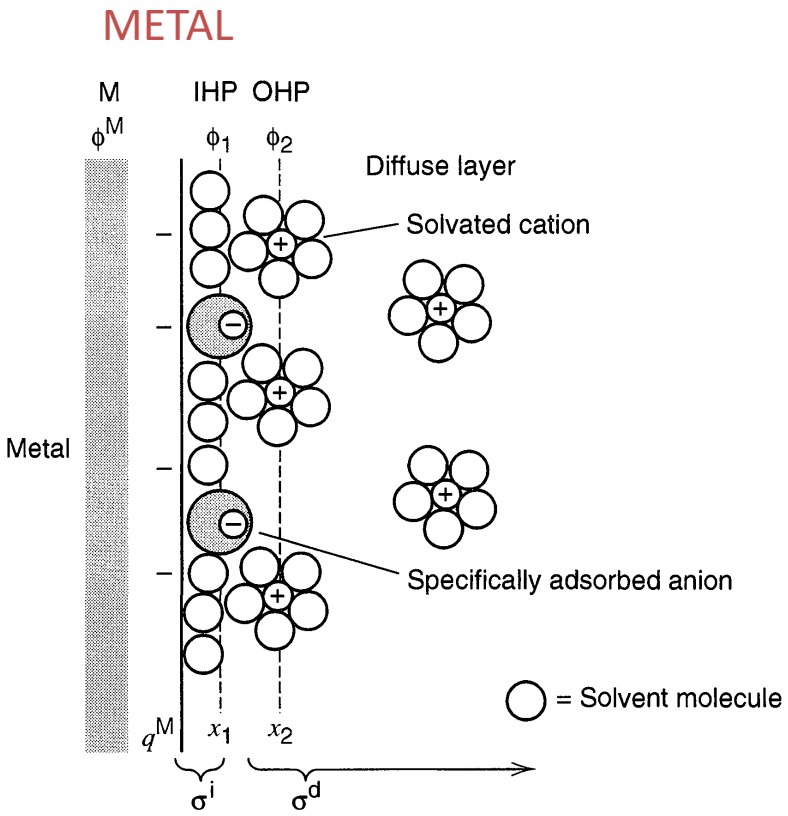
(8) ELECTRODES

Electrical Double layer (Metal). – Electrified interface 1879



Stern layer: first molecular layer. water molecules and Specifically Adsorbed Ions (non necessarily counterions)

IHP: inner Helmholtz plane: locus of the electrical center of the Specifically Adsorbed Ions

Diffuse layer: counterions surrounded by water molecules. Thickness of the diffuse layer: less than 100 Å for 10^{-2} M electrolyte.

OHP: outer Helmholtz plane: locus of the electrical center of the Non Specifically Adsorbed Ion

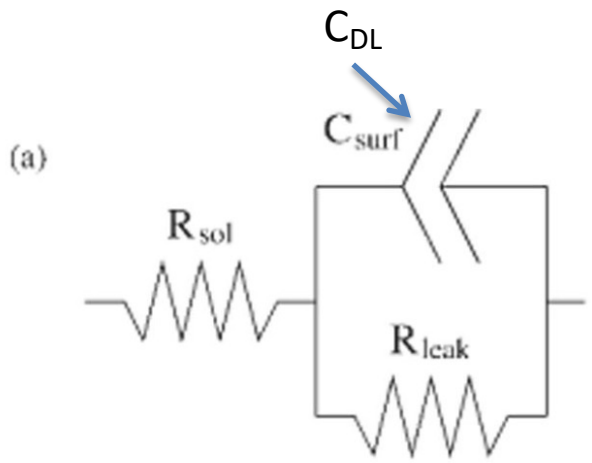
Electrode/solution interface as a sensor

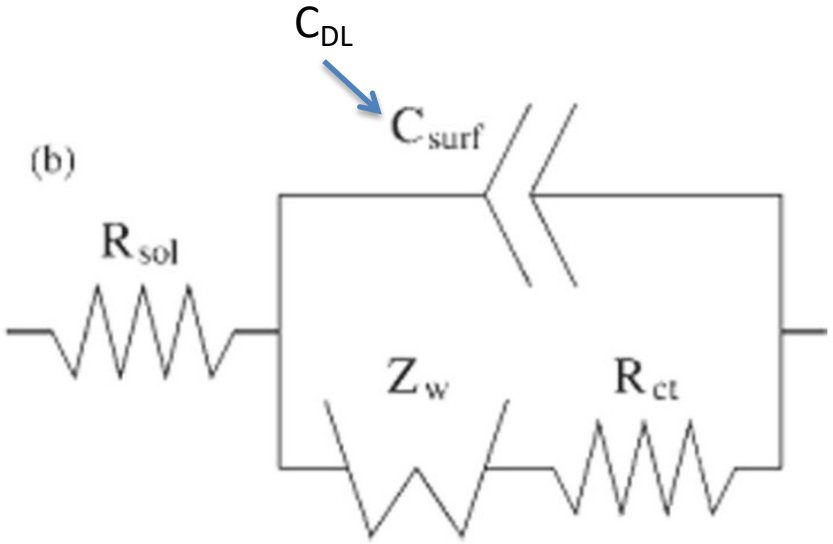
- Measurement of either the electrical parameters, the electrical potential or the current
- Observable phenomena
  - Cell growth
  - Cell membrane potential spikes
  - Presence and changes in molecular layers/coatings on electrodes
  - Binding of molecules on electrodes
  - Change in conformation of molecules bound to electrodes

Electrolyte/electrode interfaces

- Ideally nonpolarizable interface
  - Potential difference is fixed. R_{CT} -> 0.
    - Such electrodes are called "reference electrodes" or non polarizable interfaces.
- Ideally polarizable interfaces
  - The potential difference changes as a consequence of any variation of the potential difference across the whole system which includes the interface. R_{CT} -> ∞
    - Called Ideally polarizable interfaces or blocking interface
- Equivalent circuit with R_{CT} and C_{DL}

Electrical model of the interface





Non faradaic processes

Minor charge transfer effects

Z_w Warburg impedance, small for high frequencies, large for low frequencies. It is caused by diffusion of species

Faradaic processes (resulting in a non negligible net current through the interface)

- Charge transfer due to oxidation/reduction reactions at the interface
- Charge transfer resistance (R_{CT}) due to:
  - Overpotential
  - energy barrier of the redox species reaching the electrode

Integrating electrodes on silicon chip

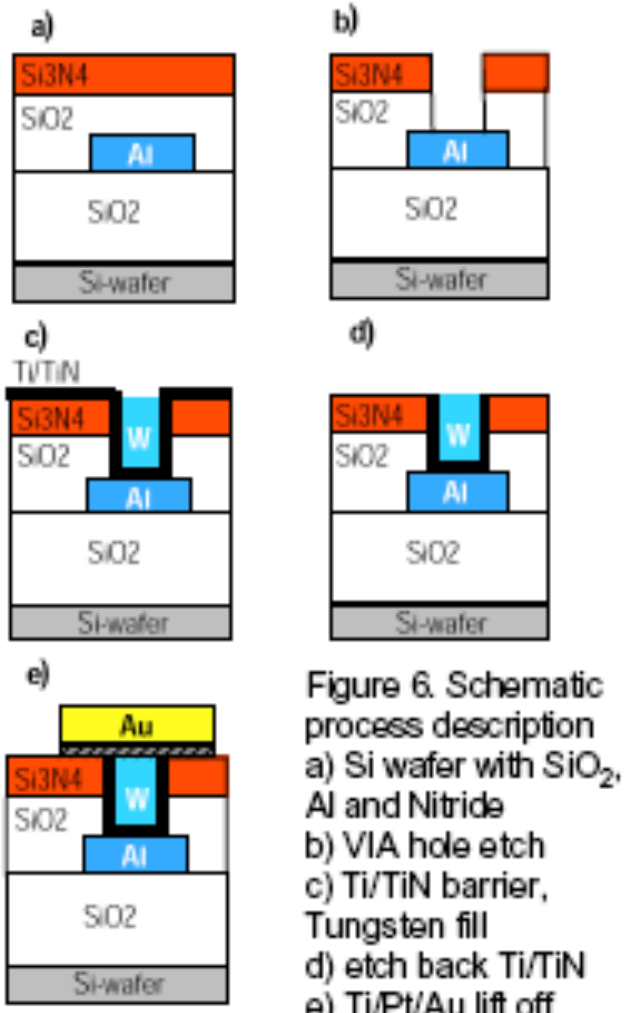
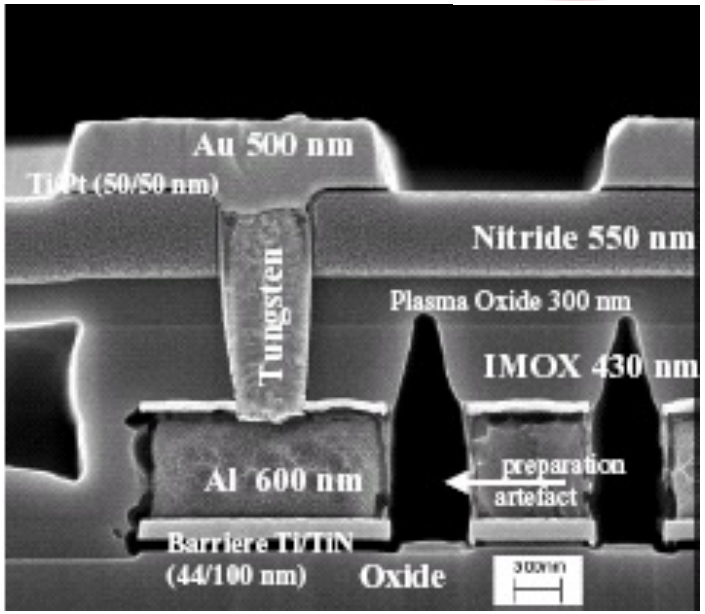


Figure 6. Schematic process description
a) Si wafer with SiO_2, Al and Nitride
b) VIA hole etch
c) Ti/TiN barrier, Tungsten fill
d) etch back Ti/TiN
e) Ti/Pt/Au lift off



Additional process steps needed to expose and contact gold sensor electrodes

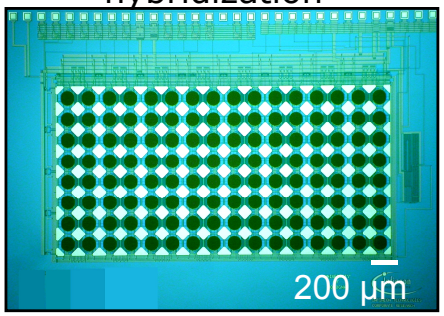
Applications of integrated electrodes

Microarrays.
Electrodes use to drive and fix probes and perform detection of binding

Combimatrix – Invitae Prenatal genetic tests

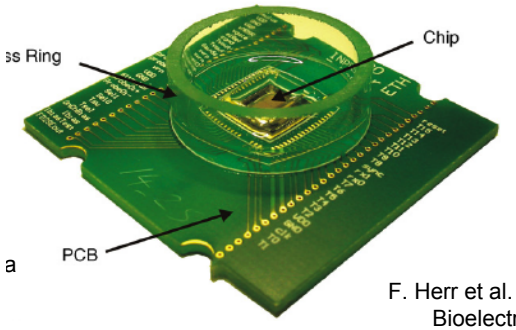
Detecting (DNA)

Electronic chip for measurement of DNA hybridization



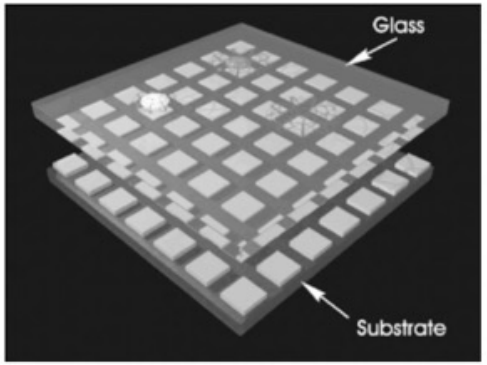
Univ.of Bologna and Infineon Tech, JSSC, 2007

Stimulating/Measuring (Neural Cells)



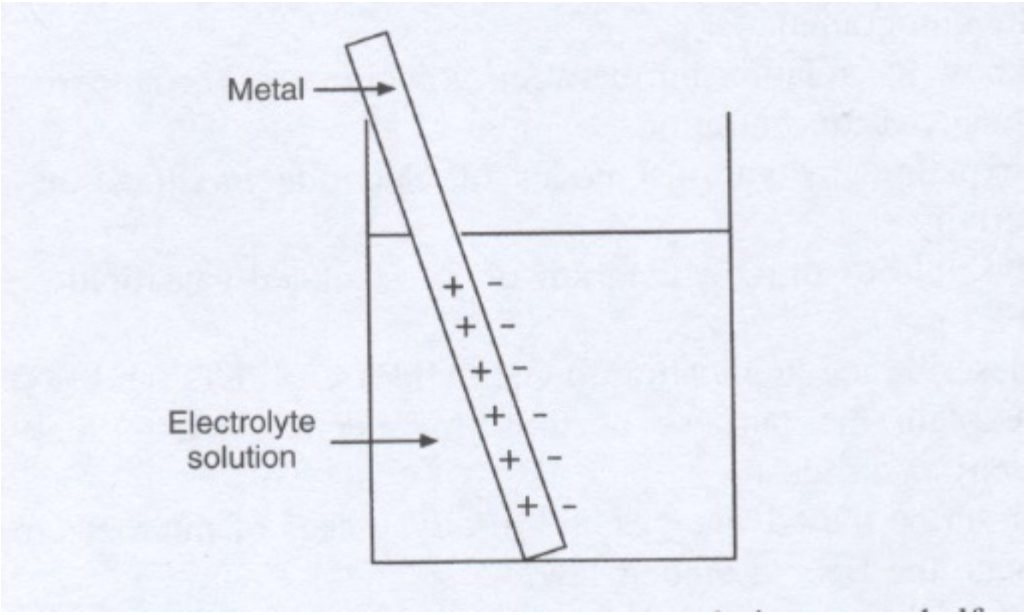
F. Herr et al. Biosensors and Bioelectronics 22 (2007) 2546–2553

Imparting movements to cells



N.Manaresi et al. IEEE J. Solid-State Circuits, VOL. 38, NO. 12, 2003

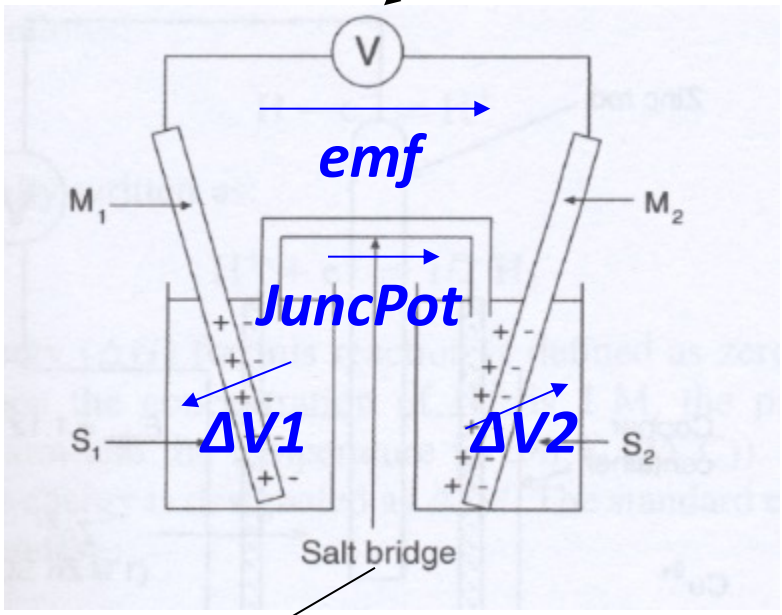
Electrical Behaviour of an electrode in solution



*When a piece of metal is placed in a solution containing ions, a charge separation takes place across the boundary between the metal and the solution. This sets up a **potential**, which cannot be measured directly but requires a second **half cell***

Electrochemical Cell (I=0)

Device which measures potential (very little current flowing through it)



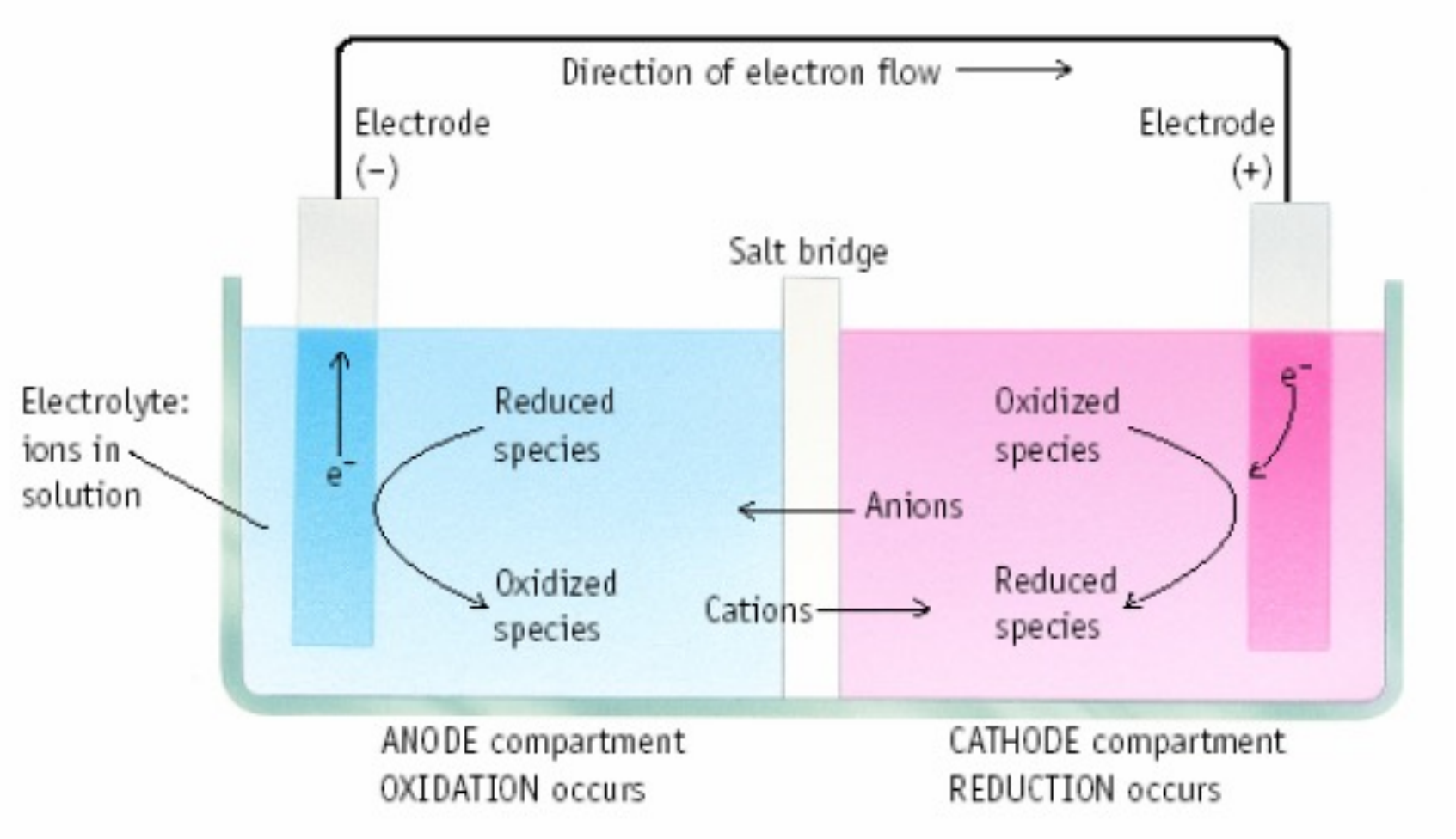
Emf (electromotive force)

- is the difference between the electrode potentials of the two half cells;
- depends on the nature of the electrodes, the nature and concentration of the solution and the liquid junction potential across the salt bridge

emf= ΔV2 +JuncPot- ΔV1

Electrically conductive bridge or membrane

Electrochemical Cell (I≠0)



Reference Electrode

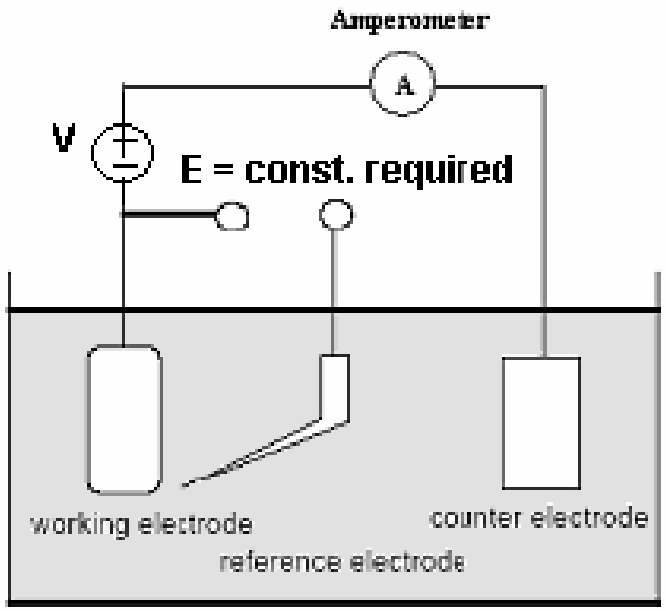
Def: An electrode which has reproducible potentials in solution with low coefficient of variation with temperature. Many varieties of these electrodes have been devised (ideally non polarizable electrodes).

Most common and available commercially:

- Standard hydrogen electrode (SHE) (E=0.000V)
- the silver-silver chloride electrode (E=0.225V saturated)
- the saturated calomel electrode (SCE) (E=+0.242V saturated)

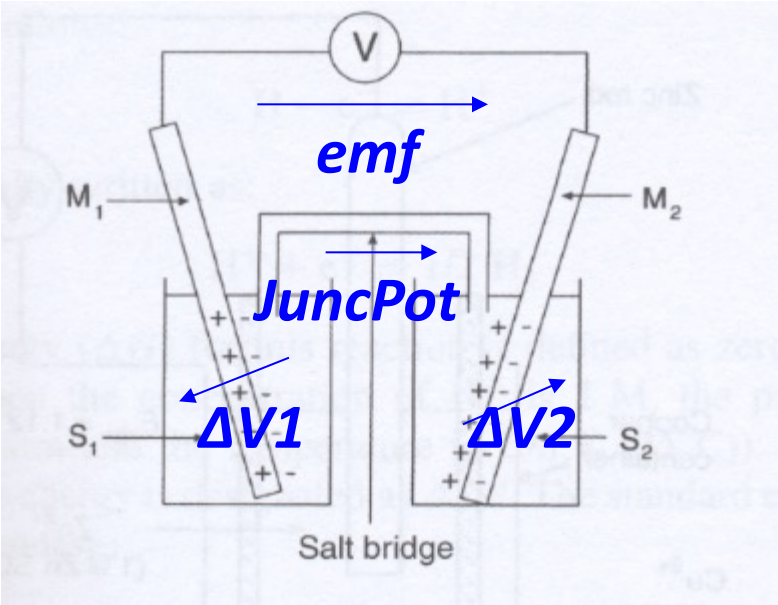
Three-electrode cell

- Requires a precise control of the potential at the electrode.
- Three electrodes:
  - Working electrode (WE),
  - Counter electrode (CE)
  - Reference electrode (RE).
- No current through the RE, ideally.
- RE is used to provide precise control of potential at the WE, and the current from WE to CE is measured.



Electrochemical Measurements techniques

Potentiometric : involves the measurement of the emf (potential) of a cell at zero current. The emf is proportional to the logarithm of the concentration of the substance being determined.



Potentiometry

Potentiometry involves the measurement of the emf of a cell at equilibrium, for example to direcly determine the concentration (activity) of an ion by using the Nernst equation.

Nernst Equation

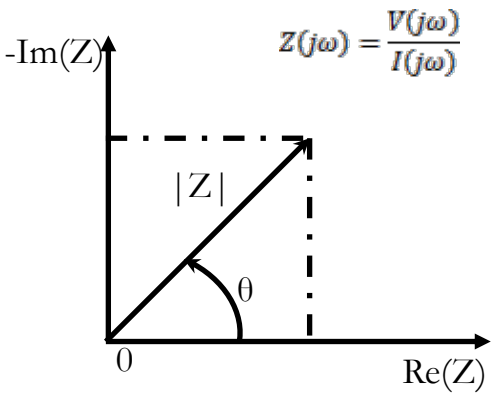
$$E = E^0 + \frac{RT}{nF} \ln\left(\frac{a_{Ox}}{a_R}\right)$$

where **R** is the universal gas constant, **T** is the absolute temperature in degrees Kelvin, **n** is the charge number of the electrode reaction (which is the number of moles of electrons involved), and **F** is the Faraday constant (96,500 C mole^{-1}). $\mathbf{a_R}$ represents the chemical activities of all of the species which appear on the reduced side of the electrode reaction and the notation

$\mathbf{a_{Ox}}$ represents the chemical activities of all of the species which appear on the oxidized side of the electrode reaction.

Impedance spectroscopy

Nyquist plot



- Electrical impedance of solid/liquid interface
- Can read Surface phenomena and changes of bulk proprieties
- Can Identify and separate contributions of different phenomena and elements to the electric and dielectric responses of the biosystem

Data presentation: Nyquist plot/Bode

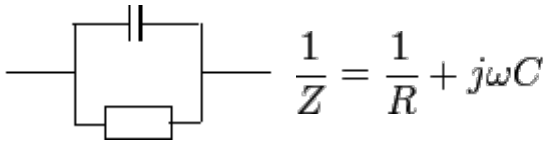
$$Z = \frac{E}{I} = Z_0 \exp(i\phi) = Z_0(\cos\phi + i\sin\phi)$$

Nyquist plot

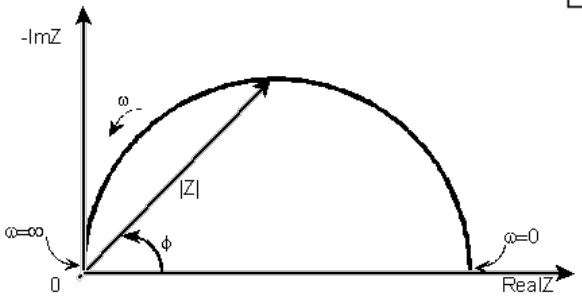
The real part of the impedance is plotted on the x-axis and the (-)imaginary part on the y-axis of a chart. The impedance can be represented as a vector of length |*Z*|. The angle between this vector and the x-axis is *f*.

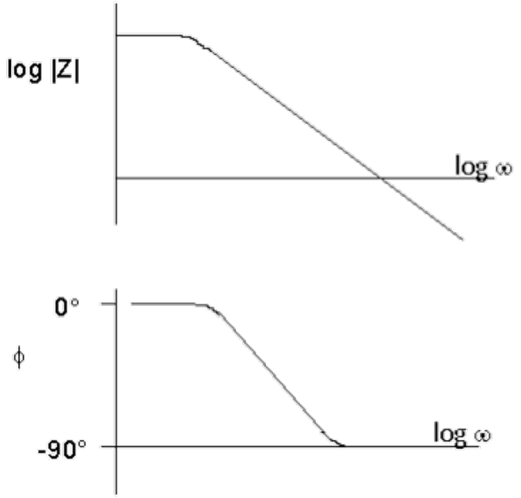
Bode plot

The impedance is plotted with log frequency on the x-axis and the log absolute value of the impedance and phase-shift on the y-axis.



$$\frac{1}{Z} = \frac{1}{R} + j\omega C$$

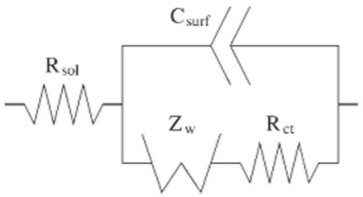




Faradaic and non-Faradaic sensors

- ***Faradaic process***: charges are transferred across an interface (metal-liquid interface). The redox species are alternately oxidized and reduced by transfer of electrons to and from the metal electrode. Faradaic EIS requires the addition of redox-active species to counteract depletion.
- ***Non-Faradaic process*: charging** transient currents flow without charge transfer across the interface (capacitive charging).

Faradaic process



Non-Faradaic process