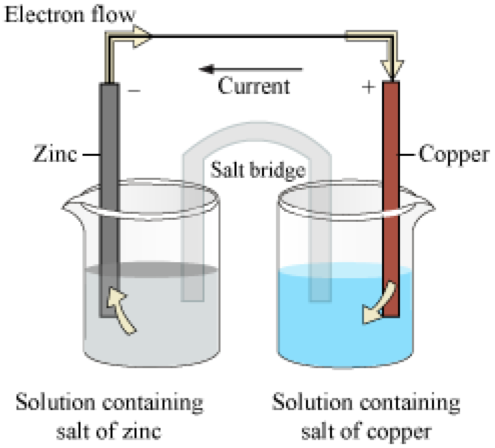
Electrochemistry

Galvanic Cells

Electrochemical Cell

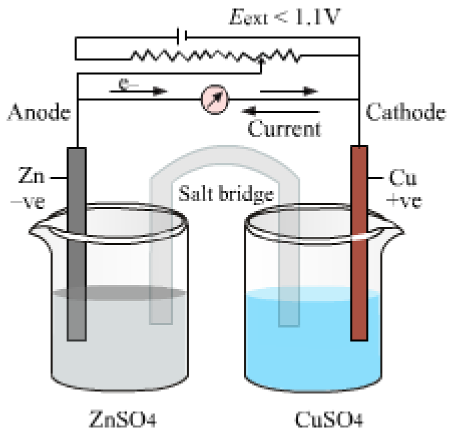
- An electrochemical cell is a cell used for generating electrical energy from chemical reactions, or for inducing chemical reactions from electrical energy.
- Daniel cell
- Generates electrical energy from the chemical reaction $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
- Electrode potential = 1.1 V, when $\left[Zn^{2+}\right] \equiv \left[Cu^{2+}\right]$ = 1 mole dm^{-3}
- Such a device is called a galvanic or voltaic cell.



- When an external potential is applied and increased slowly, the reaction continues till E_{ext} = 1.1 V. At this external potential, the reaction stops; when E_{ext} is further increased, the reaction starts again, but in the opposite direction. Now, the device becomes an electrolytic device.
- When $E_{ext} < 1.1$ V

  (i) Electrons flow from the Zn rod to the Cu rod, so current flows from Cu to Zn

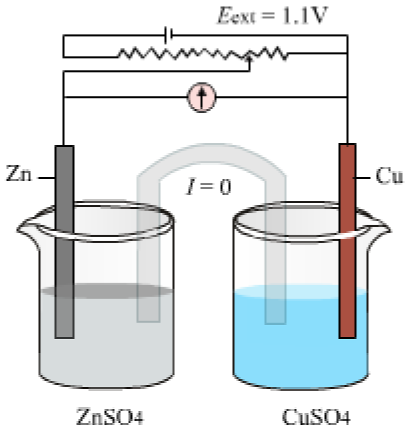
  (ii) Zn dissolves at the anode and copper deposits at the cathode



- When $E_{ext} = 1.1$ V

  (i) There is no flow of electrons, and hence, there is no current

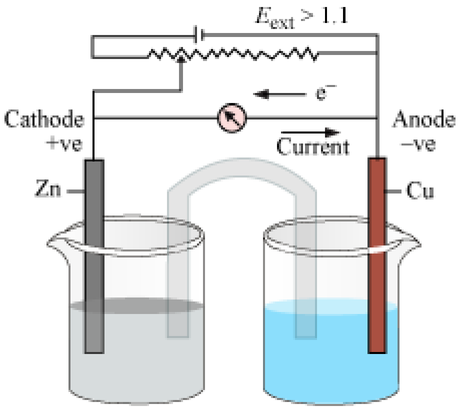
  (ii) No chemical reaction takes place



- When $E_{ext} > 1.1$ V

  (i) Electrons flow from the Cu rod to the Zn rod, so current flows from Zn to Cu

  (ii) Copper dissolves at the Cu electrode and Zn deposits at the Zn electrode.



Galvanic Cells

- Convert chemical energy of a spontaneous redox reaction into electrical energy
- Example: Daniel cell
- The overall cell reaction is

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

- Reduction half-reaction:

$$Cu^{2+} + 2e^{-} \longrightarrow Cu_{(s)}$$

- Oxidation half-reaction:

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^{-}$$

- Reduction half-cell: $Cu^{2+}_{(aq)} / Cu_{(s)}$

  Oxidation half-cell: $Zn_{(s)}/Zn^{2+}{}_{(aq)}$

- Electrode potential – Potential difference developed between the electrode and the electrolyte
- Standard electrode potential – Electrode potential when the concentration of the species of the half-cell is unity
- Anode – Electrode where oxidation takes place
- Cathode – Electrode where reduction takes place
- Cell potential – Potential difference between the cathode and the anode

- Cell electromotive force (emf) – Potential difference between cathode and anode when no current is drawn
- Emf of a galvanic cell is positive, and it is given by $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$
- For example:

  Cell reaction

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

  Half-cell reactions are:

  Reduction half-reaction (cathode): $2Ag^{+}{}_{(aq)} + 2e^{-} \longrightarrow 2Ag_{(s)}$

  Oxidation half-reaction (anode): $Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^{-}$

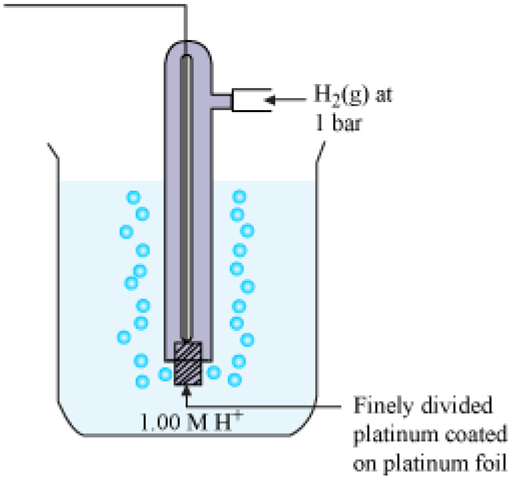
  The given cell can be represented as

  $$Cu_{(s)}\left|Cu^{2+}_{(aq)}\right|\left|Ag^{+}{}_{(aq)}\right|Ag_{(s)}$$

  Therefore, $E_{\text{cell}} = E_{\text{right}} - E_{\text{left}} = E_{Ag^{+}/Ag} - E_{cu^{2+}/Cu}$

- Measurement of electrode potential:
- Potential of an individual half-cell cannot be measured; only the potential difference between two half-cells can be measured.
- Potential difference of a half-cell is determined with respect to the standard hydrogen electrode (SHE), $Pt_{(s)}\left|H_{2(g)}\right|H^{+}_{(aq)}$, which is assigned a zero potential at all temperatures.
- The reaction corresponding to SHE is

  $$H^{+}_{(aq)} + e^{-} \longrightarrow \frac{1}{2}H_{2(g)}$$



- A negative standard electrode potential means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.

- A positive standard electrode potential means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

Nernst Equations

Let us start by solving a simple puzzle.

- For a general electrochemical reaction

$$aA + bB \xrightarrow{ne^-} cC + dD$$

Nernst equation is given by

$$\begin{aligned} E_{(cell)} &= E^{\theta}_{(cell)} - \frac{RT}{nF} \ln Q \\ &= E^{\theta}_{(cell)} - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b} \end{aligned}$$

Where,

R = Gas constant

= 8.314 J K^{-1} mol^{-1}

F = Faraday constant

= 96487 C mol^{-1}

T = Temperature in Kelvin

Equilibrium Constant from Nernst Equation

- $E^{0}_{(cell)} = \frac{2.303RT}{nF} \log K_c$

Where, K_c = Equilibrium constant

Electrochemical cell and Gibbs Energy of Reaction

- The relationship between Gibbs energy and cell potential is given by

$\Delta_r G = -nFE_{(cell)}$

Where,

ΔG_r = Gibbs energy of the reaction

E_{cell} = Emf of the cell

nF = Amount of charge passed

- If the concentration of all the reacting species is unity, then $E_{(cell)} = E^{0}_{(cell)}$, and we have

$\Delta_r G^{0} = -nFE^{0}_{(cell)}$

Where, $\Delta_r G^{0}$ = Standard Gibbs energy of the reaction

- The relationship between Gibbs energy and equilibrium constant (K) is given by

$\Delta_r G = -RT \ln K$

Conductance of Electrolytic Solutions

- Electrical resistance (R) of any object is directly proportional to its length (l) and inversely proportional to its cross-sectional area (A), i.e.,

$R \propto \frac{l}{A}$

Or, $R = \rho \frac{l}{A}$

Where, ρ= Proportionality constant, known as resistivity or specific resistance

Its SI unit is ohm metre (Ω m) and is often expressed in ohm centimetre.

- Resistivity − Resistance of a substance when it is 1 metre long and has 1 m^2 cross-sectional area.
- Conductance, $G = \frac{1}{R} = \frac{A}{\rho l} = \kappa \frac{A}{l}$
- SI unit of conductance is siemens (S), S = ohm^{-1}
- κ is called conductivity or specific conductance

$$\kappa = \frac{1}{\rho}$$

- Conductivity − Conductance of a substance when it is 1 m long and has 1 m^2 cross-sectional area. Its SI unit is S m^{-1}, but is often expressed in S cm^{-1}.
- Conductivity of a solution at any given concentration is the conductance of one unit volume of the solution kept between two platinum electrodes with the unit cross-sectional area at a distance of unit length.
- Electrical conductance through a metal (i.e., metallic or electronic conductance) depends upon −
- Nature and structure of the metal
- Number of valence electrons per atom
- Temperature (decreases with increase in temperature)
- Conductivity of an ionic (electrolytic) solution depends upon −
- Nature of the electrolyte added
- Size of the ions produced and their solvation
- Nature of the solvent and its viscosity
- Concentration of the electrolyte
- Temperature (increases with increase in temperature)

Molar Conductivity of ionic solutions

- Molar conductivity of a solution at a given concentration is the conductance of volume *V* of a solution containing 1 mole of the electrolyte, kept between two electrodes with the cross-sectional area of *A* and distance of unit length.

- It is denoted as Λ_m.

$$\wedge_m = \kappa \frac{A}{l}$$

Now, *l* = 1cm and *A* = *1sq. cm* (volume containing 1 mole of the electrolyte)

Therefore, $\Lambda_m = \kappa V$

Molar conductivity=Specific conductivity×V

Or, molar conductivity is given by

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

Variation of Conductivity and Molar Conductivity with Concentration

- For both weak and strong electrolytes, conductivity decreases with decrease in concentration.

- Reason: Decrease in the number of ions per unit volume carrying the current in a solution

- For both weak and strong electrolytes, molar conductivity increases with decrease in concentration.

- Reason: $\Lambda_m = \kappa V$

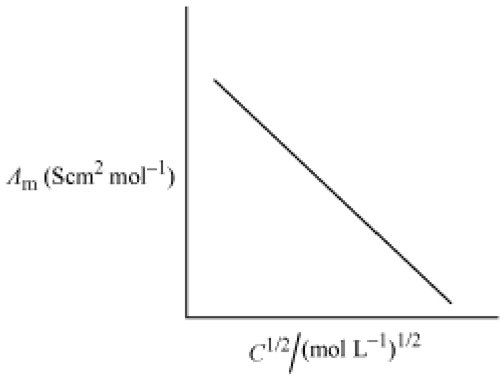
  With dilution, *V*increases; hence, molar conductivity increases.

- When concentration approaches zero, the molar conductivity is known as limiting molar conductivity.

Molar Conductivity for Strong Electrolytes

$$\Lambda_m = \Lambda_m^0 - AC^{\frac{1}{2}}$$

The plot of Λ_m against $C^{\frac{1}{2}}$ is a straight line, with the intercept equal to Λ_m^0 and the slope equal to '$-A$'. The value of '*A*' depends on the type of electrolyte.



- Kohlrausch law of independent migration of ions:
- This law states that the limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of its anion and cation.

If $\lambda_{Na^+}^0 =$ Limiting molar conductivity of Na^+ions

$\lambda_{Cl^-}^0 =$ Limiting molar conductivity of Cl^-ions

$\Lambda_{m(NaCl)}^0 =$ Limiting molar conductivity of NaCl

Then,

$$\Lambda_{m(NaCl)}^0 = \lambda_{Na^+}^0 + \lambda_{Cl^-}^0$$

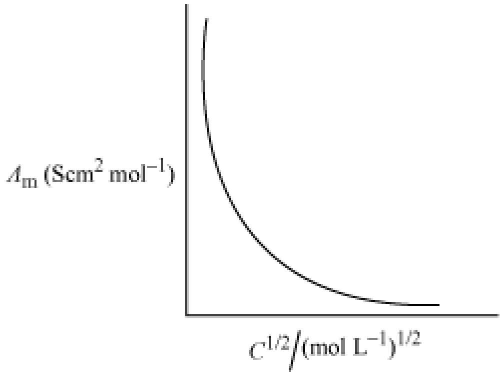
In general, if an electrolyte gives ν_+ cations and ν_- anions, then its limiting molar conductivity is given by

$$\Lambda_m^0 = \nu_+\lambda_+^0 + \nu_-\lambda_-^0$$

Where, λ_+^0, λ_-^0 = Limiting molar concentration of cations and anions respectively

Molar Conductivity for Weak Electrolytes

The plot of Λ_m against $C^{\frac{1}{2}}$ is given below.



- Λ_m^0 for weak electrolytes is obtained by using Kohlrausch law of independent migration of ions.
- If α is the degree of dissociation, then

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0}$$

- For a weak electrolyte like acetic acid, the dissociation constant is given by

$$K_a = \frac{C\alpha^2}{(1-\alpha)} = \frac{C\Lambda_m^2}{\left(\Lambda_m^0\right)^2\left(1-\frac{\Lambda_m}{\Lambda_m^0}\right)} = \frac{C\Lambda_m^2}{\Lambda_m^0\left(\Lambda_m^0-\Lambda_m\right)}$$

Electrolytic Cells and Electrolysis

Electrolytic Cell

- It consists of two copper strips dipped in an aqueous solution of copper sulphate.
- Copper is dissolved (oxidised) at the anode and is deposited (reduced) at the cathode.
- Reactions at the two electrodes:–

At anode: $\mathrm{Cu}_{(s)} \longrightarrow \mathrm{Cu}^{2+}_{(aq)} + 2\mathrm{e}^-$

At cathode: $\mathrm{Cu}^{2+}_{(aq)} + 2\mathrm{e}^- \longrightarrow \mathrm{Cu}_{(s)}$

Quantitative Aspects of Electrolysis

- Faraday’s law of electrolysis

- First law – The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolytic solution or melt.

  Let 'm' be the mass of substance collected or deposited at the electrode and 'Q' be the charge passed. Let the unit of 'm' be kg and that of 'Q' be Coloumb.

$$\begin{aligned} &\mathrm{m} \propto \mathrm{It} \quad ----- \qquad \left(\text{ as } \mathrm{I} = \frac{\mathrm{Q}}{\mathrm{t}}\ ,\ \mathrm{Q} = \ \mathrm{It}\right) \\ &\mathrm{m} \propto \mathrm{Q} \\ &\mathrm{m} = \ \mathrm{ZQ} \\ &\mathrm{Z} = \ \text{Proportionality} \ \ \text{Constant} \\ &\mathrm{Z} = \mathrm{mQ} \end{aligned}$$

- 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.

  Chemical equivalent weight $= \dfrac{\text{Atomic mass of metal}}{\text{Number of electrons required to reduce the cation}}$

- If Q = Quantity of electricity passed

  I = Current (which is constant)

  t = Time

  Then, Q (coulomb) = I (ampere) × t (second)

- 1F (Faraday) = 96487 C mol^{-1} ≈ 96500 C mol^{-1}

  Products of Electrolysis

- Products of electrolysis depend upon –
- Nature of material being electrolysed
- Type of electrodes: If inert (like Pt or Au), they act only as source or sink for electrons instead of participating in the reaction. On the other hand, if reactive, they participate in the reaction. Therefore, for different electrodes, the products of electrolysis may be different.
- Different oxidising and reducing agents present, and their standard electrode potentials

- In some cases, extra potential (called over potential) has to be applied because some electrochemical processes are kinetically so slow that they do not occur at lower voltages.

- For example, the products of electrolysis of molten NaCl are Na metal and Cl_2 gas, while the products of electrolysis of aqueous solution of NaCl are NaOH, Cl_2 and H_2.

Batteries

- Battery is a galvanic cell in which chemical energy of the redox reaction is converted into electrical energy.

- Mainly two types:

- Primary batteries
- Secondary batteries

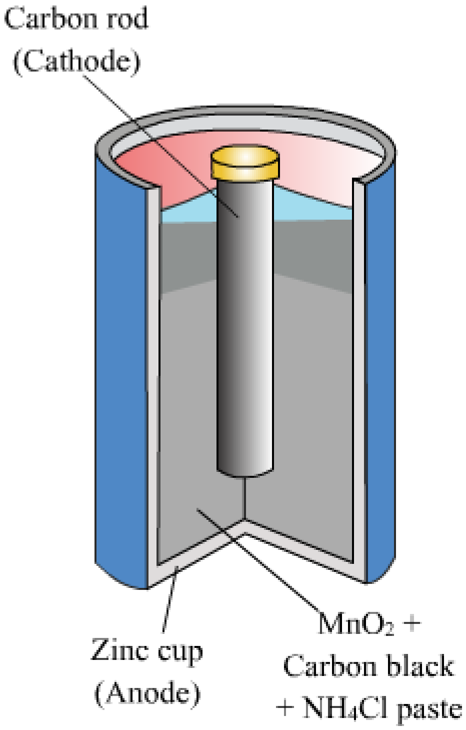
Primary Batteries

- In primary batteries, reaction occurs only once.

- After use over a period of time, these become dead and cannot be reused.

- Examples:Dry cell (or Leclanche cell), Mercury cell

Dry cell



- The reactions taking place at the anode and cathode are –

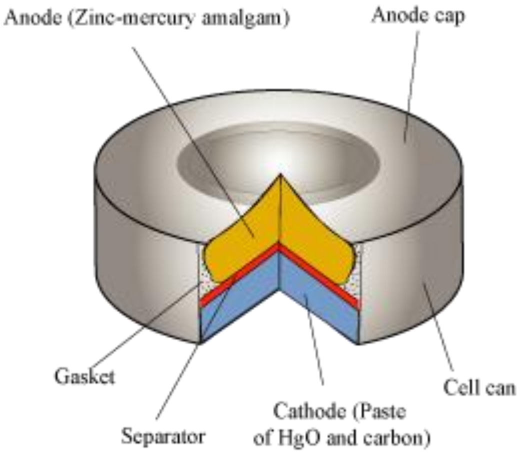
  At anode: $Zn \longrightarrow Zn^{2+} + 2e^-$

  At cathode: $2\overset{+4}{Mn}O_2 + 2NH_4^+ + 2e^- \rightarrow \overset{+3}{Mn}_2O_3 + 2NH_3 + H_2O$

  NH_3 formed in the reaction combines with Zn^{2+} to form a complex $[Zn(NH_3)_2Cl_2]$

- Cell potential is nearly 1.5 V.

  Mercury cell



- A paste of KOH and ZnO is used as electrolyte.
- The reactions taking place at the anode and cathode are –

At anode: $\mathrm{Zn}_{(s)} + 2\mathrm{OH}^- \longrightarrow \mathrm{ZnO}_{(s)} + \mathrm{H_2O}_{(l)} + 2e^-$

At cathode: $\mathrm{HgO}_{(s)} + \mathrm{H_2O}_{(l)} + 2e^- \longrightarrow \mathrm{Hg}_{(l)} + 2\mathrm{OH}^-$

The overall reaction is

$\mathrm{Zn(s) + HgO(s) \rightarrow ZnO(s) + Hg(l)}$

- Cell potential is nearly 1.35 V.
- Cell potential remains constant.

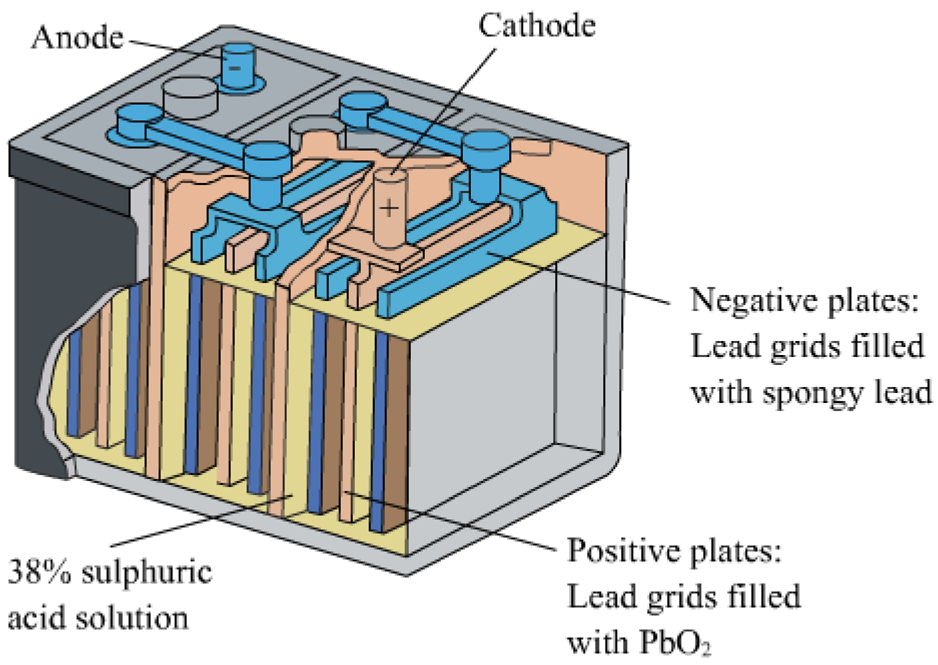
Reason – The overall reaction does not involve any ion whose concentration can vary with time.

Secondary Batteries

- Secondary batteries can be recharged again by passing current through them in the opposite direction.
- Examples:Lead storage battery, Nickel-cadmium cell

Lead storage battery

- Commonly used in automobiles and invertors



Anode → Lead

Cathode is a grid of lead packed with PbO_2

Electrolyte is 38% solution of H_2SO_4

- The reactions taking place at the anode and cathode are –

At anode: $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)} + 2e^-$

At cathode: $PbO_{2(s)} + SO_4^{2-}{}_{(aq)} + 4H^+_{(aq)} + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

Overall reaction: $Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

- On charging the battery, the reaction is reversed. The $PbSO_{4(s)}$ on the anode and cathode is converted into Pb and PbO_2 respectively.

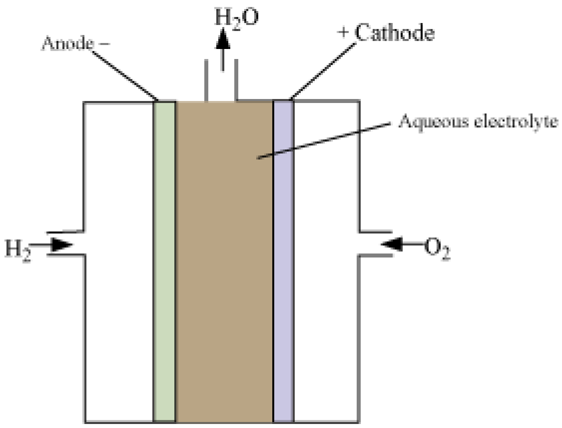
Nickel-cadmium cell

- Longer life than lead storage battery
- The overall reaction during discharging is

$$Cd(OH)_2 + 2Ni(OH)_{2(s)} \longrightarrow Cd_{(s)} + 2NiOOH_{(s)} + 2H_2O_{(l)}$$

Fuel Cells

- Fuel cells are galvanic cells in which the energy of combustion of fuels is directly converted into electrical energy.
- Fuels used are hydrogen, methane, methanol, etc.
- **Fuel cell using H_2 and O_2 to produce H_2O**



- The electrode cell reactions −

At anode: $2H_{2(g)} + 4OH^{-}_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^{-}$

At cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^{-} \rightarrow 4OH^{-}_{(aq)}$

- The overall reaction is

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

- Its efficiency is 70% whereas the efficiency of thermal plants is about 40%.
- It was used for providing electricity to the Apollo space programme.
- The water vapours produced during the reaction were condensed and supplied to astronauts for drinking purposes.
- The cell consists of porous carbon electrodes, which are incorporated with catalysts like finely divided Pt or Pd.
- Hydrogen and oxygen are bubbled through the electrodes into the electrolyte, which is an aqueous solution of NaOH or KOH.

- Advantages:

  (i) Pollution free – No harmful products are formed during the reaction.

  (ii) High efficiency – Its efficiency is about 70% whereas the efficiency of thermal plants is about 40%.

  (iii) Continuous source of energy – It runs continuously as long as the reactants are supplied.

Corrosion

- It is the process of slow conversion of metals into their oxides (undesirable) by the action of moisture, oxygen and other gases of the atmosphere.
- Certain metals (except the least reactive metals like Au, Pt, Pd) undergo corrosion and become coated with their oxides and other salts of the metals.
- Examples:
- Rusting of iron
- Tarnishing of copper
- Development of a green coating on copper and bronze
- In the process of corrosion, metals lose electrons to oxygen and get oxidised.

Corrosion of Iron

- Known as rusting
- The spot where oxidation takes place behaves as anode.
- The reaction taking place at anode is given by

$$2Fe_{(s)} \longrightarrow 2Fe^{2+}_{(aq)} + 4e^-;\ \ E^{\ominus}_{\left(Fe^{2+}/Fe\right)} = -0.44V$$

- The electrons released at the anodic spot move through the metal and reduce oxygen at another spot in the presence H^+ ion. This spot behaves as cathode.
- The reaction taking place at cathode is given by

$$O_{2(g)} + 4H^+_{(aq)} + 4e^- \longrightarrow 2H_2O_{(l)}; E^{\ominus}_{H^+/O_2/H_2O} = 1.23V$$

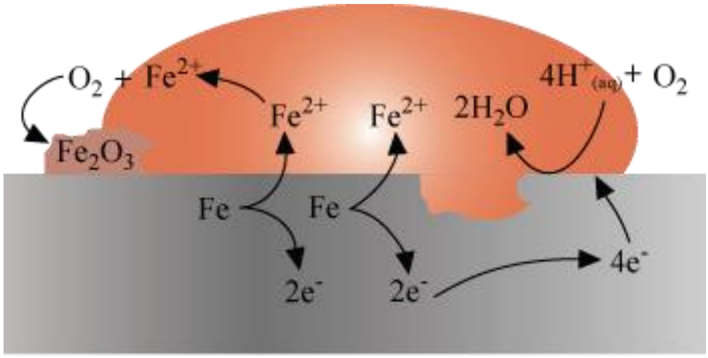
- Sources of H^+ ions may be
- H_2CO_3, formed due to the dissolution of CO_2 from air into water
- Water, formed due to the dissolution of other acidic oxides from atmosphere
- The overall reaction is

$$2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)}; E^{\ominus}_{cell} = 1.67 \text{ V}$$

- The Fe^{2+} ions thus formed are further oxidised by atmospheric oxygen to Fe^{3+} ions, and finally, it comes out as rust.

$$2Fe^{2+}_{(aq)} + \frac{1}{2}O_{2(g)} + 2H_2O_{(l)} \longrightarrow Fe_2O_{3(s)} + 4H^+$$

$$Fe_2O_{3(s)} + xH_2O_{(l)} \longrightarrow \underset{\substack{\text{Hydrated ferric oxide}\\ \text{(Rust)}}}{Fe_2O_3 \cdot x2H_2O}$$



Prevention of Corrosion

- Preventing the surface of the metal from coming in contact with atmosphere
- By covering the surface with paint or chemicals such as bis-phenol
- By covering the surface with other metals such as Sn, Zn, Mg.

Hydrogen Economy

Use of hydrogen as a renewable and non-polluting source of energy.