Y. , 1970
2. J. Dvořák, J. Koryta: Elektrochemie, Academia, Praha, 1975
3. J. Zýka et al.: Analytická příručka, 3rd ed. SNTL, Praha, 1979
4. J. Koryta: Iontově selektivní elektrody, Academia, Praha, 1984
5. J. Wang: Analytical Electrochemistry, VCH Publishers, N.Y., 1984, 1994
6. Ch.M.A.Brett, A.M.O.Brett: Electrochemistry, Oxford, 1993
7. P. Klouda: Moderní analytické metody, P.K., Ostrava, 1994
8. J.O´M. Bockris, A.K.M.Reddy: Modern Electrochemistry 1,2A,2B, Plenum Press, N.Y. 1998
9. K. Markušová: Elektrochemické metódy, PF UPJŠ, Košice, 2003
10. J. Barek, K. Štulík, F. Opekar: Elektroanalytická chemie, Uč. Texty UK, 2005
11. F. Scholtz: Electroanalytical methods, Spriner, Berlin/Heidelberg,2002.

Distribution of EAM



based on **electrode processes**

$\mathrm{Ox} + n\mathrm{e} \Leftrightarrow \mathrm{Red}$

current is very low
equilibrium electrochemistry (potentiometry)

current is non-zero
dynamic electrochemistry

the analyte concentration practically does not change by electrolysis
voltammetry (polarography)
amperometry

the analyte is converted qualitatively by electrolysis

coulometry; electrogravimetry,

based on **electrical properties** of analyte solutions

conductivity
conductometry

capacitance
dielectrometry

Introduction

Some Terms - Potentiometry

- Galvanic cell
- Electrolytic cell
- Reduction
- Oxidation
- Half Reactions
- Redox Couple
- Anode
- Cathode
- Standard Electrode Potential

$$E_{redox} = E^{0}_{redox} - \frac{RT}{zF} \ln Q$$

$$Ox + ze^{-} = Red$$

$$E_{redox} = E^{0}_{redox} + \frac{RT}{zF} \ln \frac{a_{Ox}}{a_{Red}}$$

E^{0}_{redox}

Nernst equation
equilibrium

equilibrium constant

$$\ln K = \frac{zFE^{0}_{redox}}{RT}$$

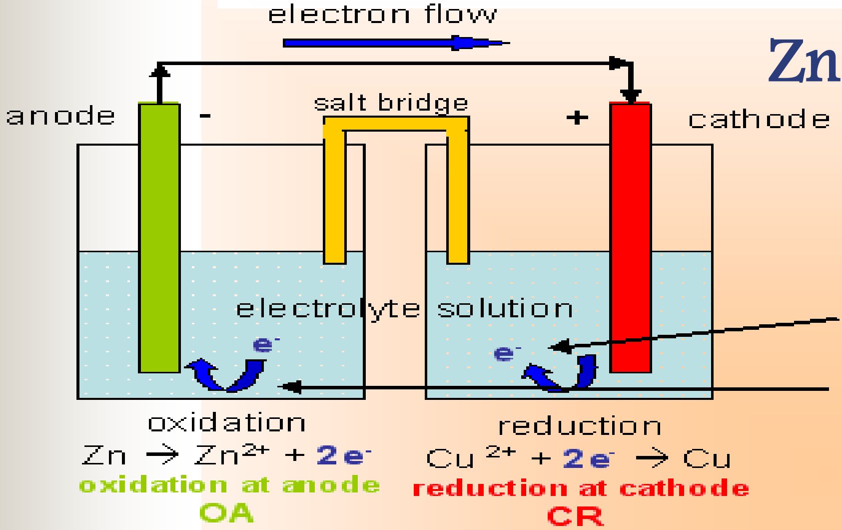
electrochemical potential; thermodynamic functions ($\Delta_r G$ $\Delta_r S$ $\Delta_r H$)
activity; activity coefficients, product of solubility, solubility

Ion selective electrodes, potentiometric titrations

Electrochemical cells

galvanic vs. electrolytic

ELECTROCHEMICAL CELLS



oxidation

$Zn \rightarrow Zn^{2+} + 2e^-$

oxidation at anode

OA

reduction

$Cu^{2+} + 2e^- \rightarrow Cu$

reduction at cathode

CR

$Zn(s)|ZnSO_4(aq)||CuSO_4(aq)|Cu(s)$

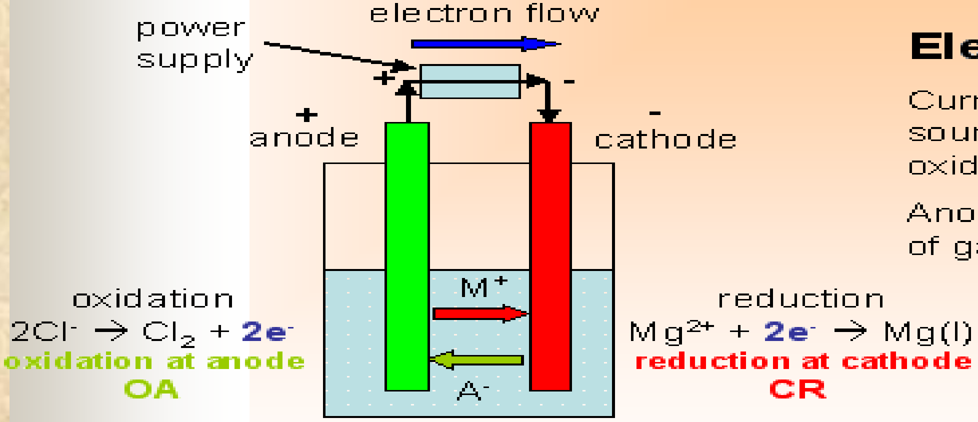
$E^o_{Zn2+/Zn} = -0.76V$ $E^o_{Cu2+/Cu} = +0.34V$

Galvanic Cell

Spontaneous rx. draw e^- into cell from cathode where reduction occurs and release them at anode where oxidation occurs

Example:

$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$



oxidation

$2Cl^- \rightarrow Cl_2 + 2e^-$

oxidation at anode

OA

reduction

$Mg^{2+} + 2e^- \rightarrow Mg(l)$

reduction at cathode

CR

Electrolytic Cell

Current supplied by external source drive nonspontaneous oxidation/reduction reaction.

Anode + and cathode -, opposite of galvanic cell

Example:

$2Cl^- + Mg^{2+} \rightarrow Cl_2 + Mg(l)$

Cations (M^+) move to cathode,
Anion (A^-) move to anodoe

After Atkins, General Chemistry, 2nd edition

Potentiometry – sample

Ag^{+} / Ag In aqueous solution of NH_3

$$Ag^{+} + e \rightleftarrows Ag \qquad Ag^{+} + 2NH_3 \rightleftarrows Ag(NH_3)_2^{+}$$

$$K_f = \frac{\left[Ag(NH_3)_2^{+}\right]}{\left[Ag^{+}\right]\left[NH_3\right]^2} = 6.10^8$$

equilibrium constant

Nernst equation $E_{Ag} = E^{0}_{Ag^{+}/Ag} + 0.059\,log\left[Ag^{+}\right]$

$$E_{Ag} = E^{0}_{Ag^{+}/Ag} + 0.059\,log\frac{1}{K_f\left[NH_3\right]^2} + 0.059\,log\left[Ag(NH_3)_2^{+}\right]$$

The potential shift due to the complex agent

The determination of:

- the constant complexity
- NH_3, organic amines, other ligands

(*concentration or activity*)

Redox potentials

… to understand and predict the electrochemistry of the chemical reactions.

- **Standard electrode potential** (E^o or $E^{\o}$)

  \- relative to a standard hydrogen electrode (**SHE**)with $E^o = 0V$ (a =1)

- **Normal redox potential** (E_{normal} or E_n)

  \- relative to a normal hydrogen electrode (NHE - potential of a Pt electrode in 1 M acid solution, not $a_{H^+}=1$ (1,18M)

- **Absolute redox potential** (E_{abs})

$$\boxed{E^{M}_{abs} = E^{M}_{SHE} + (4.44 \pm 0.02)\ V}$$

\- is the difference in electronic energy between a point inside the metal electrode (Fermi level) and a point outside the electrolyte (an electron at rest in a vacuum). The absolute electrode potential of SHE = 4.44±0.02 V at 25°C

- **Formal redox potential** ($E^{o\prime}$ or E^{f})

$$Ox + ze^- = Red$$

$$E = E^0 - \frac{0.05916}{z} log \frac{[Red][\gamma_{red}]}{[Ox][\gamma_{Ox}]} = \underbrace{E^0 - \frac{0.05916}{z} log \frac{[\gamma_{red}]}{[\gamma_{Ox}]}}_{E^{o\prime}} - \frac{0.05916}{z} log \frac{[Red]}{[Ox]}$$

the effect of pH and ionic strength

POLAROGRAPHY/ VOLTAMMETRY

Dynamic electrochemistry

- ***Linear Sweep Voltammetry (LSV)***
- ***Cyclic Voltammetry (CV)***
- ***Normal Pulse Polarography/Voltammetry(NPP/NPV)***
- ***Differential Pulse Polarography/Voltammetry(DPP/ DPV)***
- ***Square Wave Voltammetry (SWV)***
- ***Alternating Current (AC) Polarography /Voltammetry***
- *Elimination Polarography (EP)*
- *Elimination Voltammetry with Linear Scan(EVLS)*

Red-Ox in electrochemistry

negatively charged positively charged

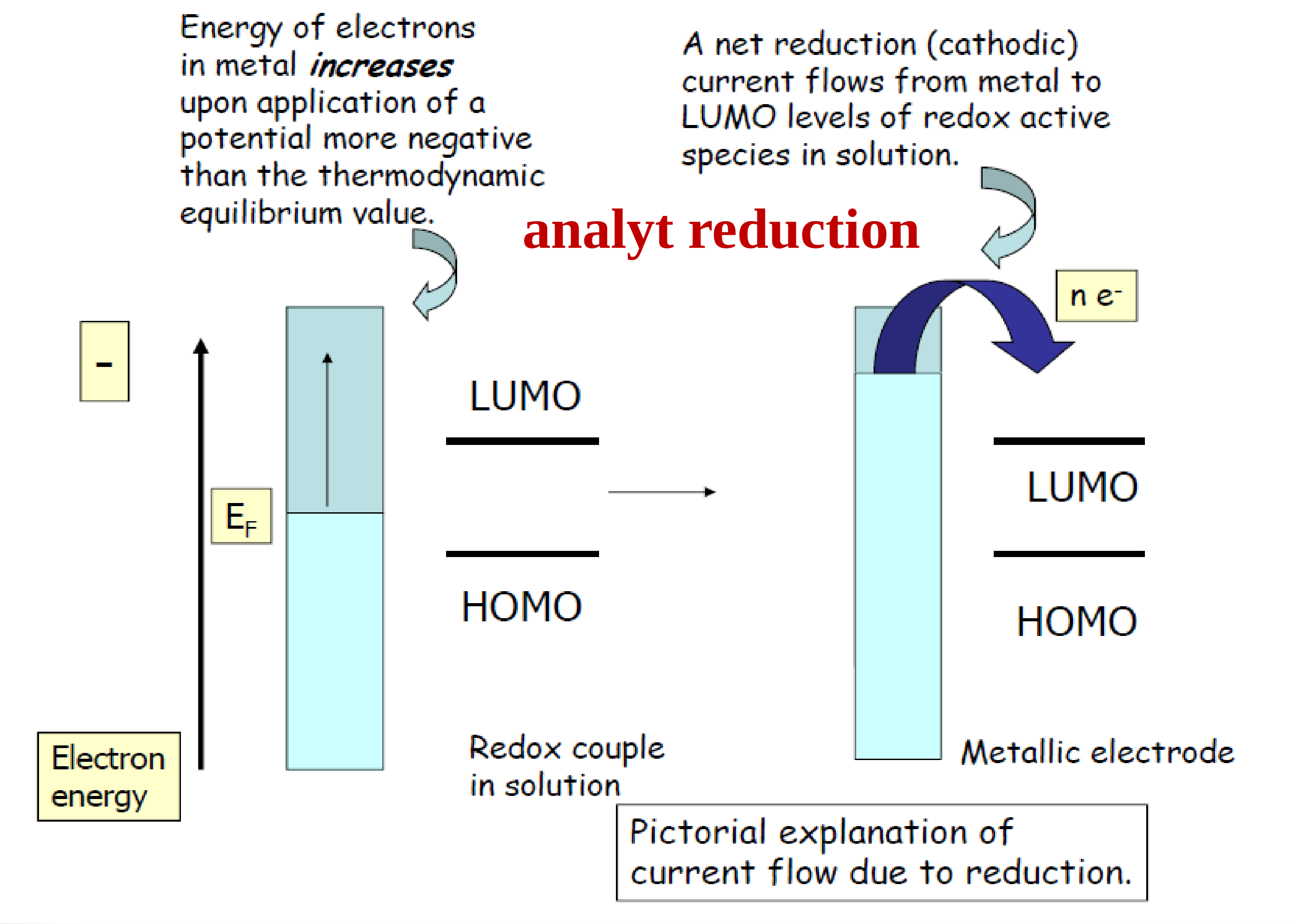
Red **electrode** **Ox**

- the same reaction as in the chemistry? (often an analogous mechanism)
  !!! reaction **in a solution** (homogeneous) X **on a electrode surface**(heterogeneous)
- **continuous selection of potentials** (selectivity in the generation of intermediates / products
- **continuous change of potential** (order of electron transfer)
- **acquisition of thermodynamic data (**potentials or energy, ox., red., E_{1ox} - E_{1red})
- **different rate of potential changes or their modulation in real time**
  reversibility, kinetics, precursor, parallel and subsequent reactions, mechanism

new dimension – a newest and most exciting part of electrochemistry

Electrode kinetics – dynamics in EAM

the electrode acts as an electron source and is termed a cathode



Energy of electrons in metal *increases* upon application of a potential more negative than the thermodynamic equilibrium value.

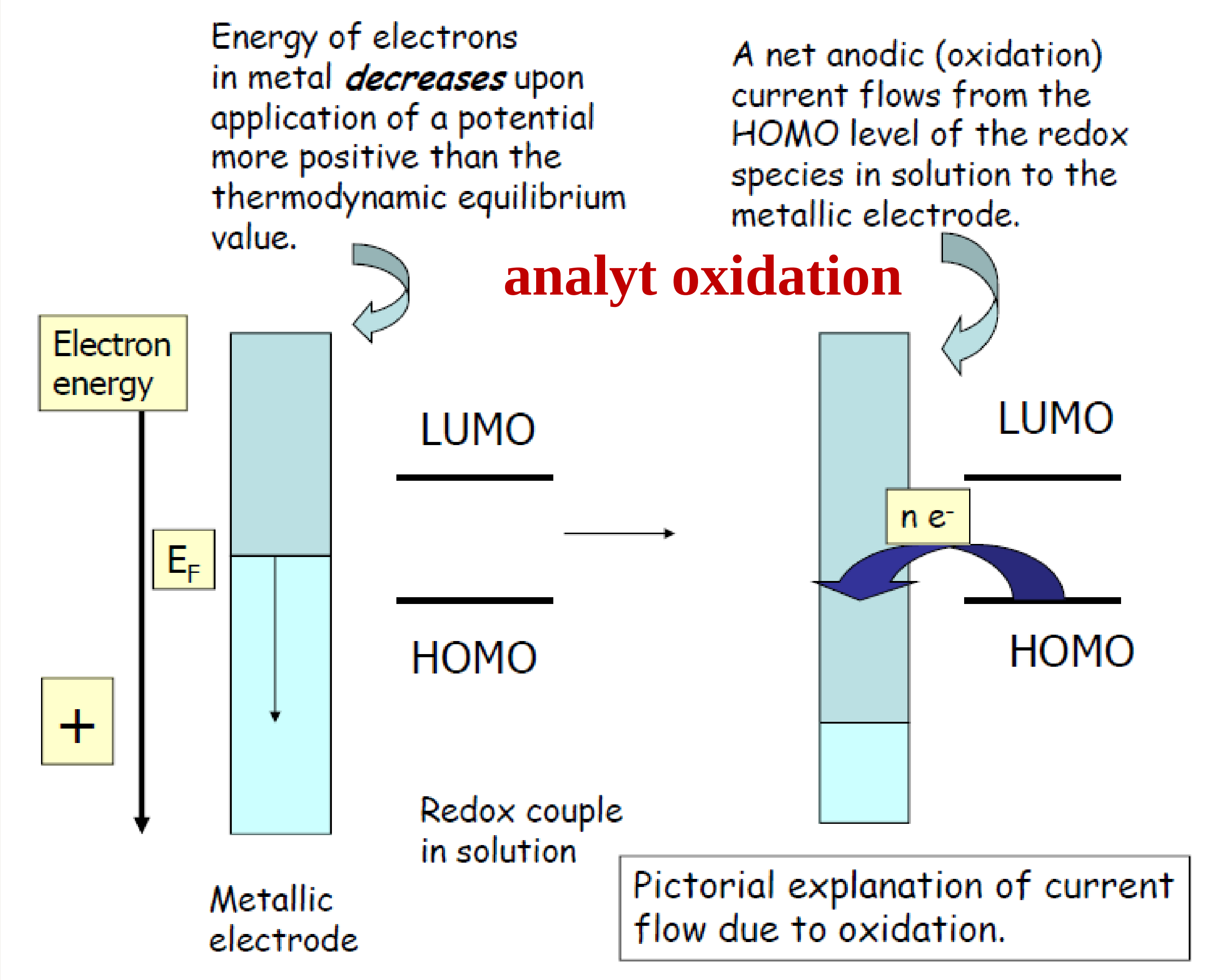
A net reduction (cathodic) current flows from metal to LUMO levels of redox active species in solution.

analyt reduction

Pictorial explanation of current flow due to reduction.

Electrode kinetics – dynamics in EAM

the electrode acts as an electron sink and is termed an anode



Energy of electrons in metal ***decreases*** upon application of a potential more positive than the thermodynamic equilibrium value.

A net anodic (oxidation) current flows from the HOMO level of the redox species in solution to the metallic electrode.

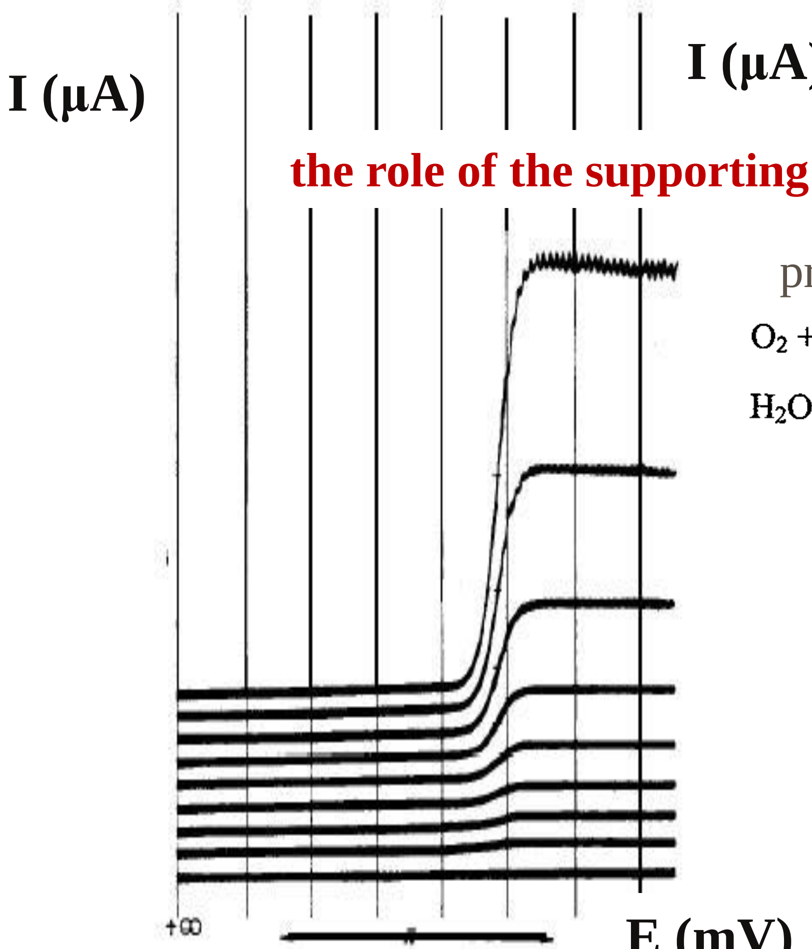
analyt oxidation

Pictorial explanation of current flow due to oxidation.

Polarography

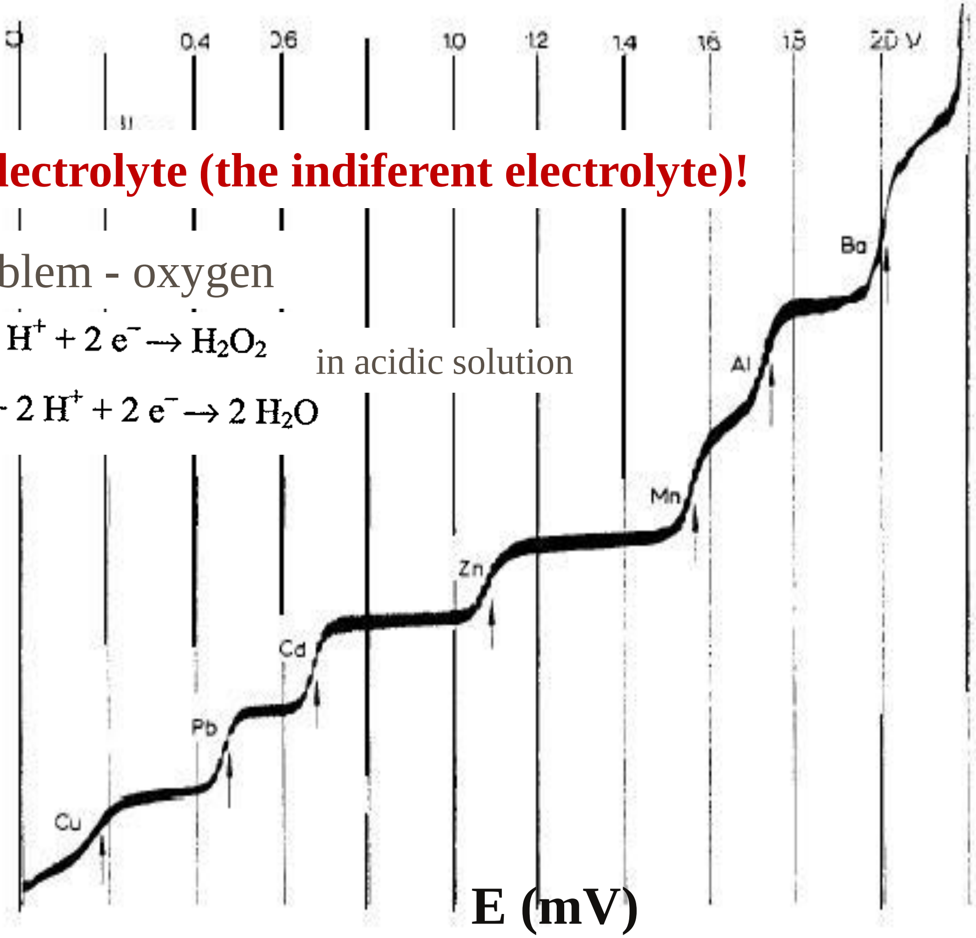
Historical polarograms

570 1959 J.HEYROVSKÝ



Constancy of the half-wave potential in solution of various concentratio
$CdCl_2$.

TRENDS OF POLAROGRAPHY 571



Polarographic spectrum showing seven cations in the solution.

the role of the supporting electrolyte (the indiferent electrolyte)!

problem - oxygen

$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2$

$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O$

in acidic solution

History

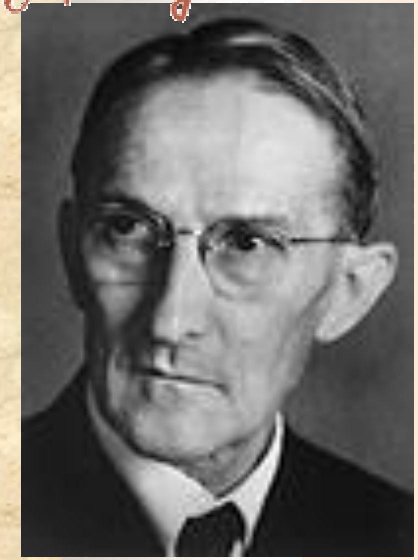
J. Heyrovský

Jaroslav Heyrovský

***The Nobel Prize in Chemistry** 1959*

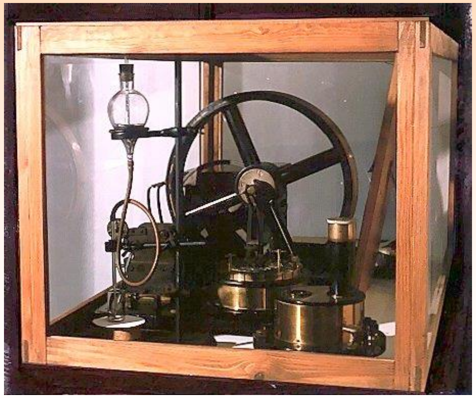
"for his discovery and development of the polarographic methods of analysis"

was an inventor of the polarographic method, **father of electroanalytical chemistry**. His contribution to electro-analytical chemistry can not be overestimated. All voltammetry methods used now in electroanalytical chemistry originate from polarography developed by him.



1890-1967

J. Heyrovský + M. Shikata (1924)



J. Heyrovský
Institute of Physical Chemistry
Academy of Sciences of the Czech Republic

Instrumentation, common techniques

Two-electrode set

WE – working electrode

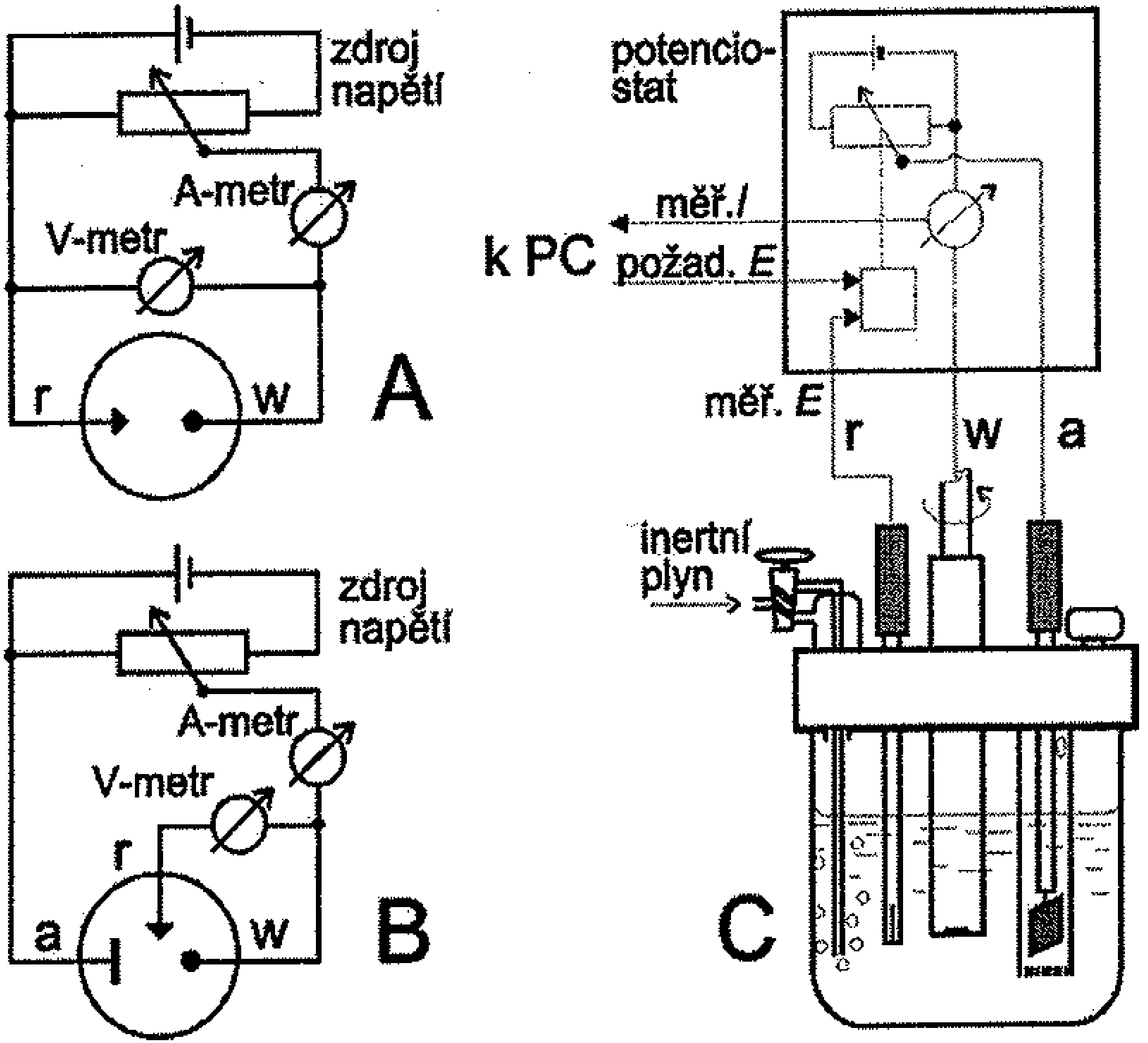
RE – reference electrode
(an electrode of the II. type!)

Three-electrode set

WE – working electrode

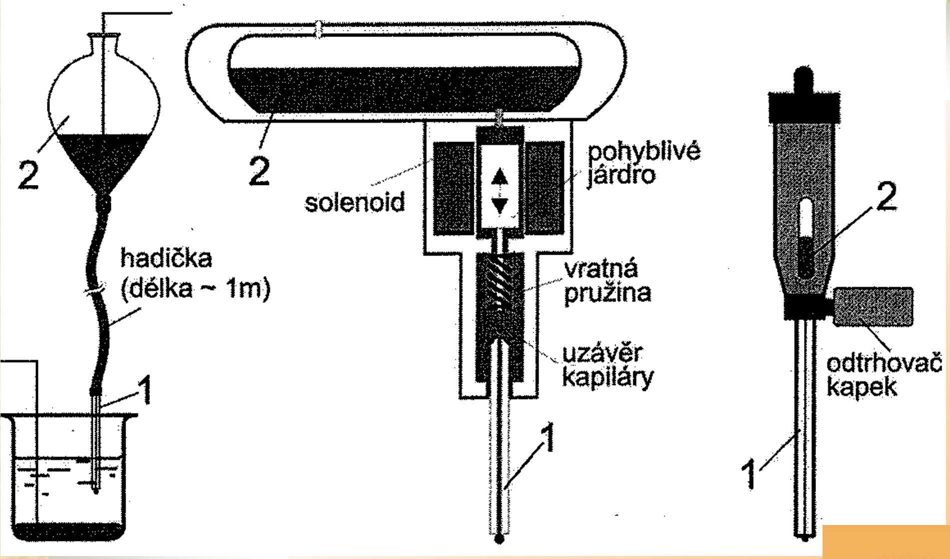
CE – counter electrode
(auxiliary)

RE – reference electrode
(an electrode of the II. type!)

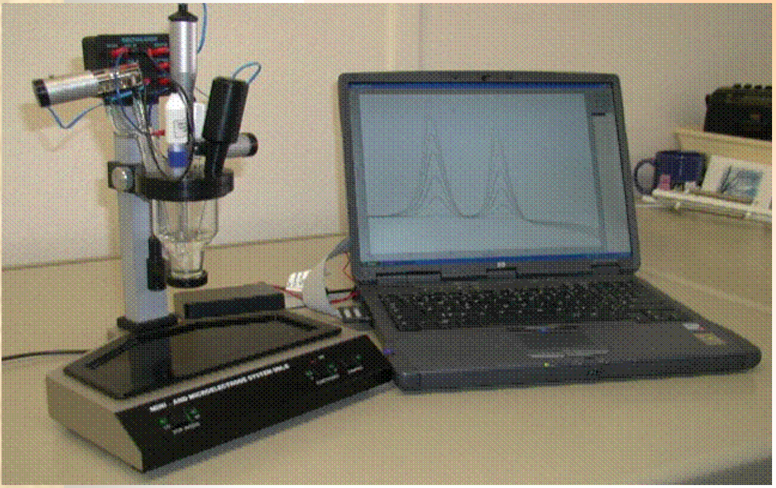


Advantage of three-electrode set !

Instrumentation, common techniques

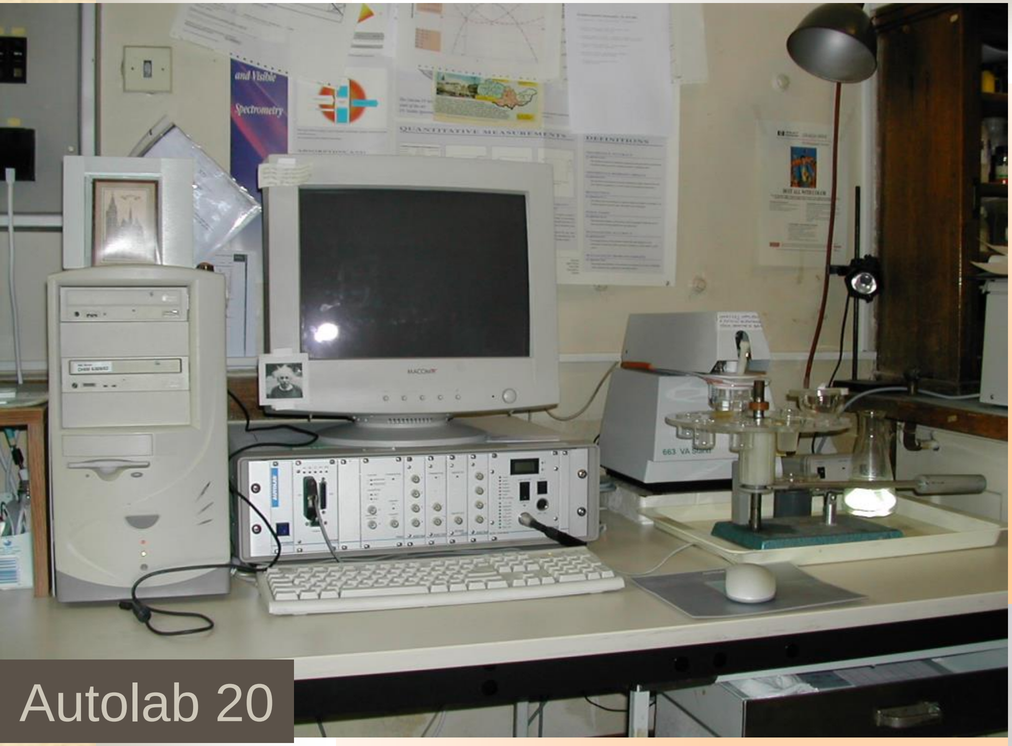


EcoTribo Polarograph
Polaro Sensors - Eco Trend
Prague, Czech Republic



Instrumentation, common techniques

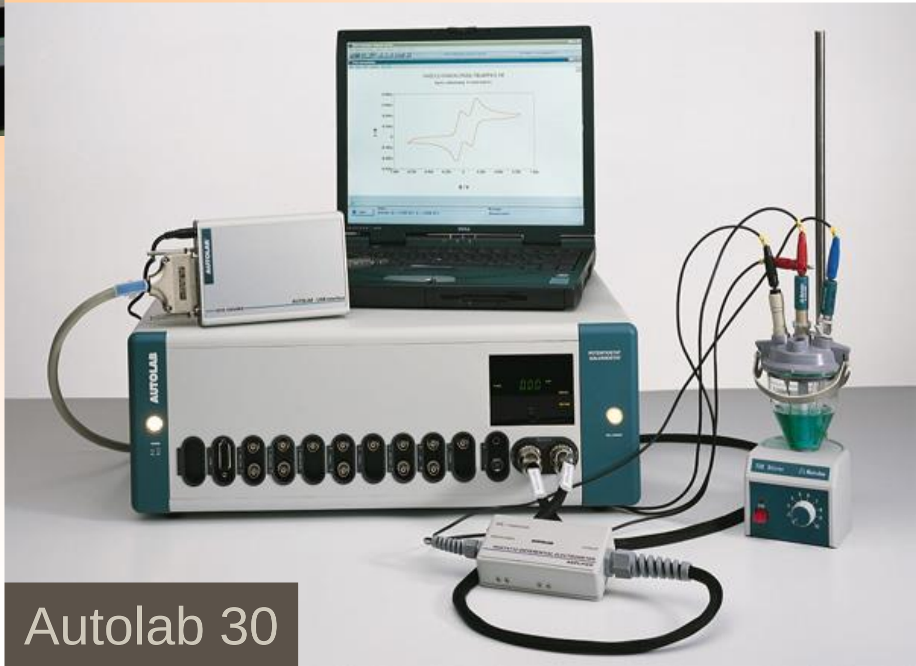
Electrochemical
analyzer
AUTOLAB



Autolab 20

Autolab
Ecochemie
Utrecht
The Netherlands

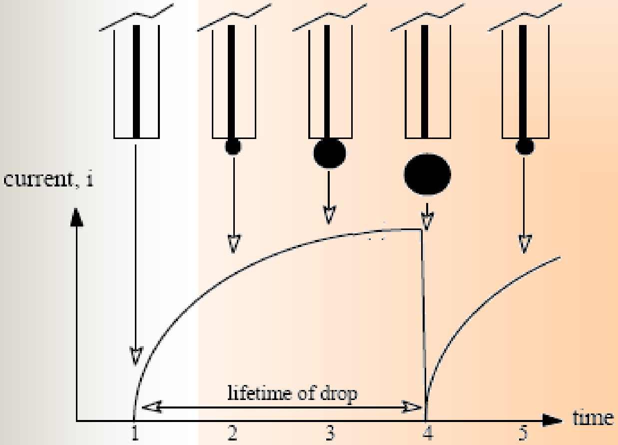
VA-Stand 663
Metrohm
Zurich
Switzerland



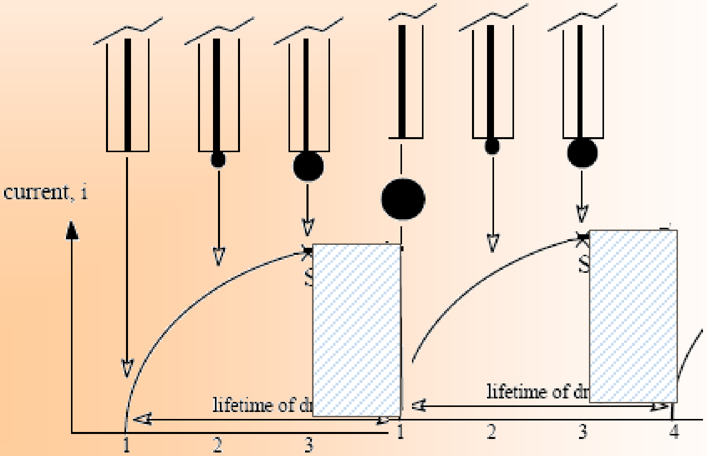
Autolab 30

Mercury electrode

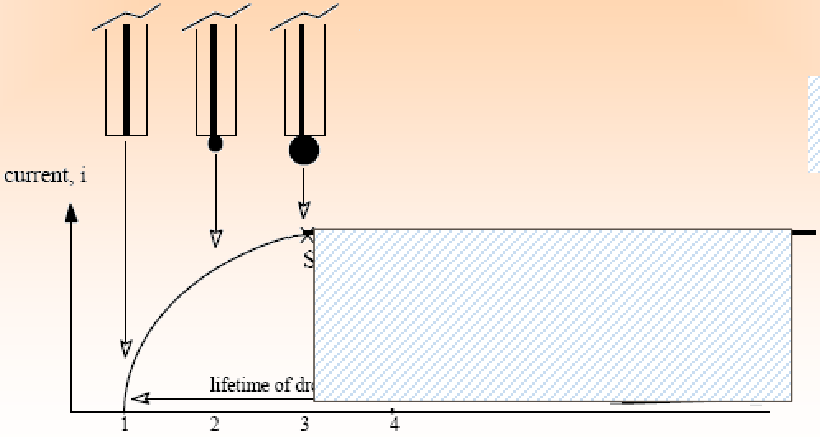
Dropping Mercury Electrode - **DME**



Static Mercury Drop Electrode - **SMDE**



Hanging Mercury Drop Electrode - **HMDE**



▨ sampling window

Mercury electrodes (DME, SMDE, HMDE)

Dropping Mercury Electrode - DME

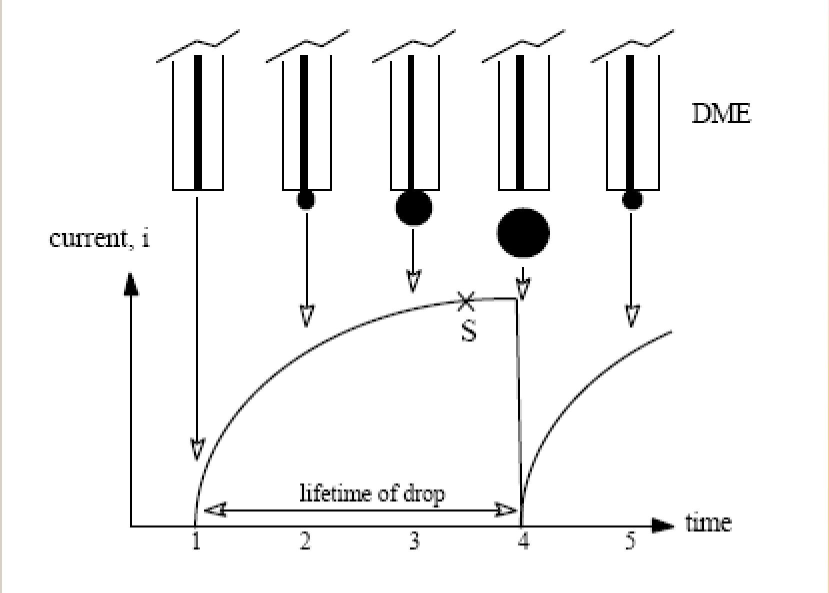
Static Mercury Drop Electrode - SMDE

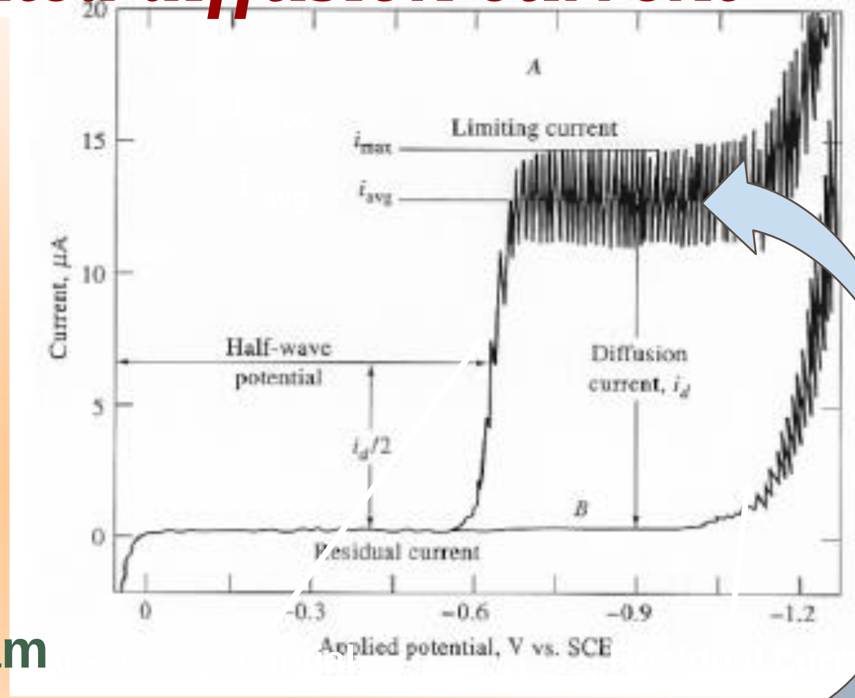
Hanging Mercury Drop Electrode - HMDE

- its liquid state at ambient temperature, renewable surface
- high purity material availability
- high conductivity
- high surface tension
- high overvoltage potential for hydrogen
- hydrophobic surface
- Hg(I) ions form sparingly soluble salts with many anions
- inertness chemically at low potentials (because of its)
- formation of amalgams with numerous metals (stripping)
- microelectrodes (Hg drop diameter smaller than a millimeter)
- reduction and oxidation of many simple and complex ions speciation
  Ce(IV) + Ce(III), Cr(III)+Cr(II),Cr(IV)+Cr(III), Eu(III)+Eu(II),Fe(III)+Fe(II),Mo(VI)+Mo(V), Sn(IV)+Sn(II),Ti(IV)+Ti(III)…..
- reduction and oxidation of numerous organic substances mechanism
  azo, carbonyl, sulphide nitro, quinone, heteroaromatic compounds

Direct Current (DC) polarography

Half-wave potential, limited diffusion current





$M^{n+} + ne^{-} + Hg = M(Hg)$ amalgam

a) ½ wave potential ($E_{½}$) characteristic of M^{n+} (E)
b) height of either average current maxima (i_{avg})
or top current max (i_{max}) is ~ analyte concentration
c) **i_{max}** is governed by:
rate of growth of DME > drop time (**t**, sec)
rate of mercury flow (**m**, mg/s)
diffusion coefficient of analyte (**D**, cm^2/s)
number of electrons in process (***z***)
analyte concentration (**c**, mol/ml)

Ilkovič equations

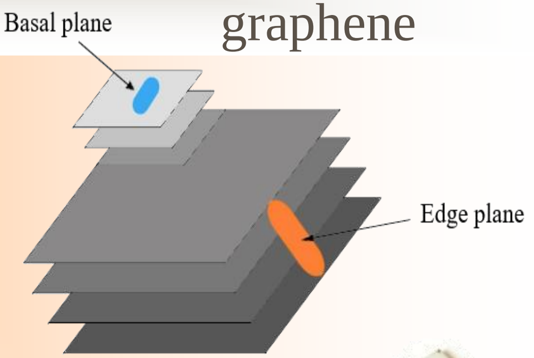
$$(i_d)_{max} = 0.706\, z\, D^{1/2} m^{2/3} t^{1/6} c$$
$$(i_d)_{avg} = 0.607\, z\, D^{1/2} m^{2/3} t^{1/6} c$$

Dionýz Ilkovič
1907 -1980 Slovensko

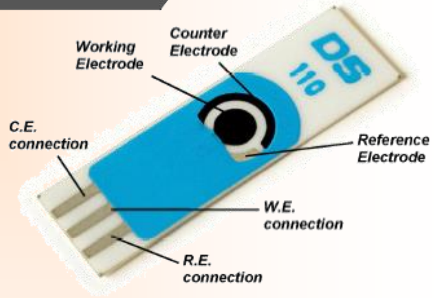
Electrode materials

- **Carbon electrodes**

graphene



- **graphite of spectral quality**
- **glassy carbon (<u>GC</u>) or vitreous carbon (VC)**
- **graphite powder with liquid or solid binders**
- **carbon paste electrode**
- **carbon fibers, highly oriented pyrolytic graphite – HOPG** (basal hexagonal and edge one, at the edge plane the electrode processes are usually much faster)
- **paraffin impreganted graphite electrode (PIGE)**



- **Optically transparent electrodes (spectroelectrochemistry)**

can be made by evaporating 10-100nm thick layers of Pt, Au, SnO_2, TiO_2, Ag, Cu, Hg, C on glass or quartz substrates, grids

- metal, metal oxide, various forms of oligomers, polymers

Pt, Au Ag (Rh, Pd, Ge, Ga, Pb)

- WE has to be tested before an analyte is added
- oligomers and polymers can spoil the electrode surface (!!!)

Electrode materials

- **Chemically modified electrodes**

it is difficult to give a definition of ChME

preliminary step or in situ

modified by:

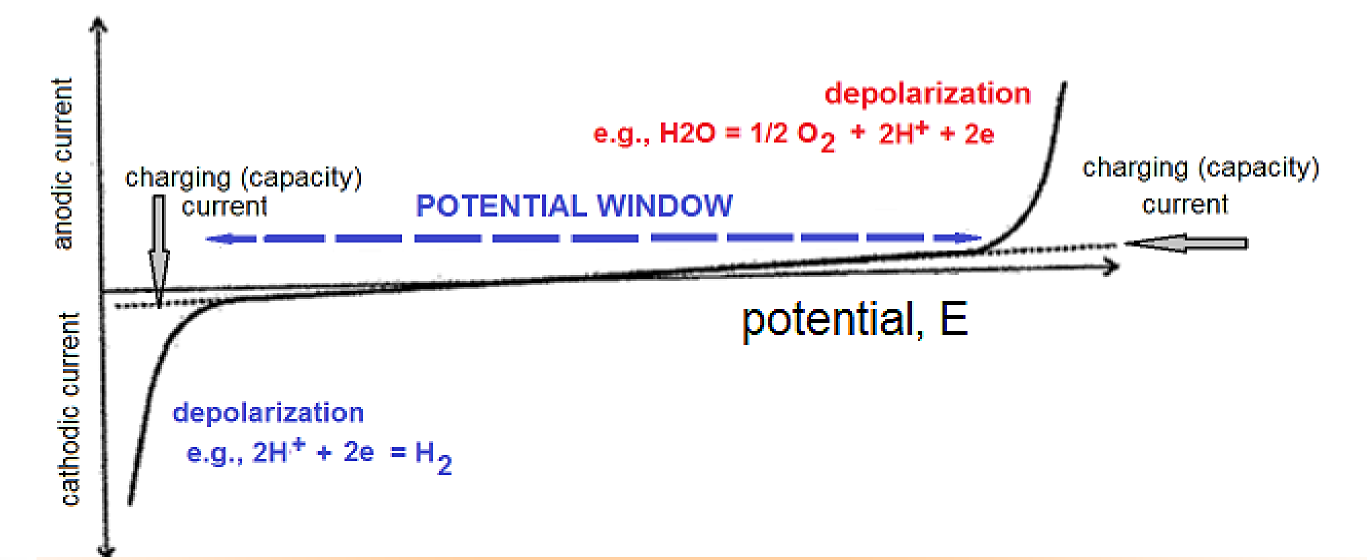
- **adsorption** (quinhydron, trioctylphosphine oxide, PAA oxime on GC)
- **chemical reaction** (substituted silanes, metal porphyrins on CE)
- **formation of polymer film** (Nafion containing dicyclohexyl-18-crown-6ether, polypyrrole-N-carbodithionate)
- **preconcentration** of analytes by complex-formation reactions

  ion exchange or ion extraction

  adsorptive accumulation (AdTS technique)
- **electrocatalysis** – attached the ET mediators which accelerate electrode reactions. The catalyst is regenerated by the fast and reversible electrode reaction, it is better to incorporate catalyst into a polymer or copolymer film.

Potential window

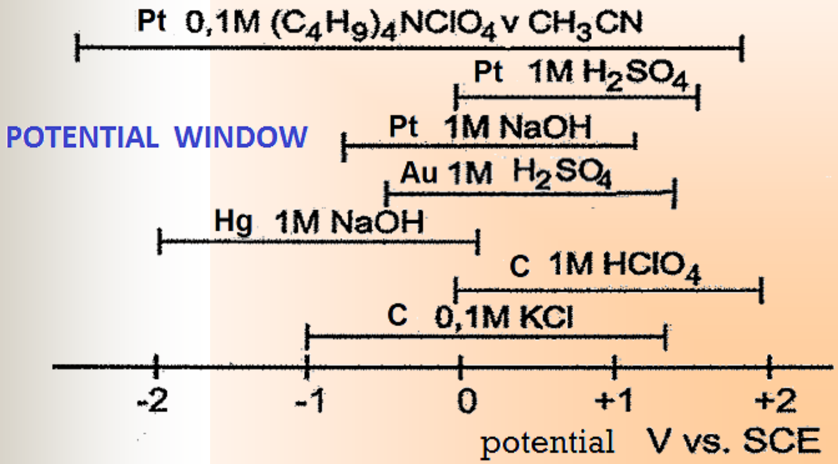
Instrumentation, common techniques

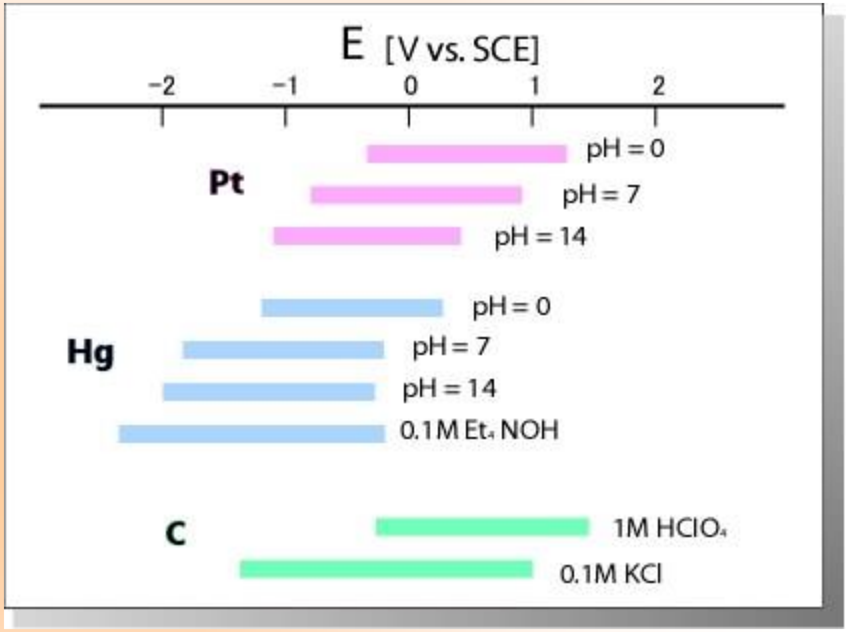


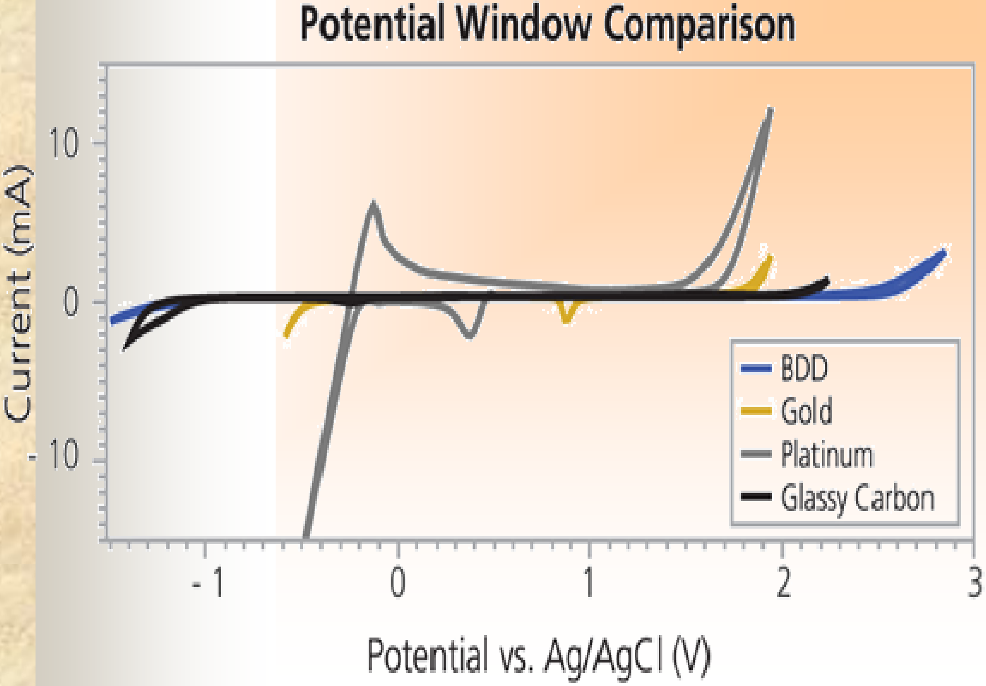
solution	**cathodic part**	**anodic part**
aqueous	reduction of H^+ (pH dependence)	oxidation of water oxidation of the electrode material ($Hg = Hg^{2+} + 2e^-$)
non-aqueous	reduction of cations of electrolytes (e.g., $-R_4N^+$, Li^+)	oxidation of electrode material oxidation of trace amont of water oxidation of supporting electrolyte components

Potential window

for different electrodes and supporting electrolyte






Potential Window Comparison

Platinum – Pt

Carbon – C

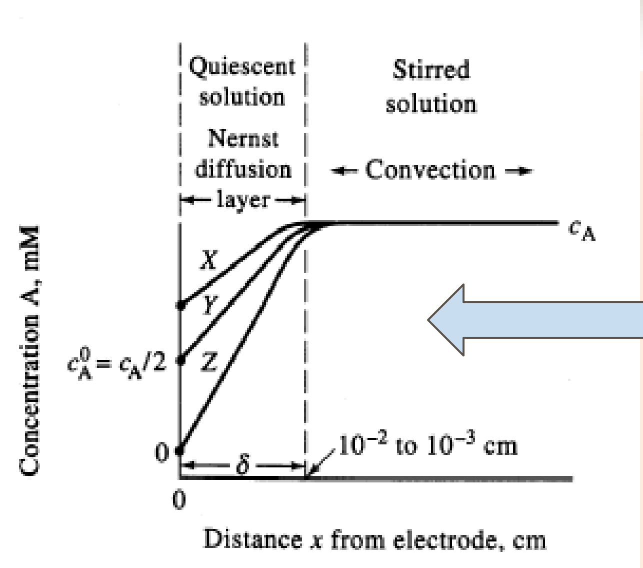
Gold - Au

Diamond - BDDE

Direct Current (DC) polarography

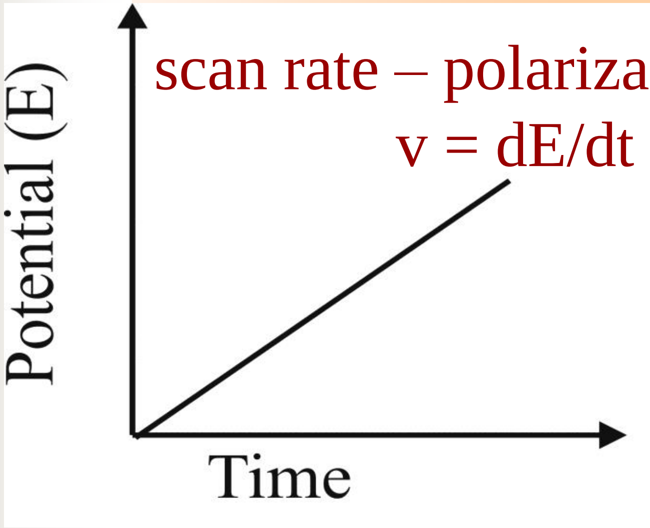
Apply

Potential
E << Eº



Diffusion

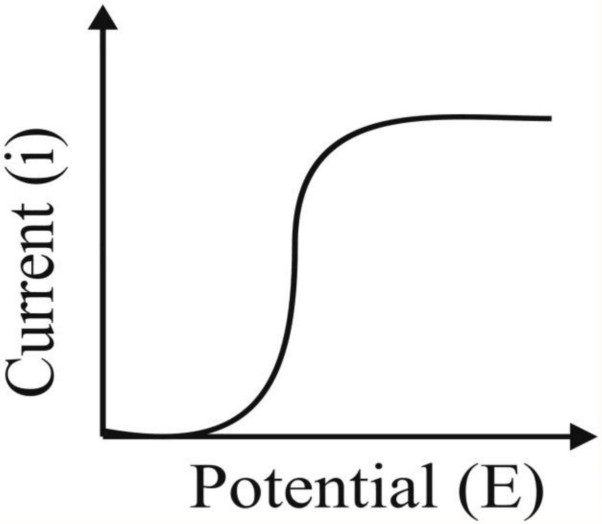
Apply Linear Potential with Time



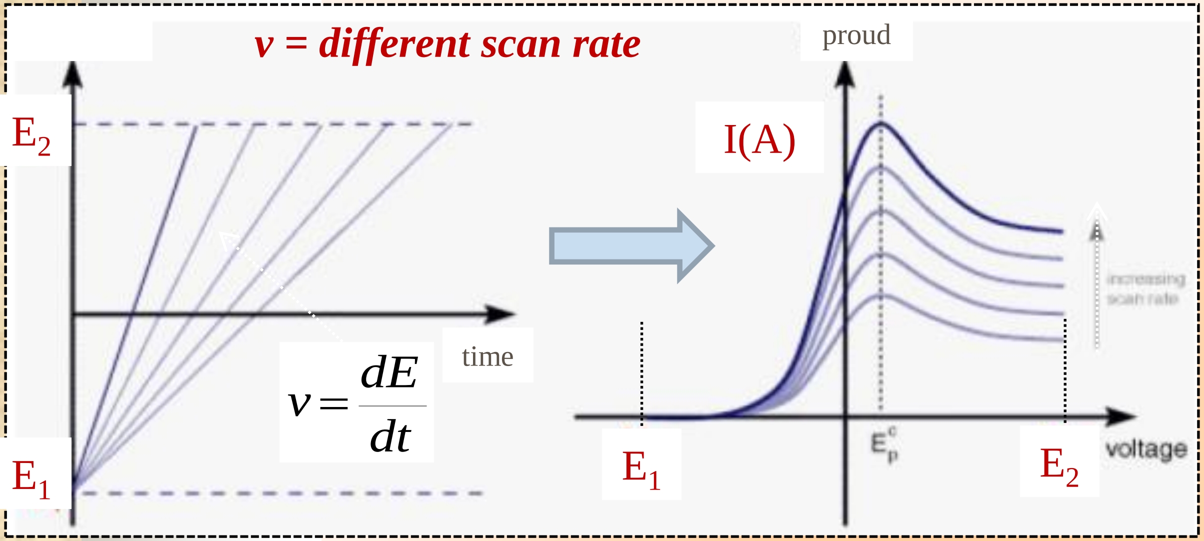
scan rate – polarization rate

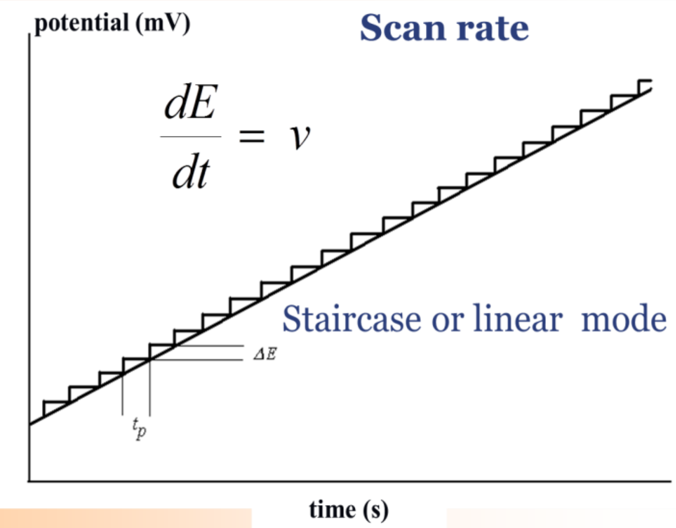
$v = dE/dt$

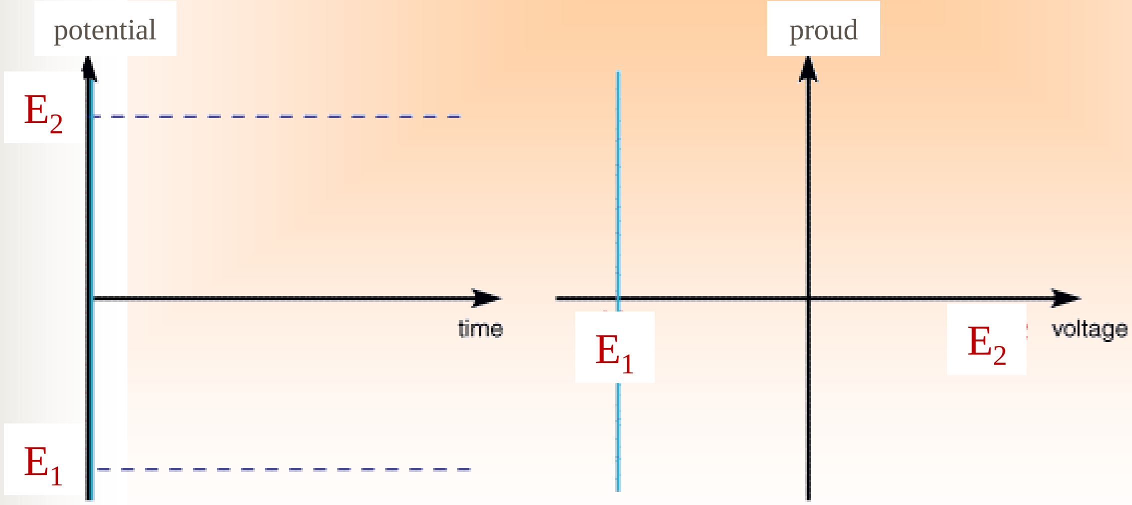
Observed Current Changes with Applied Potential



Linear sweep voltammetry (LSV)







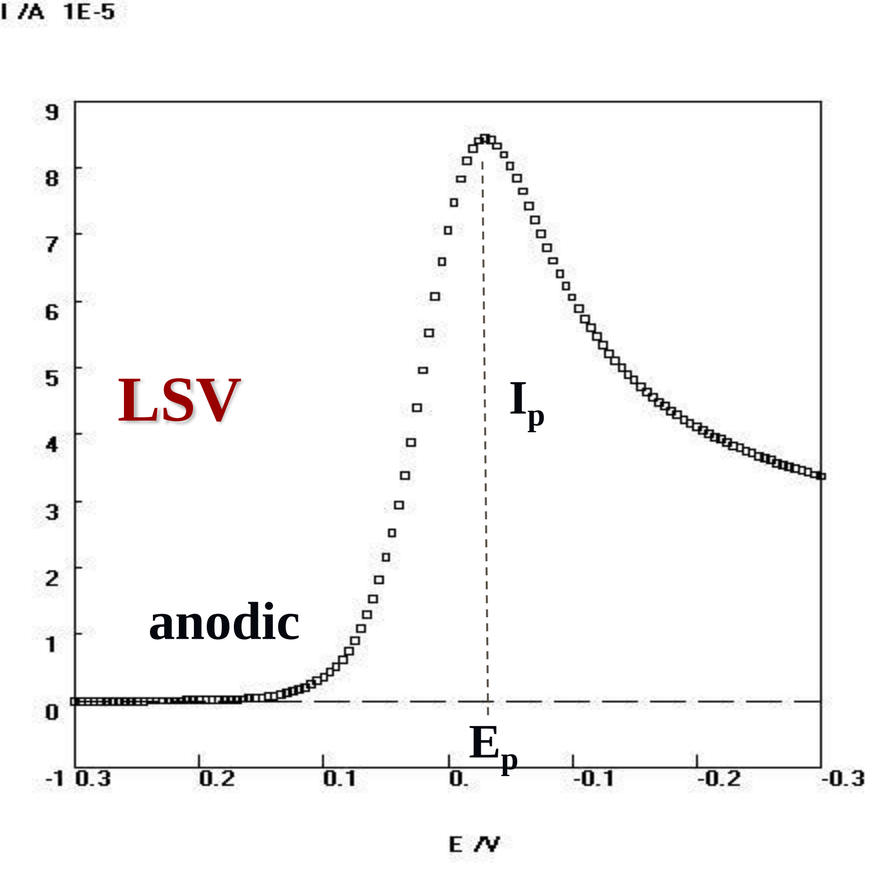
Oxidation

Electron Transfer (ET)

Reduction

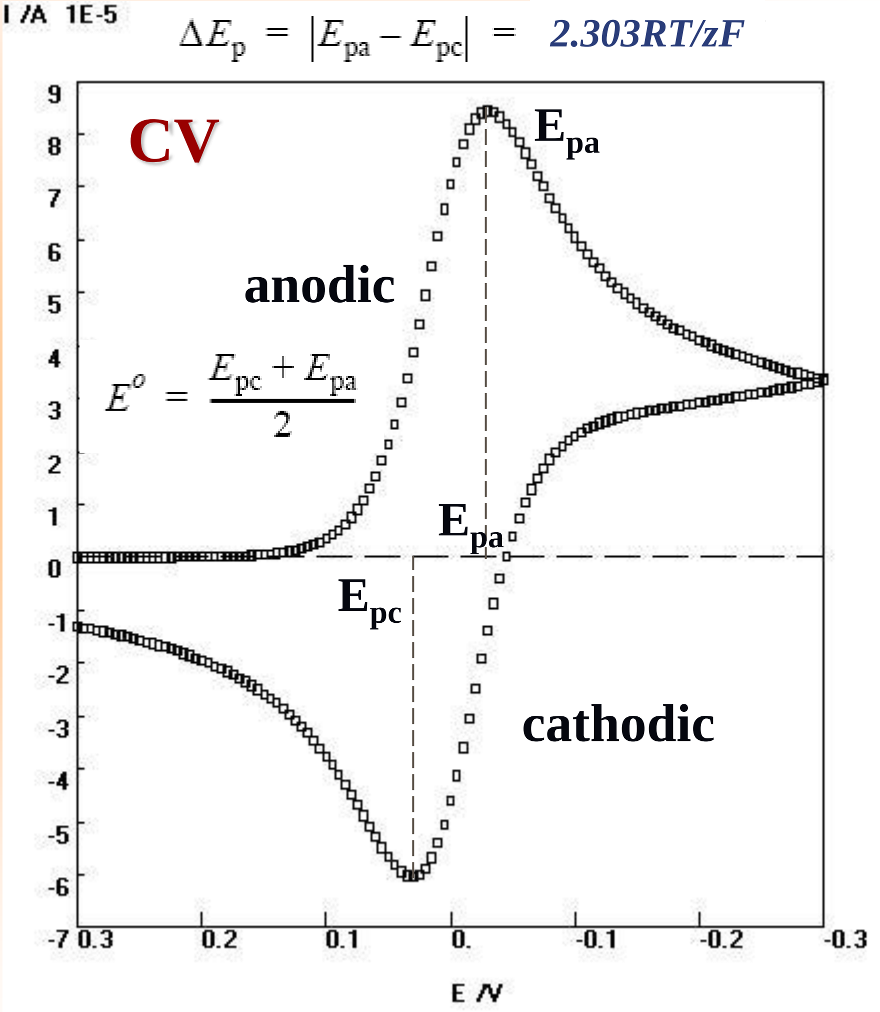
Voltammetry

Linear sweep (LSV)



Cyclic (CV)

$$\Delta E_p = |E_{pa} - E_{pc}| = 2.303RT/zF$$



$$E^o = \frac{E_{pc} + E_{pa}}{2}$$

- **Randles-Sevcik equations**

$$I_p = const.z^{2/3} A D^{1/2} c_{bulk} v^{1/2}$$ → diffusion control

const. – according to the dimension of parameters, including also F, D – the diffusion coeficient, A - the electrode surface

Cyclic and linear sweep voltammetry

- **heterogenous kinetics ($\Delta G^{\#}$ ~activation in electron transfer ~ Arrhenius ~ exp. function)**
- **I-E curves (exp. dependence)**

activation overpotential

$\eta = E_{polarization} - E_{equilibrium}$

$$j = j_0 \left\{ exp\left[\frac{(1-\alpha)zF\eta}{RT}\right] - exp\left[-\frac{\alpha zF\eta}{RT}\right]\right\}$$

Butler- Volmer equation for electrode process,
where rds is charge transfer

j - current density , j_0 - exchange current density, α - charge transfer coefficient

diffusion overpotential

$$J = -D\frac{dc_{electrode}}{dx}$$

- **I-E curves under both overpotential**
- **fast ET~ Nernst equation**

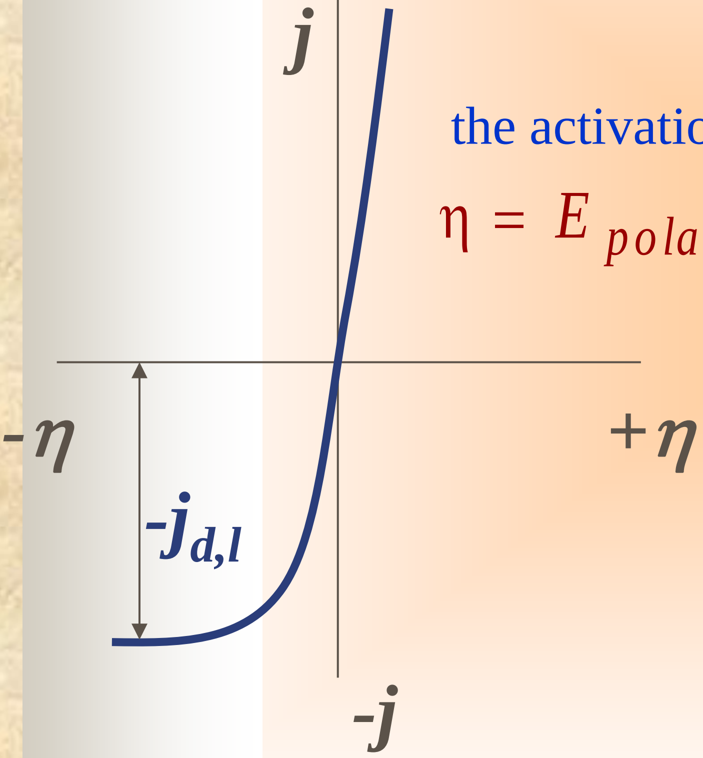
J- flux of matter, D -diffusion coefficient

Direct Current (DC) polarography

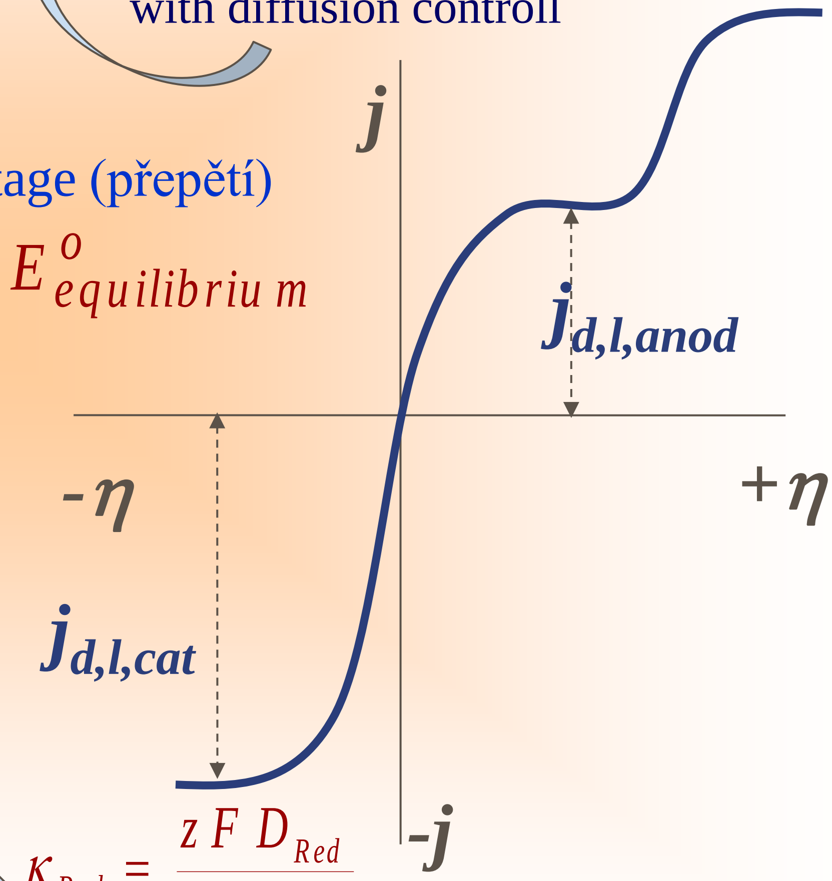
$$E = E_c^o + \frac{RT}{zF}\ln\frac{\kappa_{Red}}{\kappa_{Ox}} + \frac{RT}{zF}\ln\frac{j_{dl} - j}{j}$$

$$\kappa_{Ox} = \frac{zFD_{Ox}}{\delta_{Ox}}$$

without diffusion controll



with diffusion controll



the activation overvoltage (přepětí)

$$\eta = E_{polarization} - E^{o}_{equilibrium}$$

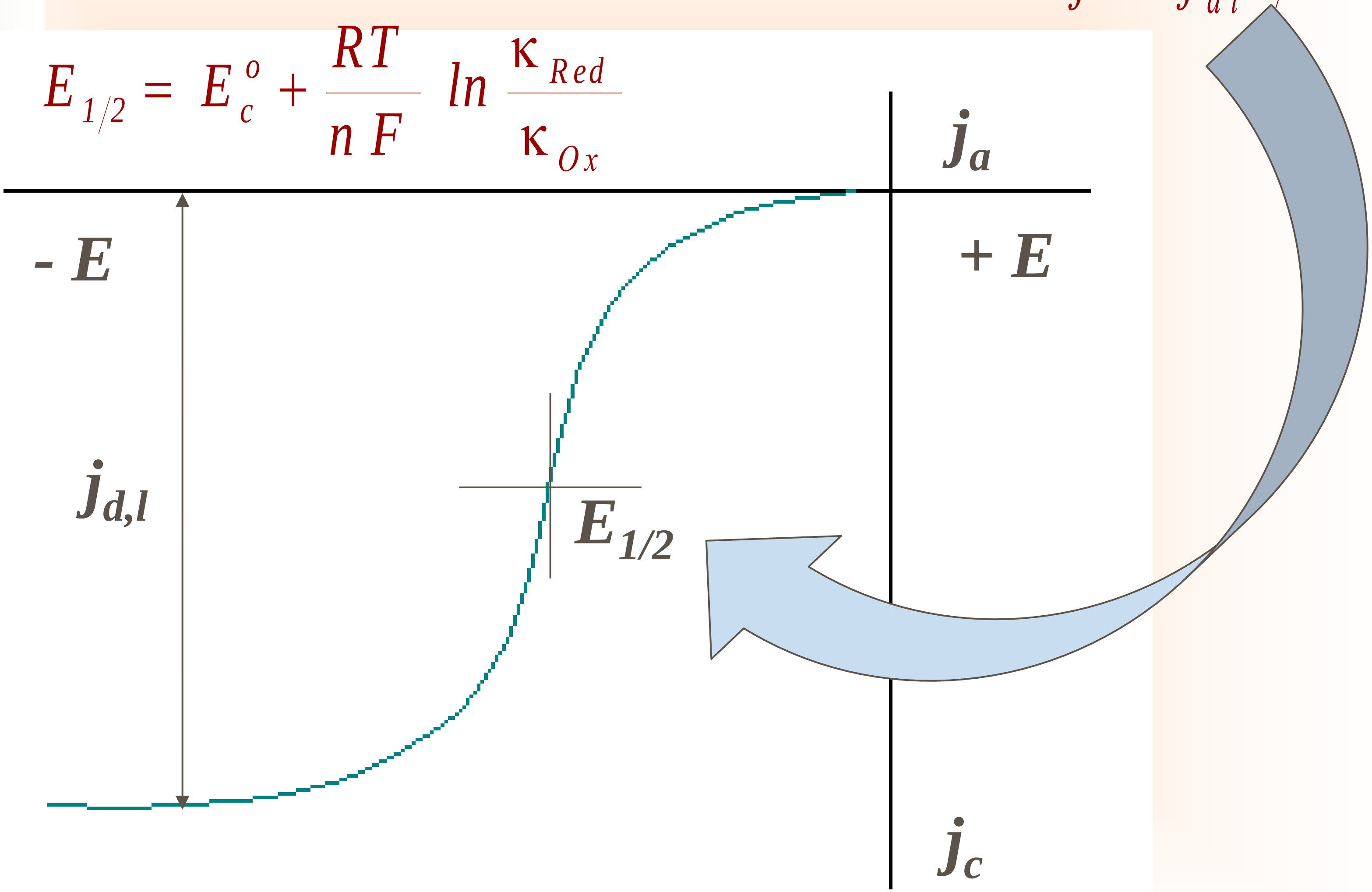
the concentration overvoltage → limit currents → $\kappa_{Red} = \frac{zFD_{Red}}{\delta_{Red}}$

Polarization curves for diffusion controlled processes

Direct Current (DC) polarography

$$j = j_{dl}/2$$

$$E_{1/2} = E_c^o + \frac{RT}{nF} \ln \frac{\kappa_{Red}}{\kappa_{Ox}}$$



Diffusion overpotential – polarography/voltammetry

Voltammetry

General Uses of Voltammetric Techniques

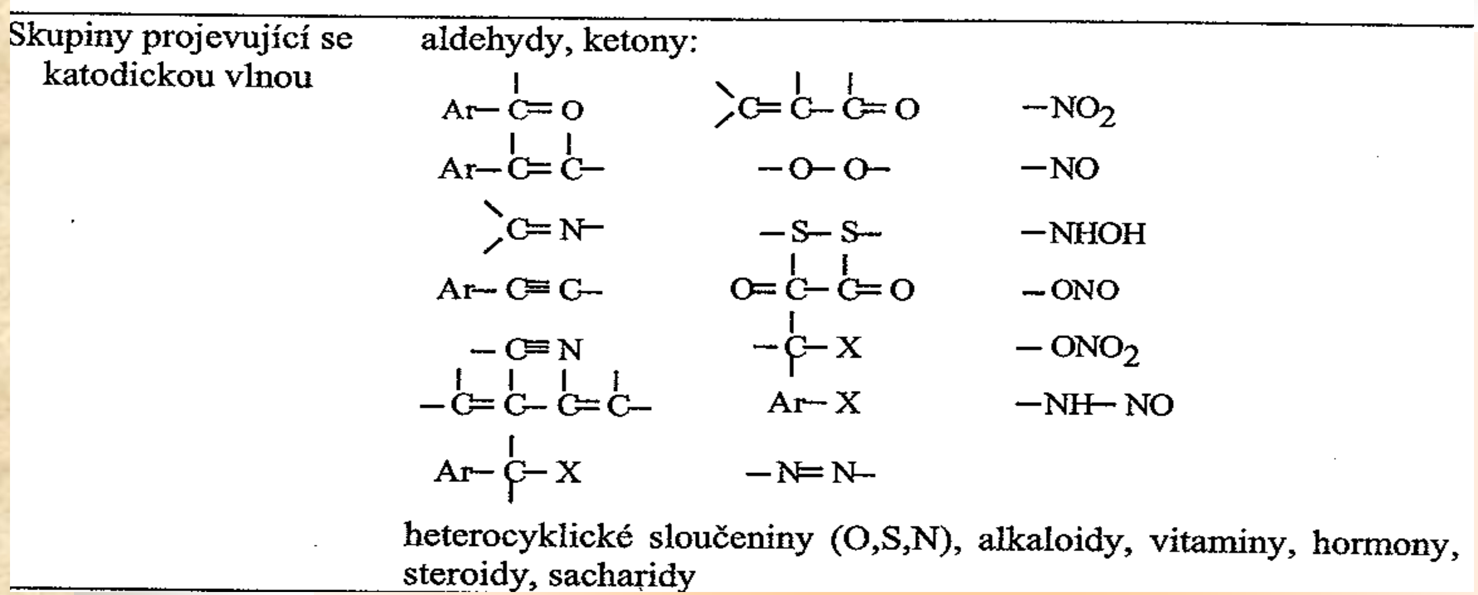
- Determination of org.and inorg.compounds in aqueous and nonaq.solutions
- Study of structures of organic and inorganic compounds
- Determination **adsorption processes** on surfaces
- Determination **electron transfer** and **reaction mechanisms**
- Measurement of kinetic rates and constants
- Determination of **thermodynamic properties of solvated species**
- Fundamental studies of oxidation and reduction processes in various media
- Determination of **complexation and coordination values**
- Determination of equilibrium **protonation constants**
- **Electrochemical sensors**

Common Applications

- Quantitative determination of pharmaceutical compounds
- Determination of metal ion concentrations in water to sub–parts-per-billion levels
- Determination of redox potentials
- Detection of eluted analytes in HPLC and flow injection analysis
- Determination of number of electrons in redox reactions
- Kinetic and mechanistic studies of reactions

Voltammetry

Analytical applications



Skupiny projevující se katodickou vlnou

aldehydy, ketony:

$Ar{-}C{=}O$ $\quad >C{=}C{-}C{=}O$ $\quad -NO_2$

$Ar{-}C{=}C{-}$ $\quad -O{-}O{-}$ $\quad -NO$

$>C{=}N{-}$ $\quad -S{-}S{-}$ $\quad -NHOH$

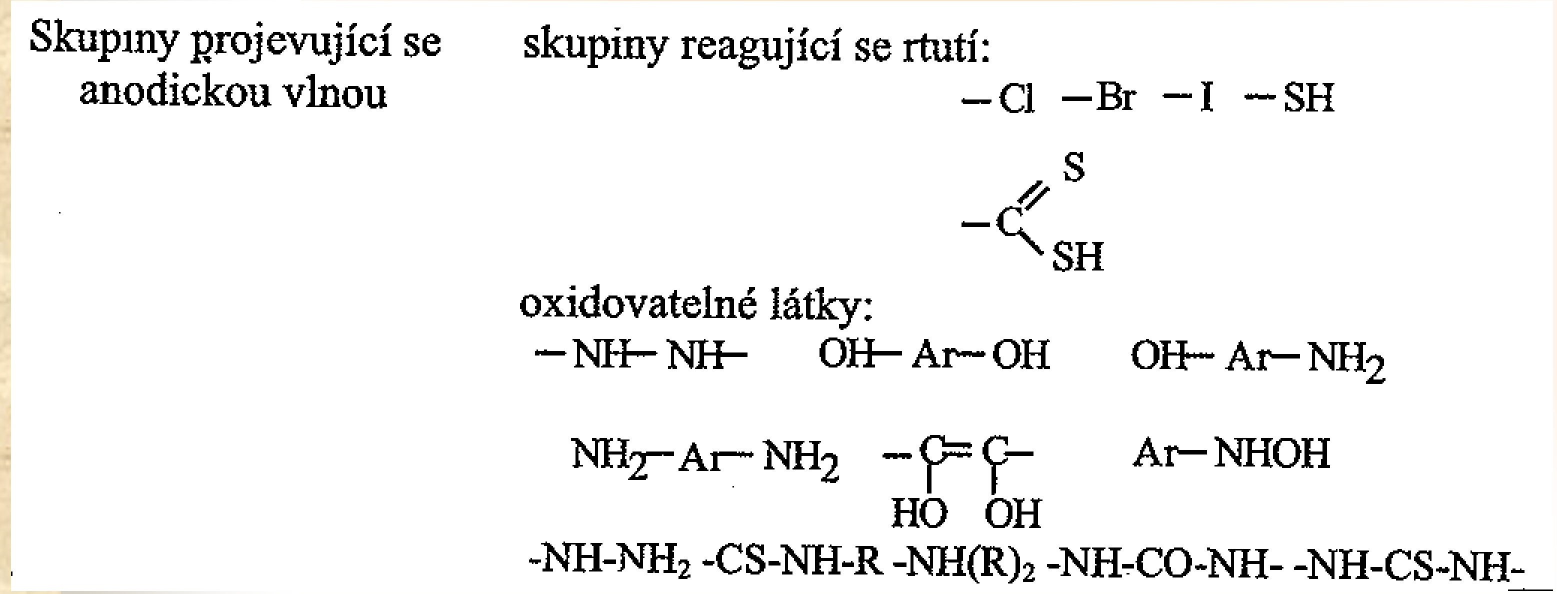
$Ar{-}C{\equiv}C{-}$ $\quad O{=}C{-}C{=}O$ $\quad -ONO$

$-C{\equiv}N$ $\quad -C{-}X$ $\quad -ONO_2$

$-C{=}C{-}C{=}C{-}$ $\quad Ar{-}X$ $\quad -NH{-}NO$

$Ar{-}C{-}X$ $\quad -N{=}N{-}$

heterocyklické sloučeniny (O,S,N), alkaloidy, vitaminy, hormony, steroidy, sacharidy



Skupiny projevující se anodickou vlnou

skupiny reagující se rtutí:

$-Cl$ $\quad -Br$ $\quad -I$ $\quad -SH$

$-C(=S)SH$

oxidovatelné látky:

$-NH{-}NH{-}$ $\quad OH{-}Ar{-}OH$ $\quad OH{-}Ar{-}NH_2$

$NH_2{-}Ar{-}NH_2$ $\quad -C(HO){=}C(OH){-}$ $\quad Ar{-}NHOH$

$-NH{-}NH_2$ $-CS{-}NH{-}R$ $-NH(R)_2$ $-NH{-}CO{-}NH{-}$ $-NH{-}CS{-}NH{-}$

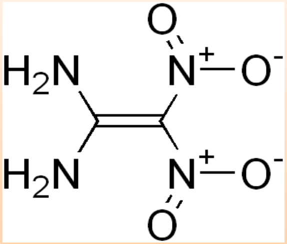
Mechanistic study (example)

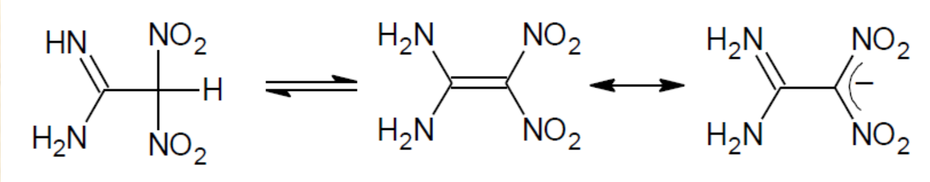
Reduction of nitro- compounds

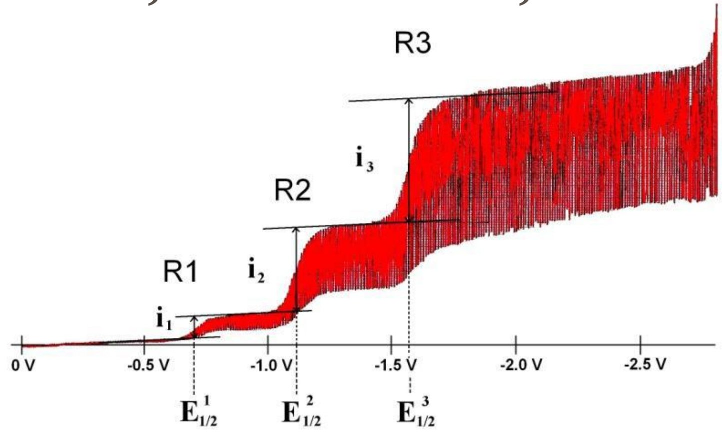
geminální diamin

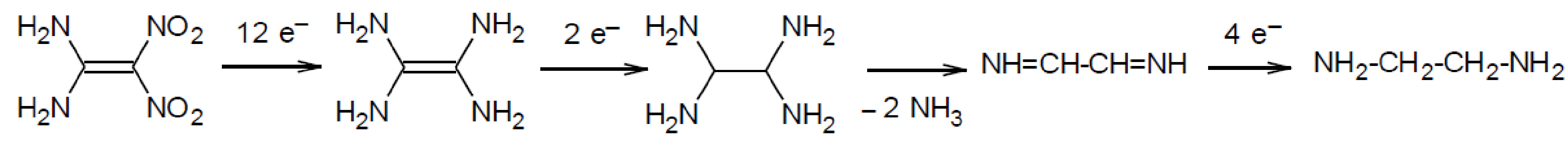
2,2-dinitroethen-l,l-diamin

FOX-7









TNT

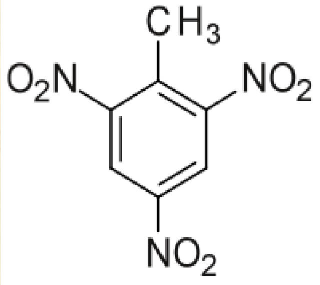
trinitrotoluen

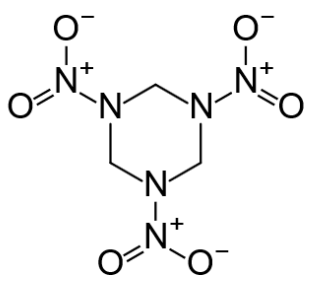
RDX Research Department Formula X

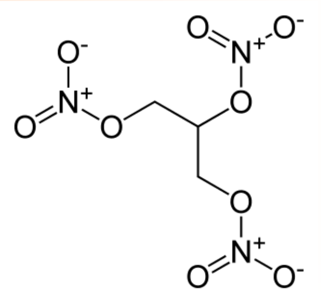
1,3,5-trinitroperhydro-1,3,5-triazine

nitroglycerin

propan-1,2,3-triyl-trinitrát



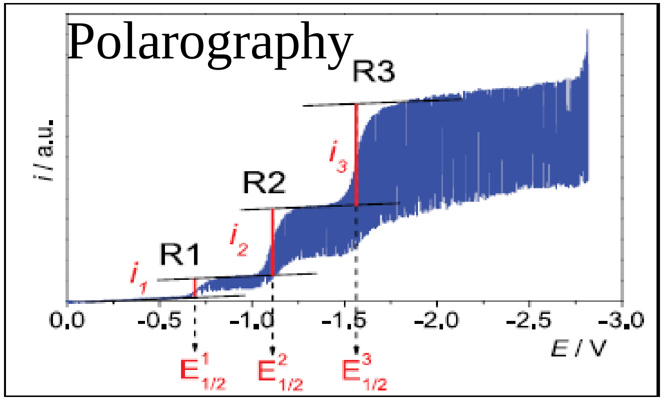


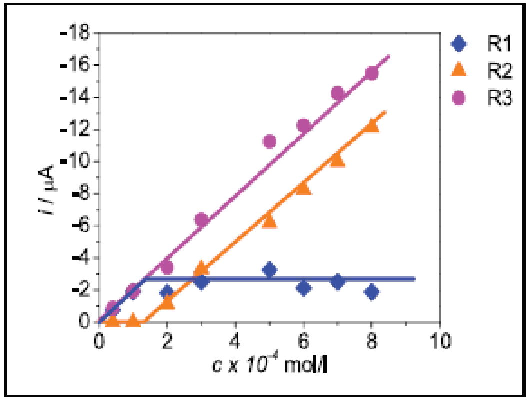


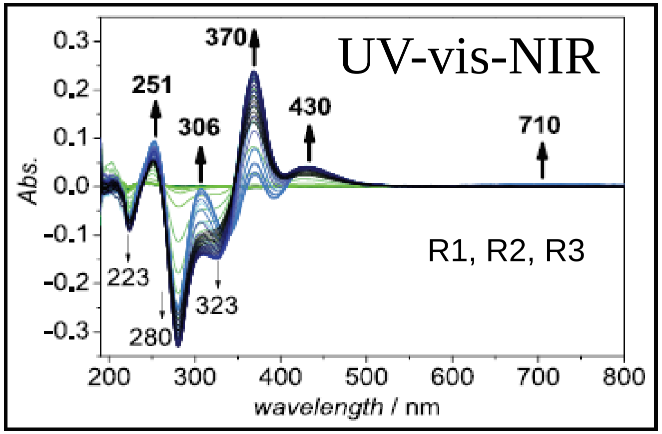
Voltammetric and spectral experiment

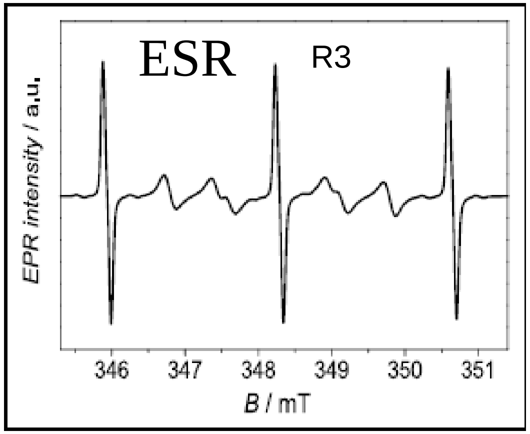
Mechanistic study - reduction of FOX-7

J Phys Org Chem. 2020;e4046.
https://doi.org/10.1002/poc.4046

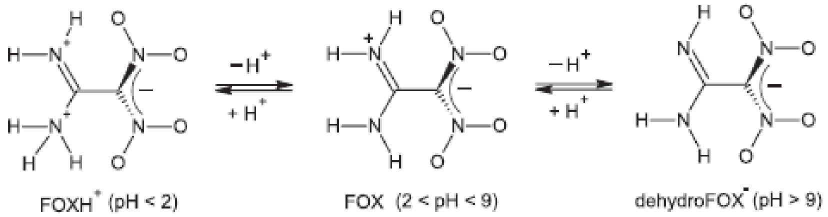


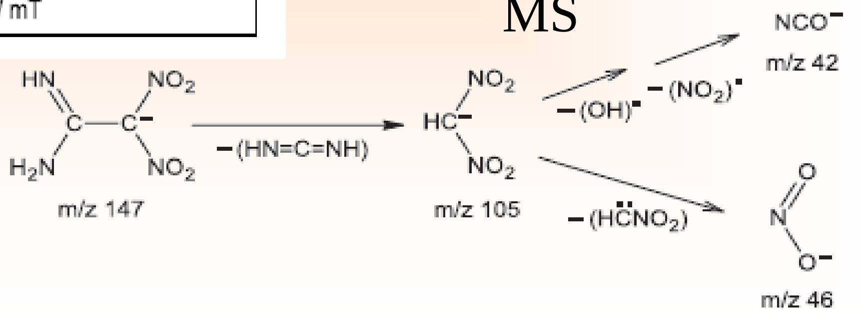






- **electrochemistry** - electroactive groups)
- **electronics**(push-pull)
- **structure** (mesomeric forms, protonation/ deprotonation forms, tautomerism, changing geometry, and planarity)

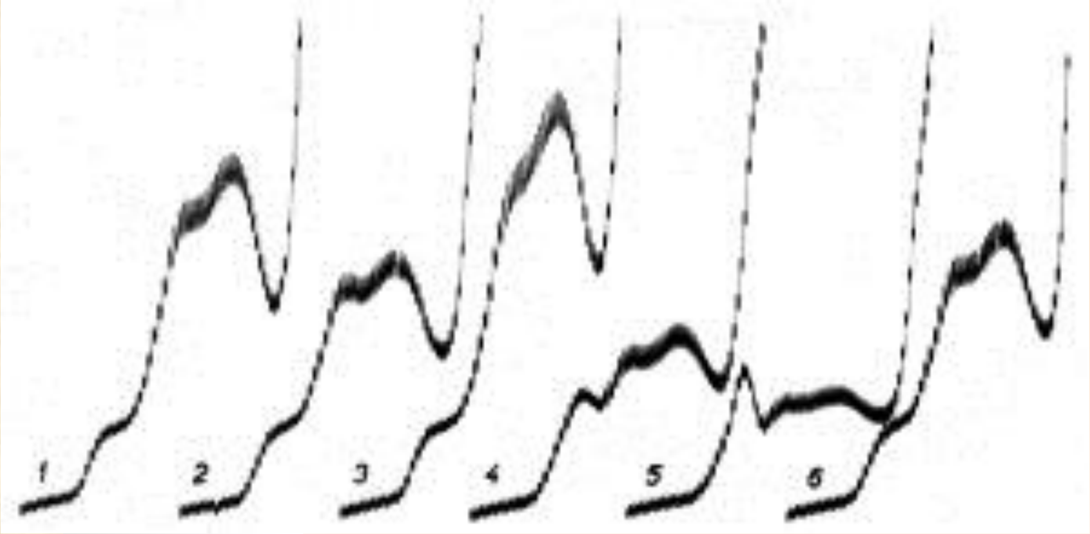


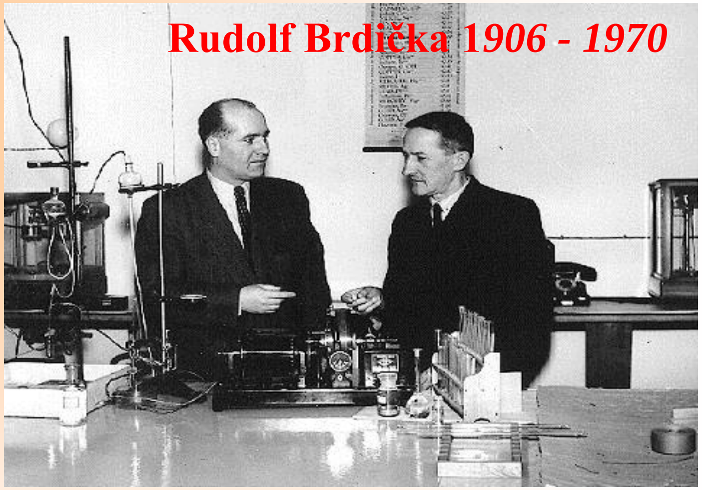


Voltammetry

Brdička reaction

*Heyrovsks's second assistant, Dr. Rudolf Brdicka, discovered a sensitive **catalytic hydrogen-evolution reaction of proteins**: in buffer solutions of pH about 9, containing ions of cobalt, proteins yield a prominent catalytic "double-wave"; this polarographic reaction was used in many countries over several decades as a diagnostic tool in treatment of cancer*

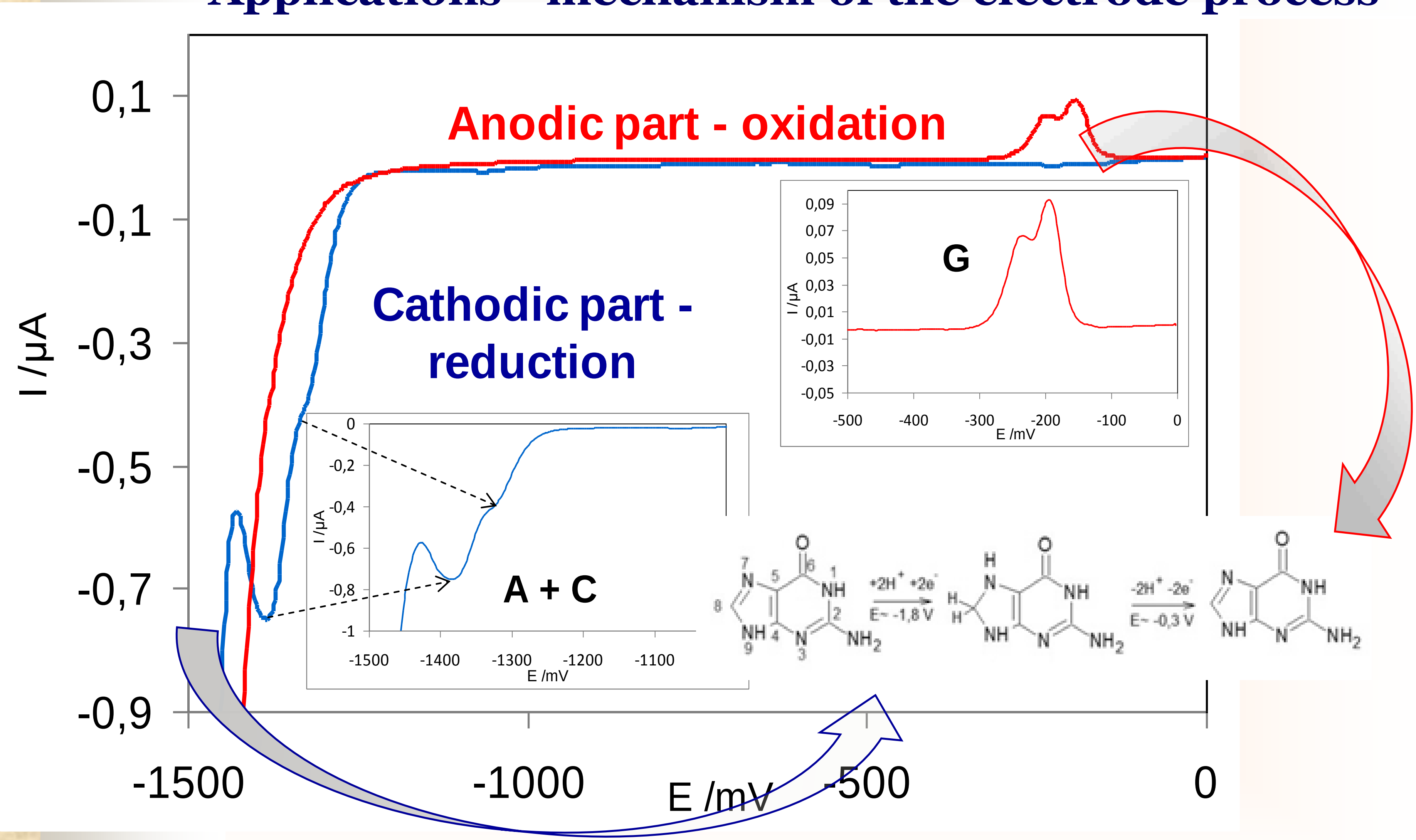



Rudolf Brdička *1906 - 1970*

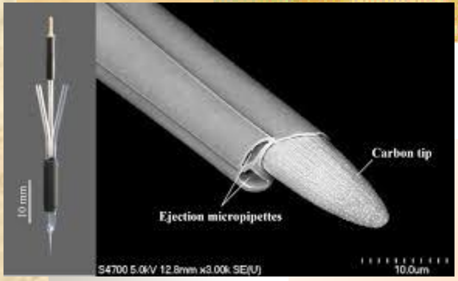
Polarographic "Brdicka reaction" of blood sera of different patients with following diagnoses: 1) status febrilis 2) tumor hepatis susp 3) ca. ventriculi susp 4) normal serum 5) cirrhosis hepatic 6) atherosclerosis.

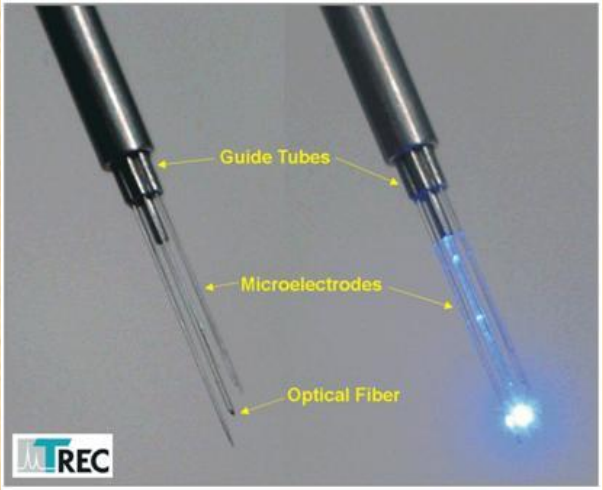
Cyclic Voltammetry

Applications –mechanism of the electrode process



Microelectrodes

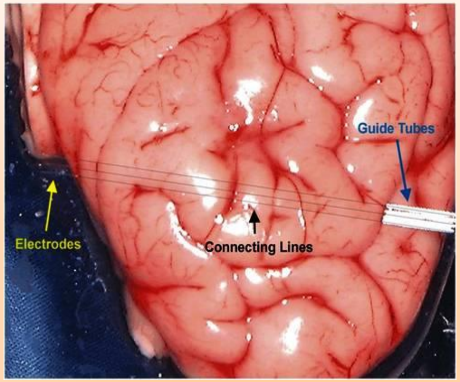




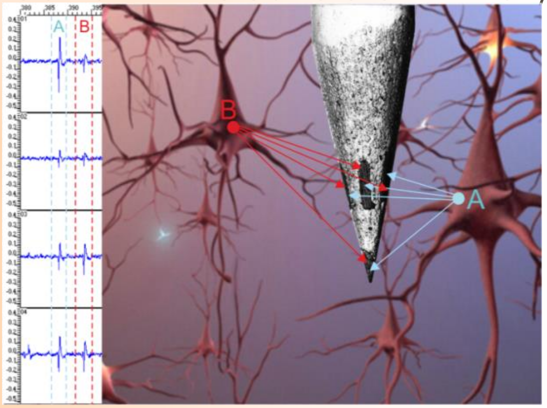
How do currents flow through electrodes?

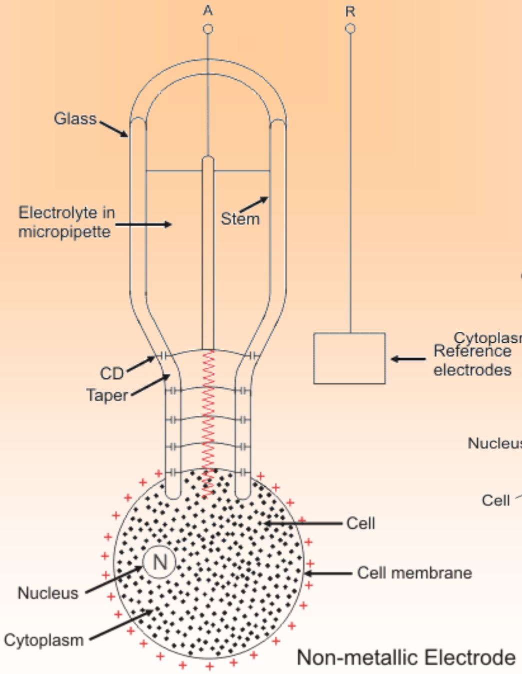
Steady state of spherical diffusion.

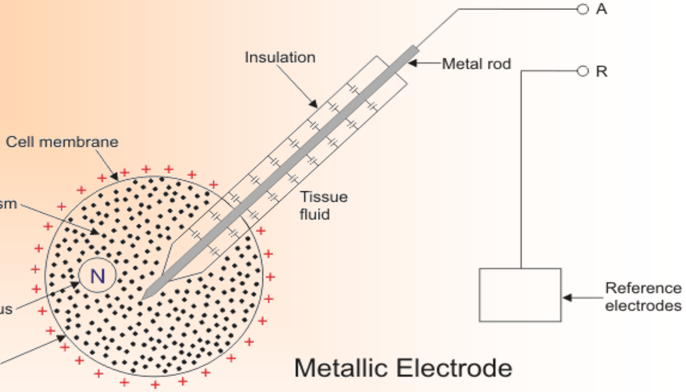
$$I_d = \frac{zFADc_\infty}{r_0} = 2\pi zFr_0Dc_\infty$$



Neural Electrode Arrays





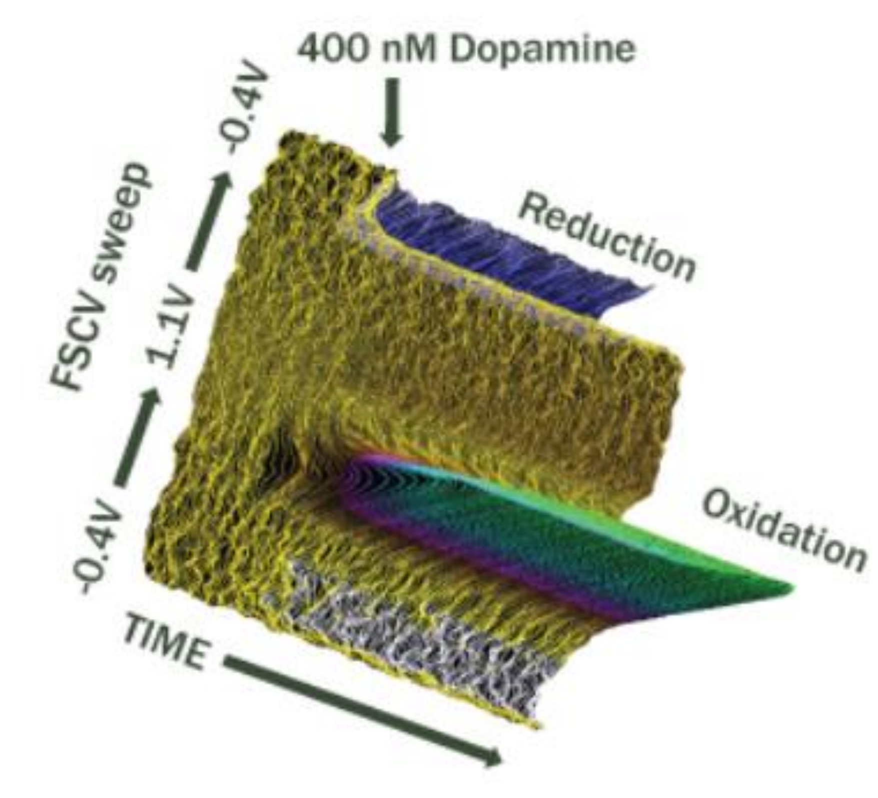


$$A = 2\pi r_0^2$$

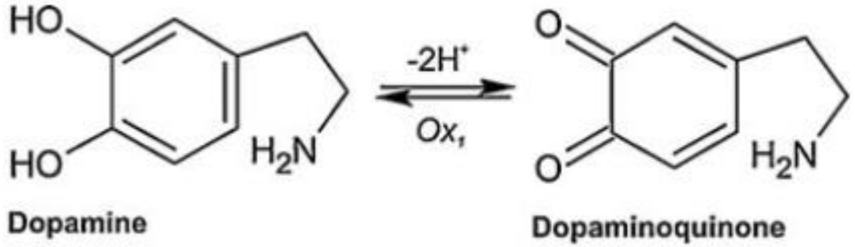
Fast Cyclic Voltammetry (FCV)

microelectrodes

Biogenic amine levels are detected by rapidly cycling a voltage across **an implanted carbon fiber sensor** and measuring the resultant current. Our systems can measure spontaneous sub-second **neurotransmitter release** events while conducting detailed behavioral studies. Both the wireless and tethered systems sweep from **250 to 400 V/s** in a user-selectable range spanning **-1.1 to +1.3 V**. All systems have built-in support for controlling an external stimulus.



3,4-dihydroxyphenethylamine



Important roles in the brain and body
Neurotransmiter
Brain dopamine pathways (neuromodulatory) are involved in motor control and controlling the release of various hormones.

Voltammetry

Applications – kinetics

Heterogeneous rate constant k_h and k_h^o

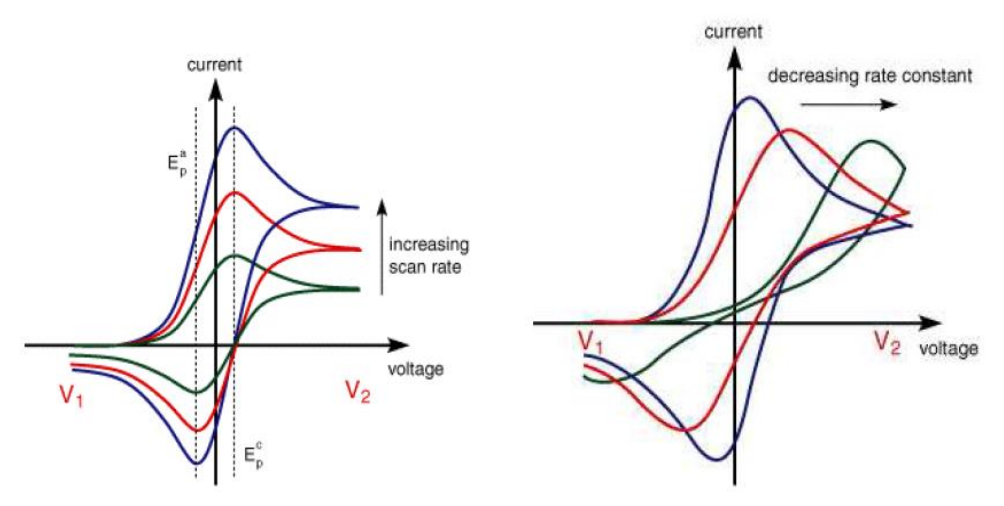
$Cd^{2+} + 2e^- \rightarrow Cd \quad k^0 = 1$ cm/s

$Pb^{2+} + 2e^- \rightarrow Pb \quad k^0 \sim 2$ cm/s

$Tl^+ + e^- \rightarrow Tl \quad k^0 \sim 2$ cm/s

$Zn^{2+} + 2e^- \rightarrow Zn \quad k^0 \sim 10^{-2} – 10^{-3}$ cm/s

ET



Dependence on parameters (E, solvent,electrode,pH, I, adsorption…)

Direct Current (DC) Voltammetry

Randles-Ševčík equation

$$I_p = 2.686 * 10^5 z^{3/2} A D^{1/2} \boxed{v^{1/2}} c$$

peak height

I_p (A) A (cm^2), D (cm^2.s^{-1}), v (V.s^{-1}),
c (in solution) (mol.cm^{-3})

diffusion control

or Delahay equation

current

$$I_p = 2.686 * 10^5 (\alpha z)^{3/2} A D^{1/2} \boxed{v^{1/2}} c$$

current density

$$i_p = \frac{I_p}{A} \quad or \quad j_p = \frac{I_p}{A}$$

Calibration redox couples:

D (cm^2.s^{-1}) (1°C, i.e., 1.7%)

$[Fe(CN)_6]^{3-/4-}$ dopamine

$[Ru(NH_3)_6]^{2+/3+}$ ferrocene

Voltammetry

Capacity (charging) current I_c

- the electric double layer charging (as a capacitance)
- $I_{capacity}$ (I_c) - the connection with surface tension (important

E_{pzc} - zero charge potential: the charges are balanced at the interface (electrode/electrolyte)

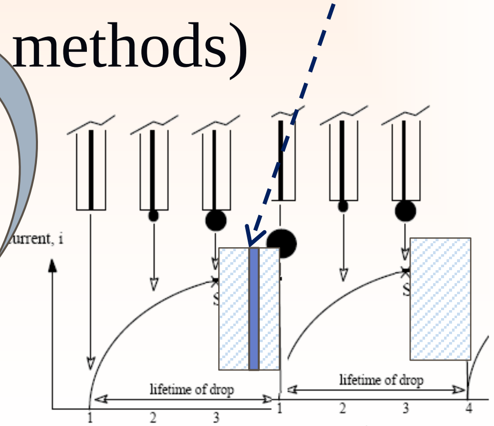
- each Hg drop is recharged
- $I_c = f(E)$ is not linear and its time dependence:

$$I_c = \frac{E}{R_s} exp\left(-\frac{t}{R_s C_{dl}}\right)$$

Elimination of I_c

1) SMDE – electronically controlled mercury drop; sampled technique (tast methods - vzorkovací)
2) Application of pulse methods (non – stationary methods)
3) AC voltammetry (phase shift between I_c and I_f
4) Elimination methods (software approaches)

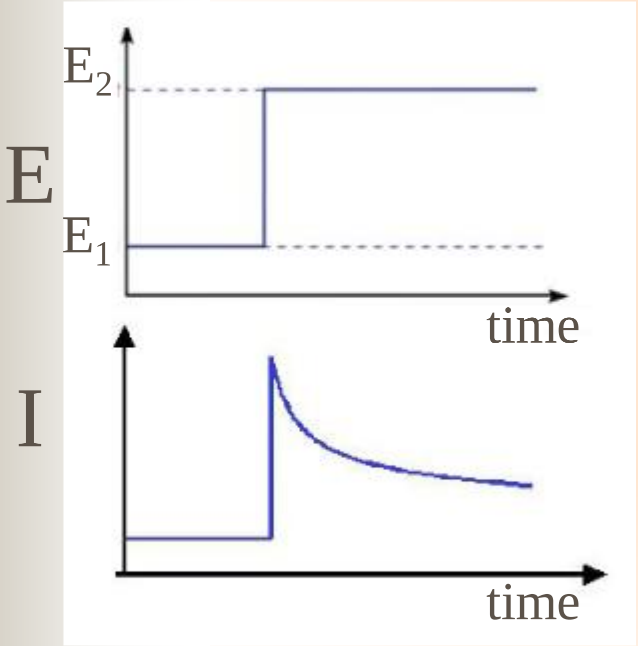
the measured quantity is a function of time

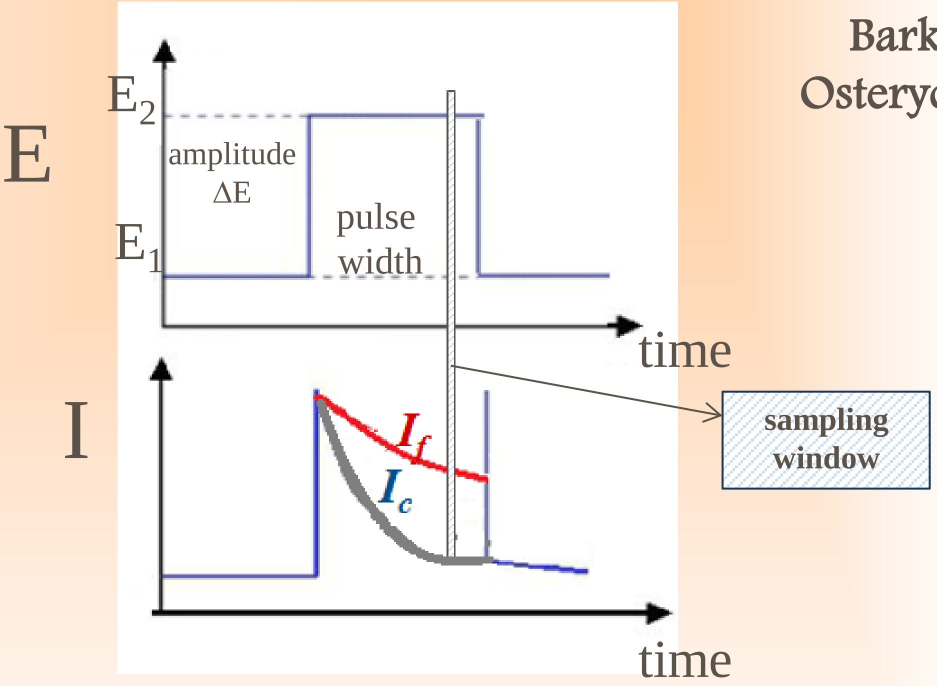


Pozn.: tast - vzorkovací

Voltammetry

Staircase technique, pulse techniques





Barker
Osteryoung

- perturbation
- measurement during short time (sampling)

In the pulse a capacity current decays faster then a faradaic current (electron transfer)

$$I_{faradaic}(t) = \frac{zFAD^{1/2}c}{(\pi t)^{1/2}}$$

Cottrell

$$I_{charging} = \frac{\Delta E}{R_s} exp\left(-\frac{t}{R_s C_{dl}}\right)$$

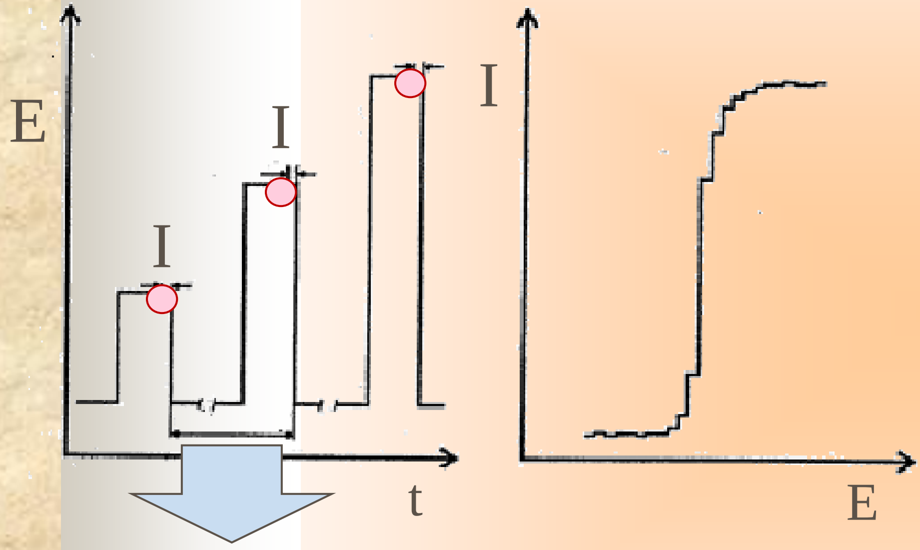
Parameters:
Pulse amplitude (mV)
Pulse width (ms)
Sample period (ms)
Pulse period (s)

$R_s C_{dl}$ time constant (5RC ~ 30ms ~ 0.68% drop of I_c]

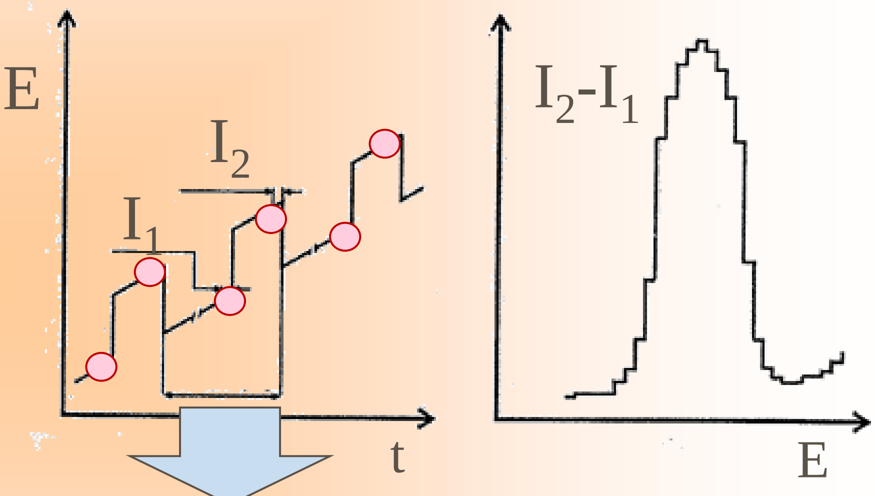
Pulse Polarography (Voltammetry)

Normal pulse (NPP, NPV)

Differential pulse (DPP, DPV)



pulse period
(drop time)



pulse period
(drop time)

$$I_{NPP} = \frac{zFAD^{1/2}c}{\sqrt{\pi t_m}}$$

Cottrell equation or Cottrell factor

t_m time after application of the pulse where the current is sampled

$$I_{DPP} = \frac{zFAD^{1/2}c}{\sqrt{\pi t_m}}\left(\frac{1-\sigma}{1+\sigma}\right)$$

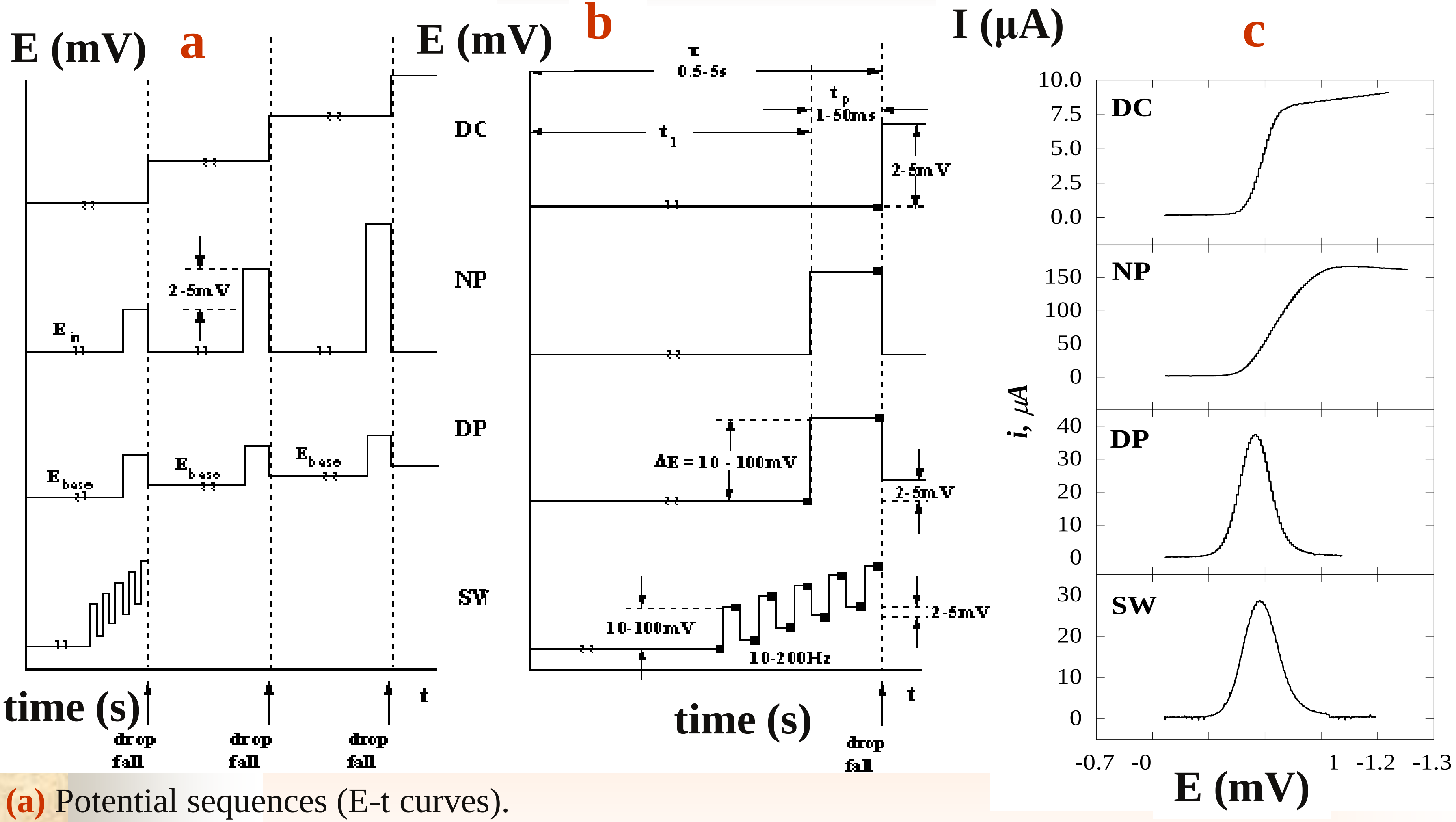
$$\sigma = exp\left[\left(zf/RT\right)\left(\Delta E/2\right)\right]$$

ΔE...pulse amplitude

f...frequency

Pulse and square wave voltammetry

Perturbation by pulses



(a) Potential sequences (E-t curves).

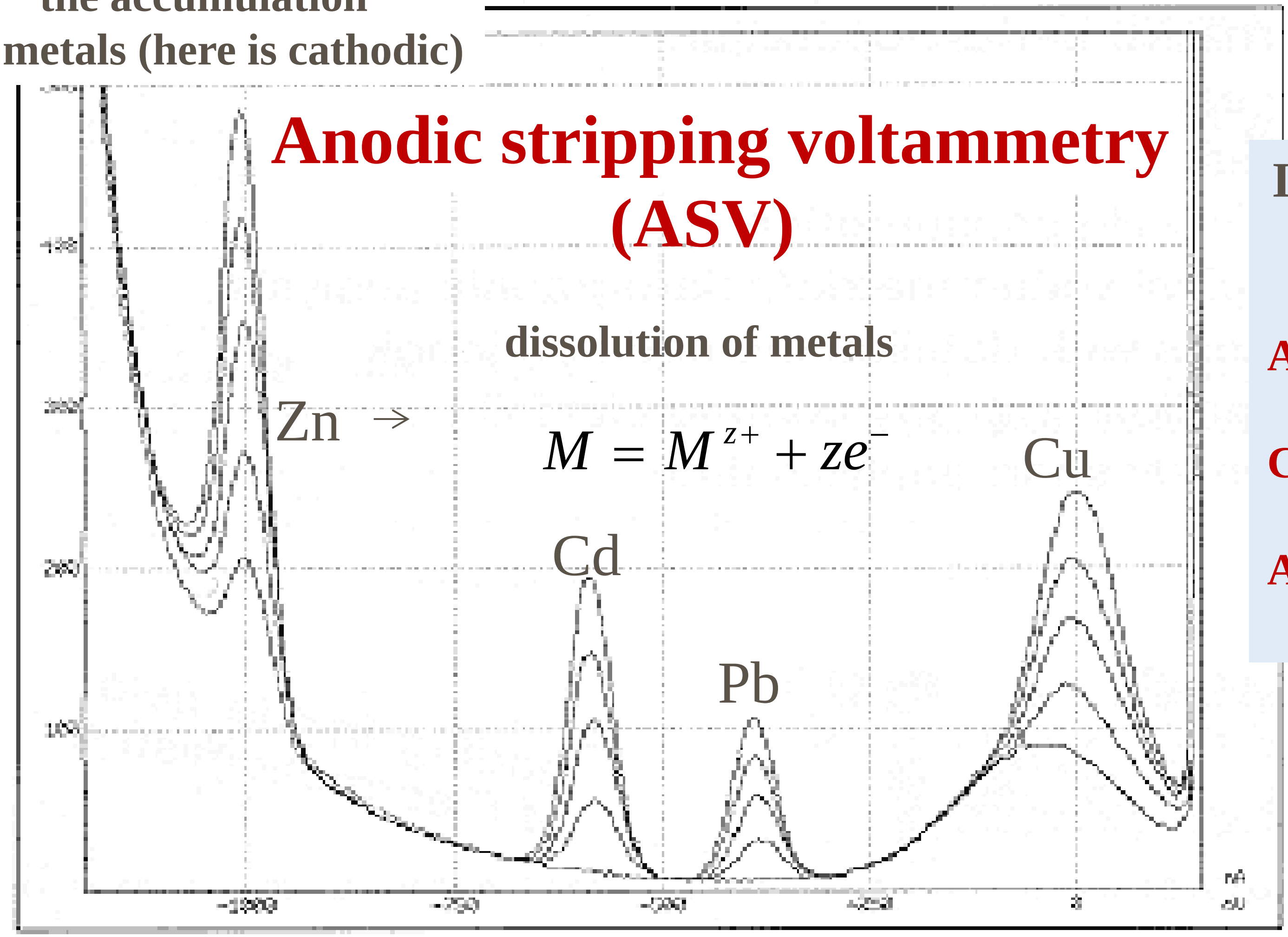
(b) Potential sequence on one drop (■ tast).

(c) Current-potential curves for 1 mM Zn^{2+} in 1 M KNO_3.

DC: τ = 2 s; **NP:** τ = 2 s, t_p = 5 ms; **DP:** τ = 2 s, t_p = 5 ms; ΔE_p = 20 mV; **SW:** ΔE_p = 20 mV, f = 100 Hz.

DPV with stripping

the accumulation
of metals (here is cathodic)



Anodic stripping voltammetry (ASV)

dissolution of metals

$$M = M^{z+} + ze^{-}$$

Improving DPV by the stripping mode:

Anodic stripping (ASV)

Cathodic stripping (CSV)

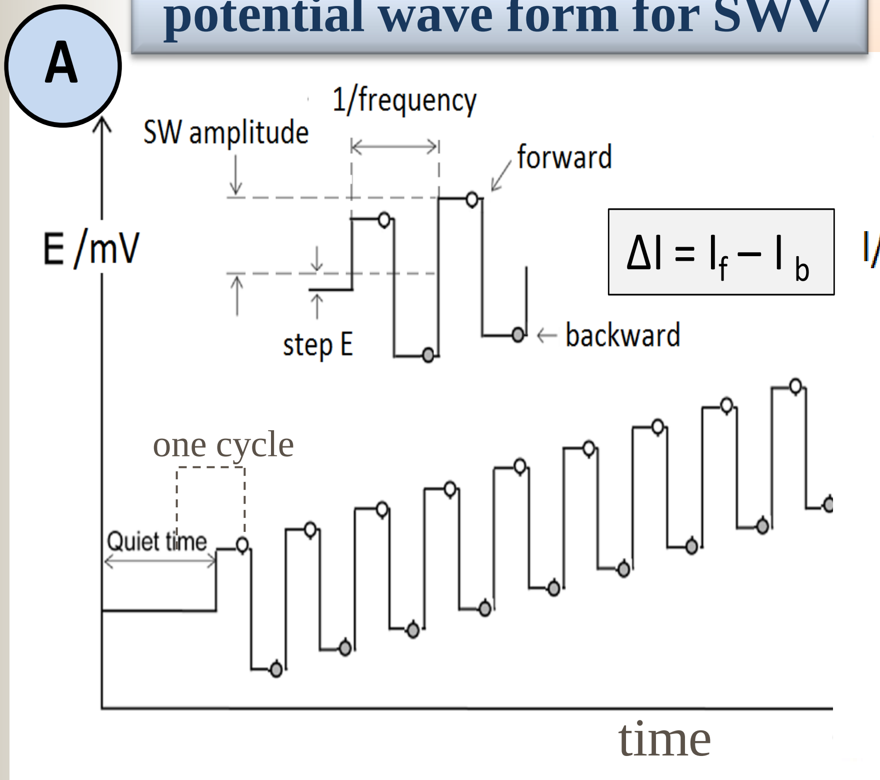
Adsorptive stripping (AdSV)

The example above shows the simultaneous determination of Zn , Cd, Pb and Cu using standard addition

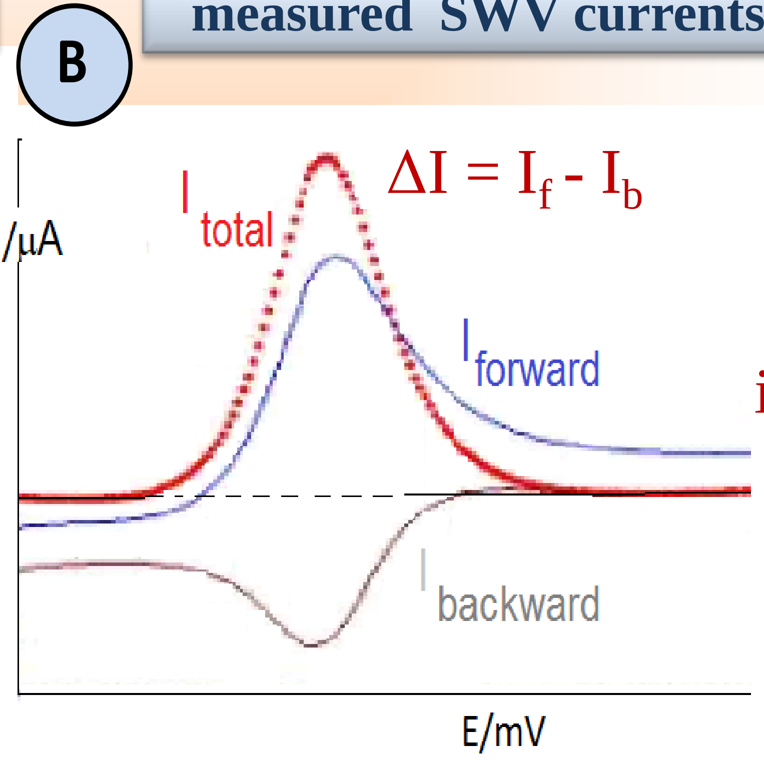
Square Wave Voltammetry (SWV)

Ramaley&Krause and Osteryoung&O´Dea

potential wave form for SWV



measured SWV currents



rev

vs.

irrev.!

$$\Delta I_{DPP} = \frac{nFAD^{1/2}c}{\sqrt{\pi t_m}}\Delta\Psi$$

ΔI – *differential current peak value*

Cottrell factor

$\Delta\Psi$ – *dimensionless parameter which gauges the peak height in SWV relative to the limiting response in normal pulse voltammetry*

$$\left(\frac{1-\sigma}{1+\sigma}\right)$$

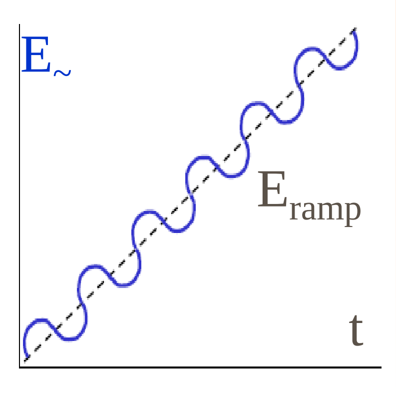
$$\sigma = exp\left[(zf/RT)(\Delta E/2)\right]$$

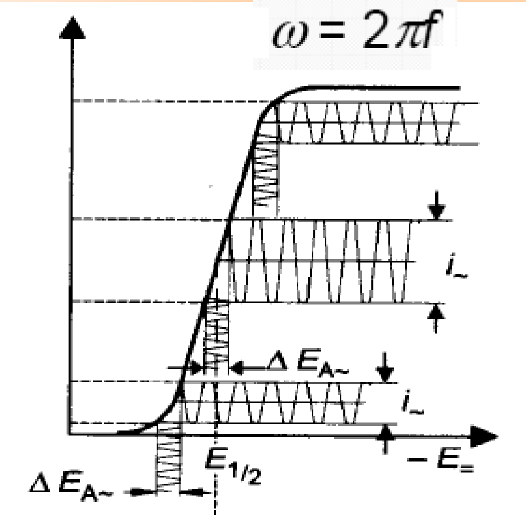
Alternating Current (AC) Voltammetry

- the application of a sinusodially oscillating voltage; alternating potential usually has a frequency of 50-200 Hz and 5-50 mV amplitude
- the AC signal causes a perturbation in the surface concentration
- an electrochemical process, mass transport, chemical and adsorption steps and electron transfer
- electric double layer EDL
- adsorption (nucleation) studies, study of surface active compounds (PAL)

the suppression of a capacity current

1) phase sensitive AC current regulation (the faradaic current component is phase shifted by π/4 compared to the input potential, the capacity current component by π/2
2) using the second harmonic current component (the frequency 2f)

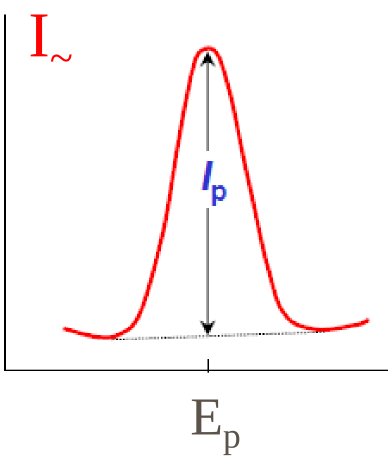


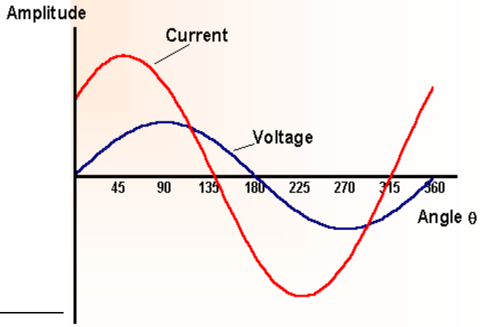

$$\omega = 2\pi f$$

$$I_p = \frac{z^2F^2}{4RT} A\Delta E(\omega D)^{1/2}c$$

reversible system

$$W_{1/2} = 3{,}52\frac{RT}{zF}$$

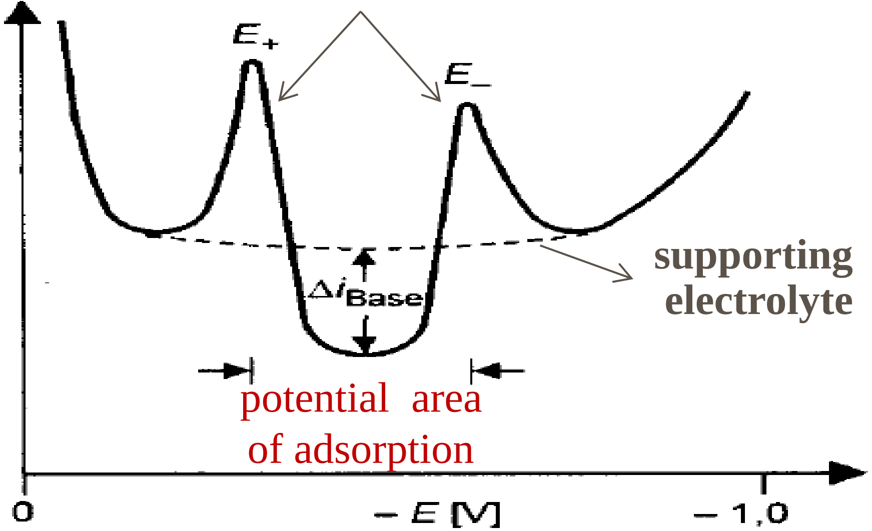




Alternating Current (AC) Voltammetry

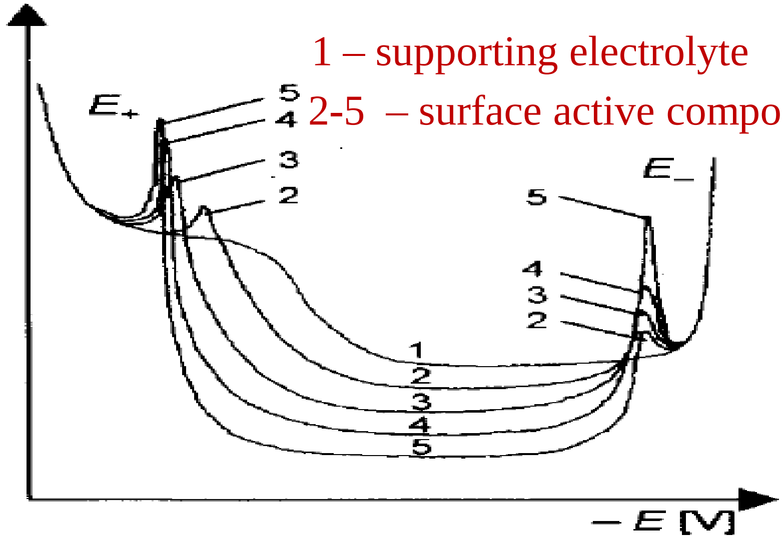
Tensammetry

adsorption/desorption peaks



supporting electrolyte

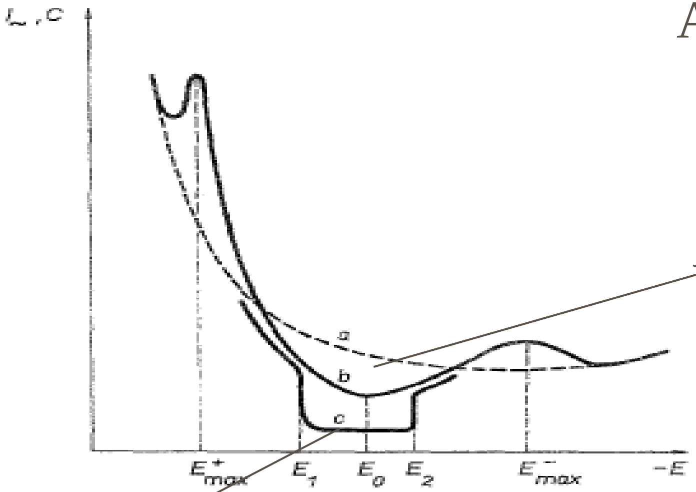
potential area of adsorption



1 – supporting electrolyte

2-5 – surface active compound

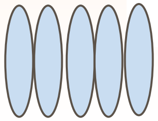
Adsorption/desorption of biomacromolecules involved in catalytic hydrogen evolution (Emil Paleček)



Adsorption of Nucleosides on Mercury Surface (Vladimír Vetterl)

non-stacked molecules

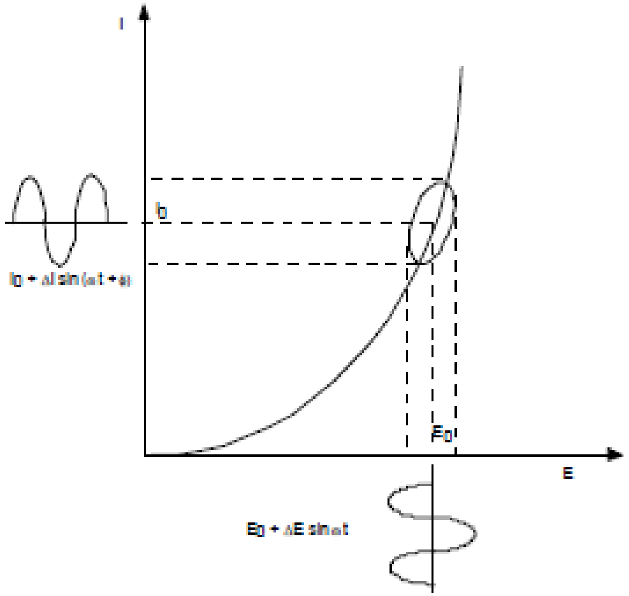
„phase transition“



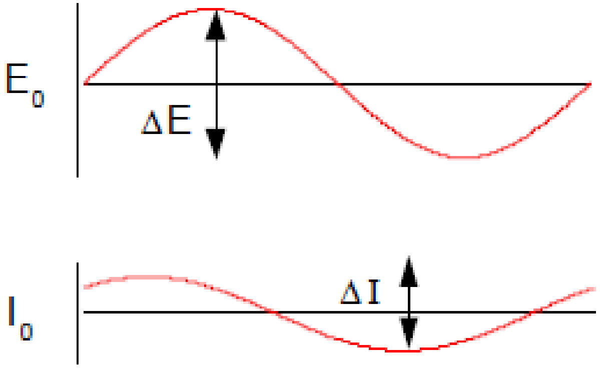
pits – stacking interactions of adsorbed molecules

Electrochemical impedance spectroscopy EIS

corrosion
electrodeposition,
electrodissolution, passivity
SAM
diffusion of ions across
membranes semiconductor
interfaces



The fundamental approach of all impedance methods is to apply a **small amplitude sinusoidal excitation signal**



Electrochemical impedance spectroscopy EIS

Principles of EIS measurements

Taylor series expansion for the current is given by

$$\Delta I = \left(\frac{dI}{dE}\right)_{E_0,I_0} \Delta E + \frac{1}{2}\left(\frac{d^2I}{dE^2}\right)_{E_0,I_0} \Delta E^2 + \ldots.$$

If the magnitude of the perturbing signal ΔE is small, then the higher order terms can be assumed to be negligible. The impedance of the system can then be calculated using Ohm's law:

$$Z(\omega) = \frac{\Delta E(\omega)}{\Delta I(\omega)}$$

$Z(\omega)$ is impedance $= \mathrm{f}(\omega)$

frequency range of 100kHz – 0.1Hz

Electrochemical impedance spectroscopy EIS

Electrode system - model

$$\frac{1}{Z}=\frac{1}{R_{ct}}+\frac{1}{1/j\omega C_{dl}}=\frac{1}{R_{ct}}+j\omega C_{dl}$$

$Z = impedance$

$R = rezistance$

$X = reaktance$

induktance L   capacitance C

$$\boxed{Z=\frac{R_{ct}}{1+j\omega C_{dl}R_{ct}}}$$

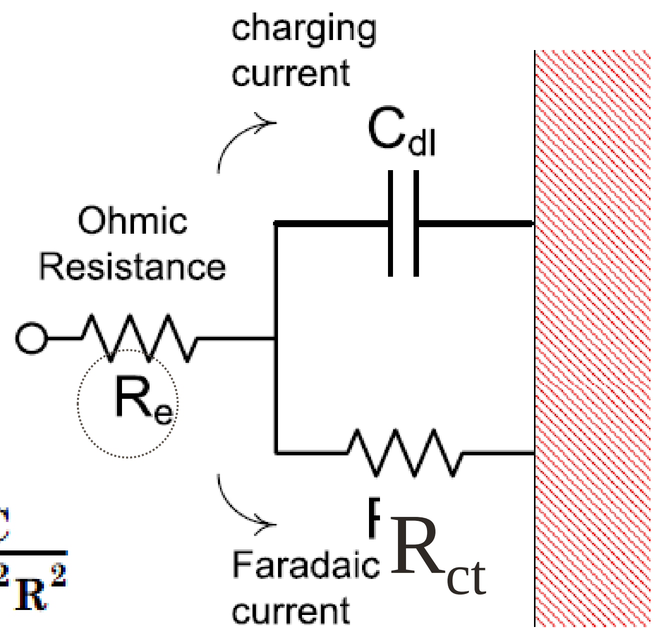
$$Z = R_e+\frac{R_{ct}}{1+j\omega C_{dl}R_{ct}}$$

$$Z_{real} = R_e+\frac{R_{ct}}{1+\omega^2 C_{dl}{}^2 R_{ct}{}^2}$$

$$Z_{im}=\frac{R_{ct}{}^2 C_{dl}\omega}{1+\omega^2 C_{dl}{}^2 R_{ct}{}^2}$$

$$\boxed{|Z|=\sqrt{R^2+X^2}}$$

Electrical Analogues



The impedance of a parallel combination

$$Z=\frac{R}{1+C^2\omega^2R^2}-j\cdot\frac{R^2\omega C}{1+C^2\omega^2R^2}$$

Electrochemical impedance spectroscopy EIS

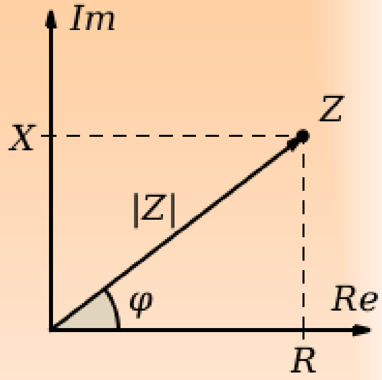
EIS plots

In cartesian co-ordinates $Z(w) = Z_r(w) + jZ_j(w)$

In polar co-ordinates $Z(\omega) = |Z(\omega)| e^{\phi\omega}$

magnitude of the impedance

phase shift



$$Z(t) = \frac{E(t)}{I(t)} = \frac{E_0 \cos(\omega t)}{I_0 \cos(\omega t - \phi)} = Z_0 \frac{\cos(\omega t)}{\cos(\omega t - \phi)}$$

The plot of the imaginary part against the real part of impedance - **Nyquist plot.** The shape of the curve is important in making qualitative interpretations of the data. The disadvantage of the Nyquist representation is that one loses the frequency dimension of the data. One way of overcoming this problem is by labelling the frequencies on the curve. The absolute value of impedance and the phase shifts are plotted as a function of frequency in two different plots giving a **Bode plot.** The relationship between the two ways of representing the data is as follows:

Electrochemical impedance spectroscopy EIS

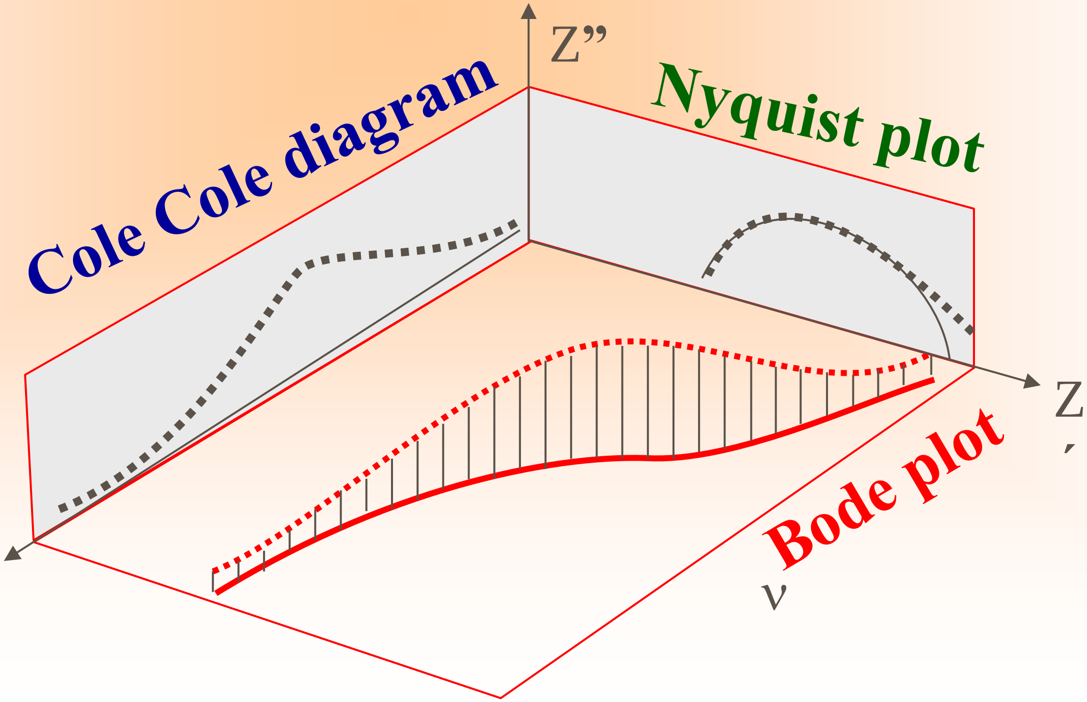
The different views on impedance data

The absolute value of Z and the phase shifts are plotted as a function of frequency in two different plots giving a **Bode plot**

The impedance data are the red points.

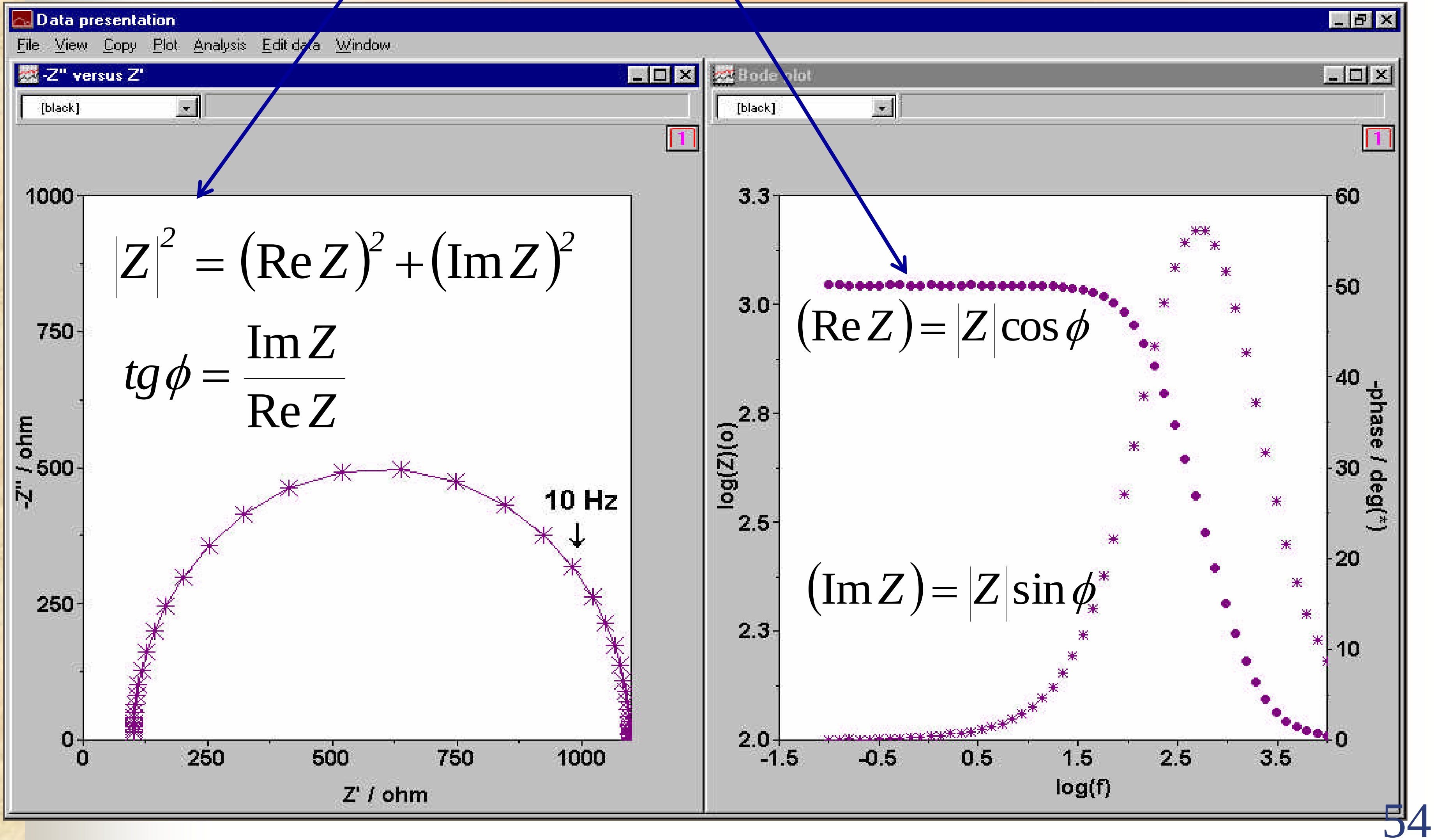
Their projection onto the Z“-Z‘ plane is called the **Nyquist plot**

The projection onto the Z“-ν plane is called the **Cole Cole diagram**



Electrochemical impedance spectroscopy EIS

Nyquist and Bode plot



$$|Z|^2 = (\operatorname{Re} Z)^2 + (\operatorname{Im} Z)^2$$

$$tg\,\phi = \frac{\operatorname{Im} Z}{\operatorname{Re} Z}$$

$$(\operatorname{Re} Z) = |Z| \cos\phi$$

$$(\operatorname{Im} Z) = |Z| \sin\phi$$

EIS: experiment parameters

FRA parameters or settings

$$Z_R = R$$

$$Z_C = -\frac{j}{\omega C}$$

$$Z_L = j\omega L$$

1. *AC mode (single sine or multi sine)*
2. *perturbation (sine wave) amplitude (10 mV)*
3. *Open Circuit Potential (OCP)*
4. *three electrode set*
5. *frequency range (1MHz – 0.1Hz)*
6. *frequency distribution* (linearly, logarithmically or with a square root distribution)

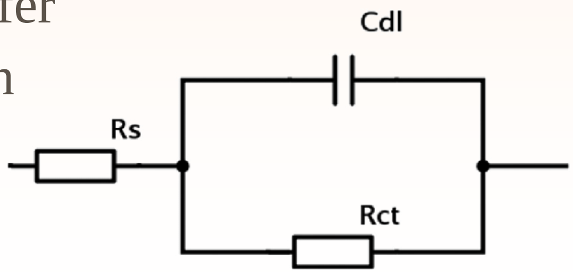
Output parameters from circuit models

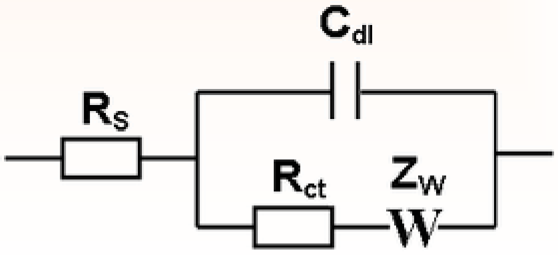
C_{dl} capacitance of double layer

R_{ct} resistance of electron transfer

R_s or R_Ω resistance of solution

Randles circuit



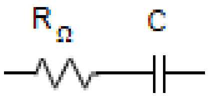


Electrochemical impedance spectroscopy EIS

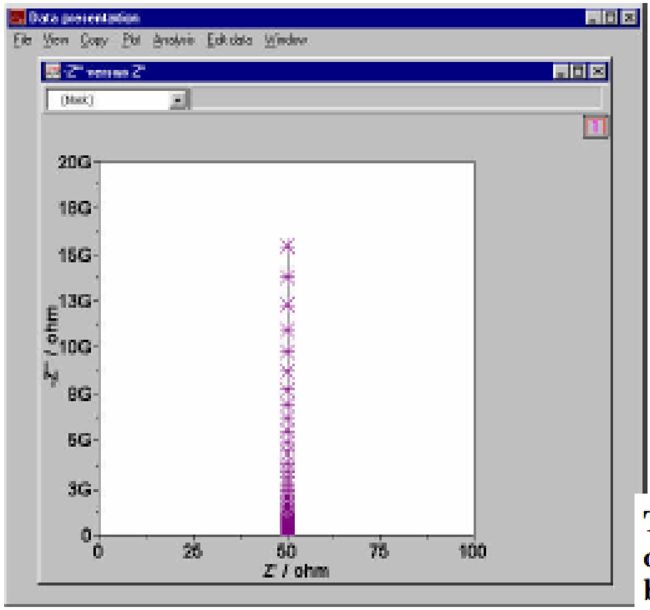
equivalent circuit models

Model 1

A resistance and a capacitance in series

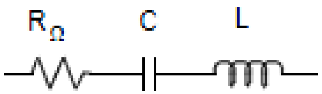


Model 1 can be used, for example, to model a metal with an undamaged high impedance coating.

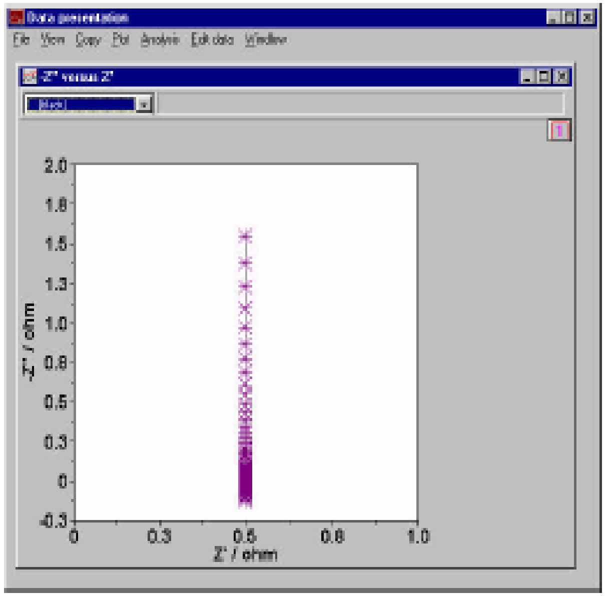


Model 2

A resistance, a capacitance and an inductance in series

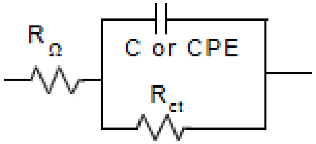


Model 2 can be used to model the response of a supercapacitor.

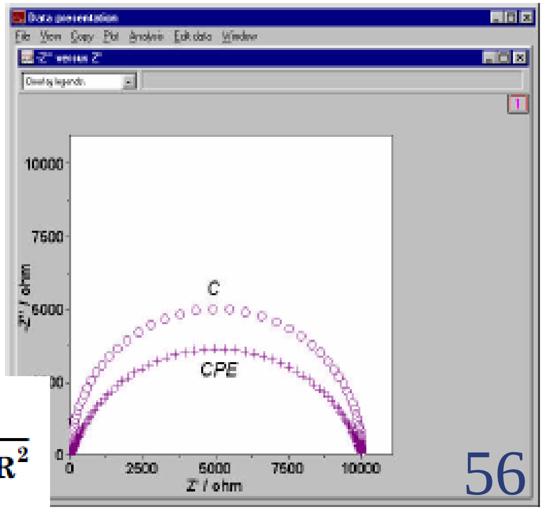


Model 3

A resistance and a capacitance in parallel (Randles circuit)



The Randles circuit is one of the simplest and most common cell models. It includes a solution resistance, a double layer capacitor or a CPE and a polarization resistance. It is used to model corrosion processes and is often the starting point for other more complex models.



The impedance of a parallel combination

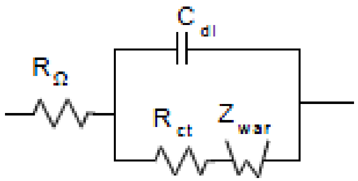
$$Z = \frac{R}{1 + C^2\omega^2R^2} - i \cdot \frac{R^2\omega C}{1 + C^2\omega^2R^2}$$

Electrochemical impedance spectroscopy EIS

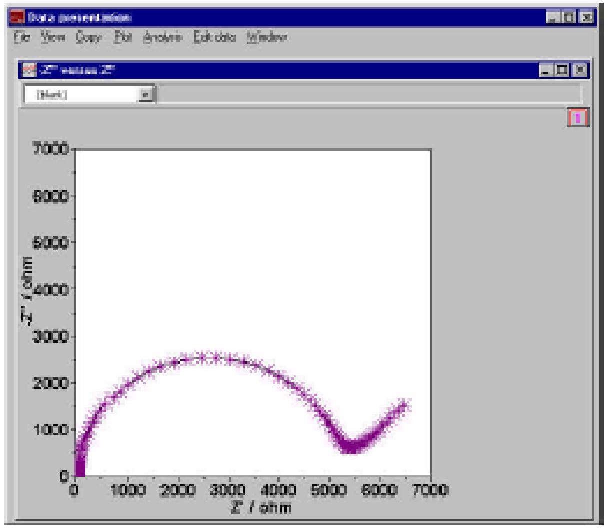
equivalent circuit models

Model 4

Mixed kinetic and diffusion control

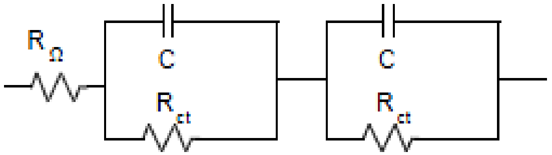


Model 4 can be used to describe electrode processes when both kinetics and diffusion are important.

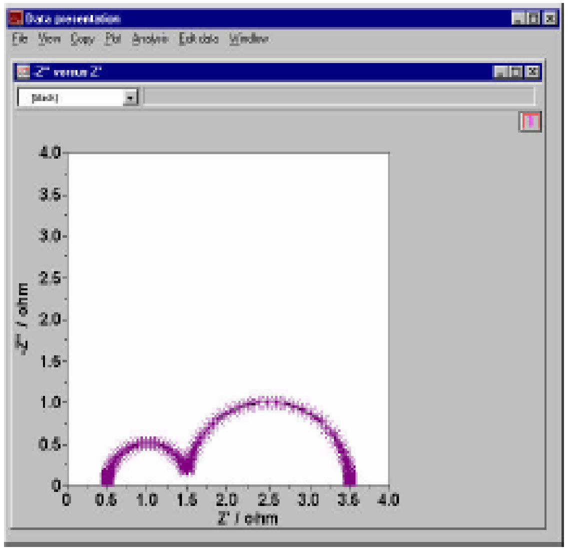


Model 5

Two Randles circuits in series



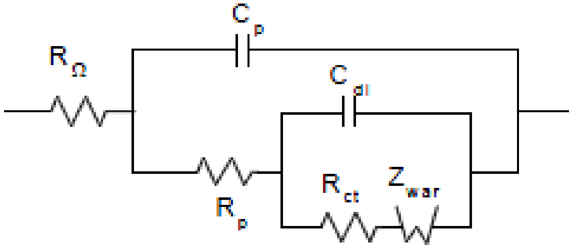
Model 5 can be used, for example, to model the response of batteries.



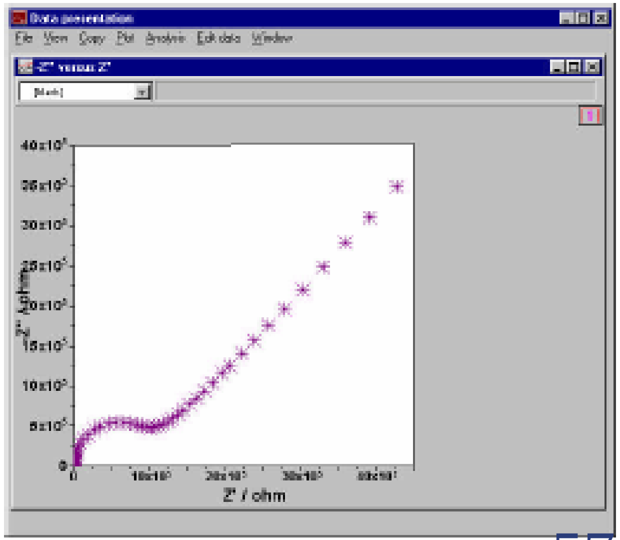
e.g., porous electrodes

Model 6

A complex circuit



Model 6 can be used, for example, to describe the impedance of an organic coating on a metal substrate in contact with an electrolyte.



Hyphenated methods (HEM)

Complementary or Related Techniques *in-situ*

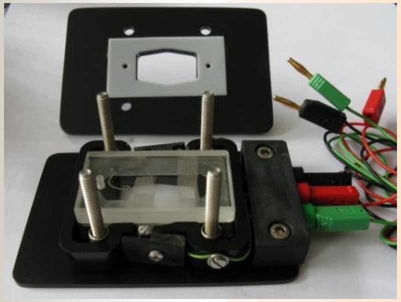
Other electroanalytical techniques may provide additional or preliminary information

- **Spectroelectrochemistry SE:** Simultaneous use of spectroscopic methods can identify species undergoing reaction, *in-situ study.*
- **EQCMB (EQCNB) with CV** *in situ* the study of layers on electrode surfaces together with cyclic voltammetry
- **HPLC - ED** Liquid chromatography is often used to separate individual analytes before analysis.
- **EC - AFM** *in situ* the study of layers on electrode surfaces by means of microscopy.

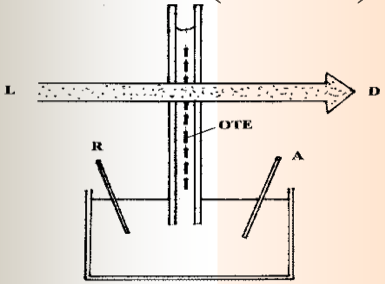
Spectroelectrochemistry

an experimental method that combines an electrochemical measurement coupled to an:

- *in situ* spectroscopical measurement (UV-Vis, IR, ESR, NMR)
- *ex situ* spectroscopical measurement (LEED, AES, XPS, AFM)

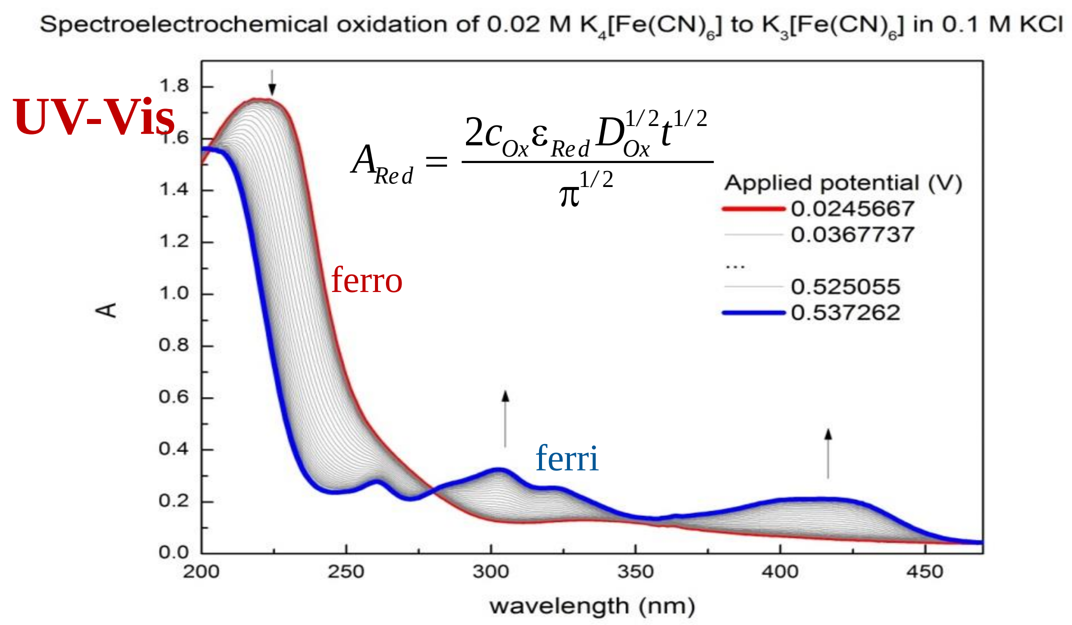


Optically Transparent Thin Layer Electrochemical (OTTLE) Cell



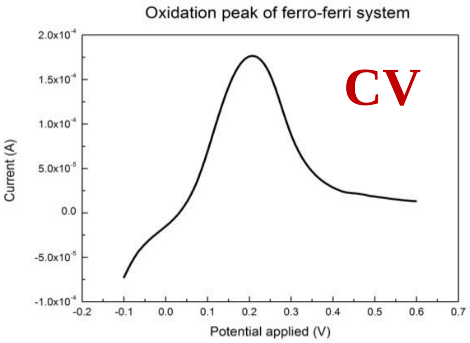
Applications

- mechanism
- kinetics
- $E^{0\prime}$, z: log $(A_{Ox}/A_{red}) = f(E)$
- $dA/dt = f(E)$
- ↑ selectivity in complex reactions

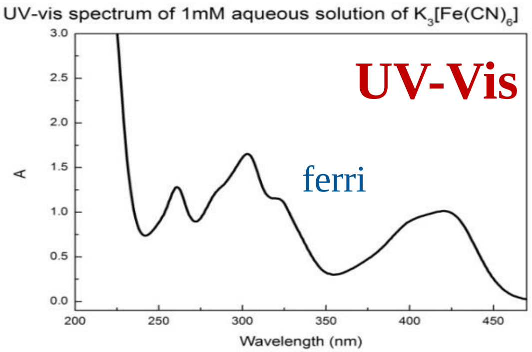


Spectroelectrochemical oxidation of 0.02 M $K_4[Fe(CN)_6]$ to $K_3[Fe(CN)_6]$ in 0.1 M KCl

$$A_{Red} = \frac{2c_{Ox}\varepsilon_{Red}D_{Ox}^{1/2}t^{1/2}}{\pi^{1/2}}$$



Oxidation peak of ferro-ferri system



UV-vis spectrum of 1mM aqueous solution of $K_3[Fe(CN)_6]$

Spectroelectrochemistry

UV-Vis

$$A_{Red} = \frac{2c_{Ox}\varepsilon_{Red}D_{Ox}^{1/2}t^{1/2}}{\pi^{1/2}}$$

diffusion of **Ox** to the electrode - the absorbance A_{red} as a function of time can be observed

$$A_{Ox} = \frac{2c_{Red}\varepsilon_{Ox}D_{Red}^{1/2}t^{1/2}}{\pi^{1/2}}$$

diffusion of **Red** to the electrode - the absorbance A_{Ox} as a function of time can be observed

$$A = f\left(t^{1/2}\right)$$

Applications

kinetics and mechanism of electrode processes

- *formal redox potentials:* $E^{0\prime}$, z: log $(A_{Ox}/A_{red}) = f(E)$
- *evaluation as the derivative function: dA/dt = f(E) (greater accuracy)*
- *selectivity in complex reactions*

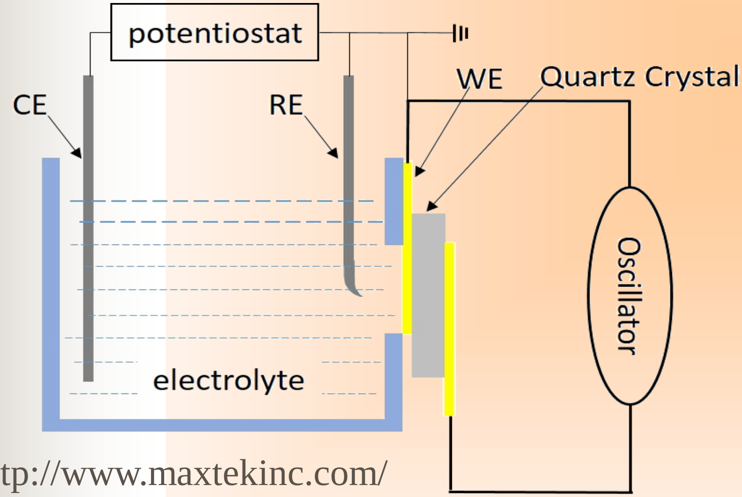
(not affected by capacity)

(EQCM)

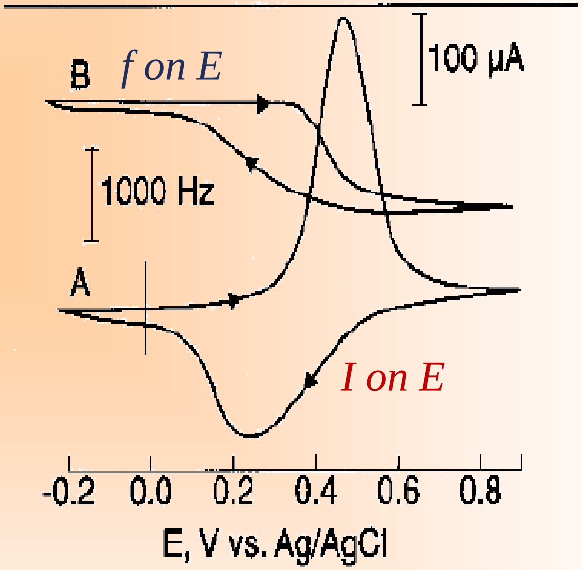
Electrochemical Quartz Crystal Microbalance

- A mass variation (Δm) per unit area (A) by measuring the change in frequency (f) of a quartz crystal resonator
- The resonance is disturbed by the addition or removal of a small mass due to oxide growth/decay or film deposition at the surface of the acoustic resonator.

Quartz crystal the heart of the QCM



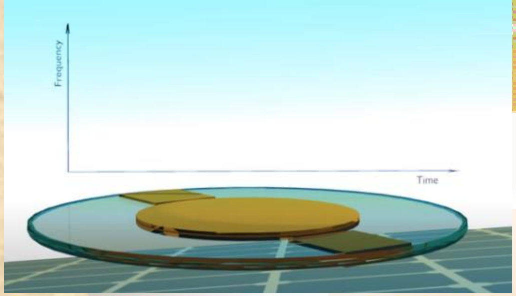
http://www.maxtekinc.com/
http://chinstruments.com

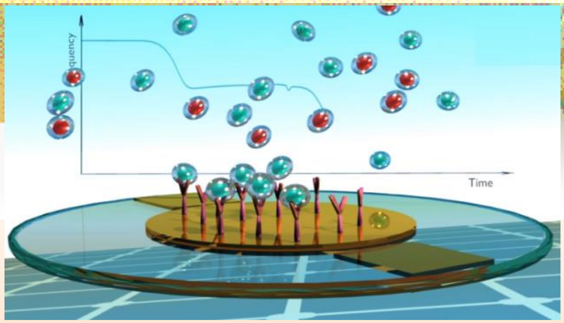


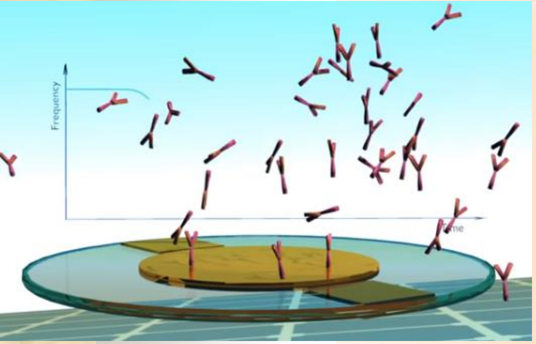
Piezoelectric effect (brothers Curie – 1880)

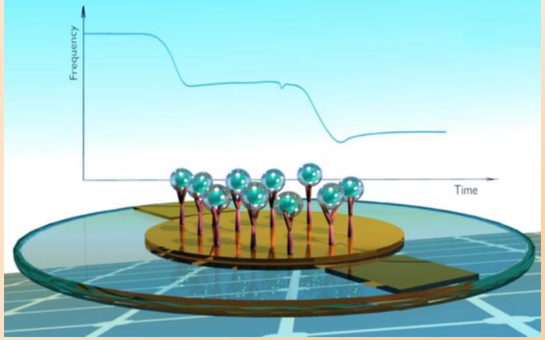
Some crystal could produce electricity when pressure is applied in certain crystalographic directions.

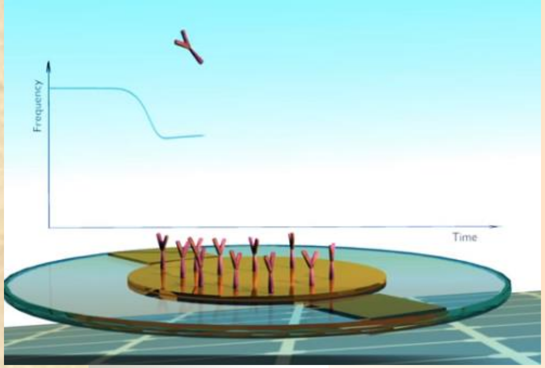
- sensitivity – 0.1-1 ng/cm^2
- the calibration is necessary (C_f)

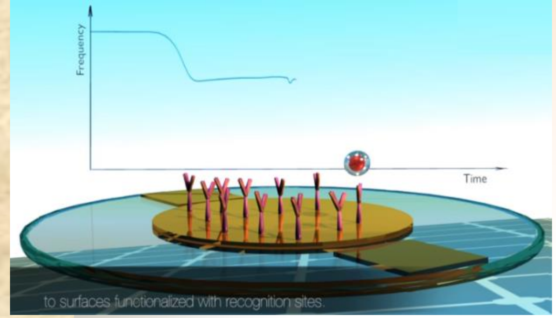








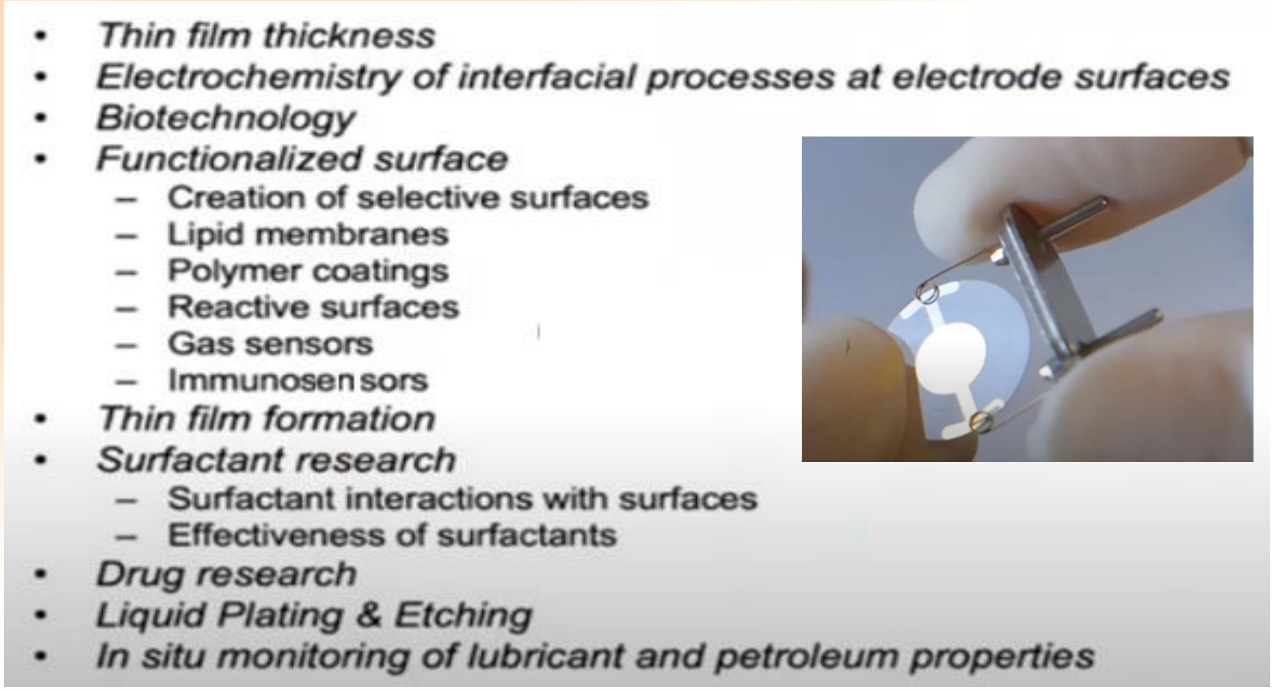




QCM or QCN

- Surface film mass
- Thickness
- Viscoelasticity
- Surface roughness
- Kinetics time dependence

Applications



- *Thin film thickness*
- *Electrochemistry of interfacial processes at electrode surfaces*
- *Biotechnology*
- *Functionalized surface*
  - Creation of selective surfaces
  - Lipid membranes
  - Polymer coatings
  - Reactive surfaces
  - Gas sensors
  - Immunosensors
- *Thin film formation*
- *Surfactant research*
  - Surfactant interactions with surfaces
  - Effectiveness of surfactants
- *Drug research*
- *Liquid Plating & Etching*
- *In situ monitoring of lubricant and petroleum properties*

Quartz crystal microbalance and nanobalance (QCM, QCN)

A mass variation (*Δm*) per unit area (*A*) by measuring the change in frequency (*f*) of a quartz crystal resonator Gűnter Sauerbrey (1959)

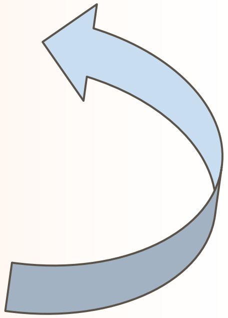
Sauerbrey equation

$$\Delta f = -\frac{2 f_0^2}{A\sqrt{\rho_q \mu_q}} \Delta m$$

where f_0 is the resonant frequency (Hz), Δf is frequency change (Hz), Δm is mass change (g), A is piezoelectrically active crystal area (Area between electrodes in cm^2), ρ_q is density of quartz (2.643 g/cm^3) and μ_q is the shear modulus of quartz for AT-cut crystal ($2.947 x 10^{11}$ $g \cdot cm^{-1} \cdot s^{-2}$).

Faraday:

$$\Delta m = \frac{M}{zF} Q = \frac{M}{zF} I t$$



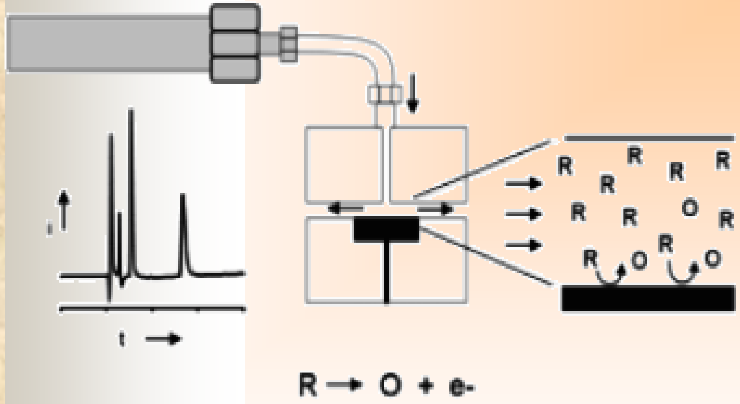
$$\Delta f = -C_f \Delta m$$

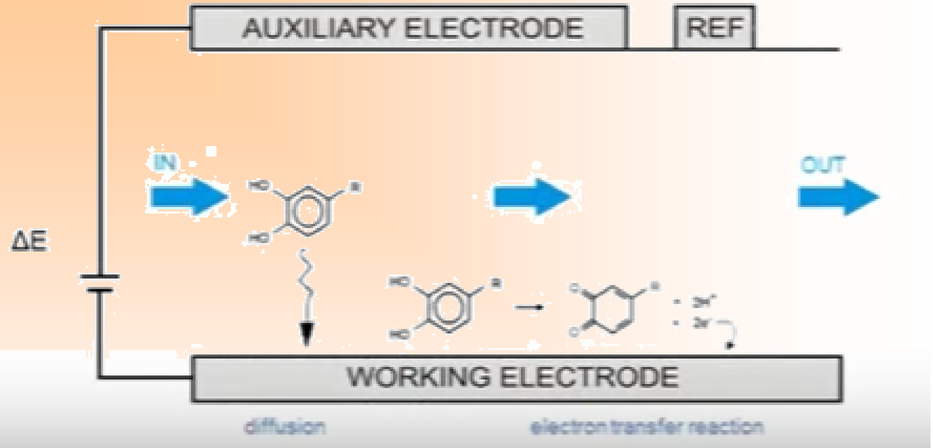
- thin and rigid film
- sensitivity – 0.1-1 ng/cm^2
- for vacuum or for gas phase (correction)
  (in water - decrease in *f* ~ 750Hz)
- the calibration is necessary (C_f)

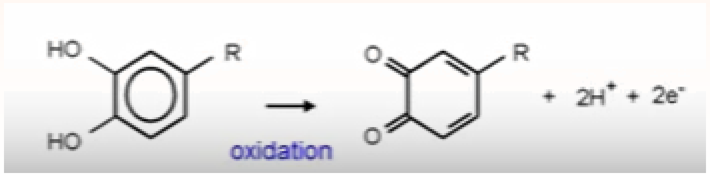
polyvinyferrocene

HPLC with Electrochemical Detection (ECD)

- An extremely selective and sensitive detection technique that is applied in a number of analyses such as the neurotransmitters (dopamine, serotonin and noradrenalin – neurotransmiter analyzer). In combination with the proper electronics, ECD has an enormous linear dynamic range of more then 6 orders of magnitude (50 pmol/L - 100 µmol/L).
- Amperometric electrochemical detection (hydrodynamic mode)
- Interest: electrochemical detectors; electrochemical flow cells; electrodes (carbon); electroactive compounds







HPLC with Electrochemical Detection (ECD)

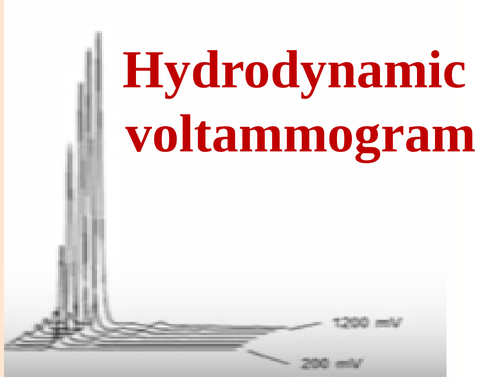
- DC or pulse mode; S/N ratio; optimal ***E***, (low ***E*** – no signals, high ***E*** – interference and noise)
- Difference between UV-Vis detection and ECD

Lambert-Beer equation vs. Cottrell equation

$$absorbance \simeq \varepsilon_{\lambda} d \boxed{c}$$

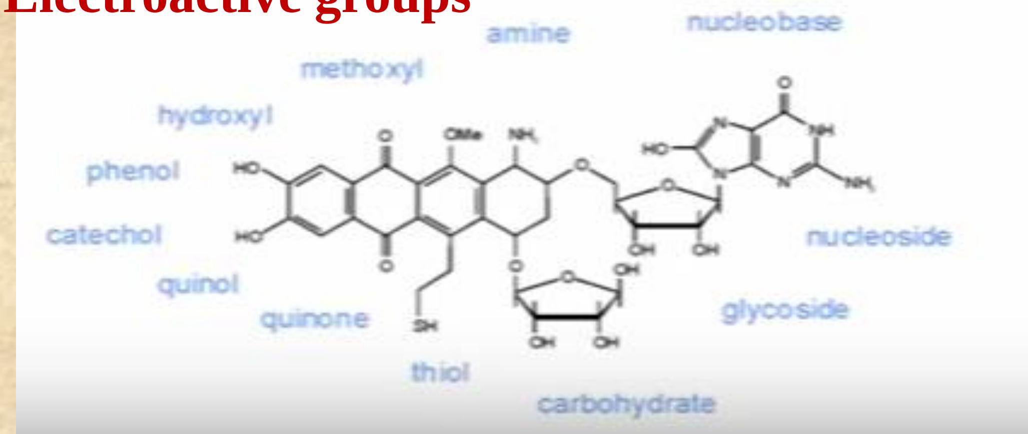
$$current \simeq \frac{zFA\boxed{c}\sqrt{D}}{\sqrt{\pi t}}$$

Hydrodynamic voltammogram



- Aplications: 1) neurotransmitter (in blood and brain)
  2) vitamins, carbohydrates (in food)
  3) phenols (in enviromental samples)

Electroactive groups



Applications

EC-AFM

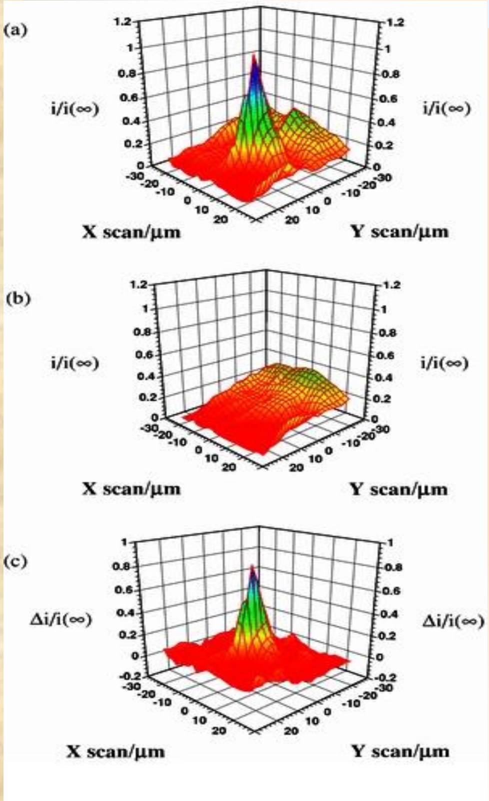
Electrochemical Atomic Field Microscopy

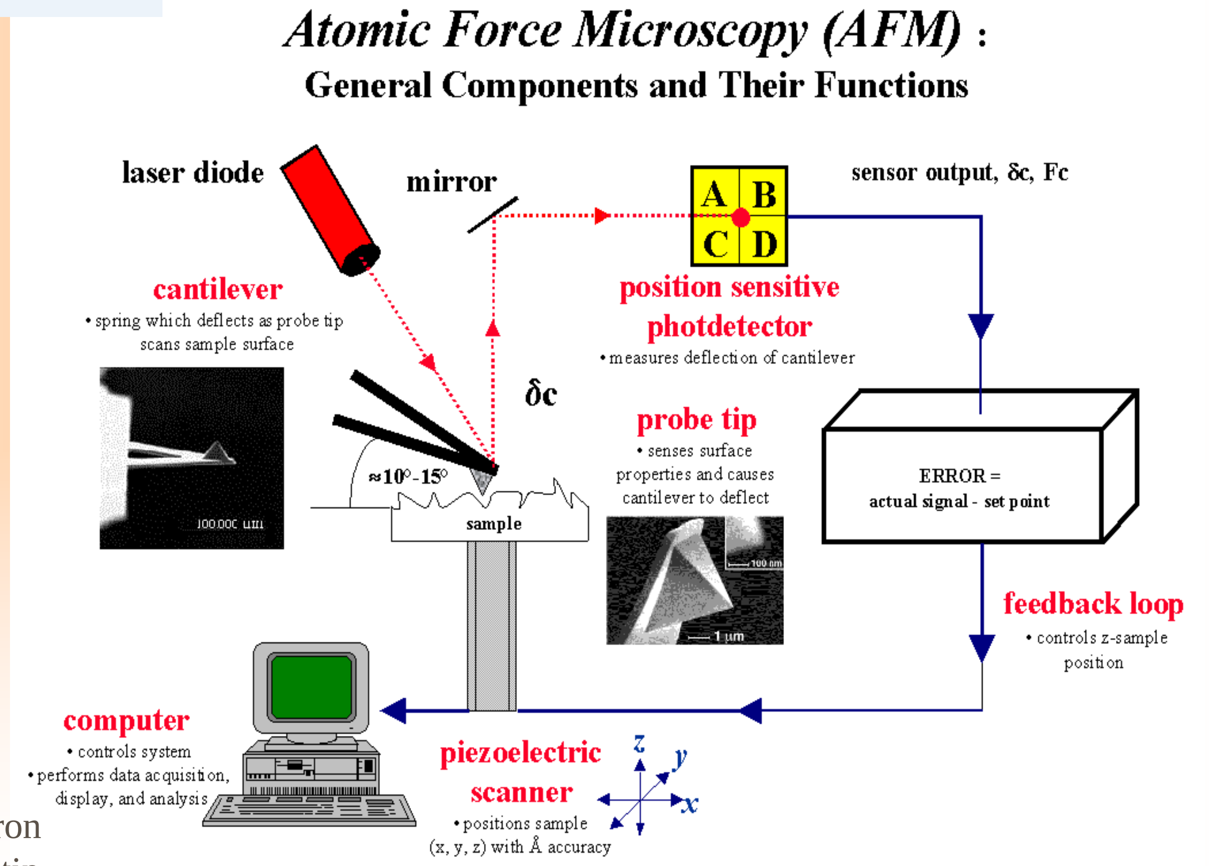
- combines atomic force microscopy (AFM) together with electrochemical measurements
- allows to perform *in-situ* AFM measurements in an electrochemical cell, in order to investigate the actual changes in the electrode surface morphology during electrochemical reactions (increasing interest, „gnome“)
- AFM apparatus is integrated with a three electrode electrochemical cell
- The AFM probe is monitored: surface changes as a function of time, when a potential is applied to the sample.
- Several electrochemical experiments (CV, DPV); E is applied to the tip, with respect to a suitable RE, to drive the process of interest at the tip and the current that flows is typically amplified by a current-to-voltage converter
- During the potential sweeping, the current flows through the sample and the morphology is monitored.

Electrochemical Atomic Field Microscopy

Scanning electrochemical microscopy: principles and applications to biophysical systems: Martin A Edwards et al 2006 Physiol. Meas. 27 R63 doi:10.1088/0967-3334/27/12/R01

EC-AFM





transport-limited current for the one-electron oxidation of ferrocyanide as a function of tip position under pressure); dentin - substrate

Confucius

Slyšel jsem a zapomněl jsem.
Viděl jsem a pamatuji si.
Dělal jsem a pochopil jsem.
(Confucius)

I hear and I forget.
I see and I remember.
I do and I understand.
(Confucius)

"Co slyším, to zapomenu. Co vidím, si pamatuji. Co si vyzkouším, tomu rozumím."

551 BC – 479 BC

Moral philosophy
Social philosophy
Ethics