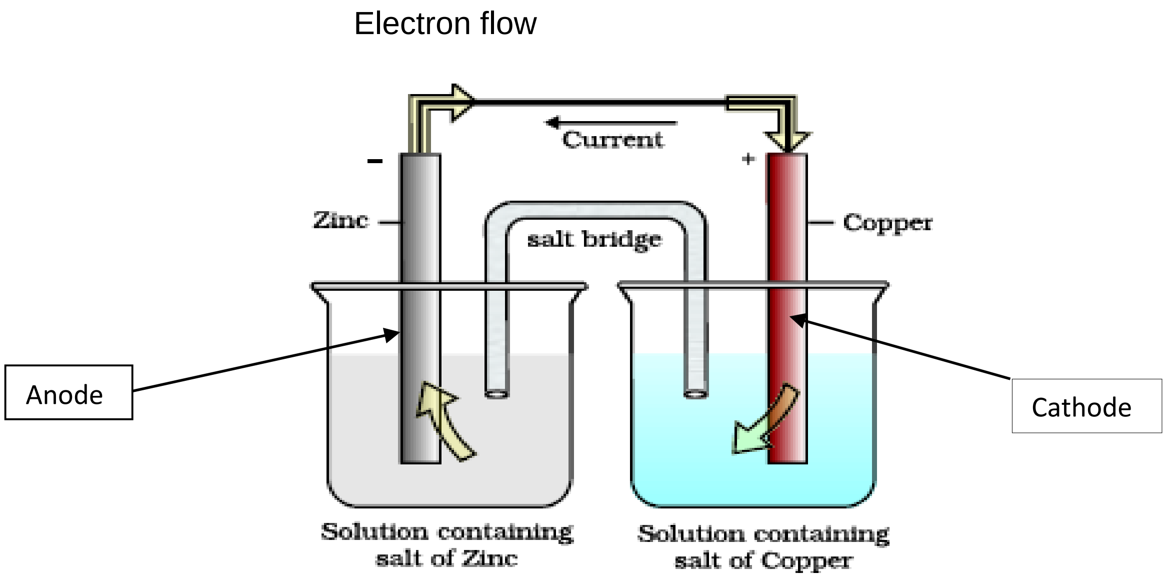
UNIT 3 : ELECTROCHEMISTRY

Electrochemistry deals with relationship between electrical energy and chemical energy and their inter-conversion.
Electrochemical cell is a device in which chemical energy is converted into electrical energy


Electron flow
Current
−
+
Zinc
salt bridge
Copper
Anode
Cathode
Solution containing salt of Zinc
Solution containing salt of Copper

The electrode at which oxidation occurs is called **anode** and at which reduction occurs is called **cathode**.

Salt bridge

It is inverted U like tube containing saturated solution of some electrolyte like KCl,KNO_3, NH_4NO_3 with agar-agar jelly or gelatine and connects the anode and cathodce in an electrochemical cell.

Functions of salt bridge:-

→ It allows the flow of current by completing the inner circuit.
→ It maintains electrical neutrality in both the half cells.

Cell representation:

A cell with the following chemical reaction:

$$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\ Ag(s)$$

may be represented as

$$Cu(s) \mid Cu^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$$

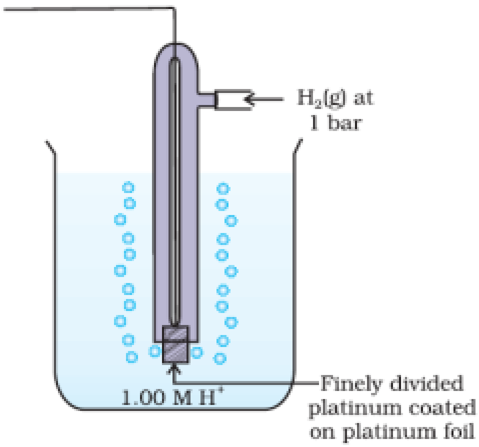
Electrode potential: - The potential difference set up between the metal and the solution of its ions is known as electrode potential

Standard electrode potential is the electrode potential of a metal in contact with it's ions when the concentration of ions is 1 molar at 1 bar pressure and 298K.It may be standard reduction potential or standard oxidation potential.

EMF of the cell: - It is defined as the potential difference between the two terminals of the cell when either no or very little current is drawn from it.

$$E_{cell} = E_{right} - E_{left} = E_{Ag^+|Ag} - E_{Cu^{2+}|Cu}$$

Standard Hydrogen electrode (SHE) OR Normal Hydrogen Electrode (NHE)



This is a half cell having zero electrode potential. Electrode potential of any element is determined in relative term of it.

$$H_2(g) \longrightarrow 2H^+ + 2e$$

if SHE acts as anode

$$2H^+ + 2e \longrightarrow H_2(g)$$

if SHE acts as cathode

Any half cell whose electrode potential is to be determined is connected to this & e.m.f measured so is called electrode potential of that electrode. Presentation of the cell having SHE and a copper electrode:

$$Pt(s) \mid H_2(g,\ 1\ bar) \mid H^+(aq,\ 1\ M) \parallel Cu^{2+}(aq,\ 1\ M) \mid Cu$$

Nernst equation:

This equation is used to measure the electrode potential of any half cell at any concentration with respect to SHE.

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

$$E_{(M^{n+}/M)} = E^{\ominus}_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

The concentration of a solid is unity, so the equation becomes

$$E_{(M^{n+}/M)} = E^{\ominus}_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

In Daniell cell, the electrode potential for any given concentration of Cu^{2+} and Zn^{2+} ions, we write

For Cathode:

$$E_{(Cu^{2+}/Cu)} = E^{\ominus}_{(Cu^{2+}/Cu)} - \frac{RT}{2F} \ln \frac{1}{[Cu^{2+}(aq)]}$$

For Anode:

$$E_{(Zn^{2+}/Zn)} = E^{\ominus}_{(Zn^{2+}/Zn)} - \frac{RT}{2F} \ln \frac{1}{[Zn^{2+}(aq)]}$$

The cell potential, $E_{(cell)} = E_{(Cu^{2+}/Cu)} - E_{(Zn^{2+}/Zn)}$

$$E_{(cell)} = E^{\ominus}_{(cell)} - \frac{RT}{2F} \ln \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Relationship between equilibrium constant and standard electrode potential

$$E^{\ominus}_{(cell)} = \frac{2.303RT}{nF} \log K_C$$

Relationship between standard Gibbs free energy and standard electrode potential

$$\Delta_r G^{\circ} = -nFE^{\ominus}_{(cell)}$$

Relationship between standard Gibbs free energy and equilibrium constant

$$\Delta_r G^{\circ} = -RT \ln K.$$

Metallic and Electrolytic Conductance

Metallic or electronic conductance: It isdue to flow of electrons.

Electrolyte or ionic conductance:–It is due to the movement of ions when an electrolyte decomposes in a solvent.

Metallic conductance depend upon

i) The nature & structure of metal.
ii) The no. of valence electrons per atom.
iii) Temperature (decreases with increasing temperature.)

Ionic Conductivity depends upon-

- i) The nature of electrolyte & solvent.
- ii) size of ion & solvation.
- iii) concentration of electrolyte.
- iv) temperature (increases with increasing temperature.)

Molar conductivity

$$\text{Molar conductivity} = \Lambda_m = \frac{\kappa}{c}$$

In the above equation, if κ is expressed in S m^{-1} and the concentration, c in mol m^{-3} then the units of Λ_m are in S m^2 mol^{-1}. It may be noted that:

1 mol m^{-3} = 1000(L/m^3) × molarity (mol/L), and hence

$$\Lambda_m(\text{S cm}^2\ \text{mol}^{-1}) = \frac{\kappa\ (\text{S cm}^{-1})}{1000\ \text{L m}^{-3} \times \text{molarity (mol L}^{-1})}$$

If we use S cm^{-1} as the units for κ and mol cm^{-3}, the units of concentration, then the units for $\ddot{E}_m$ are S cm^2 mol^{-1}. It can be calculated by using the equation:

$$\Lambda_m(\text{S cm}^2\ \text{mol}^{-1}) = \frac{\kappa\ (\text{S cm}^{-1}) \times 1000\ (\text{cm}^3/\text{L})}{\text{molarity (mol/L)}}$$

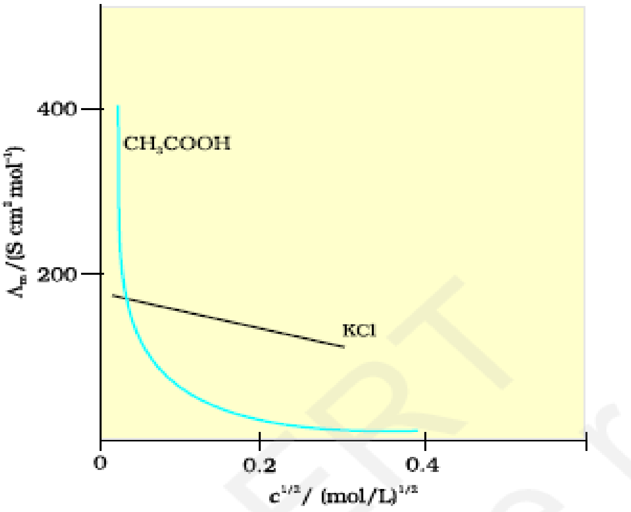
Both type of units are used in literature and are related to each other by the equations:

$1\ \text{S m}^2\text{mol}^{-1} = 10^4\ \text{S cm}^2\text{mol}^{-1}$ or

$1\ \text{S cm}^2\text{mol}^{-1} = 10^{-4}\ \text{S m}^2\text{mol}^{-1}$.

Variation of conductivity and molar conductivity with concentration: conductivity always decreases while Molar conductivity increases with decrease in concentration for both weak and strong electrolytes.

Limiting Molar conductivity: When concentration approaches zero, molar conductivity is called Limiting molar conductivity.



Kohlrauschlaw of independent migration of ions: It states that limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

Thus, if λ^{o} Na+ and λ^{o} Cl are limiting molar conductivity of the sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation:

$$\ddot{E}^{\circ}_{m\ (\mathrm{NaCl})} = \lambda^{0}_{\mathrm{Na}^{+}} + \lambda^{0}_{\mathrm{Cl}^{-}}$$

Applications of Kohlrausch law: This law is used to measure the limiting molar conductivity degree of dissociation and dissociation constant of weak electrolytes.

Electrolytic cell In this cell electric energy is used to carry non spontaneous chemical reaction. An electrochemical cell works as electrolytic cell if external voltage supplied is more than the emf of the cell.

Faraday's Laws of Electrolysis

(i) First Law: The amount of chemical reaction occurs at any electrode during electrolysis proportional to the quantity of electricity passed through the electrolyte (solution or melt).

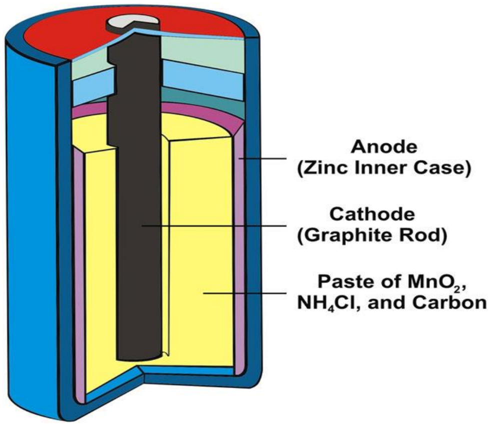
M = Zit (M=Mass of substance obtained at electrode, i = current in Ampere, t= time in seconds)

(ii) Second Law: The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights. (Atomic Mass of Metal ÷ Number of electrons required to reduce the cation).

Batteries: Any battery (actually it may have one or more than one cell connected in series) or cell that we use as a source of electrical energy is basically a galvanic cell. There are mainly two types of batteries.

Primary batteries In the primary batteries, the reaction occurs only once and after use over a period of time battery becomes dead and cannot be reused

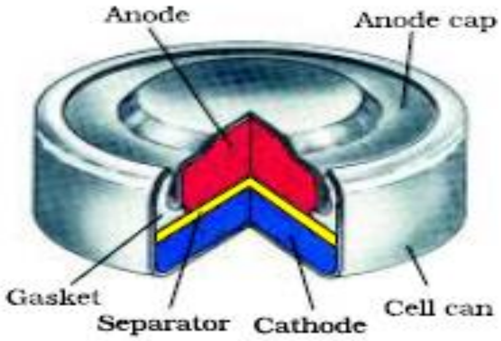
Dry cell or Leclanche cell:


Anode
(Zinc Inner Case)
Cathode
(Graphite Rod)
Paste of MnO₂,
NH₄Cl, and Carbon

Anode: $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

Cathode: $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

Mercury or Button cell:


Anode
Anode cap
Gasket
Separator
Cathode
Cell can

Anode: $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2$

Cathode: $HgO + H_2O + 2e^- \longrightarrow Hg(l) + 2OH^-$

T

The cell potential is 1.35 V and remains constant during its life as the overall reaction does not involve any ion in solution whose concentration can change during its lifetime.

Secondary Batteries: A secondary cell after use can be recharged by passing current through it in the opposite direction so that it can be used again.

Lead Storage Cell:

The cell reactions when the battery is in use are

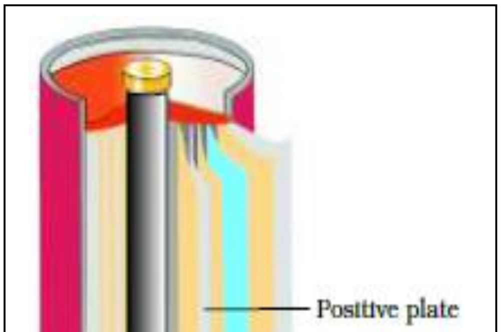
Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

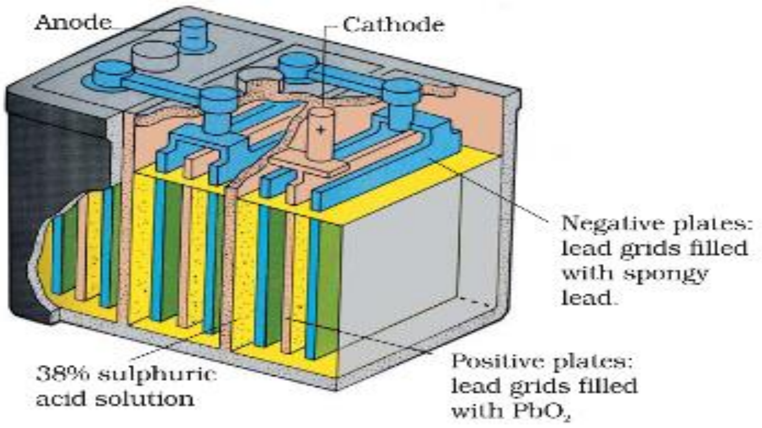
Cathode: $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

overall cell reaction consisting of cathode and anode reactions is:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

On charging the battery the reaction is reversed


Positive plate

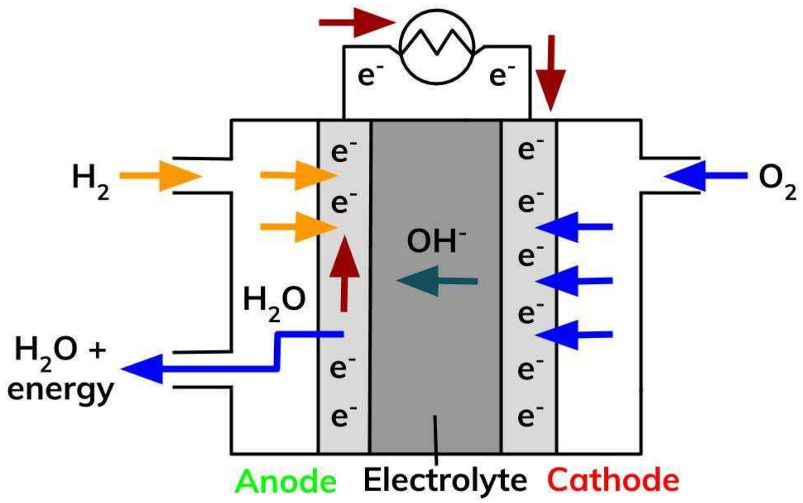

Anode
Cathode
Negative plates: lead grids filled with spongy lead.
38% sulphuric acid solution
Positive plates: lead grids filled with PbO_2

Nickel Cadmium Cell

Nickel Cadmium cell:

$$Cd\ (s) + 2Ni(OH)_3\ (s) \rightarrow CdO\ (s) + 2Ni(OH)_2\ (s) + H_2O\ (l)$$

Fuel Cell : fuel cell are galvanic cell that convert energy of combustion of fuel directly in to electrical energy. Fuel used are hydrogen, methane , methanol. Its efficiency is about 70% .


e⁻
e⁻
H₂
O₂
OH⁻
H₂O
H₂O + energy
Anode
Electrolyte
Cathode

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

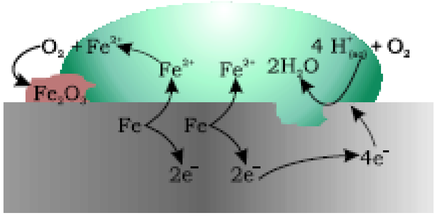
Anode: $2H_2\ (g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

Overall reaction being:

$$2H_2(g) + O_2(g) \longrightarrow 2\ H_2O(l)$$

Corrosion: the phenomenon of degradation of upper layer of metal in presence of oxygen, moisture and atmospheric gases etc.

e.g rusting of Iron



Anode: $2\,Fe\,(s) \longrightarrow 2\,Fe^{2+} + 4\,e^-$ $\quad E^{\ominus}_{(Fe^{2+}/Fe)} = -\,0.44\ V$

Cathode: $O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O\,(l)$ $\quad E^{\ominus}_{H^+|O_2|H_2O} = 1.23\,V$

The overall reaction being:

$2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2\,H_2O\,(l)$ $\quad E^{\ominus}_{(cell)} = 1.67\ V$

Prevention of Corrosion-

1. Barrier protection through coating of paints or electroplating.
2. By the use of antirust solutions (bis phenol).
3. By cathodic protection in which a metal is protected from corrosion by connecting it to another metal that is more easily oxidized.