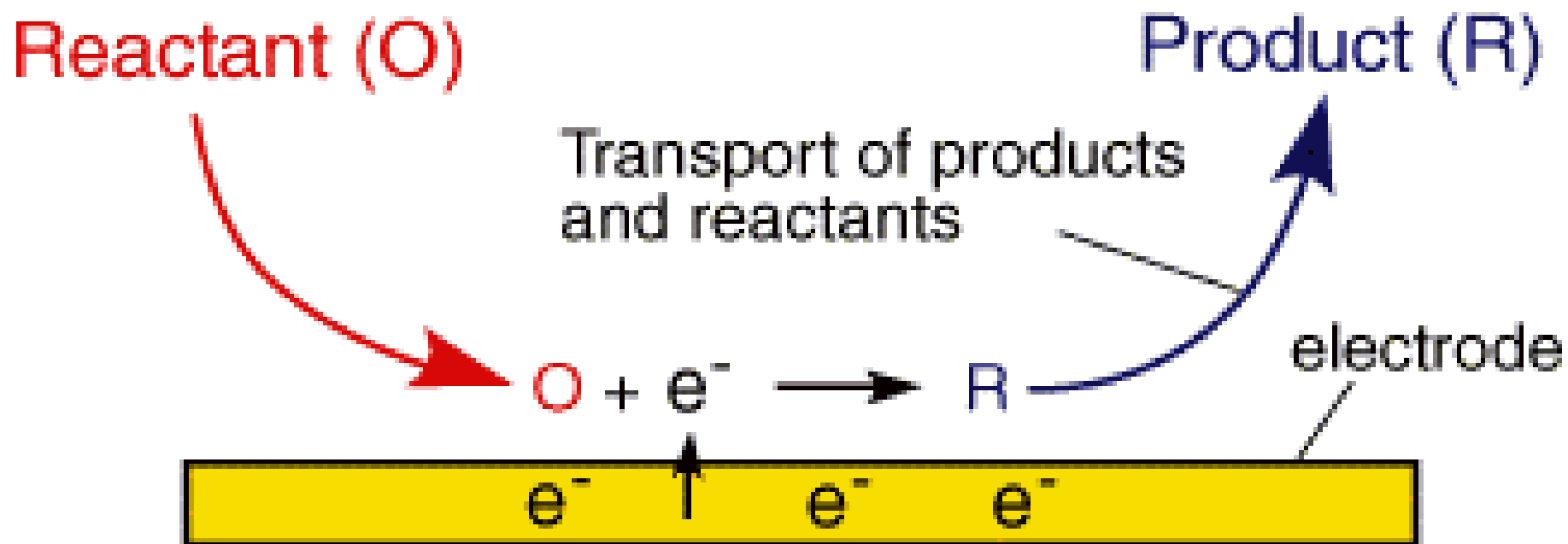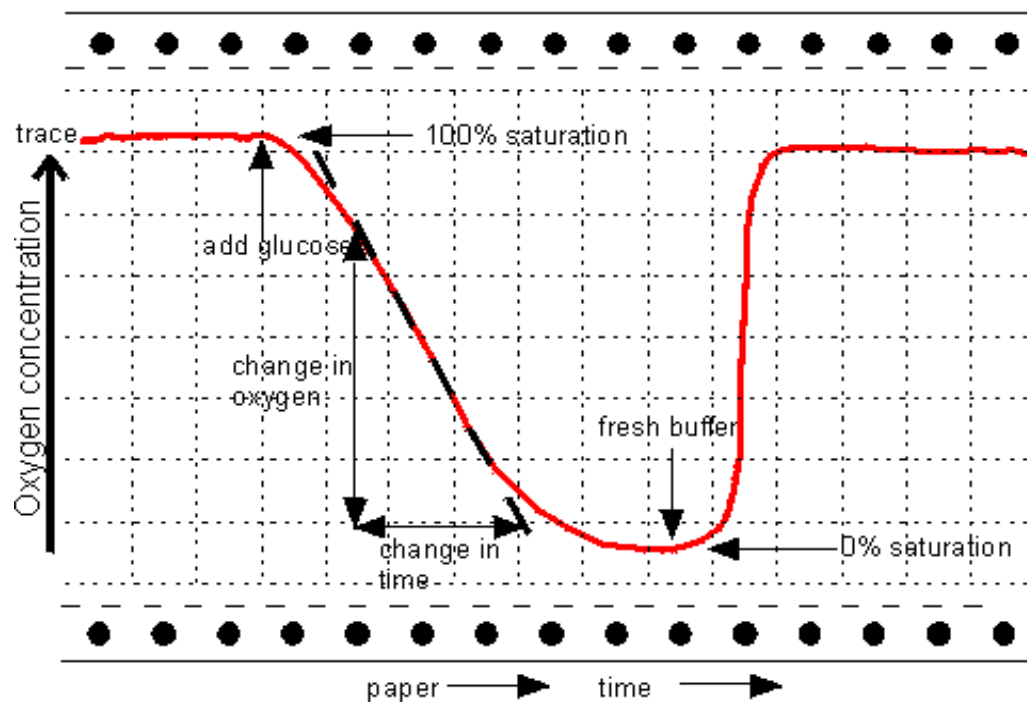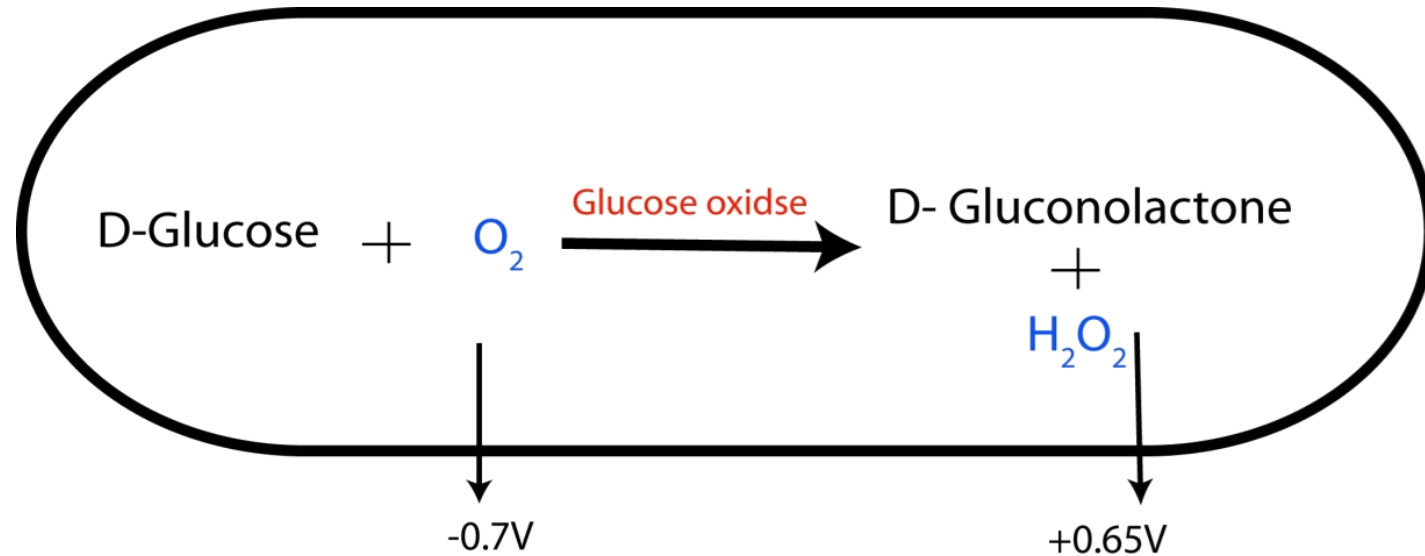# ELECTROCHEMICAL BIOSENSORS

Electrochemistry is the study of electricity and how it relates to chemical reactions. In electrochemistry, electricity can be generated by movements of electrons from one element to another in a reaction known as redox or oxidation-reduction reaction.

- ✓ Amperometric Biosensors
- ✓ Potentiometric Biosensors
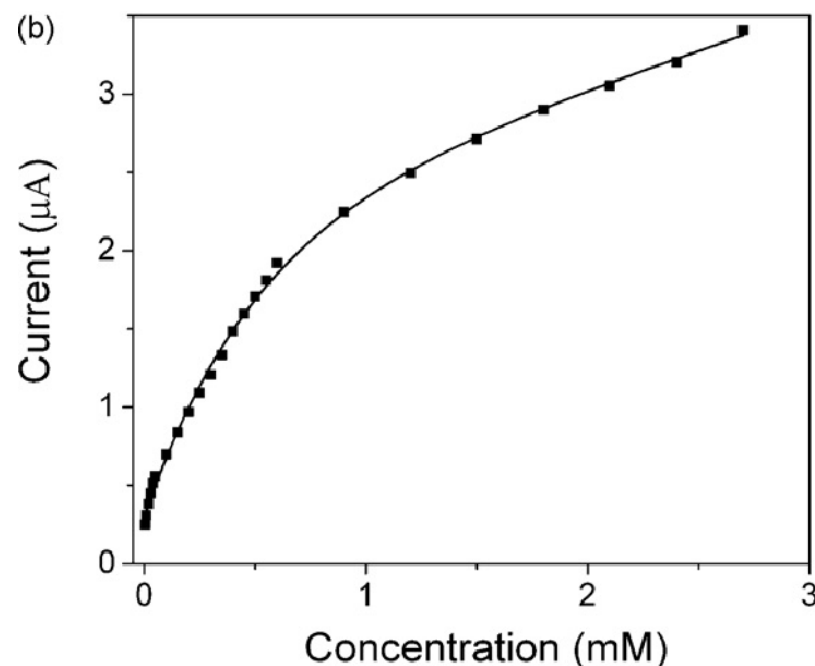- ✓ Conductometric Biosensors

Prof. Eduardo Corton, eduardo@qb.fcen.uba.ar

AMPEROMETRIC BIOSENSORS

Reactant (O)

Product (R)

Transport of products
and reactants

$O + e^- \longrightarrow R$

electrode

e^- e^- e^-

D-Glucose + O_2 →(Glucose oxidse) D- Gluconolactone + H_2O_2

-0.7V   +0.65V

O_2 as redox entity

H_2O_2 as redox entity

What is volt?

- volt is simply the energy (*J*) required to move charge (*c*).
- Reactions are initiated by applying a potential,

$$V = Joule/Coulomb$$

- Application of a voltage to an electrode therefore supplies electrical energy.
- Since electrons possess charge an applied voltage can alter the 'energy' of the electrons within a metal electrode.

Which electron in a metal?

•Electrons of the Fermi-level (E_F).

•The Fermi-level corresponds to the energy of the highest occupied orbitals.

•This level is not fixed and can be moved by supplying electrical energy.

•Electrochemist's are therefore able to alter the energy of the Fermi-level by applying a voltage to an electrode.

•Depending upon the position of the Fermi level it may be thermodynamically feasible to reduce/oxidise a species in solution.

$$O \ + \ e \ \rightleftharpoons \ R$$

The figure below shows the Fermi-level within a metal along with the orbital energies (HOMO and LUMO) of a molecule (*O*) in solution.
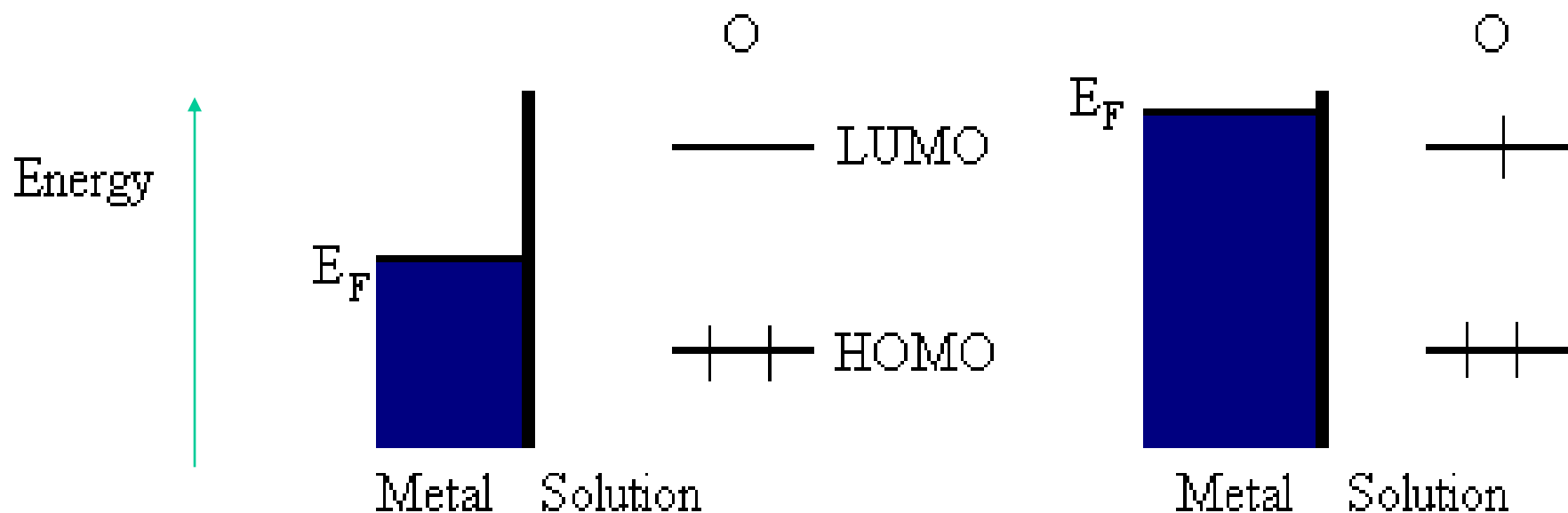
Voltage

- Left: E_F < the E of LUMO of (*O*), hence ***thermodynamically unfavourable*** for an e to jump from the electrode to O.
- Right: E_F > the E of LUMO of (*O*), it is ***thermodynamically favourable*** for the electron transfer to occur to O.

The fundamental relationship between the current flowing and the applied voltage is given by the following Butler-Volmer equation,.

$$i = i_o \left\{ \frac{[O]_o}{[O]_{bulk}} e^{\frac{-\alpha n F (E - E_s)}{RT}} - \frac{[R]_o}{[R]_{bulk}} e^{\frac{(1 - \alpha) n F (E - E_s)}{RT}} \right\}$$

This expression shows how the current will respond to changes in potential, the value of **alpha** and the quantity i_o which is called the exchange current (density). The term **alpha** reflects the sensitivity of the transition state to the applied voltage. If **alpha = 0** then the transition state shows no potential dependence. Typically **alpha = 0.5** this means that the transition state responds to potential in a manner half way between the reactants and the products response.

Here we wish to see how the voltage influences the current in the absence of concentration effects. To do this we will assume that the a solution is well mixed ie that the surface and bulk concentrations are identical which will be reasonable under condition of small current flow. Now the Butler-Volmer equation simplifies to
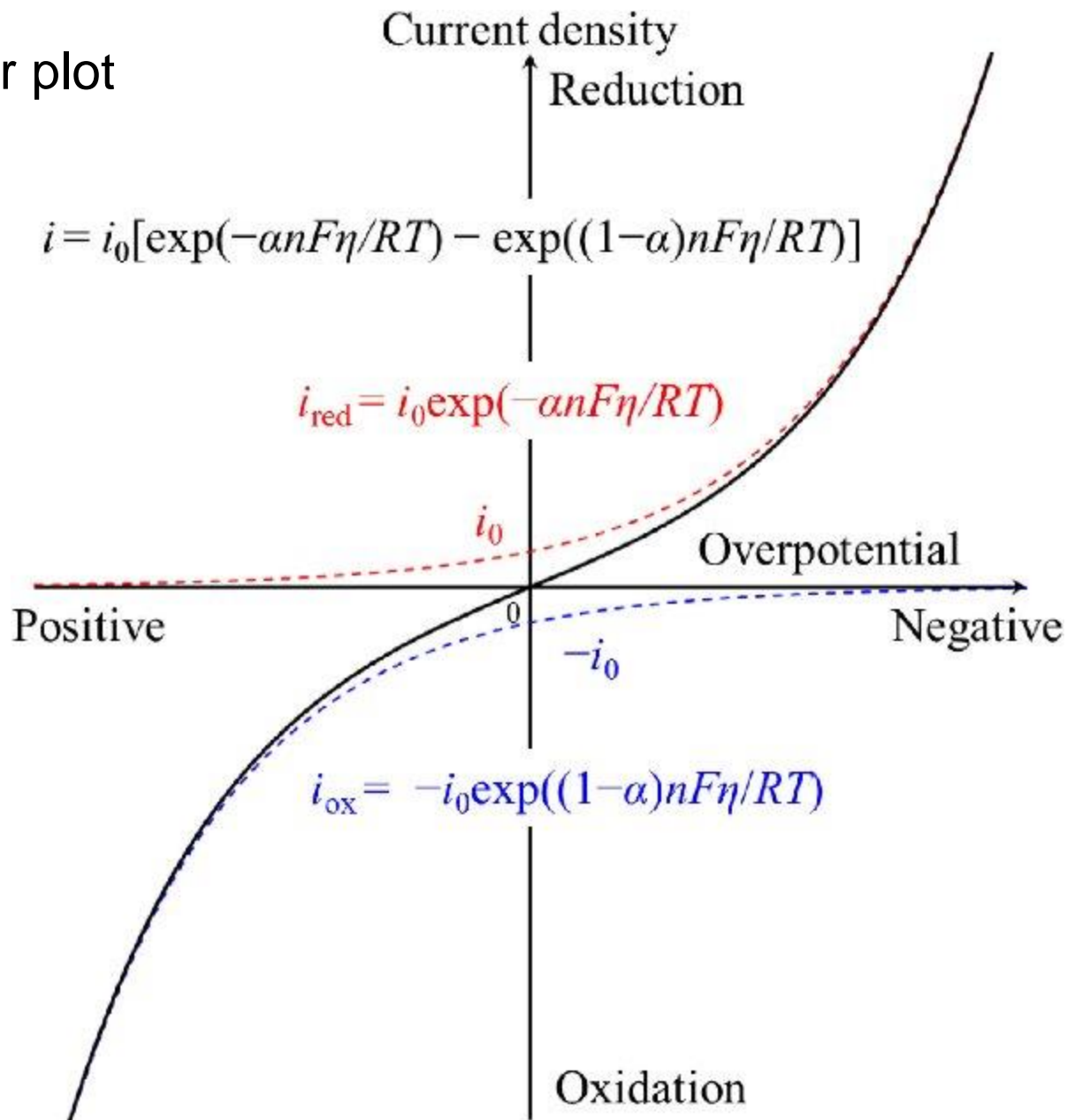
$$i = i_o \left\{ e^{\frac{-\alpha n F (E - E_s)}{RT}} - e^{\frac{(1 - \alpha) n F (E - E_s)}{RT}} \right\}$$

Without concentration and therefore mass transport effects to complicate the electrolysis it is possible to establish the effects of voltage on the current flowing. In this situation the quantity **E - E_e** reflects the activation energy required to force current **i** to flow.

Buttler-Volmer plot

$E - E_{equi}$ = overpotential (eta, η)

$$i = i_0[\exp(-\alpha nF\eta/RT) - \exp((1-\alpha)nF\eta/RT)]$$

Current density

Reduction

$$i_{\mathrm{red}} = i_0\exp(-\alpha nF\eta/RT)$$

i_0

Overpotential

Positive

0

Negative

$-i_0$

$$i_{\mathrm{ox}} = -i_0\exp((1-\alpha)nF\eta/RT)$$

Oxidation

- **Amperometry** is a subclass of voltammetry in which the electrode is held at constant potentials for various lengths of time.
- Voltammetry applies a constant and/or varying potential at an electrode's surface and measures the resulting current with a three electrode system.
- To conduct such an experiment requires at least two electrodes.
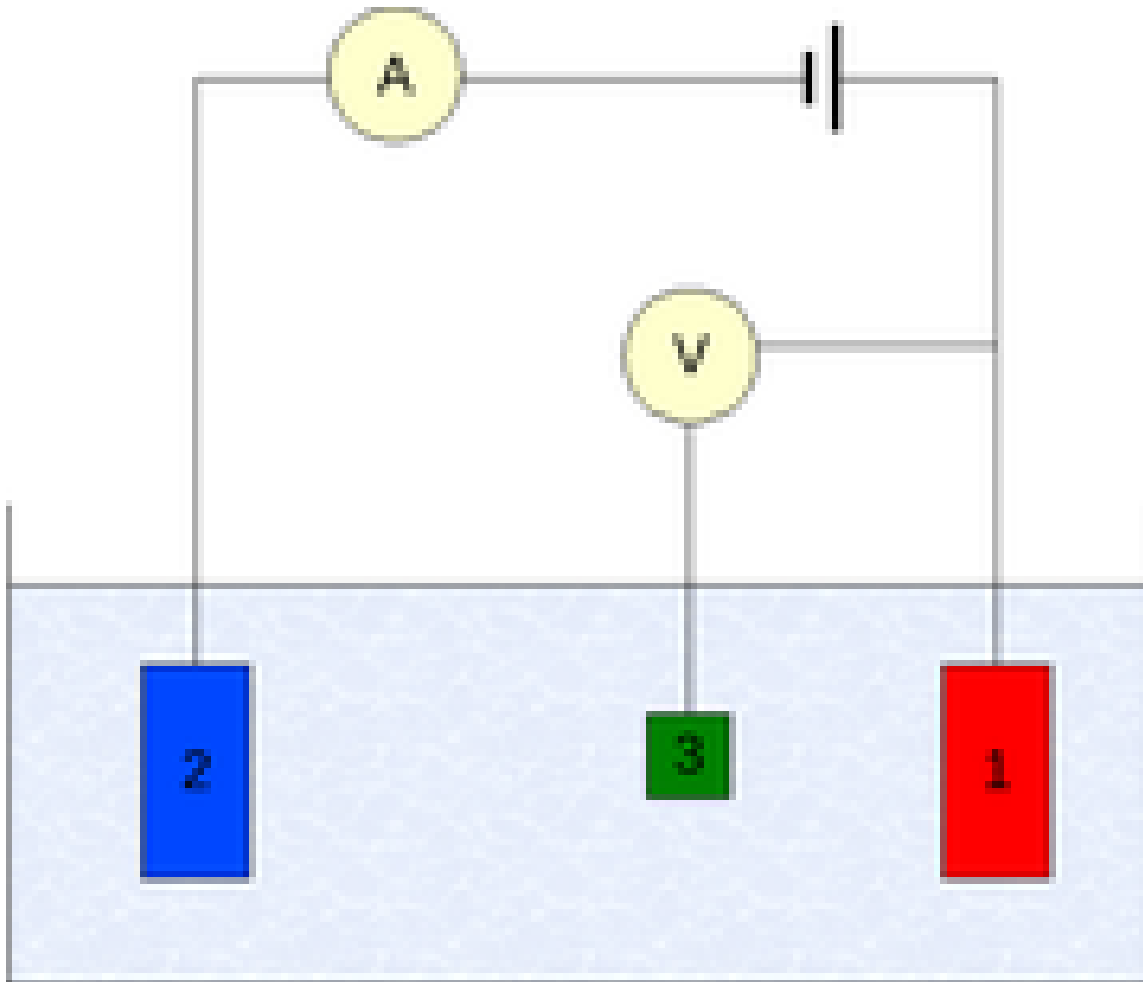
Three-electrode setup:
(1) working electrode;
(2) auxiliary electrode;
(3) reference electrode

<u>Working electrode</u>: It makes contact with the analyte, must apply the desired potential in a controlled way and facilitate the transfer of <u>electrons</u> to and from the analyte.
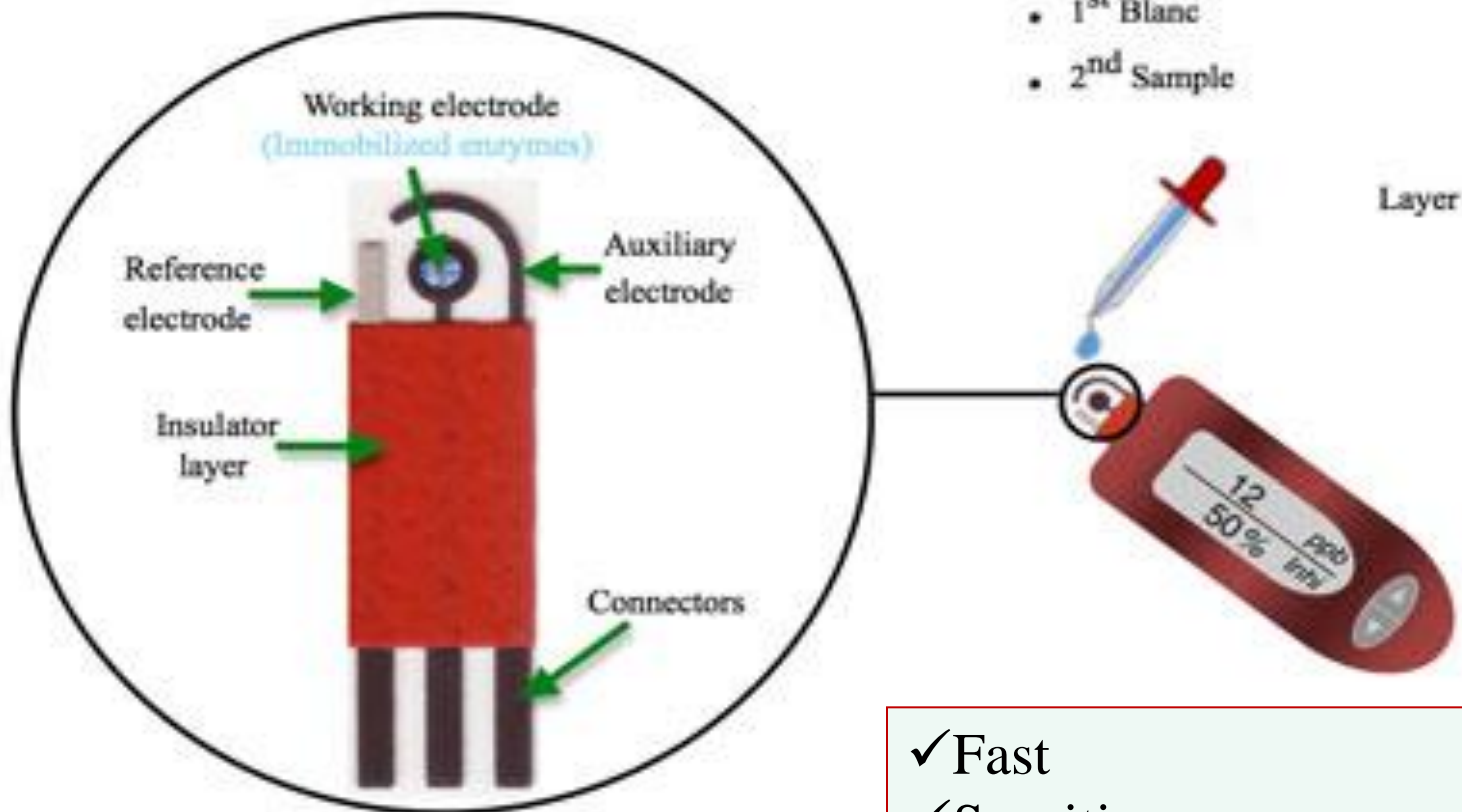
<u>Reference electrode</u>: It acts as the other half of the cell, has a known potential with which to gauge the potential of the working electrode.

It may use to balance the electrons added or removed by the working electrode. While this is a viable setup, it is extremely difficult for an electrode to maintain a constant potential while passing current to counter redox events at the working electrode. To solve this problem, the role of supplying electrons and referencing potential has been divided between two separate electrodes.

<u>Aauxiliary electrode</u>: <u>It</u> passes all the current needed to balance the current observed at the working electrode. To achieve this current, the auxiliary will often swing to extreme potentials at the edges of the solvent window, where it oxidizes or reduces the solvent or supporting electrolyte.

These electrodes, the <u>working</u>, <u>reference</u>, and <u>auxiliary</u> make up the modern three electrode system.

Disposable 3 electrode cell,
Made by screen printing technique

Working electrode
(Immobilized enzymes)

Reference electrode

Auxiliary electrode

Insulator layer

Connectors

Two steps

- 1st Blanc
- 2nd Sample

Layer

12
50 % ppb
Inhi

✓Fast
✓Sensitive
✓Selective
✓Label free
✓Min. or no sample clean-up
✓Small size-low cost

Potentiostats

Reference
Electrode

Working
Electrode

Counter
Electrode
(Pt)

Potentiostat

Electrochemical
Cell
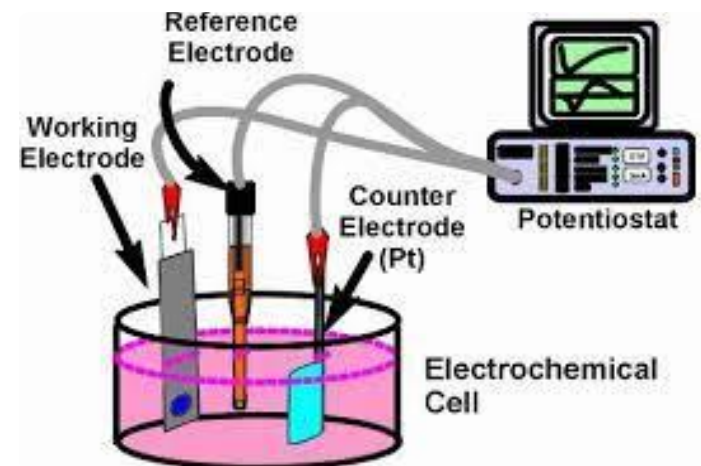
Low cost potentiostats

Electrochemistry- Open Source Potentiostats

Rodeostat FeatherWing
Rodeostat
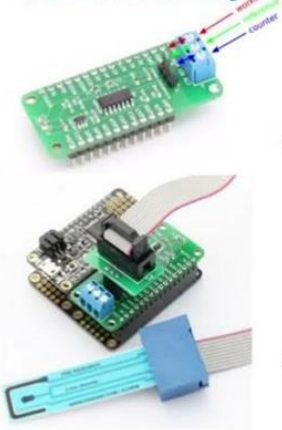
- 3 electrodes - working, counter, reference
- control potential between working and reference
- utilize feedback for control
- simultaneously measure working electrode current
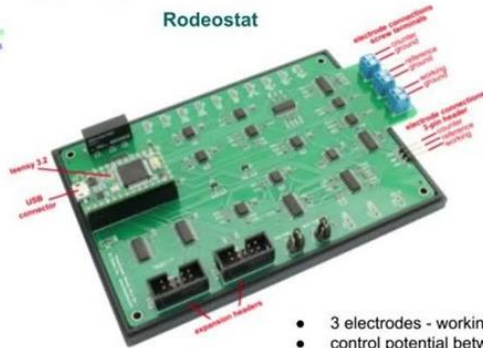
Applications include:
- characterization of processes
- coatings and corrosion
- biosensor development

OSHW
US002129

IO Rodeo

github.com/iorodeo/rodeostat_featherwing   github.com/iorodeo/potentiostat
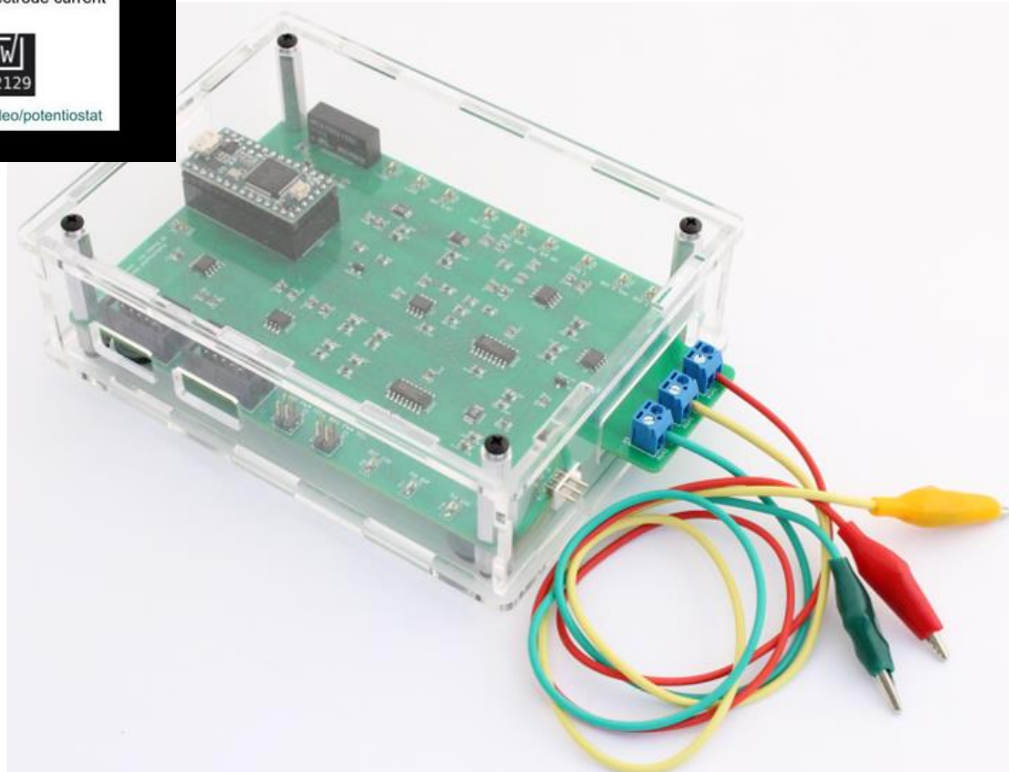
Redox reactions
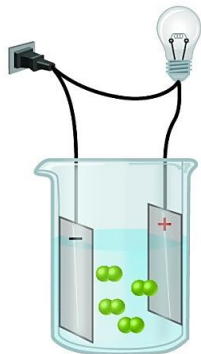# Check out the basics!

A substance is oxidized when it gives up electrons (it is a reducing agent).

A substance is reduced when it takes electrons (it is an oxidizing agent)
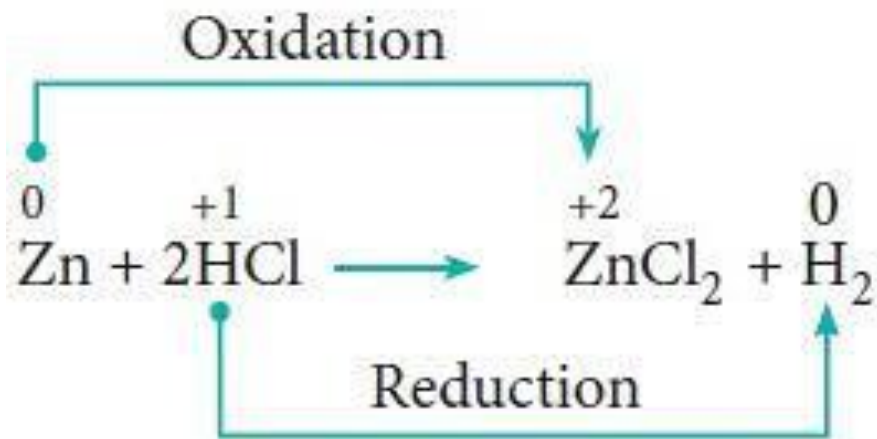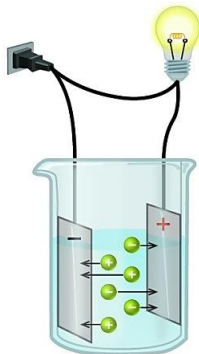
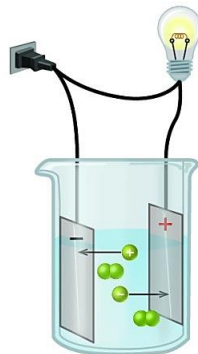# Basic electrochemical nomenclature

ELECTROLYTE: Substance that conducts electric current in solution (because it is dissociated into ions).

ethanol
No conductivity

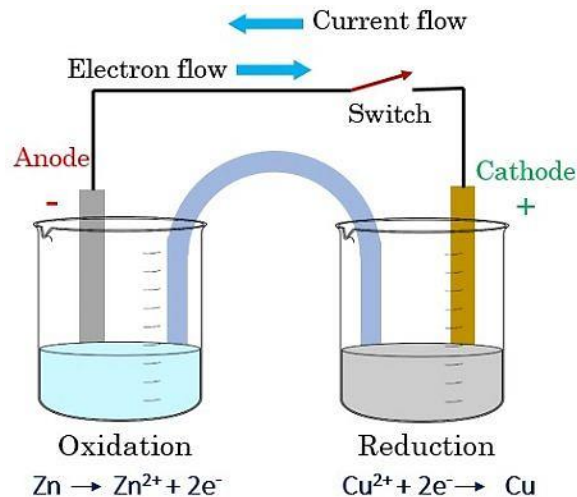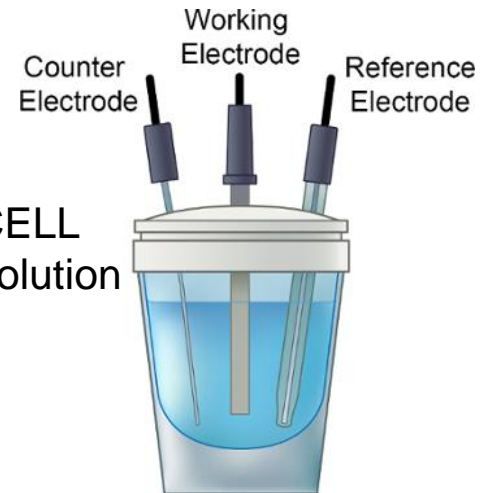KCl
High conductivity

acetic acid solution
Low conductivity

ELECTROCHEMICAL CELL
Container containing the solution and the electrodes.

Working Electrode
Counter Electrode
Reference Electrode

ELECTRODES
Conductors, normally metallic, placed in contact with the electrolyte solution.

Current flow
Electron flow
Switch
Anode
−
Cathode
+

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

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

Set-up for Galvanic Cell

Circuit Globe
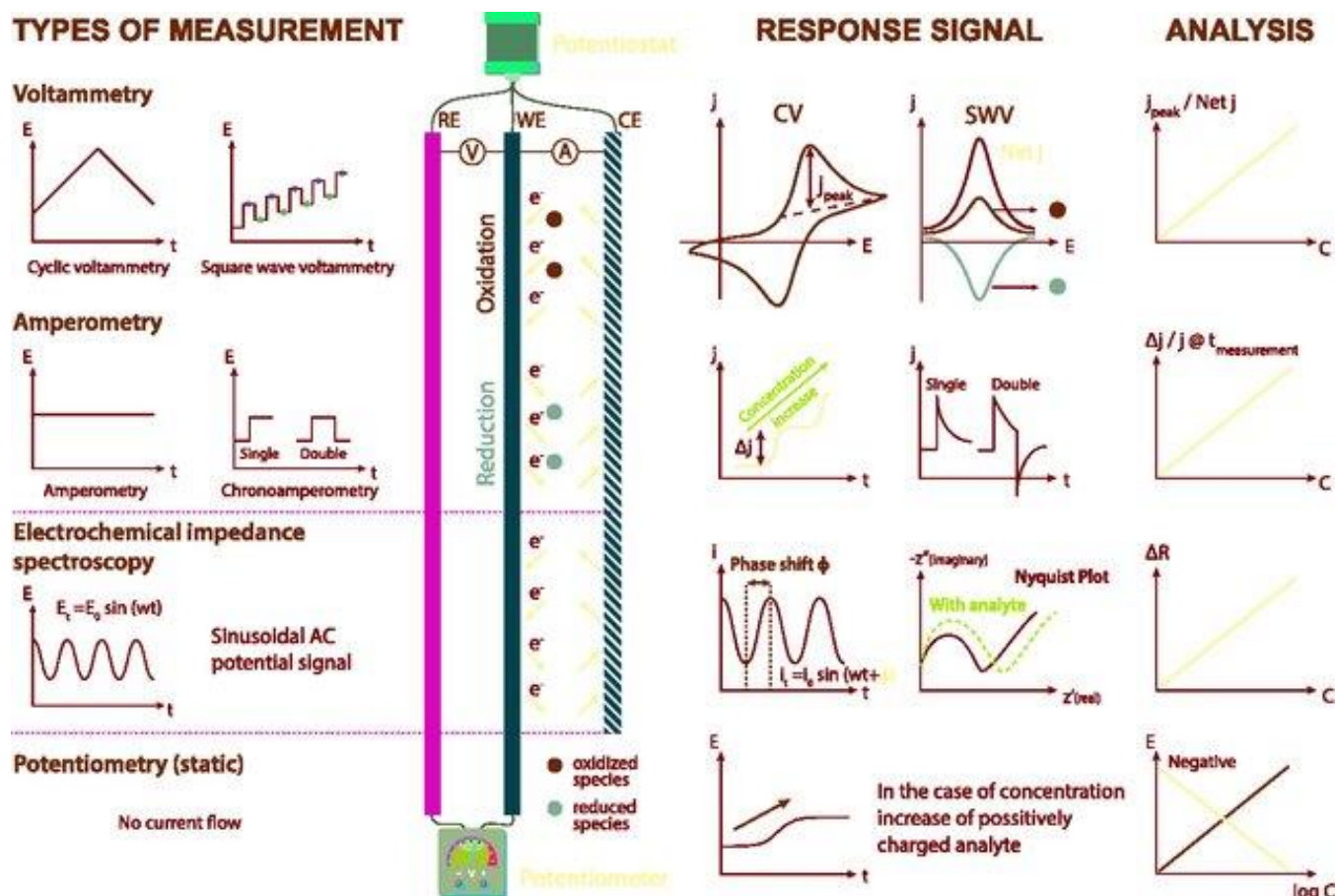
ELECTROLYTIC CELL: The externally generated current causes a non-spontaneous chemical reaction. Spend energy
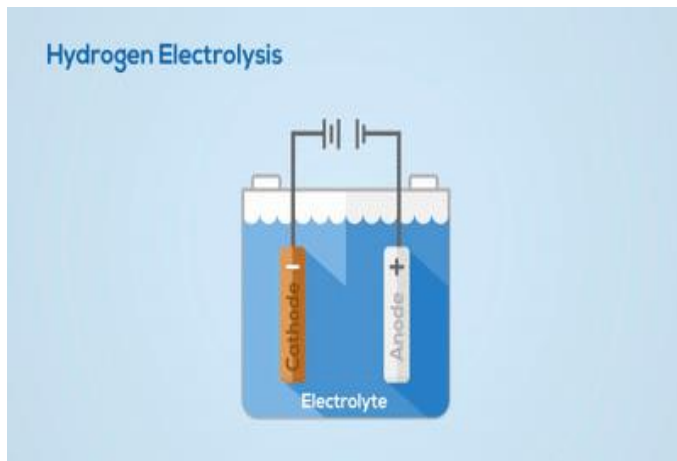
GALVANIC or VOLTAIC CELL: It is a spontaneous chemical reaction. Produces energy
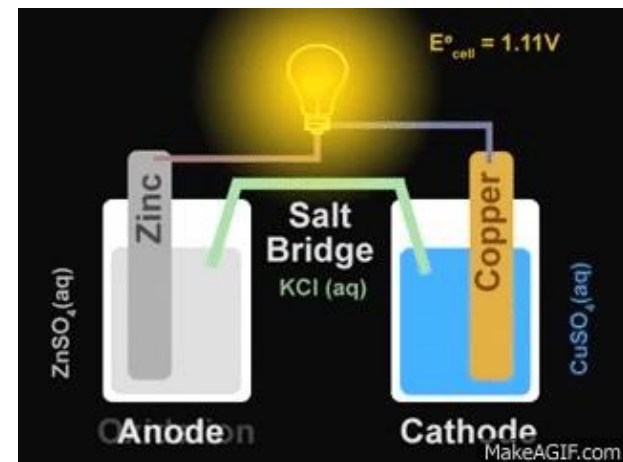
Types of electrochemical techniques (just to check the almost endless possibilities)

Electrochemical signal transduction. There are four main types of electrochemical methods of analysis: voltammetry, amperometry, electrochemical impedance spectroscopy (EIS), and potentiometry. In voltammetry, a potential sweep (linear, cyclic, i.e., cyclic voltammetry (CV), or pulsed, e.g., square-wave voltammetry (SWV)) with respect to the reference electrode (RE) is applied by a potentiostat (an electronic instrument) between the working (WE) and counter (CE) electrodes and the current generated is measured as the analytical signal. In amperometry, a constant or stepped (chronoamperometry) potential is employed instead. In potentiometry, the open-circuit voltage between the WE and RE is measured as the analytical signal which can increase or decrease depending on concentration of the analyte. In EIS, a sinusoidal potential over a frequency range is applied to an electrochemical cell. By measuring the current response, the impedance (resistance, capacitance etc.) of the system can be estimated, allowing the study of the surface and material properties.