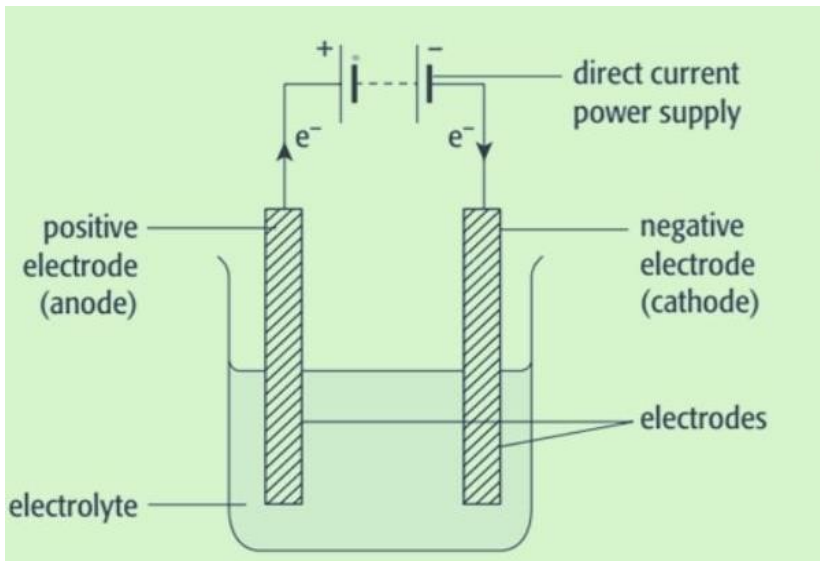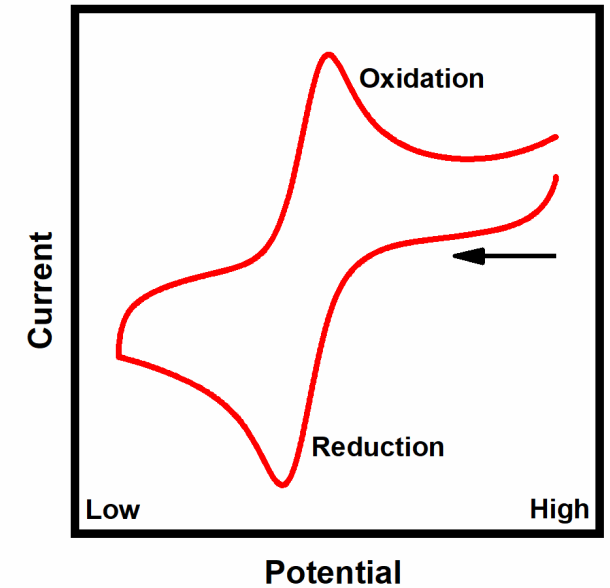# electrochemistry

Electrochemistry is the study of the generation of electricity from the energy released during spontaneous chemical reactions, as well as the application of electrical energy to non-spontaneous chemical transformations.

Outlines

Electrochemistry: Definition and Importance

Type of electrochemical cells

Typical setup of an electrochemical cell

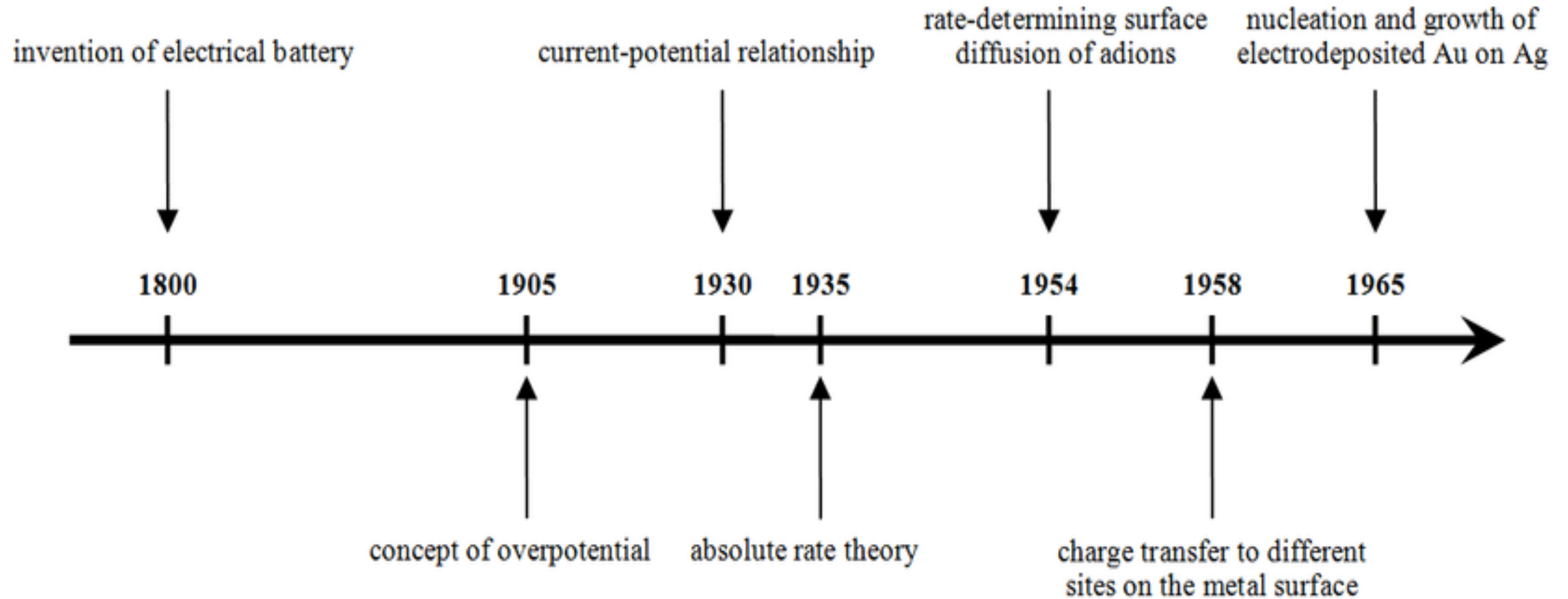**Electrode and their functions**

Electrolytes

Electrochemistry

Electrochemistry is the study of the generation of electricity from the energy released during spontaneous chemical reactions, as well as the application of electrical energy to non-spontaneous chemical transformations.
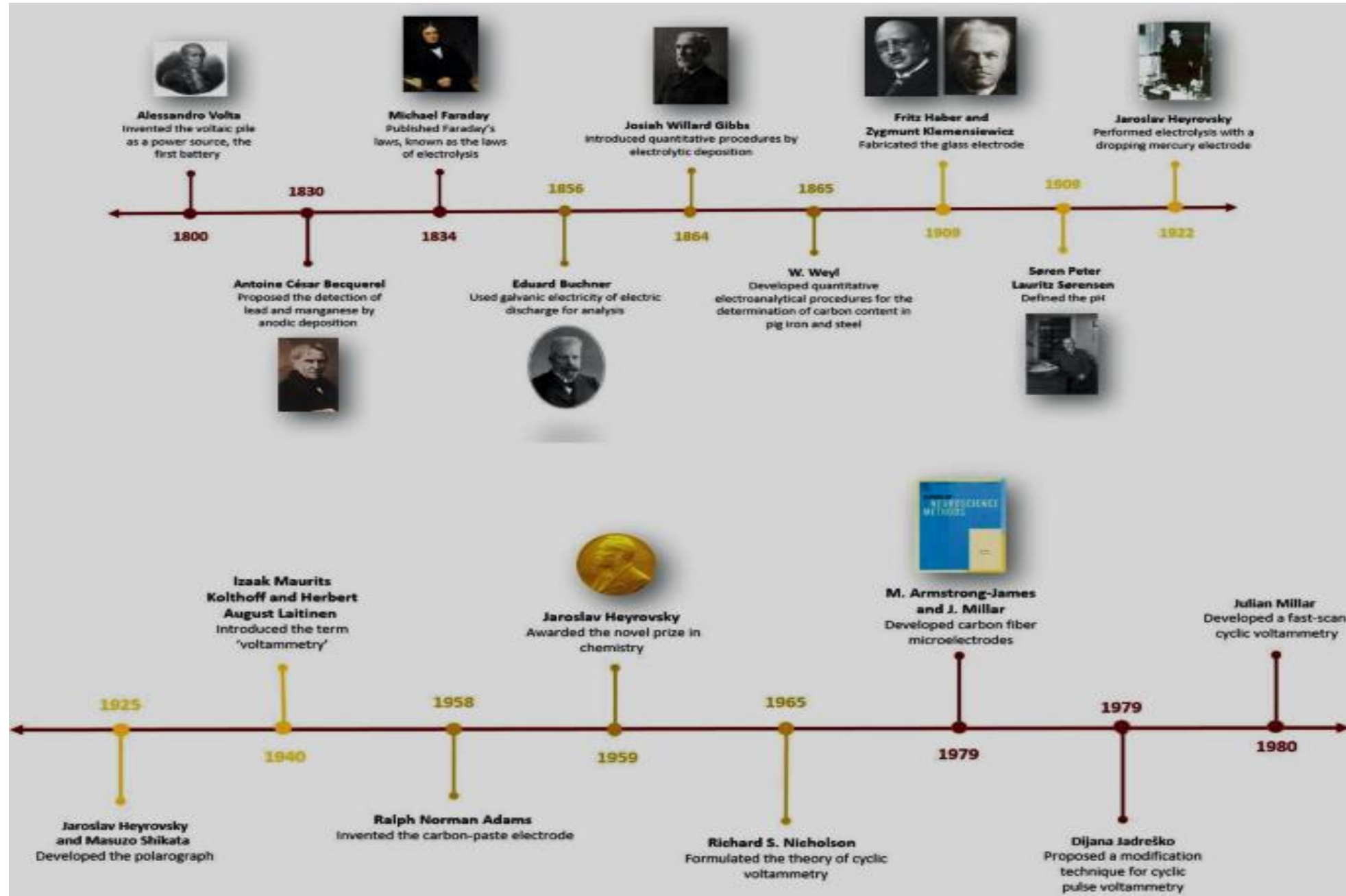
It is the branch of physical chemistry concerned with the relationship between electrical potential difference and identifiable chemical change. These reactions involve electrons moving via an electronically conducting phase (typically an external electrical circuit, but not necessarily, as in electroless plating) between electrodes separated by an ionically conducting and electronically insulating electrolyte (or ionic species in a solution).

When a chemical reaction is driven by an electrical potential difference, as in electrolysis, or if a potential difference results from a chemical reaction as in an electric battery or fuel cell, it is called an electrochemical reaction. Unlike in other chemical reactions, in electrochemical reactions electrons are not transferred directly between atoms, ions, or molecules, but via the aforementioned electronically conducting circuit. This phenomenon is what distinguishes an electrochemical reaction from a conventional chemical reaction.
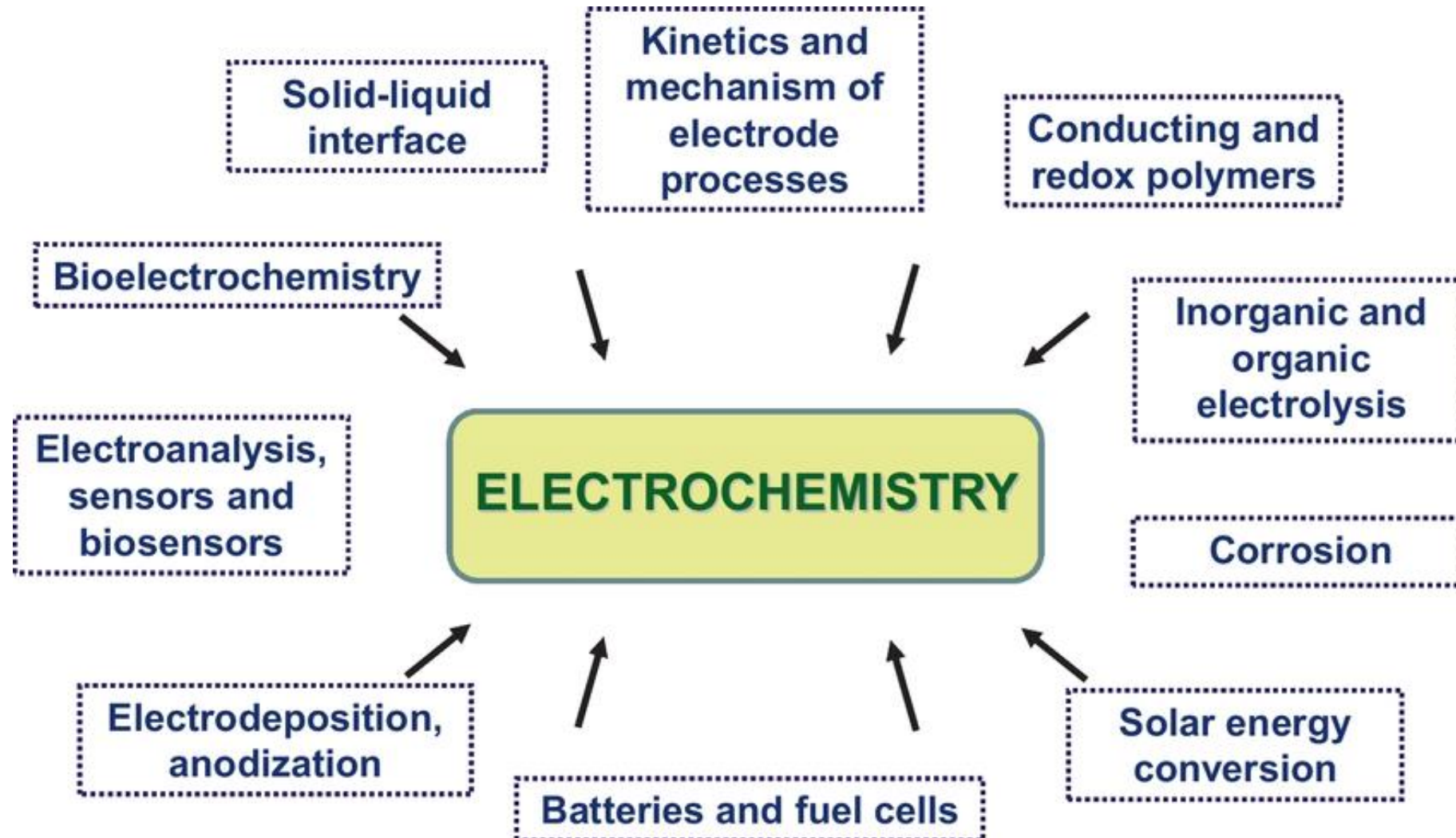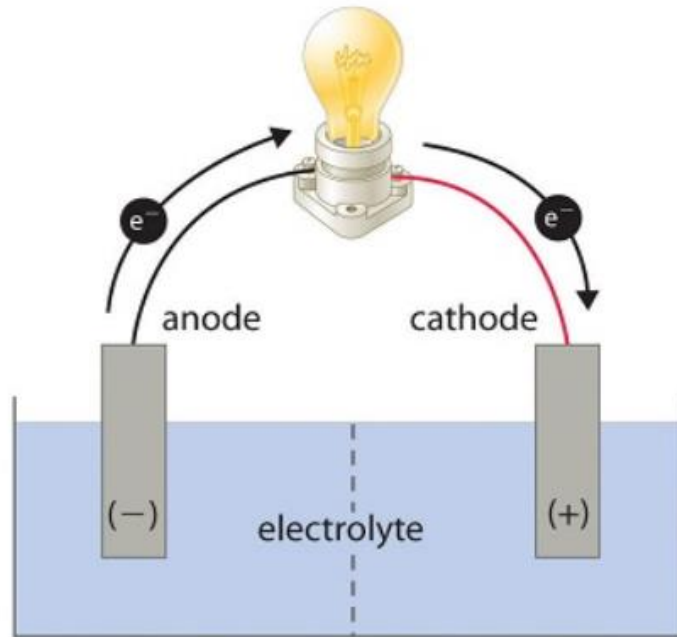
Timeline

Timeline

Alessandro Volta
Invented the voltaic pile as a power source, the first battery

Michael Faraday
Published Faraday's laws, known as the laws of electrolysis

Josiah Willard Gibbs
Introduced quantitative procedures by electrolytic deposition

Fritz Haber and Zygmunt Klemensiewicz
Fabricated the glass electrode

Jaroslav Heyrovsky
Performed electrolysis with a dropping mercury electrode

1830   1856   1865   1909

1800   1834   1864   1909   1922

Antoine César Becquerel
Proposed the detection of lead and manganese by anodic deposition

Eduard Buchner
Used galvanic electricity of electric discharge for analysis

W. Weyl
Developed quantitative electroanalytical procedures for the determination of carbon content in pig iron and steel

Søren Peter Lauritz Sørensen
Defined the pH

Izaak Maurits Kolthoff and Herbert August Laitinen
Introduced the term 'voltammetry'

Jaroslav Heyrovsky
Awarded the novel prize in chemistry

M. Armstrong-James and J. Millar
Developed carbon fiber microelectrodes

Julian Millar
Developed a fast-scan cyclic voltammetry

1925   1958   1965   1979

1940   1959   1979   1980

Jaroslav Heyrovsky and Masuzo Shikata
Developed the polarograph

Ralph Norman Adams
Invented the carbon-paste electrode

Richard S. Nicholson
Formulated the theory of cyclic voltammetry

Dijana Jadreško
Proposed a modification technique for cyclic pulse voltammetry
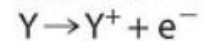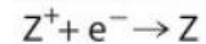
Applications

Type of electrochemical cells

GALVANIC CELL

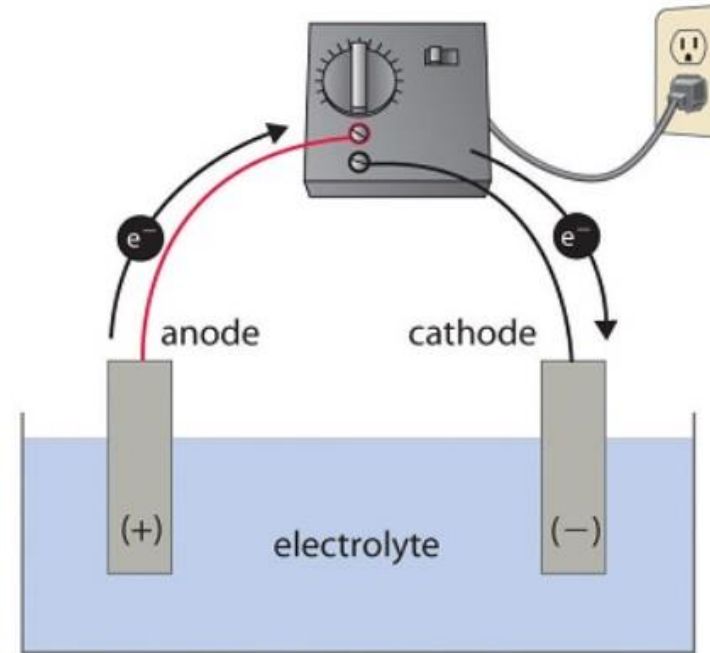Energy released by spontaneous redox reaction is converted to electrical energy.

Oxidation half-reaction:
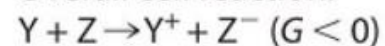$Y \rightarrow Y^+ + e^-$

Reduction half-reaction:
$Z^+ + e^- \rightarrow Z$
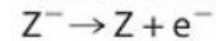
Overall cell reaction:
$Y + Z \rightarrow Y^+ + Z^-$ $(G < 0)$

ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

Oxidation half-reaction:
$Z^- \rightarrow Z + e^-$

Reduction half-reaction:
$Y^+ + e^- \rightarrow Y$

Overall cell reaction:
$Y^+ + Z^- \rightarrow Y + Z$ $(G > 0)$

A Typical Electrochemical Setup

Electrode connections

Holes for degassing
or reagent addition

Teflon cap

Glass solution reservoir

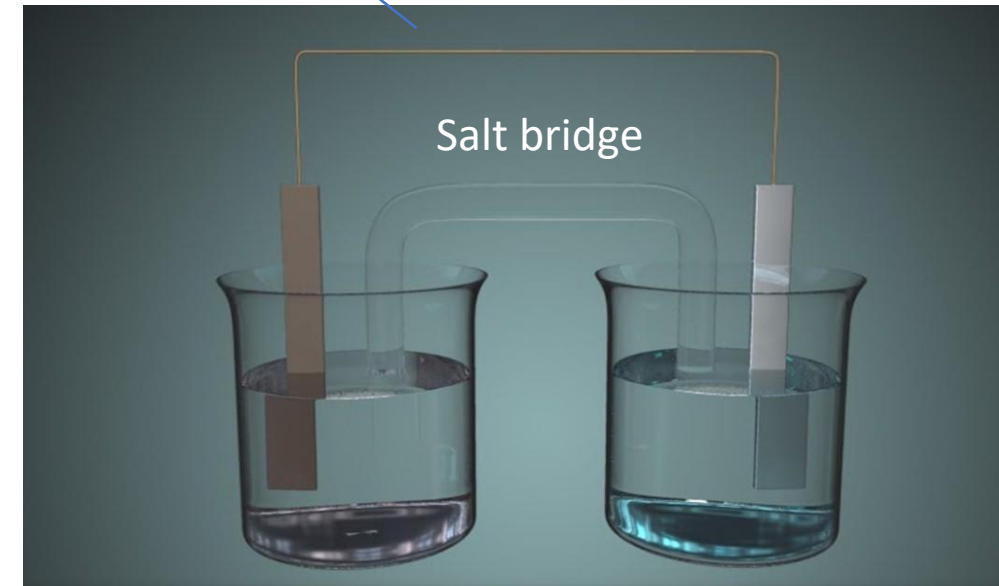Electrolyte solution

Working electrode

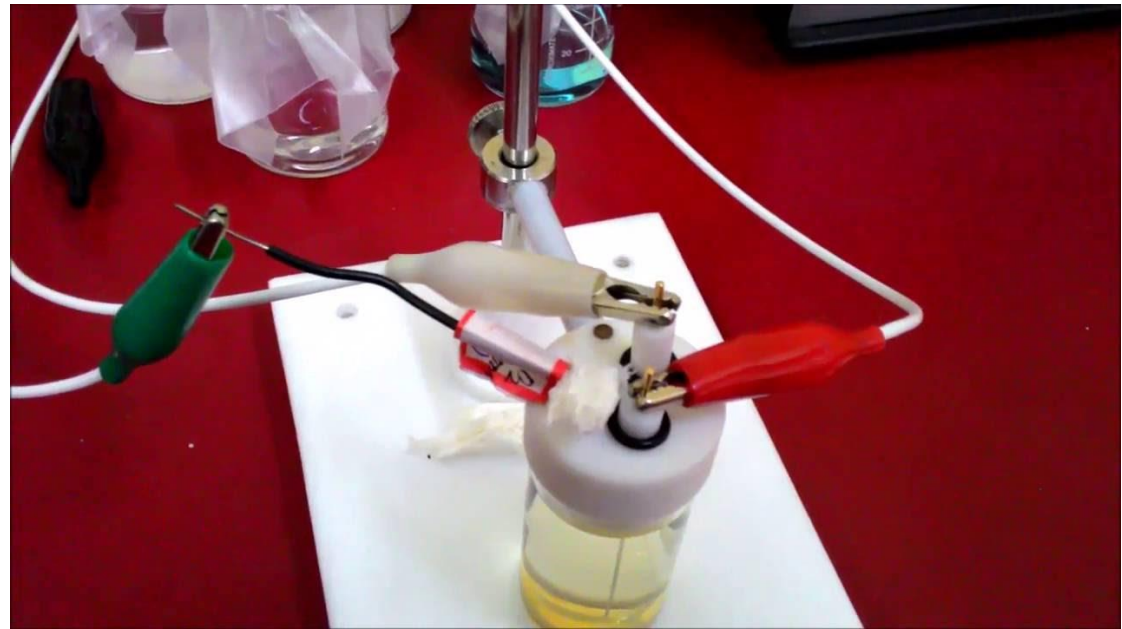Reference electrode

Counter elctrode

Potentiostat

One-compartment
Two-compartment

Two-electrode
Three-electrode

Salt bridge

Electrochemical System

Potentiostat / Galvanostat

Potentiostats/Galvanostats are designed to perform *electrochemical measurements* in applications.

Potentiostats: It measures and controls the *voltage difference (ΔV)* between a WE and a RE. It also measures the current flow between the WE and CE (that completes the cell circuit).

Example: *Cyclic Voltammetry*

Galvanostats: controls the *cell current (i)* rather than the cell voltage.

Example: Galvanostatic Charge-Discharge (*Chronopotentiometry)*

1. Electrodes and their functions

Anode: through which the conventional current enters into a polarized electrical device (oxidation)
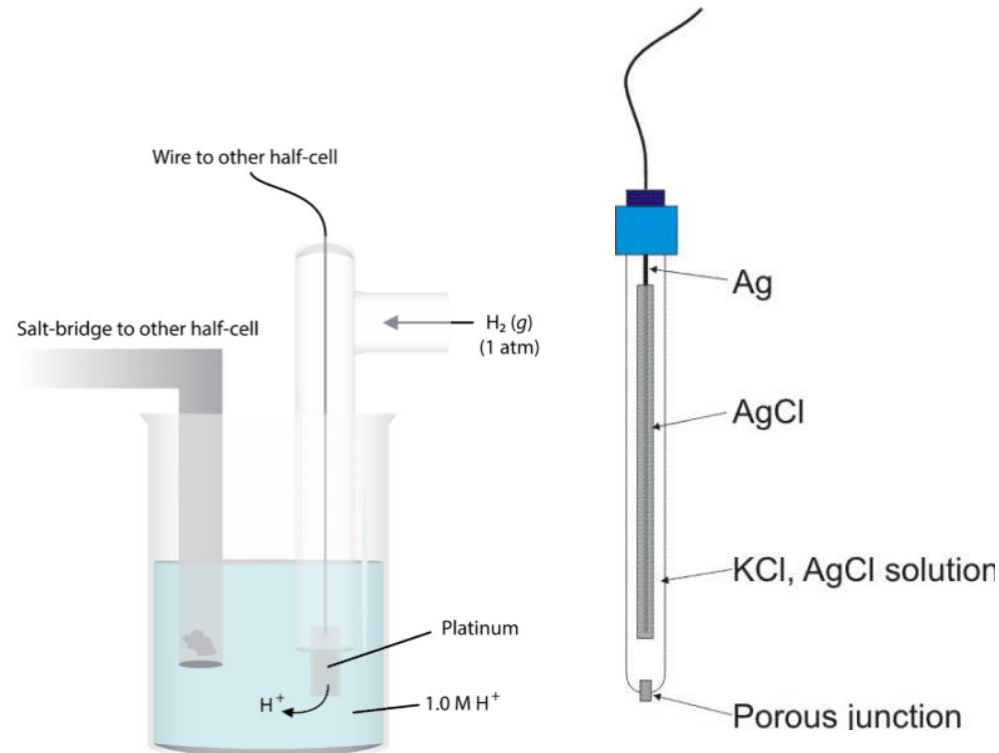Cathode: an electrode through which conventional current leaves an electrical device (reduction)

Working Electrode

On which the reaction of interest occurs

- Glassy carbon electrode
- Graphite electrode
- Fluorine doped Tin Oxide (FTO) Glass electrode
- Ni foam electrode
- Ni foil electrode
- Pt Electrode
- Au Electrode
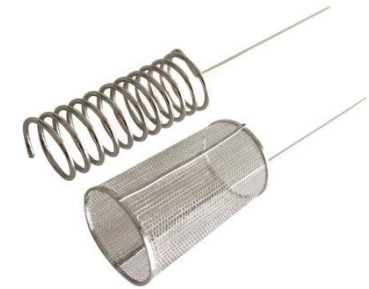- Carbon pest electrode
- Carbon Cloth electrode
- Pd electrode

Reference Electrode

Has a stable and well known electrode potential

Wire to other half-cell

Salt-bridge to other half-cell

H_2 (g) (1 atm)

Platinum

H^+

$1.0\,M\,H^+$

Ag

AgCl

KCl, AgCl solution

Porous junction

Counter Electrode

Opposite to working electrode
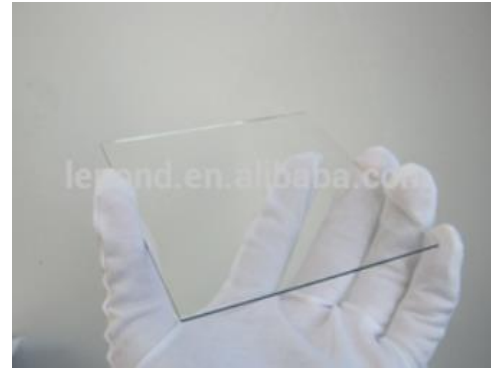

Pt mess electrode
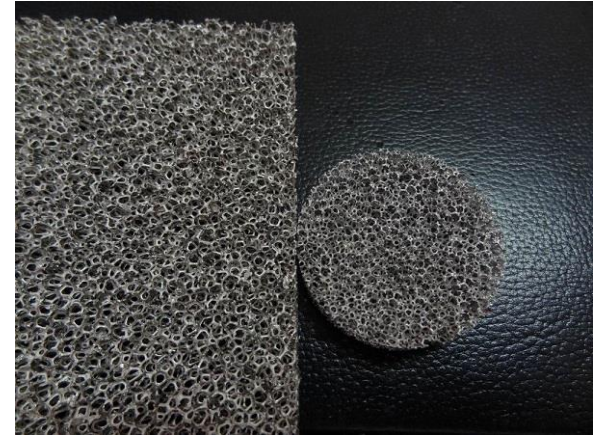
Working Electrodes

Glassy carbon electrode

Graphite electrode

Fluorine doped Tin Oxide (FTO) Glass electrode
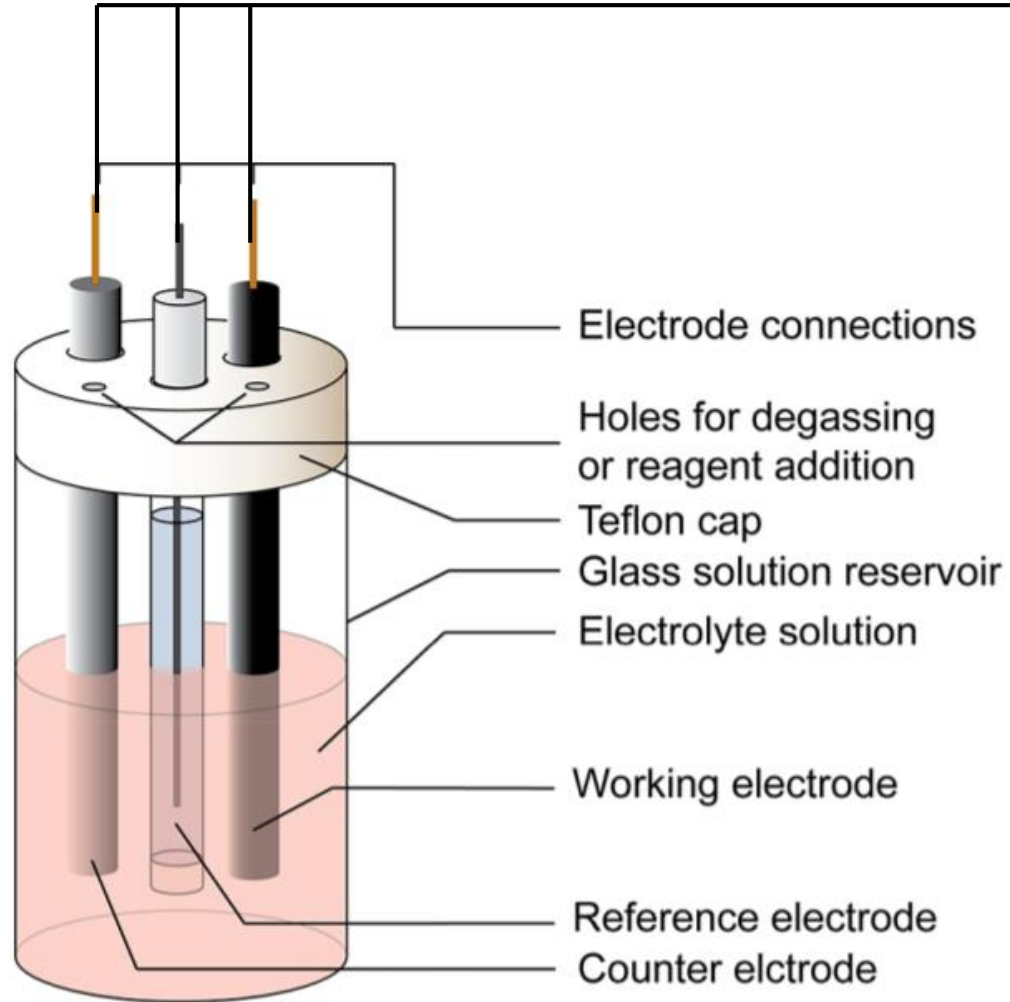
Ni foam electrode

Ni foil electrode

Au electrode

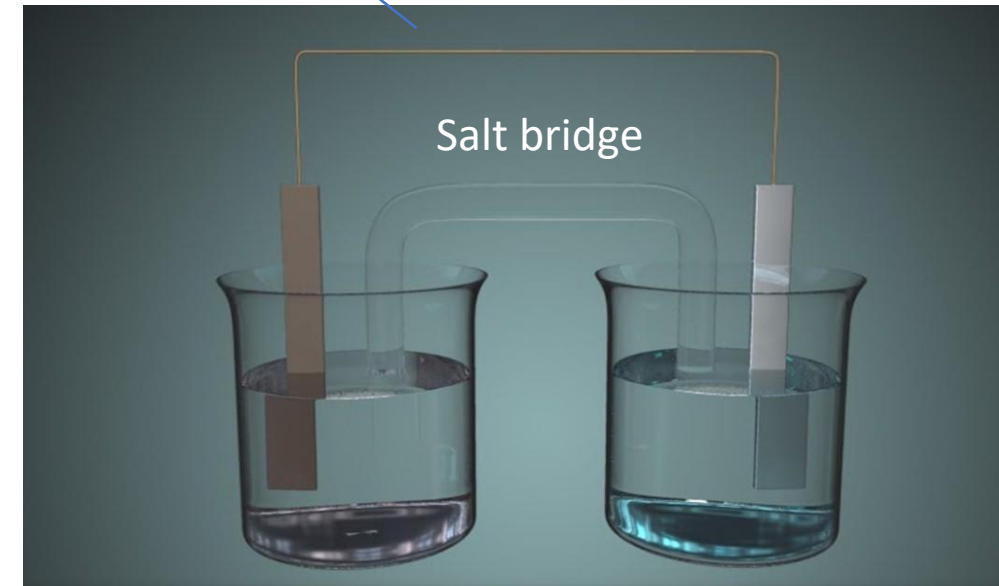Carbon pest electrode

Carbon cloth electrode
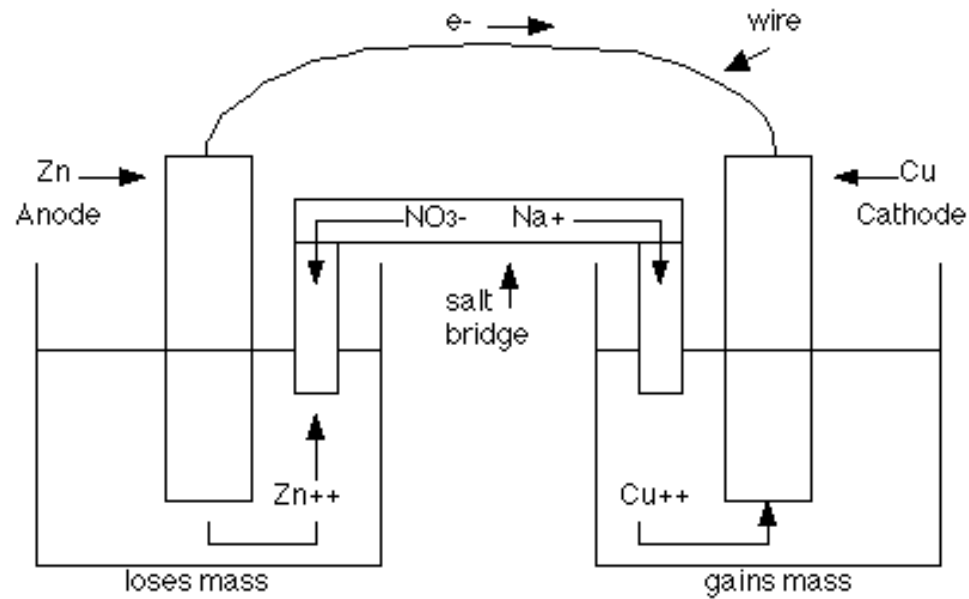
A Typical Electrochemical Setup

Potentiostat

Electrode connections

Holes for degassing or reagent addition

Teflon cap

Glass solution reservoir

Electrolyte solution

Working electrode

Reference electrode

Counter elctrode

One-compartment
Two-compartment

Two-electrode
Three-electrode

Salt bridge

Electrolytic conduction: Why necessary?
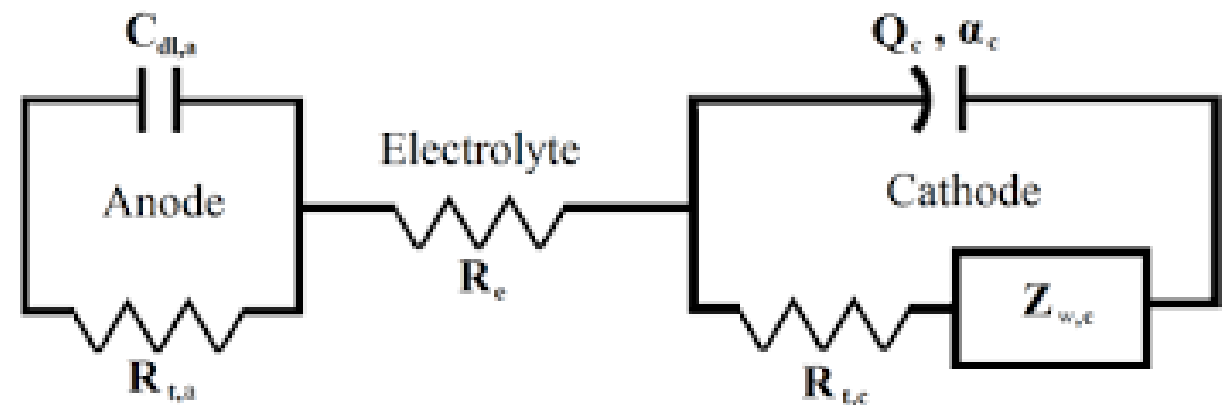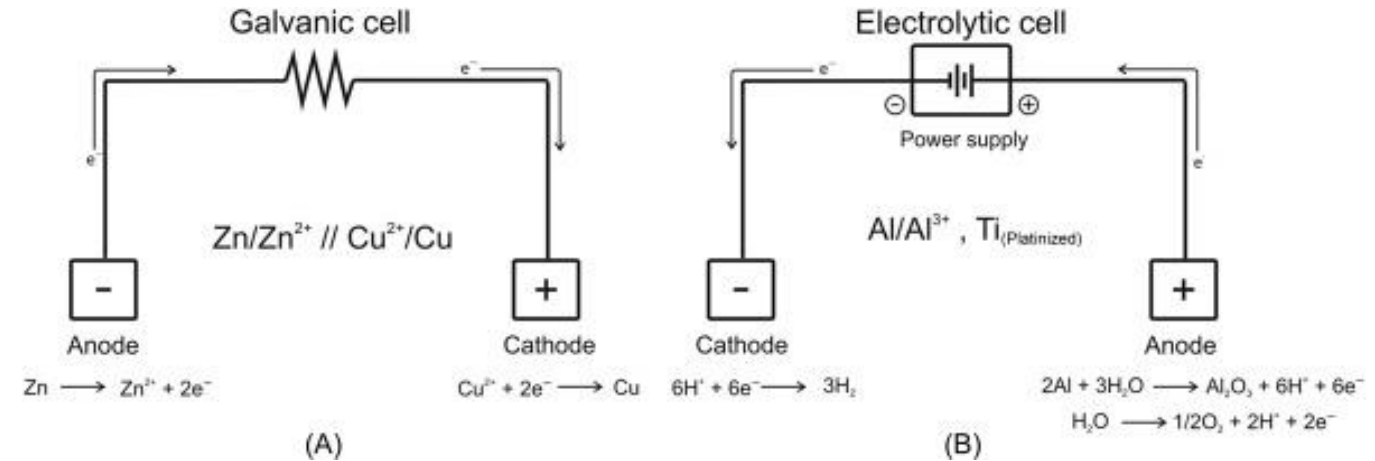
Electrochemical cell

Circuits
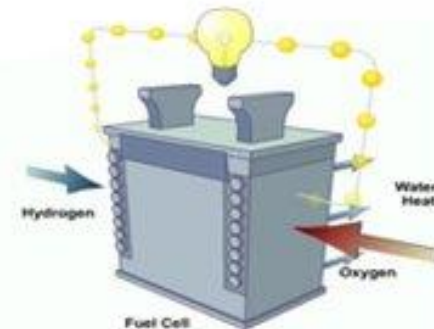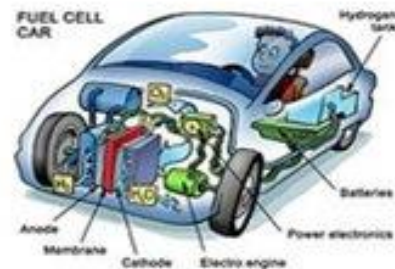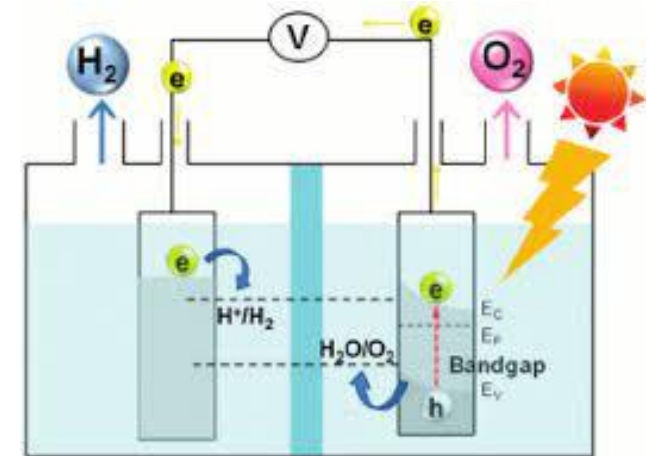
Types of electrolytes
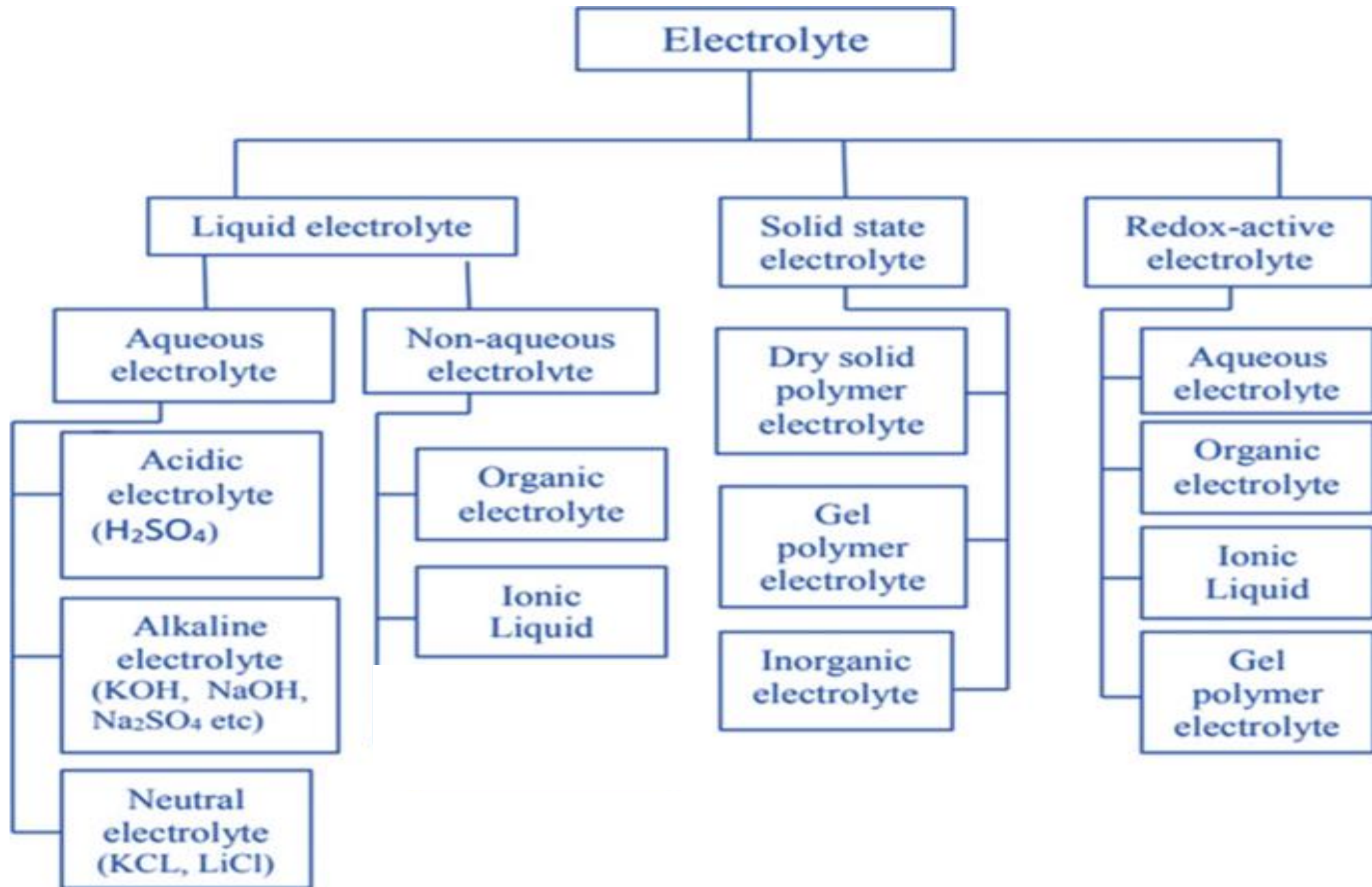
Liquid Electrolytes

Electrolyte Solution: Solvent + Supporting electrolyte (ionic compounds)

Solvent: **A good solvent has these characteristics:**
- **It is liquid at experimental temperatures.**
- **It dissolves the analyte and high concentrations of the supporting electrolyte completely.**
- **It is stable toward oxidation and reduction in the potential range of the experiment.**
- **It does not lead to deleterious reactions with the analyte or supporting electrolyte.**
- **It can be purified.**

Supporting Electrolyte: **A good supporting electrolyte has these characteristics:**
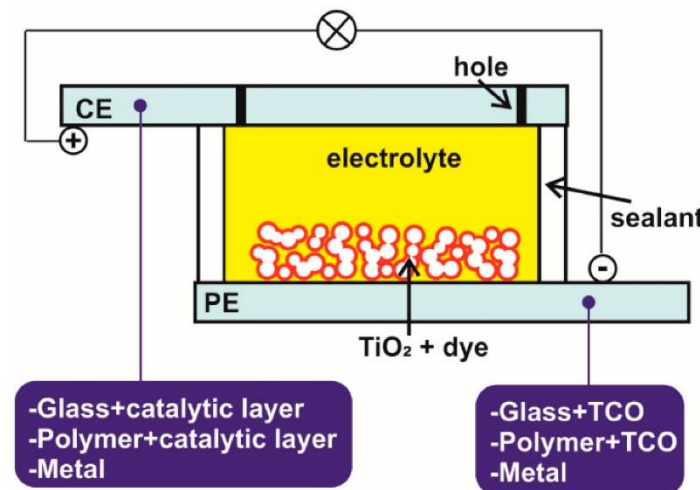- **It is highly soluble in the solvent chosen.**
- **It is chemically and electrochemically inert in the conditions of the experiment.**
- **It can be purified.**

Aqueous electrolytes

A *weak electrolyte* dissociates partially.
- Weak electrolyte solutions are poor conductors.
- Different weak electrolytes dissociate to different extents.

Weak electrolytes include:
- Weak acids and weak bases (NH_4OH)
- A few insoluble ionic compounds
- A water H_2O

A *strong electrolyte* dissociates completely.
- A strong electrolyte is present in solution almost exclusively as *ions*.
- Strong electrolyte solutions are good conductors.

Strong electrolytes include:
- Strong acids (HCl, HBr, HI, HNO_3, H_2SO_4, $HClO_4$)
- Strong bases (IA and IIA metals hydroxides)
- Most water-soluble ionic compounds (salts)

Molten salts

Molten salts are ionic compounds with high melting ranges, consisting of positively and negatively charged ions. They are used in energy technologies at high temperatures, such as in nuclear reactor systems and thermal energy storage.

- ❑ Molten sodium chloride, table salt has a melting point (m.p.) of 801 °C (1,474 °F).

- ❑ LiCl melts at approximately 605-614°C (1121-1137°F)

- ❑ KCl melts at approximately 770°C (1420°F)

- ❑ Eutectic mixture (Lithium chloride + potassium chloride) m.p. 450 °C (842 °F) .

Ionic liquids

Ionic liquids, which are salts in a liquid state at ambient temperatures, are increasingly being used as electrolytes in various electrochemical applications, including batteries and supercapacitors. They offer several advantages over traditional liquid electrolytes, such as higher thermal stability, non-flammability, and the ability to be tailored for specific applications by adjusting the cation and anion.
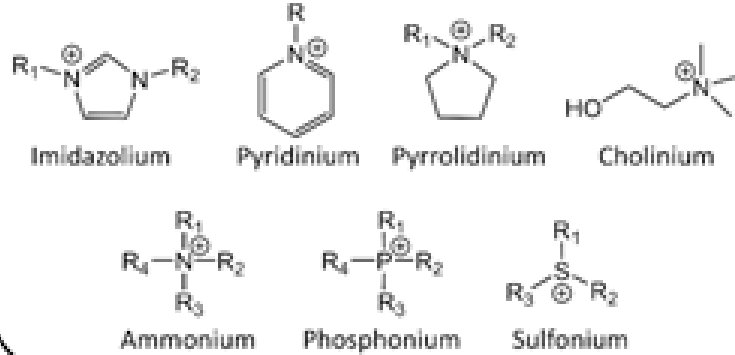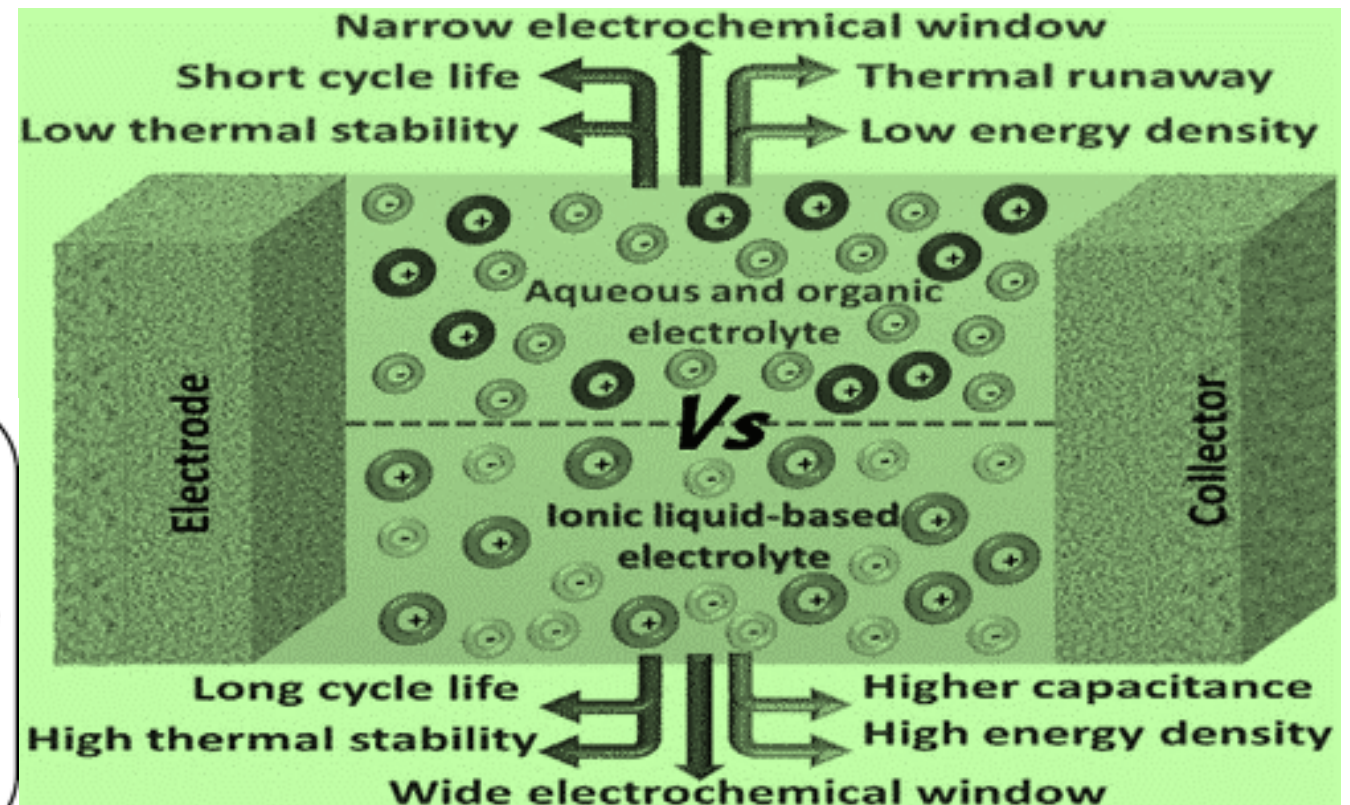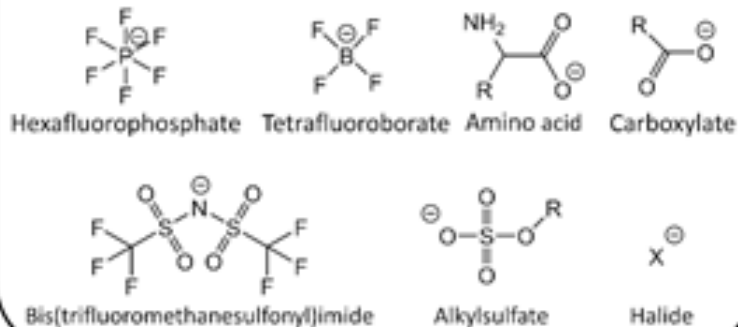
Conductivity: Conductance

Property of the conductor (metallic as well as electrolytic) which facilitates the flow of electricity through it

Conductance

Conductance of a solution of definite dilution enclosed in a cell having two electrodes of unit area separated by one centimeter apart

Specific Conductance

Conductancae of all the ions produced by one gram equivalent of an electrolyte in a given solution.

Equivalent conductance

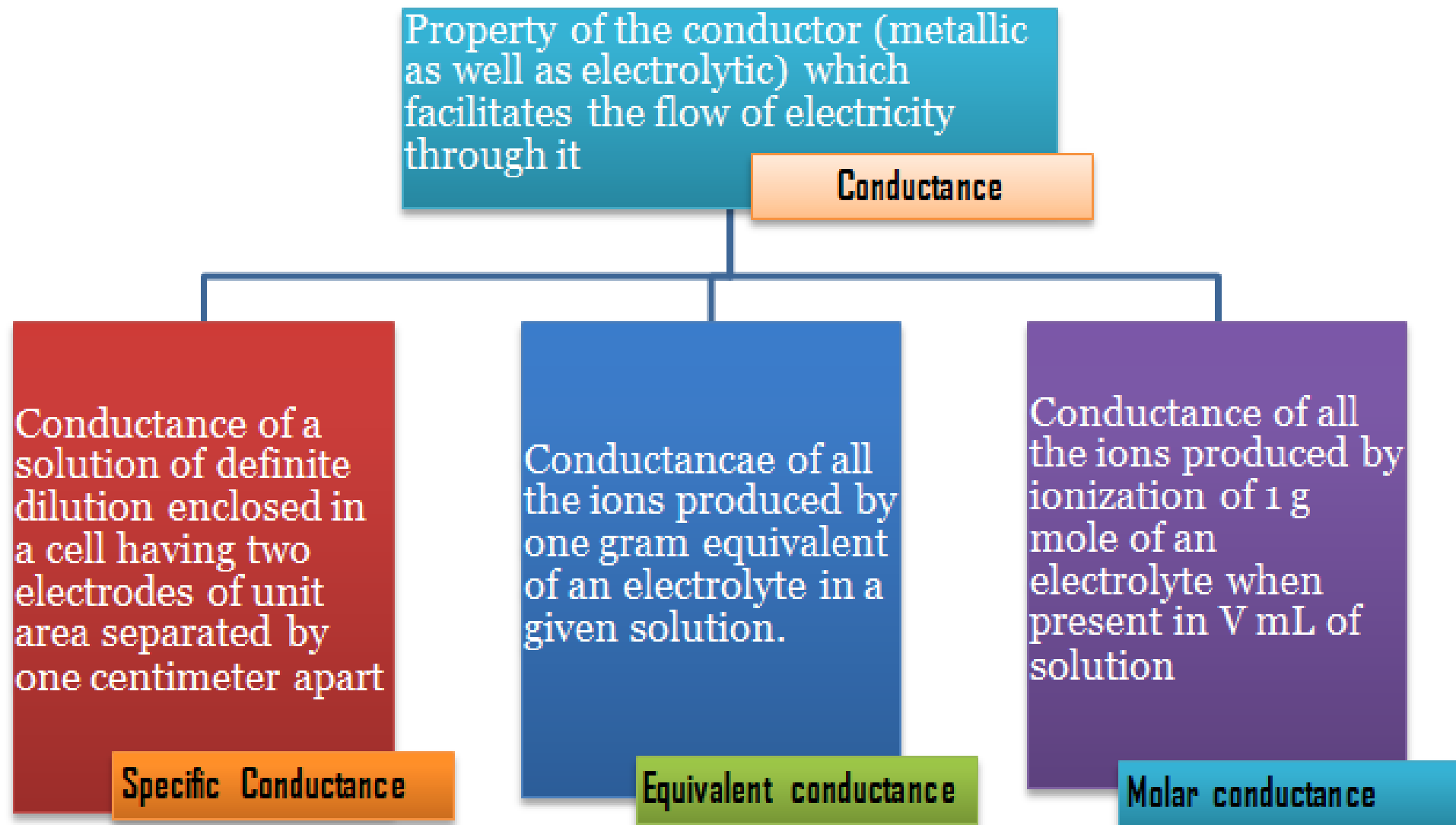Conductance of all the ions produced by ionization of 1 g mole of an electrolyte when present in V mL of solution

Molar conductance

Specific Conductance

- Specific conductance or conductivity is defined as the conductance of unit volume of a cell. It is reciprocal of resistivity.

$$\kappa = 1/\rho \quad \text{and} \quad \rho = \frac{aR}{l}$$

Therefore,

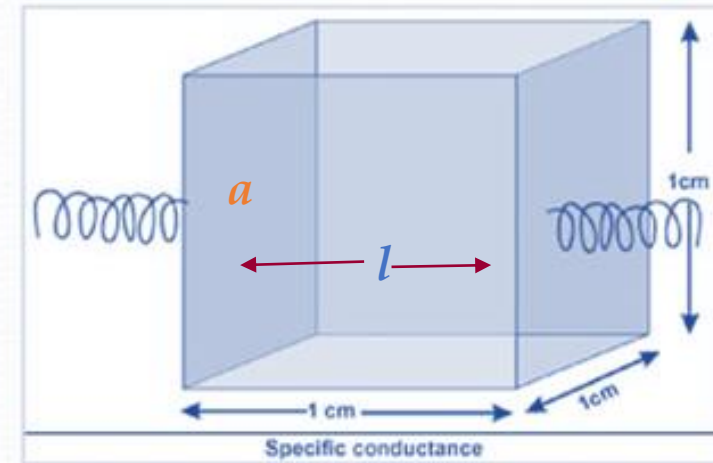$$\kappa = \frac{l}{aR}$$

Specific conductance

or $\kappa = (l/a) \times \text{Conductance}$

The quantity "l/a" is called cell constant .

Specific conductance has units $ohm^{-1}cm^{-1}$. SI Unit of specific conductance is Sm^{-1} where S is Siemen.

Molar Conductance

- It is the conductance of all ions furnished when one mole of the electrolyte is dissolved in V cc of the solution. Molar conductance is represented by λ_m

Mathematically, $\lambda_m = \kappa \times V$

$$\lambda_m = \frac{\kappa \times 1000}{\text{Molarity}}$$

Where, κ = Specific conductivity

V = Volume of solution in "cc" containing one gram equivalent of the electrolyte.

Determination of conductance
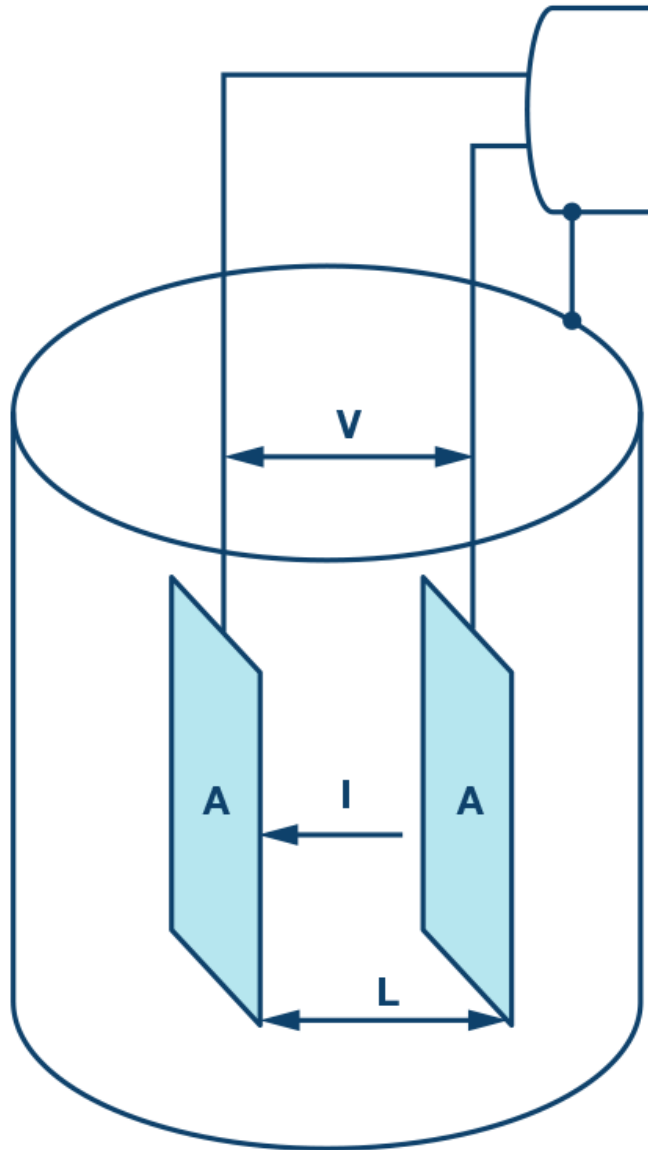
A = Area of Electrode Surface (cm^2)
L = Distance Between Electrodes (cm)
V = Excitation Voltage
I = Cell Current
K = L/A = Cell Constant (cm^{-1})
Y = Measured Conductance = I/V (S)
Y_X = Water Conductivity = K × Y (S/cm)

Factors affecting electrolytic conduction

- <u>Nature of electrolyte</u>: Strong electrolytes ionize almost completely in the solution whereas weak electrolytes ionize to a small extent.

- <u>Size of ions</u>: larger the ion, smaller will be its conductance.

- <u>Nature of solvent and viscosity:</u> Greater the polarity of the solvent, greater is the conductance. Greater the viscosity, lesser will be the conductance.

- <u>Concentration of solution</u>: Higher the concentration of the solution, less is the conduction.

- <u>Temperature</u>: On increasing the T, the dissociation increases and the conduction increases.

Molar conductivity, λ

Table 14.3 Molar conductance ($ohm^{-1} \, cm^2 \, mol^{-1}$) of different electrolytes in aqueous solutions at 25°C

C mol L^{-1}	NaCl	KCl	HCl	AgNO₃	HAc
0.0000	126.45	149.86	426.16	133.4	(390.7)
0.0005	124.50	147.81	422.74	131.4	67.7
0.001	123.74	146.95	421.36	130.5	49.2
0.01	118.51	141.27	412.00	124.8	16.3
0.10	106.74	128.96	391.32	109.1	5.2

Figure 14.6 Molar conductance vs square root of concentration

Remarks :
(i) at low concentration
(ii) at High concentration
(iii) decrease in λ with increasing c

Molar conductivity, λ

Strong electrolytes:

- The molar and equivalent conductance at infinite dilution can be obtained by extrapolating the line.

- It is denoted by λ_∞

- Increase in the Molar and equivalent conductance is due to weakening of intermolecular forces upon dilution.

- Follow Debye Hückel Theory ($\lambda^c_m = \lambda^\infty_m - A\sqrt{C}$)

Weak electrolytes:

- The molar and equivalent conductance at infinite dilution can be obtained by **Kohlrausch's Law**

- Increase in the Molar and equivalent conductance is due to increase in the number of ions upon dilution.
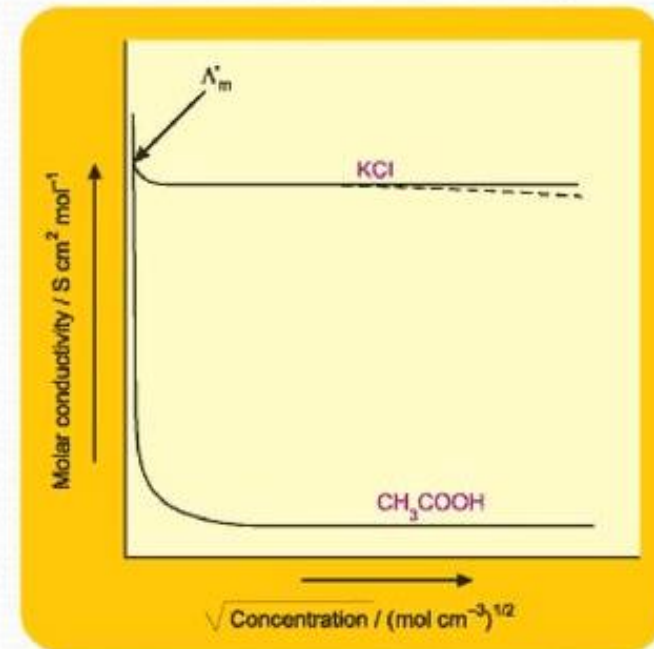
Kohlrasuch's Law

Statement: "At time infinite dilution, the molar conductance of an electrolyte can be expressed as the sum of the contributions from its individual ions"

i.e. $\Lambda^{\infty}_m = v_+ \lambda^{\infty}_+ + v_- \lambda^{\infty}_-$.

where, v_+ and v_- are the number of cations and anions per formula unit of electrolyte respectively and, λ^{∞}_+ and λ^{∞}_- are the molar conductivities of the cation and anion at infinite dilution respectively.

For e.g. The molar conductivity of HCl at infinite dilution can be expressed as,

$\Lambda^{\infty}_{HCl} = v_H^+ \lambda^{\infty}_{H^+} + v_{Cl^-} \lambda^{\infty}_{Cl^-}$; For HCl, $v_H^+ = 1$ and $v_{Cl^-} = 1$.

So, $\Lambda^{\infty}_{HCl} = (1 \times \lambda^{\infty}_{H+}) + (1 \times \lambda^{\infty}_{H-})$; Hence,

$\Lambda^{\infty}_{HCl} = \lambda^{\infty}_{H+} + \lambda^{\infty}_{Cl-}$

The Debye-Hückel-Onsager theory is a theoretical framework used to explain the behavior of strong electrolytes in solution, particularly concerning their electrical conductivity. It addresses the deviations from ideal behavior caused by interionic interactions and provides a method for calculating ionic mobility and electrical conductivity, including the effects of relaxation and hydrodynamics.

Key Concepts:

1.1. Ionic Atmosphere:

2.The theory posits that each ion in a solution is surrounded by a cloud of oppositely charged ions, creating an "ionic atmosphere".

3.2. Non-ideal Behavior:

4.Interionic interactions disrupt the ideal behavior of the solution, affecting properties like electrical conductivity.

5.3. Relaxation and Electrophoretic Effects:

6.The theory accounts for the "relaxation effect," where the ionic atmosphere must rearrange when an ion moves, and the "electrophoretic effect," where the movement of the ionic atmosphere creates a hydrodynamic drag.