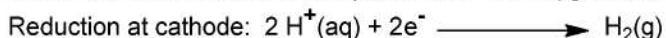


Unit III: Electrochemistry and Applications

Electrode potential, Nernst equation, reference electrodes (Calomel electrode and glass electrode), electrochemical cell, cell potential calculations. Primary cells – dry cell, alkali metal sulphide batteries, Secondary cells – lead acid, lithium ion batteries, Fuel cells - Hydrogen-oxygen fuel cell, Methanol-oxygen fuel cell, Solid-oxide fuel cell.
Corrosion: Introduction, Definition, types of corrosion- wet (galvanic corrosion, concentration cell corrosion) and dry corrosion, Factors influencing corrosion, control of corrosion- sacrificial anodic protection, Impressed current cathodic protection, electroplating method (Nickel).

1) Introduction:

- ❖ In 1791 Luigi Galvani discovered electrical activity in the nerves of the frogs that he was dissecting. He thought that electricity was of animal origin and could be found only in living tissues.
- ❖ The connection between chemistry and electricity is a very old one. Alexander Volta's discovery, in 1793, that electricity could be produced by placing two dissimilar metals on opposite sides of a moistened paper. In 1800, Nicholson and Carlisle, using Volta's primitive battery as a source, showed that an electric current could decompose water into oxygen and hydrogen.



- ❖ A small number of zinc atoms go into solution as Zn ions, leaving their electrons behind in the metal:



As this process goes on, the electrons which remain in the zinc cause a negative charge to build up within the metal which makes it increasingly difficult for additional positive ions to leave the metallic phase. A similar buildup of positive charge in the liquid phase adds to this inhibition. Very soon, therefore, the process comes to a halt, resulting in a solution in which the concentration of Zn^{2+} is still too low (around 10^{-10}M) to be detected by ordinary chemical means.

- ❖ Electric current is a flow of electrons generated by a battery, when the circuit is completed. The substance which allows the electric current to pass through it is called a conductor. Ex all metals, graphite, and aq. Solutions of electrolytes.
- ❖ The conductors are of two types. Metallic conductors and electrolytic conductors

Metallic conductance	Electrolytic conductance
Conductance is due to migration of electrons.	Migration of ions to different electrodes takes place in molten salts (or) electrolytic solution
It does not result in any chemical change.	It involves the decomposition of the conductor.
It decreases with increase in temperature.	It increases with increase in temperature.
It does not involve the transfer of any matter.	It involves the transfer of matter.

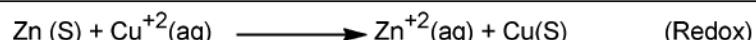
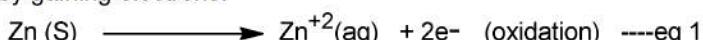
Redox reactions:

Oxidation reactions involves with the loss of electrons by a substance; while in the reduction reactions involves the gain of electrons by a substance. The, oxidation and reduction must always go side-by-side.

For example, if a zinc metal is placed in a solution of CuSO_4 , immediate precipitation of Cu takes place.



In the above redox reaction, the Zn atom is oxidized to Zn^{+2} , by losing electrons and the Cu^{+2} ions is reduced to Cu atom, by gaining electrons.

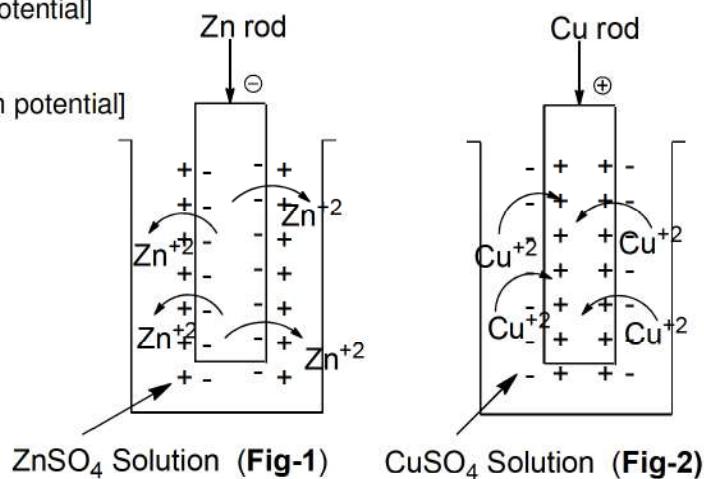
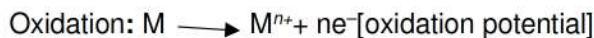


A redox reaction is obtained by adding eq-1 and eq-2 and each of these reaction, is known as half-reaction. i.e. eq 1 is called as oxidation half-reaction and eq-2 is called as reduction half reaction

2) Electrode potential and Nernst equation

Electrode potential: It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with its own salt solution of a unit molar concentration at 25 °C (298 K).

When a metal rod is dipped in its salt solution (electrolyte), the metal atom tends either to lose electrons (oxidation) or to accept electrons (reduction). In this process, there develops a potential between the metal atom and its corresponding ion called the electrode potential.



In Oxidation, a metal (M) is in contact with a solution of its own salt, the +ve ions in the metal come into the solution, leaving behind an equivalent number of electrons on the metal. As a result metal acquires a -ve charges, ex; Zn rod dipped in ZnSO₄ solution (Fig-1).

Similarly in reduction, the positive charge density is more on the surface of metal with respect to the solution. ex: Cu rod dipped in CuSO₄ solution (Fig-2).

Because of these -ve or +ve charges developed on the metal attracts the +ve or -ve charged free ions in the solution. Due to this attraction, the +ve and -ve ions remain quite close to the metal to form a layer like. This layer is called Helmholtz electrical double layer. As a result, a potential difference develops between metal and the solution, known as **electrode potential**.

There is a dynamic equilibrium between metal and metal ion and the potential difference between these two is called the electrode potential or the equilibrium potential. It is measured in volts. The potential difference for oxidation reaction is called the oxidation potential and that of reduction is called the reduction potential.

For any system, its oxidation and reduction potentials are numerically same with the opposite sign, i.e. if the oxidation potential of the electrode is +X volts, then its reduction potential will be -X volts.

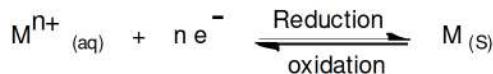
The electrode potential of an electrode at a given temperature depends upon the concentration of the ions in the surrounding solution.

If the concentration of the ions is unity at 25 °C (298 K), the potential of the electrode is termed as **the standard electrode potential** (E^0).

The value of electrode potential depends upon (i) the nature of the metal, (ii) the temperature and (iii) the concentration of the electrolyte. This can be explained in terms of Nernst equation.

The **Nernst equation** is an equation that relates the equilibrium reduction potential of a half-cell in an electrochemical cell.

Consider the general redox reaction:



In general for a reversible reaction, the free energy change (ΔG) and equilibrium constant (K) are inter-related as:

$$\Delta G = RT \ln K + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \quad \text{eq 1}$$

$$\Delta G = \Delta G^0 + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \quad \text{eq 2}$$

The energy in a physical system that can be converted to do work, is known as free energy change (ΔG) and the change in free energy when the concentration of reactant and the products are unity each is known as Standard free energy change (ΔG^0)

In a reversible reaction, the electrical energy produced at the expense of the free energy decrease i.e. $\Delta G = -nEF$ and $\Delta G^0 = -nE^0F$

Substitute ΔG and ΔG^0 in equation 2

$$-nEF = -nE^0F + RT \ln \frac{[M]}{[M^{n+}]} \quad \text{eq 3}$$

$$-nEF = -nE^0F + RT \ln \frac{1}{[M^{n+}]} \quad \text{eq 4}$$

(The concentration of metal (M) is unity)

$$-nEF = -nE^0F - RT \ln [M^{n+}] \quad \text{eq 5}$$

$$E = E^0 + \frac{RT}{nF} \ln [M^{n+}] \quad \text{eq 6}$$

$$E = E^0 + 2.303 \frac{RT}{nF} \log [M^{n+}] \quad \text{eq 7}$$

'Equation 7' is known as **Nernst's equation** for cation electrode or metal ion electrode potential at 25 °C.

Where E = electrode potential,

E^0 = standard electrode potential,

R = gas constant,

T = absolute temperature

F = Faraday constant,

n = number of electrons under redox process, and

M^{n+} = concentration of electrolyte.

From the equation 7, it is clear that with increase of concentration of the solution or with rise in temperature, the electrode potentials increases.

On substituting the values of R ($8.314 \text{ J.K}^{-1}\text{mol}^{-1}$), T (298 K) and F (96500 C), in eq 7

$$E = E^0 + \frac{0.0592}{n} \log [M^{n+}] \quad \text{----- eq 8}$$

For an electrode-electrolyte system, if the concentration of the electrolytic solution is 1 mol/L, the above equation (eq 8) can be written as

$$E = E^0 \quad \text{----- eq 9}$$

Hence, the standard electrode potential of a metal is the electrode potential *when the metal is dipped in its electrolytic solution of unit concentration at room temperature (25 °C)*.

The **Nernst's equation** for anion electrode or non-metal ion electrode potential at 25 °C

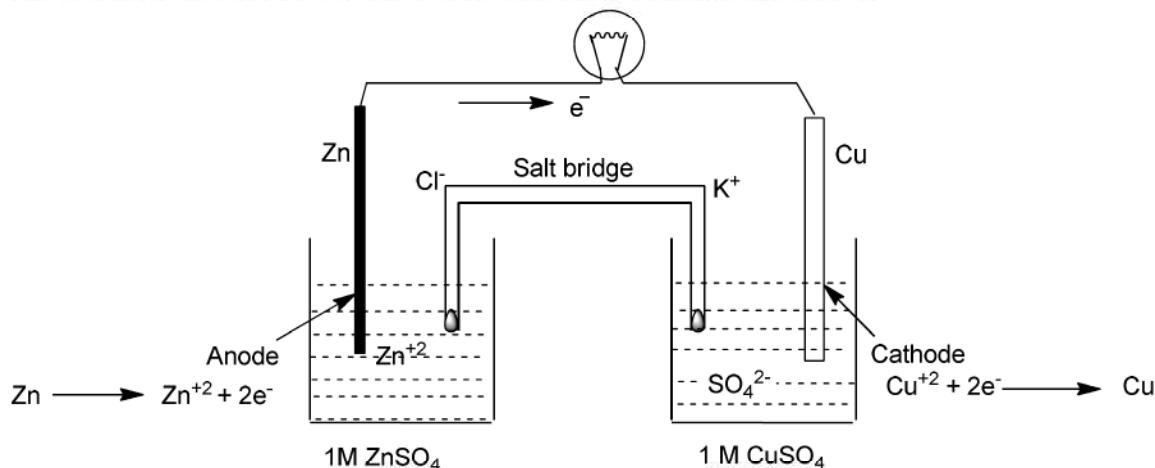
$$E = E^0 - 2.303 \frac{RT}{nF} \log [A^{n-}] \quad \text{----- eq 10}$$

A^{n-} = concentration of electrolyte.

Limitations: In dilute solutions, the Nernst equation can be expressed directly in terms of concentrations; but at higher concentrations, the true activities of the ions must be used.

3) Electrochemical cell (galvanic cell): An electrochemical cell is a device in which redox reaction is utilized to get electrical energy. The electrode where oxidation occurs is called anode; while the electrode where reduction occurs is called cathode.

An electrochemical cell can be created by placing metallic electrodes into an electrolyte. This phenomenon generates an electric current by a chemical reaction.



Galvanic cell (Daniell cell)

A simple electrochemical cell can be made from zinc and copper metals with solutions of their sulfates. As a result, electrons can be transferred from the zinc to the copper through an electrically conducting. The flow of current is due to the difference in electrode potentials of both the electrodes. Each electrode and electrolyte may consider as a half cell. The two electrolyte solutions are separated by a 'salt bridge'.

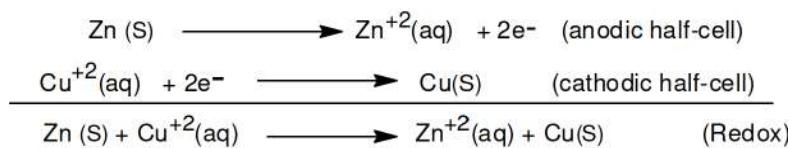
The electrode showing oxidation reaction is called as anode and the reduction reaction is called as cathode. The flow of electron will be externally from anode to cathode and internally from cathode to anode through the salt bridge.

A galvanic cell (Daniel cell) obtained by coupling Zinc half-cell and copper half-cell through a salt bridge.

The tendency of Zn to form Zn^{+2} is greater than the tendency of Zn^{+2} to get deposited as Zn and hence, Zn metal acquires a -ve charge. On the other hand the tendency of Cu^{+2} to get deposited as Cu is more and hence copper electrode becomes +vely charged. Because of the polarization of the electrodes, the flow of the current becomes slow after using them for a long time. This can be overcome by using a salt bridge.

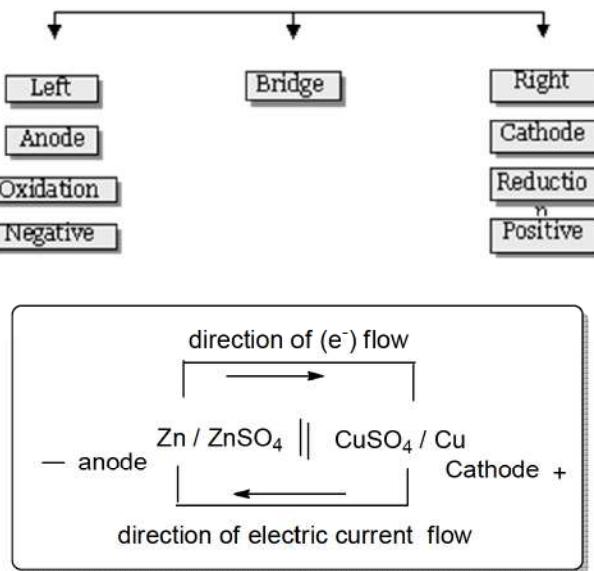
A zinc or a copper galvanic cell can be represented as $Zn/ZnSO_4 \parallel CuSO_4/Cu$. The double bar shows salt bridge, i.e. electrolyte-electrolyte junction.

The electrode reactions in galvanic cell (Denial cell) are



Representation of Galvanic cell:

As per IUPAC convention, the anode is always on the left and the cathode is always on the right.



(Flow chart)

A voltaic battery is a set of galvanic cells linked together in series to create a larger voltage than could be generated by a single galvanic cell.

Salt Bridge and its Significance:

- (i) Salt bridge is U – shaped glass tube filled with agar–agar (plant gel) mixed with an electrolyte like KCl , KNO_3 , NH_4NO_3 etc.

(ii) The electrolytes of the two half-cells should be inert and should not react chemically with each other.

(iii) The cation as well as anion of the electrolyte should have same ionic mobility and almost same transport number, viz. KCl, KNO₃, NH₄NO₃ etc.

EMF (electro-motive force)

The cell electromotive force or cell EMF is the *net voltage between the oxidation and reduction half-reactions taking place between two redox half-reactions*. The EMF of the cell (E_{cell}) is measured with the potentiometer.

The difference in potential, causes a current to flow from the electrode of higher potential to lower potential (i.e. a difference in potential that tends to give rise to an electric current), **is called the electromotive force** of the cell and expressed in volts.

$$E_{\text{cell}} = E_{\text{right}} - E_{\text{left}}$$

Or

$$E_{\text{cell}} = E_{\text{Cathode}} - E_{\text{Anode}}$$

$$E_{\text{cell}} = \text{EMF of cell}$$

E_{right} = reduction potential of right hand side electrode (reduction) [Cathode]

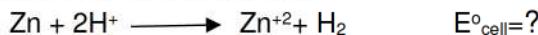
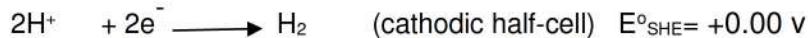
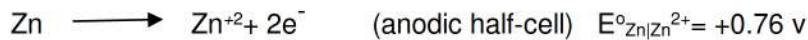
E_{left} = reduction potential of left hand side electrode (oxidation) [Anode]

If $E^{\circ}_{\text{cell}} > 0$ i.e. +ve then cell reaction is spontaneous

$E^{\circ}_{\text{cell}} < 0$ i.e. -ve then cell reaction is not feasible.

$E^{\circ}_{\text{cell}} = 0$ cell stops working

Ex: Zn/Zn²⁺is the anodic oxidation



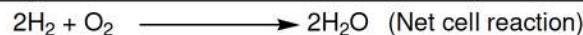
Note: The cell EMF calculated using standard reduction potentials.

$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{SHE}} - E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = +0.00 - (-0.76) = +0.76 \text{ V}$$

Because the voltage (EMF) is positive, the reaction is spontaneous and Zn will generate H_{2(g)} when added to an acid solution (but not water).

Problems with solutions:

- i) Calculate the standard EMF of the Hydrogen-oxygen fuel cell, given E⁰ value as -0.40V and 0.83V for the hydrogen and oxygen half-cells respectively.

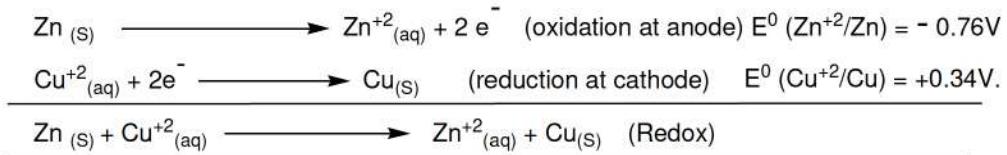


$$E_{\text{cell}} = E_{\text{Cathode}} - E_{\text{Anode}}$$

$$E_{\text{cell}} = 0.83 - (-0.40)$$

$$E_{\text{cell}} = 1.23 \text{ V}$$

- ii) Find the EMF of the Zn/Zn²⁺ (1M)// Cu²⁺ (1M)/Cu cell, gives, E⁰ (Zn²⁺/Zn) = - 0.76V and E⁰ (Cu²⁺/Cu) = +0.34V.



$$E_{\text{cell}} = E_{\text{Cathode}} - E_{\text{Anode}}$$

$$E_{\text{cell}} = +0.34 - (-0.76)$$

$$E_{\text{cell}} = 1.1\text{V}$$

Reference electrodes:

It is not possible to measure directly the electrode potential of an electrode. But the electrode potential can be measured with the help of a reference electrode. The most common reference electrode is the standard hydrogen electrode (SHE). And all other electrode potentials are expressed in comparison with this SHE.

The other reference electrodes are calomel electrodes, Silver-Silver chloride electrode etc.

The electrode, whose electrode potential, is a fixed value and it is used to determine the unknown electrode potential is called as reference electrode.

These are two types.

Primary reference electrode: eg- Standard Hydrogen Electrode (SHE)

Secondary reference electrode: eg- calomel electrode, Silver-Silver chloride electrode.

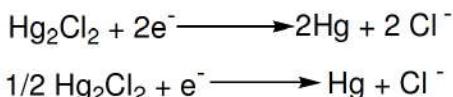
- i) **Calomel electrode:** (mercury-mercurous chloride electrode or Secondary reference electrode)

It consists of tube in the bottom of which is a layer of mercury, over which is placed a paste of Hg + Hg₂Cl₂. The remaining portion of cell is filled with a solution of 0.1 N or 1 N or saturated solution of KCl. A platinum wire dipping into the mercury layer is used for making electrical contact and rest of the Pt wire is wrapped with glass. The side tube is used to making electrical contact.

The saturated Calomel electrode is formulated as follows - Hg, Hg₂Cl₂ (s), KCl (satd. sol)

Calomel electrode acts as an anode or cathode electrode depending on the nature of the other electrode. The potential of this electrode is due to the reduction of mercurous ions to mercury

The electrode reaction taking place in this half-cell is

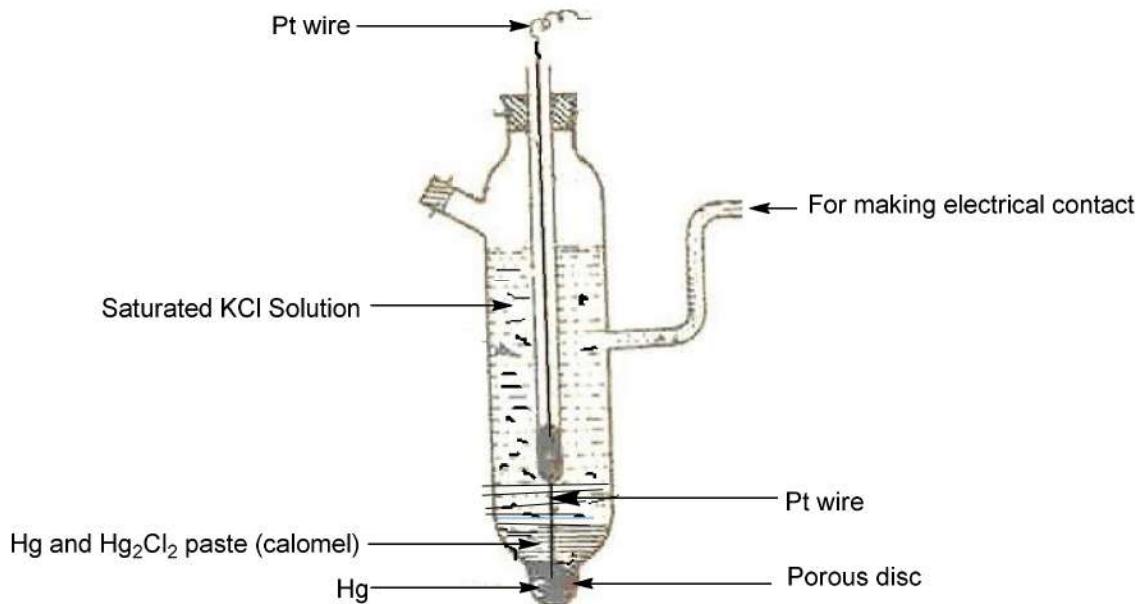


$$\text{Calomel electrode potential (}E_{\text{cal}}\text{)} = E^0_{\text{cal}} - \frac{2.303 \text{RT}}{\text{F}} \log[\text{Cl}^-]$$

$$\text{at } 25^\circ\text{C}, E_{\text{cal}} = E^0_{\text{cal}} - 0.0592 \log[\text{Cl}^-]$$

The above equation indicates that the electrode potential in the calomel electrode depends on the concentration of KCl solution used at 25 °C. The Calomel electrode potential measured by taking SHE as a reference electrode.

concentration of the KCl sol	0.1 N	1.0 N	Saturated
Electrode potential in volts (E_{cal})	0.3335	0.2810	0.2422



Applications of Calomel electrode:

- i) A calomel electrode is a much more practical electrode than a Standard Hydrogen Electrode.
- ii) Good portable reference electrode
- iii) The potential is reproducible and stable over a long period.
- iv) The Standard Calomel Electrode (SCE) is used in pH measurement.

This calomel electrode can be coupled with hydrogen electrode containing a solution of unknown pH. If the KCl used in Calomel electrode is saturated then the EMF of the cell is

$$E_{Cell} = E_{Cathode} - E_{anode}$$

$$E_{Cell} = 0.2422 - (-0.0592 \text{ pH})$$

$$E_{Cell} = 0.2422 + 0.0592 \text{ pH}$$

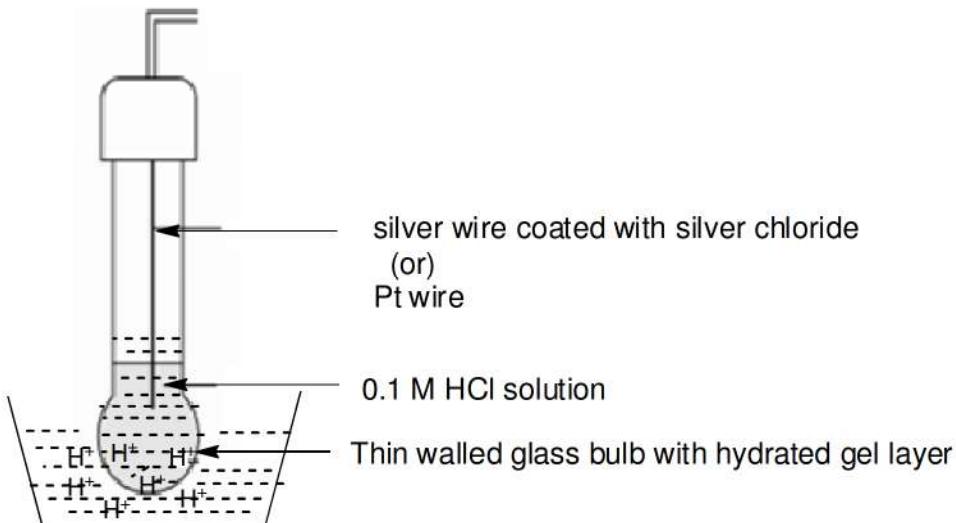
$$\text{pH} = \frac{E_{cell} - 0.2422}{0.0592}$$

Disadvantage of Calomel electrode:

- The calomel electrode contains mercury, which poses much greater health hazards.

Indicator electrode: Indicator electrode is used in conjunction with reference electrode. It is used to determine the concentration of an analyte in sample solution. ex: Glass electrode

Glass electrode: A glass electrode is a type of ion-selective electrode made of a doped glass membrane that is sensitive to a specific ion. The pH electrode is an example of a glass electrode that is sensitive to hydrogen ions and it can measure pH of various solutions.



When two solutions of different pH values are separated by a thin glass membrane, there develop a difference potential between the two surfaces of the membrane. The potential difference developed is proportional to the difference in pH value.

By keeping the pH of one of the solution inside electrode as constant the pH of the other solution can be determined.

Glass electrode is differ from the other type of electrodes, where the electrons are not involved in electrode reaction.

When electrode is in contact with the acid of unknown pH, then the potential of this electrode is given by

$$E_G = E_G^0 + 0.0592 \text{ pH}$$

E_G = potential of glass electrode

E_G^0 = standard potential of glass electrode depends on nature of the glass. _____.

Construction of glass electrode:

This glass electrode consists of special type of thin walled bulb (porous) and bulb filled with 0.1 M HCl solution. A silver wire coated with silver chloride is dipped for electrical contact. This electrode is represented by



Working of glass electrode:

The glass electrode is then coupled with reference electrode normally saturated calomel electrode (SCE). Then EMF of the cell can be measured. This cell is represented as



When the glass and the reference electrode, are immersed in a solution, a small galvanic cell is established. By using electron-tube voltmeter the potential difference between these two electrodes are measured.

$$E_{\text{Cell}} = E_{\text{SCE}} - E_G$$

Then the pH of the solution can be calculated as follows:

$$E_{\text{Cell}} = 0.2422 \text{ V} - [E_G^0 + 0.0592 \text{ pH}]$$

$$\text{pH} = \frac{0.2422 \text{ V} - E_{\text{Cell}} - E_G^0}{0.0592}$$

Advantages:

- It is simple and can easily be used.
- Equilibrium is rapidly achieved
- The results are accurate
- It can be used for turbid and colloidal solution.

Limitations:

- The glass electrode can be used in solution with pH range of 0 to 10. Above 12 pH the cations of solution affect the glass of electrode and make it useless.

Main differences between electrochemical cell (galvanic cell) and an electrolytic cell

Electrochemical cell (Galvanic Cell)	Electrolytic cell
A Galvanic cell converts chemical energy into electrical energy	An electrolytic cell converts electrical energy into chemical energy
The redox reaction is spontaneous and is responsible for the production of electrical energy	The redox reaction is not spontaneous and electrical energy has to be supplied to initiate the reaction
The two half-cells are set up in different containers, being connected through the salt bridge or porous partition	Both the electrodes are placed in a same container in the solution of molten electrolyte
The anode is negative and cathode is the positive electrode. The reaction at the anode is oxidation and that at the cathode is reduction	The anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction
The electrons are supplied by the species getting oxidized. They move from anode to the cathode in the external circuit	The external battery supplies the electrons. They enter through the cathode and come out through the anode

Batteries

An electric **battery** is a device consisting of one or more electrochemical cells that convert stored chemical energy into electrical energy.

Each battery consists of a three parts; i) negative electrode material, ii) positive electrode material, iii) electrolyte that allows ions to move between the electrodes. Terminals of electrodes allow current to flow out of the battery to perform work.

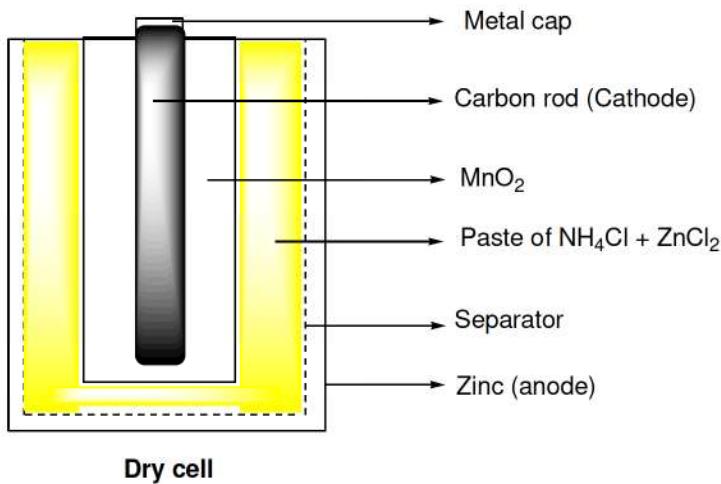
Unfortunately there is no single battery technology available on the market today that can be considered as "The Solution" for all classes of portable battery operated devices. There are a variety of batteries in use, each with its own advantages and disadvantages.

Batteries are divided into following types. based on their recharging capacity.

- I) **Primary battery** (single-use or "disposable") - batteries are used once and discarded.
eg: galvanic cell, dry cell, alkali metal sulphide batteries
- II) **Secondary battery** (rechargeable batteries) - can be discharged and recharged multiple times; eg: Ni-Cd storage battery, lithium ion batteries and lead-acid batteries.

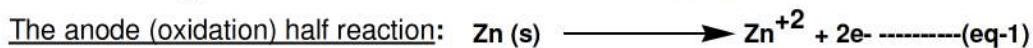
I) Primary battery-(Primary cell):- in this type, the cell reactions are irreversible. So when all the reactants are converted into product, no more electricity is produced and the batteries become dead. **Ex:** galvanic cell, dry cell, alkali metal sulphide batteries

Dry cell or Laclanche cell (or) Zinc-Carbon Dry-Cell / Battery



The zinc-carbon dry cell is made up of an outer zinc container, which acts as the anode. The cathode is a central carbon rod, surrounded by electrolyte paste. Electrolyte paste is a mixture of carbon, NH_4Cl , ZnCl_2 , MnO_2 (manganese (IV) oxide) and with only enough moisture to allow current to flow. A fibrous fabric separates the two electrodes, and a metal cap in the center of the cell conducts electricity to the outside circuit.

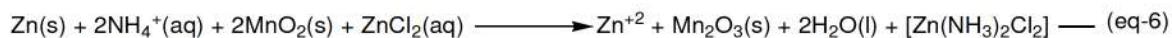
Chemical reactions occur in every part of the battery, converts the chemical energy into electrical energy. These reactions can be described as follows.



The cathode (reduction) half reaction: The MnO_2 reduces to Mn_2O_3 (Manganese trioxide)(eq-2). An acid-base reaction between OH^- and NH_4^+ leads to form the NH_3 . Formation of ammonia may disrupt the current flow (eq-3). This is prevented by the reaction between $\text{NH}_3(\text{g})$ and ZnCl_2 (eq-4).



Net cell reaction(eq-6) obtained by combining the eq-1 and eq-5:



Advantages of dry cell:

- Unlike wet cell, dry cell can operate in any orientation without spilling, as it contains no free liquid. This versatility makes it suitable for portable equipment.

- The dry-cell battery allowed for a major advance in battery safety and portability

Disadvantages of dry cell:

- When current is drawn rapidly from battery, products build up on the electrodes causes drop in voltage.
- Due to the acidic nature of NH_4Cl , zinc metal dissolves slowly, as result the cell run down slowly.

Alkali metal sulphide batteries:

The most important are Lithium–sulfur batteries, sodium sulfur batteries. Among all the metal-sulfur batteries, the Li-S battery was the first one to be investigated in 1940s.

The Na-S battery is usually made in a cylindrical configuration. The entire cell is enclosed by a steel casing that is protected, usually by chromium and molybdenum, from corrosion on the inside. In this Na-S battery, the Na metal anode and sulfur cathode were separated by a solid ceramic, β -Alumina (Al_2O_3), which also served as the electrolyte. This ceramic is electronical insulator and allows only positively charged Na^+ to pass through.

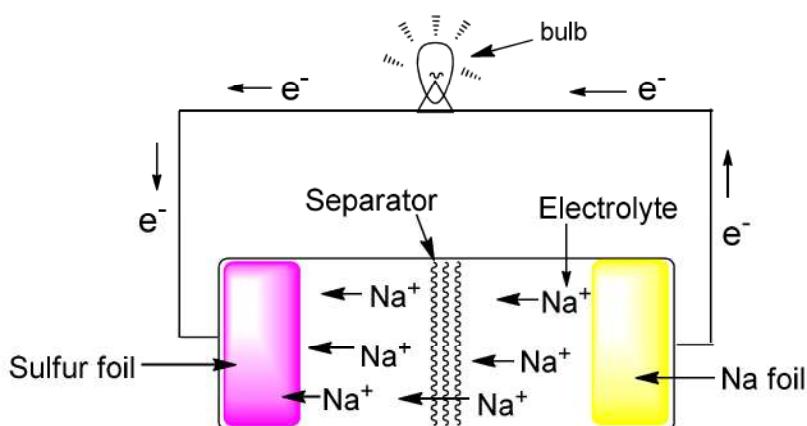
However, the battery must maintain at a high operating temperature (typically >300 °C) to promote the diffusion of Na ions. Thus, the high operation temperature limits its practical application due to the safety issues caused by molten Na and sulfur.

In 2006 a Na-S battery is developed which works at room temperature, just by using polyvinylidene fluoride hexafluoropropylene (PVDF-HFP) gel as electrolyte.

In all types of Na-S batteries, the following chemical reactions take place.



During the discharge process, the Na^+ migrate from anode to the cathode through the electrolyte, and a series of Na polysulfide (Na_2S_3 , Na_2S_2 , and eventually Na_2S) will be formed on the cathode side. Before this at cathode electron reacts with sulfur to form $\text{S}_{n^{2-}}$. i.e. the sulfur is reduced to form sodium polysulfides by reacting with Na^+ ions on the cathode electrode.



Discharge process of Alkali metal sulphide batteries

Applications of Alkali metal sulphide batteries:

- Primarily make them suitable for stationary energy storage applications _____.
- The cell becomes more economical with increasing size.
- Because of its high energy density, the NaS battery has been proposed for space applications. _____.

Disadvantages of Alkali metal sulphide batteries:

- In practice, the achieved capacity is much lower than the theoretical capacity
- Pure sodium presents a hazard, because it spontaneously burns in contact with air and moisture, thus the system must be protected from water and oxidizing atmospheres.
- Sodium polysulfides formed at cathode are highly corrosive nature.

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II) Secondary battery: is called as rechargeable battery or storage battery and is a type of energy accumulator. They can be recharged by applying electric current, which reverses the chemical reactions that occur during its use. These batteries are designed for repeated use just by recharging them. Ex: lithium ion, lead-acid etc.

Lithium battery(Rechargeable Li-battery):

Lithium shows highest reduction potential (-3.05 V) than any metal, so it produces high voltage.

Further, lithium is a very light metal, as results the Lithium batteries are light in weight.

Ex: Lithium-ion batteries, Lithium- Polymer batteries

Li-ion batteries:

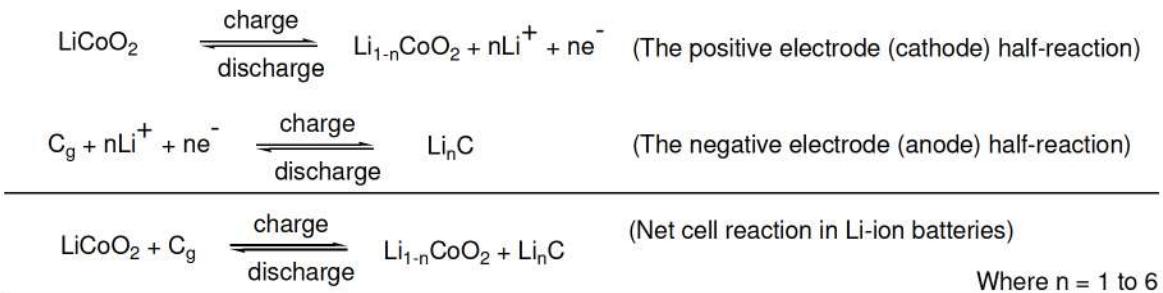
These Li-ion batteries do not contain metallic lithium and inthese batteries the conductivity is due to the transport of Li^+ ions through the electrolyte from one electrode to another and accompanied by the transport of electrons through the external circuit to maintain charge balance. They named as 'Li-ion batteries' since they uses lithium ions.

Li-ion battery consists of four parts namely, Cathode, Anode, electrolyteand separator. _____

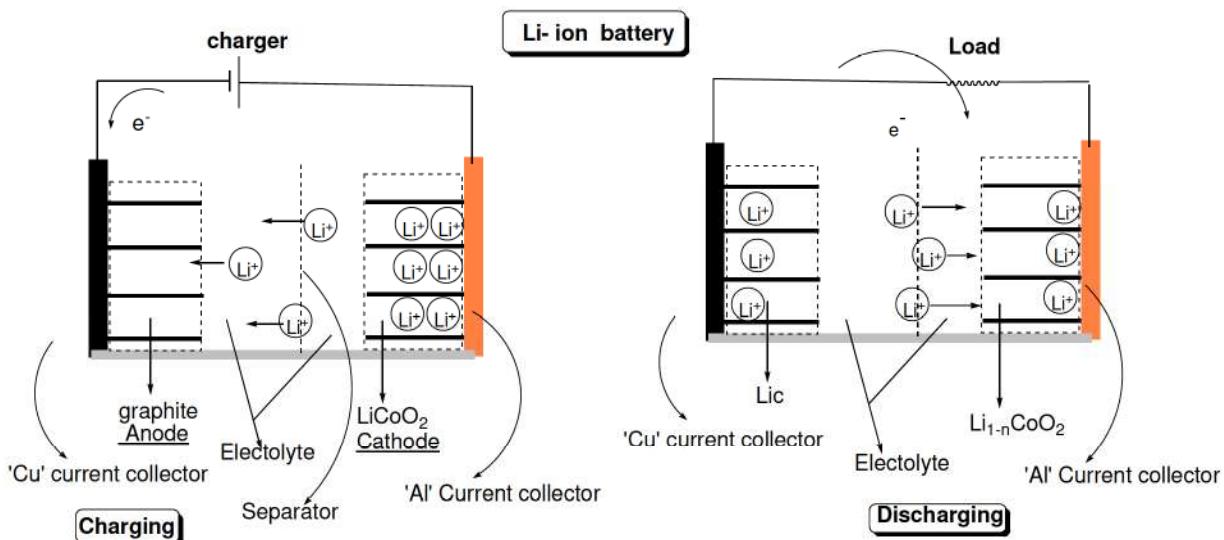
- a) Anode: finely dividedGraphiteadhere well to the copper foil
- b) Cathode: Layered Lithium Metal Oxide, e.g. Lithium Cobalt Oxide (LiCoO_2) adheres well to the aluminium foil. But in latest batteries lithium iron phosphate (LiFePO_4) is in use.
- c) Electrolyte: Lithiumhexafluorophosphate (LiPF_6) salt, dissolved in organic solvent mixture dimethylcarbonate, ethylene carbonate. Since water reacts with lithium, only non-aqueous electrolytes are used.
- d) Separator is a micro-porous film of polyethylene (PE) or polypropylene (PP). It prevent the electrodes from touching each other directly, and allows only the ions and not the electrode particles to migrate from one side to the other

Working:When the lithium ion battery is constructed, it is in its uncharged state and no Li^+ ions between the graphite layers. When battery is charged, Lithium ions move from LiCoO_2 to the graphite (C_6) through the electrolyte materials and remains there. In this process, battery stores

energy. When the battery is discharging, the lithium ions move back across the electrolyte to the LiCoO₂ electrode, producing the energy.



The fact is this battery operation does not actually involve true oxidation and reduction. In both cases, electrons flow through the external circuit to carry the charges. The electrons do not flow through the electrolyte, because as per electrons concerned it acts as an insulator. But Li⁺ ions can move easily in between these electrodes through electrolyte material due to the layer structure of both graphite and LiCoO₂. The movement of Li⁺ ions through the electrolyte and electrons through external circuit are interconnected processes.

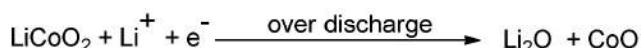


The overall reaction has its limits:

Overcharge leads to the synthesis of cobalt (IV) oxide, as evidenced by x-ray diffraction



Over discharge leads to the production of lithium oxide and cobaltous oxide as evidenced by x-ray diffraction studies



Applications of Li-ion batteries:

- i) these Li-ion batteries are used in high-performance devices

- ii) Used as power suppliers in portable electronics such as cell phones digital cameras, personal computers and in telecommunications.
- iii) For Transportation - in electric bikes and electric cars which runs with electricity

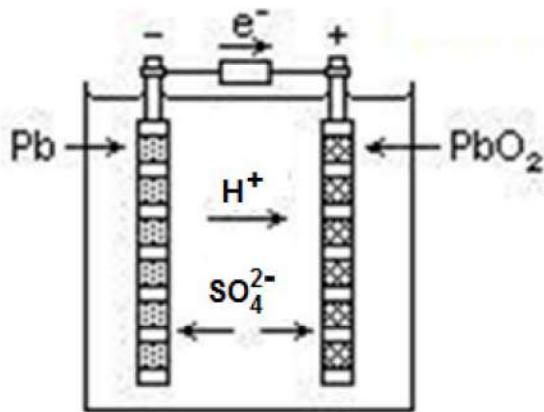
Advantages of Li-ion batteries:

- a) Energy densities are high.
- b) Voltages are high, with average operating voltages at 3.6 V, these are approximately three times the cutoff voltage of Ni-Cd battery.
- c) *Lithium-ion (Li-ion)* batteries are less environmentally damaging than batteries containing heavy metals such as cadmium and mercury.
- d) Charge / discharge cycles characteristics are excellent.
- e) Self-discharge is minimal when the battery is fully charged. (@ 3.3 % of its capacity in three months compared to 8% loss per month for Ni-Cd batteries)

Disadvantages of Li-ion batteries:

- They start degrading as soon as they leave the factory. Their life time is only two or three years from the date of manufacture whether it is in use or not.
- They are extremely sensitive to high temperatures. Heat causes lithium-ion battery packs to degrade much faster than they under normal conditions.
- If the lithium-ion batteries are completely discharged, it is ruined.
- If a lithium-ion battery pack fails, it will burst into flame.

Lead-acid battery:



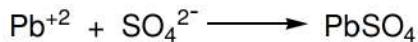
Lead-acid battery is the example for a storage cell. A storage cell is one that can operate both as a voltaic cell and as an electrical cell. When operating as a voltaic cell, it supplies electrical energy and as result it becomes run down. So it must be recharged from time to time and while charging it is considered as electrolytic cell.

Lead-acid battery consists of two types of electrodes, out of which one type are made of lead (-Ve) and others are with lead dioxide (PbO_2) (+Ve) or rather a paste of PbO_2 is pressed into a grid made of lead. These +Ve and -Ve electrodes are connected in parallel independently. The various plates are separated from the adjacent ones by insulators like strips of wood or rubber.

or glass fiber. The entire combination is then immersed in approximately 20-21 % dil H₂SO₄. The voltage of each cell is about 2.0 volts at these concentration at 25 °C.

During Discharging:

At -Ve (lead) terminal: The electrode loses electrons, which flow through the wire. In this reaction oxidation of lead takes place at the anode. The Pb⁺² ions then combines with sulphate ions (SO₄²⁻).



At + Ve (PbO₂) terminal: The electrons released at lead plate flows to the PbO₂ electrode. As result it undergoes reduction (+4 to +2) and resulted Pb⁺² ions then combines with sulphate ions.



So the net reaction during use or discharge is



Finally, PbSO₄ is precipitated at the both the electrodes and cell ceases to function and further it is noted that during discharging operations, the concentrations of acid decreases.

During Charging:

Electrodes can be reactivated by passing an external EMF > 2 volts and following reactions takes place at electrodes.

At -Ve terminal:



At +Ve terminal:



The net reaction during charging is:



During charging process the electrodes of cell are restored to their original conditions and the concentration of acids increases during charging operations.

Uses:

- In automobiles
- To supply current for electrical vehicles
- As gas engine ignition
- In telephone exchange, railway trains,
- Power stations
- In domestic inverters for un interruptible supply of power

Limitations:

Lowering of temperature causes the significant changes in voltage of Pb-acid batteries, it is just because of an increase in the viscosity of the fluids leads in the power output of the battery. Its ability can be recovered by keeping the battery at room temperature to deliver normal power.

Fuel cells

Definition: A fuel cell converts the chemical energy of the fuels directly into electricity.



Difference with batteries:

- A battery has all of its chemicals stored inside, and it converts those chemicals into electricity. i.e. battery eventually "goes dead" and as result it has to either throw away or recharge it.
- Fuel cell requires a fuel to flow in order to produce electricity. i.e. Chemicals constantly flow into the cell so it never goes dead. So the fuel cell is also called as flow cell
- **About fuel cell:** In fuel cells electricity is obtained without combustion from oxygen. Fuel cell accelerates the movement of the electrons directly. Most fuel cells today use hydrogen and oxygen as the chemicals.

Fuel cells are electrochemical cells in which reactants are supplied continuously and able to operate the cell without theoretical limit. This helps for long term generation of electrical energy.

- Fuel cells were first created in 1839 by **William Grove**. Grove, a British attorney and physicist, discovered that four large cells, each containing hydrogen and oxygen, could produce electric power.

Types of fuel cell: Fuel cells are classified mainly based on the type of electrolyte. All these fuel cells have the same basic operating principle.

- $\text{H}_2\text{-O}_2$ fuel cell (or) alkaline fuel cell (AFC)
- Phosphoric acid fuel cells (PAFC)
- Solid oxide fuel cells (SOFC)
- Proton exchange membrane fuel cells (PEMFC)
- Bio-fuel cell (BFC)

First-generation fuel cells: $\text{H}_2\text{-O}_2$ fuel cell (or) alkaline fuel cell and phosphoric acid

Second-generation fuel cells: Solid oxide fuel cell and Proton exchange membrane fuel cell

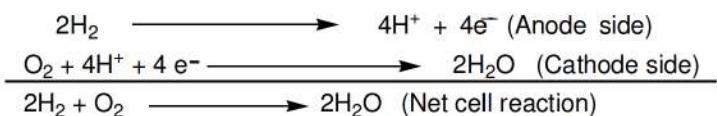
Third-generation fuel cells: hybridFuelcell(battery & fuel cell are mounted)

New third-generation zero-emission hydrogen fuel cells are in use from April 18, 2013

Fuel cell (General)

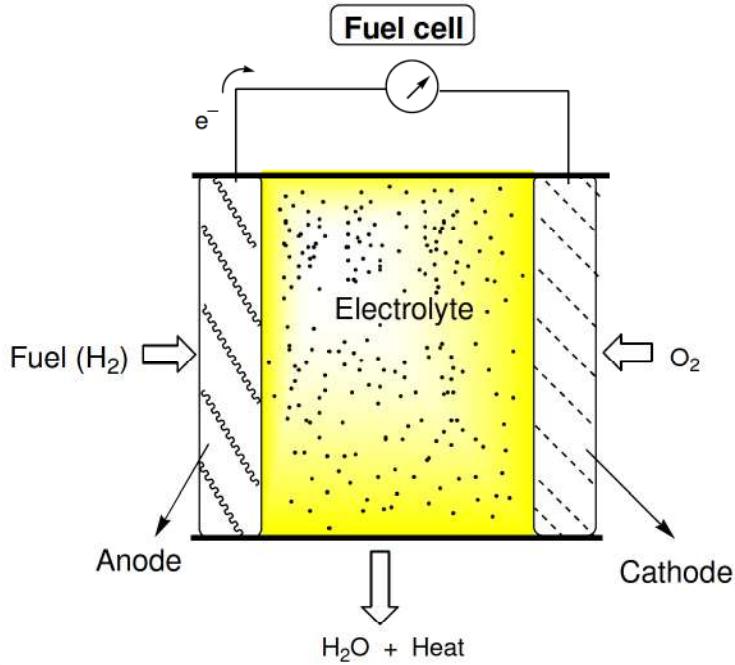
Fuel cells basic operating principle: A basic view of a single fuel cell unit is shown below.

Fuel cell's general cell reaction



- Fuel cells consist of an electrolyte material which is sandwiched in between two thin porous and rough electrodes (anode and cathode). These electrodes are coated with catalyst (platinum) to facilitate the electrode reactions. An electrolyte must be solid or liquid electrolyte that conducts protons.

- porous and rough nature of electrodes maximize surface area exposed to H₂ and O₂
- The input fuel (H₂) passes over the anode and oxygen (O₂) over the cathode where H₂ and O₂ catalytically split into ions and electrons to create an electric current.
- The electrons go through an external circuit to serve an electric load while the ions move through the electrolyte toward the oppositely charged electrode.
- Depending on the input fuel and electrolyte, different chemical reactions will occur at electrodes.
- At the electrode, ions combine to create by-products, primarily water and CO₂.



Working of fuel cell:

- The pressurized hydrogen gas (H₂) entering the fuel cell on the catalytically activated anode side
- When H₂ molecule comes in contact with the platinum, it splits into H⁺ ions and electrons
- The electrons are conducted through the anode, where they make their way through the external circuit and return to the cathode side of the fuel cell
- Meanwhile, on the cathode side of the fuel cell, oxygen gas (O₂) is being forced through the catalyst, where it forms two O²⁻ ions.
- Then each O²⁻ ions attracts two H⁺ ions through the membrane, to form a water molecule (H₂O).
- The formed electrons move through the external circuit.
- To increase voltage output, several fuel cells must be combined to form a fuel-cell stack to form the heart of a clean power generator.

Characteristics of Fuel cells

- They do not store chemical energy

- The efficiency of the fuel cell is about twice that of the conventional power plant for generating electricity.
- They are free of noise, vibration, heat transfer, thermal pollution etc.

General advantages of fuel cells

- i. The reactants and products are environment friendly, except the cell material
- ii. No emission of toxic gases and chemical wastes are in safe limits.
- iii. The efficiency of fuel cells is high. They convert nearly 75-85% of chemical energy into electrical energy. So they are good alternative energy resources.
- iv. Fuel cells are simple with few or no moving parts.
- v. Low maintenance costs of the fuel cell and the cell parts are modular and exchangeable
- vi. No noise pollution like generators but only low thermal pollution may occur. So they are used in the military operations.
- vii. Unlike solar cells, fuel cells are compact and transportable.
- viii. The fuels and electrolytes materials are available in plenty and inexhaustible unlike fissile fuels.
- ix. Unlike acid cells used in automobiles the fuel cells are less or non-corrosive.
- x. Unlike nuclear energy, the fuel cell energy is safe and did not release any toxic materials into atmosphere.
- xi. Fuel cells can operate at various temperature ranges.

Limitations of fuel cells:

- a) High initial costs associate with electrode materials (contains 'Pt') and design costs
- b) Need to develop suitable conditions for their application to massive production of electricity.
- c) Storage of H₂ gas is difficult and high cost of H₂ gas makes its uses minimal.
- d) Lack of infrastructure for distribution and marketing of H₂ gas.
- e) Needs high technical skills for operating the fuel cell.

Why cannot use fuel cells in regular life?

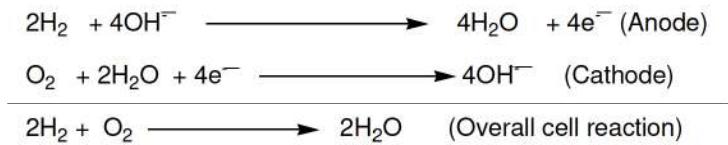
- Building inexpensive, efficient, reliable fuel cells is a far more complicated business.
- All fuel cells occupy a lot of space, much more than any other types of micro sources.

H₂-O₂ fuel cell (alkaline fuel cell)

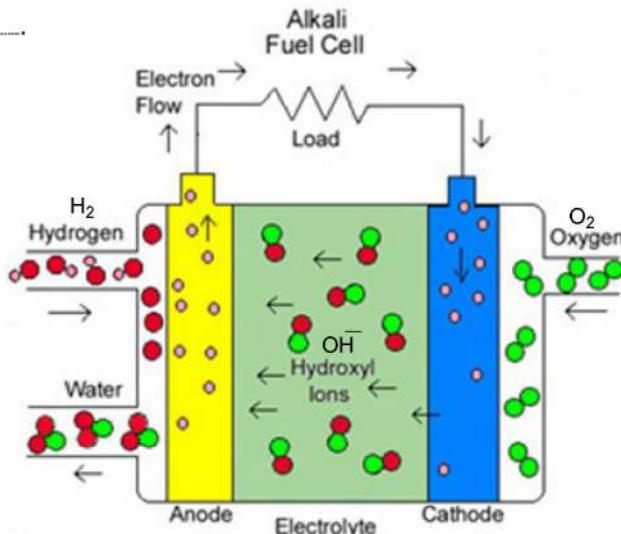
- This cell is also called the alkaline fuel cell or hydrogen fuel cell
- *H₂-O₂ fuel cell consists of two inert porous electrodes and electrolyte.*
- *Electrode: Made with graphite impregnated with finely divided platinum or alloy of palladium and silver or nickel in 3:1.*
- *Electrolyte: Aqueous KOH used as electrolyte.*
- *H₂ and O₂ gases are bubbled through the anode and cathode compartment respectively. Electrons generated at the anode move out through an external circuit creating electricity.*

- Electrical efficiency is about 75%
- Operating range is about 60 to 120 °C.
- *The cell output is 0.8 to 1.0 KW.*

H₂-O₂ fuel cell reaction:



The reaction at the anode is the combining of hydrogen gas (the fuel) with the electrolyte to form water and release electrons. At the cathode oxygen gas consumes electrons and so reacts with water in the electrolyte, this produces hydroxide ions. In this way the electrolyte is never used up, but is replenished at the same rate as it is consumed. This allows continuous operation of the hydrogen fuel cell.



Applications of H₂-O₂ fuel cell:

- H₂-O₂ fuel cell is used as auxiliary energy source in space vehicles, submarines and military-vehicles.
- The byproduct is H₂O, which can be used by astronauts.

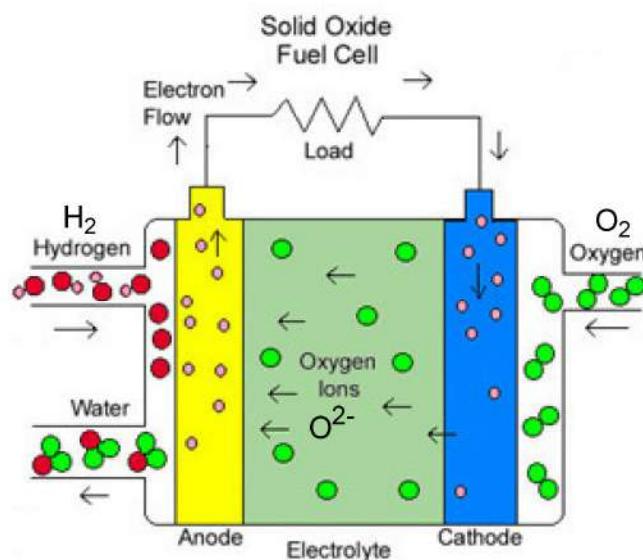
Advantages of H₂-O₂ fuel cell:

- Hydrogen fuel cells are attractive alternative to gasoline powered engine, because they are pollution free.
- The thermodynamic efficiency of fuel cells is high. They convert 75% of available energy to useful work. Whereas about 25 – 30 % for gasoline engines.
- For low temperature (-54°C to -72°C) operations potassium thiocyanate dissolved in liquid ammonia is employed as electrolyte.

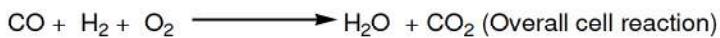
Disadvantages of H₂-O₂ fuel cell:

- Difficult to store and transport of highly flammable hydrogen
- Availability of alternative low price fuels.
- Productivity cost is very high
- Expensive catalysts (Platinum)

Solid Oxide fuel cells (SOFC):



- Solid oxide fuel cell consists of three components cathode, anode, and electrolyte.
- Solid oxide fuel cells use a hard, ceramic substances or calcium oxide or zirconium oxide as electrolyte. This electrolyte is sandwiched between the two electrodes.
- Solid oxide fuel cell electrodes are made with ceramic substances
- A fuel gas containing hydrogen, flows through anode and oxygen from the air flows through the cathode.
- Operating temperature is about 1000°C. At this high operating temperature, oxygen ions (O^{2-}) are formed at the cathode and these ions migrate through the electrolyte membrane react with the hydrogen to form water.
- Electrons generated at the anode move out through an external circuit creating electricity.
- Efficiency is about 60%. Cells output is up to 5 KW to 3 MW.
- Water gas ($CO+H_2$) or other hydrocarbon (CH_4) fuels can be used as fuels.
- It is designed to capture and utilize the systems waste heat, overall fuel efficiencies could top 80-85%.



Applications of SOFC:

- For commercial scale production
- Mobile power generation

Advantage of SOFC:

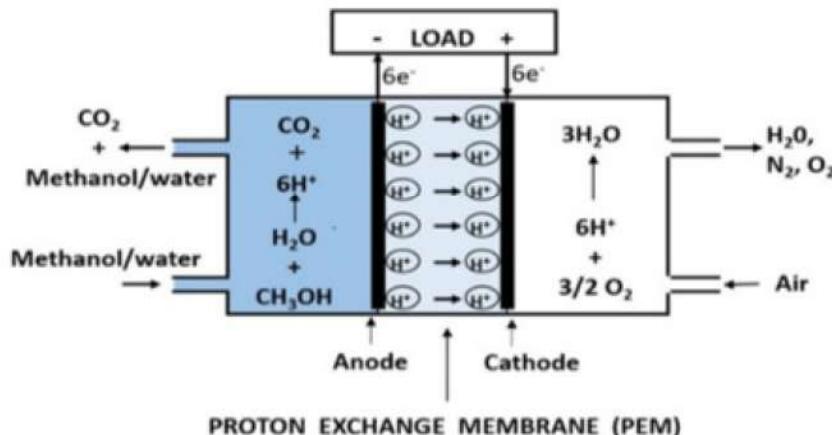
- Since cell operates at high temperature, **catalyst is not required**
- Waste heat can be recycled to make additional electricity.
- High efficiency

- Solid electrolyte reduces the electrolyte management problems
- Low cost fuel ($\text{CO} + \text{H}_2$) can be used

Disadvantage of SOFC:

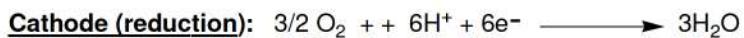
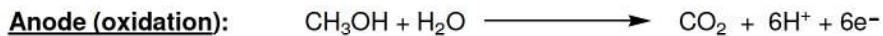
- Solid electrolytes can crack, due to high operational temperature
- High temperature enhance the corrosion and breakdown of cell composition

Methanol fuel cells (or) Directmethanol fuel cells



- Methanol fuel cell consists of two inert porous electrodes, and electrolyte
- Electrode: Made with graphite impregnated with finely divided platinum or ruthenium or gold.
- Electrolyte: Nafion (a sulfonated fluoropolymer) membrane is feasible to use between 80-120 °C and recently polybezimidazole membrane are in use, where operating temperature is 220 °C. It is not true electrolyte but it allows only migration of H^+ from anode side to cathode side. This electrolyte is sandwiched between the two electrodes.
- About 3% methanol solution was passed through the anode at 50–120 °C by applying pressure where it undergoes catalytic oxidation and forms CO_2 and protons (H^+). These H^+ are transported across the proton exchange membrane.
- Pure air is pumped into cathode chamber, where H^+ react with oxygen to produce water
- Electrons generated at the anode move out through an external circuit creating electricity.
- Electrical efficiency is about 45%
- Operating range is about 80 to 120 °C.
- The cell output is 25 W to 5 KW.

Limitations / precautions: Pure methanol cannot be used without provision of water, because under pressure, pure form of methanol diffuses directly through membrane and reached into cathode chamber, where its concentration is about zero. This methanol is rapidly consumed by oxygen at cathode and results combustion and this process finally damages the cell.



Applications of Methanol fuel cell:

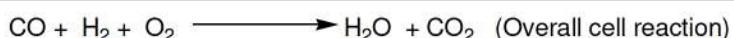
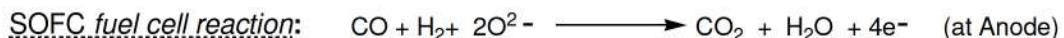
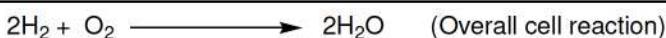
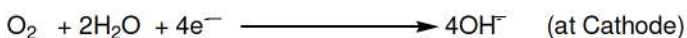
- For powering vehicles
- In space craft for continuous power supply
- In military for large scale power production
- For domestic use

Advantages of Methanol fuel cell:

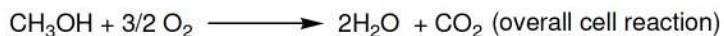
- Adoption of renewable energy sources
- Control pollution due to zero waste
- Methanol fuel cells are an emerging application since they have low noise and thermal signatures and no toxic effluent except CO_2 .

Comparison of fuel cells

Fuel cell reactions:



Methanol fuel cell reaction:



comparison of fuel cells

H₂-O₂ fuel cell (or) Alkaline fuel cell		Solid oxide fuel cell (SOFC)	Methanol-fuel cell
Fuel	H ₂	CO + H ₂	3% Methanol solution
Electrolyte	Aqueous solution of potassium hydroxide (KOH)	Solid oxide (calcium, zirconium)	no electrolyte; organic polymer membrane
Electrode	graphite <i>impregnated with finely divided platinum</i>	Ceramic substances without catalyst	Graphite covered with Pt or Ru or Au
Charge carried in electrolyte	OH ⁻	O ²⁻	H ⁺ through ion-exchange membrane
Operational temperature (°C)	60 – 120	1000	80 - 120
Efficiency (%)	converts 75% of available energy	about 60%.	about 45%
System output	10kW – 100kW	5kW – 3MW	25 W – 5 KW.
Applications	Military and space	For commercial scale production	<ul style="list-style-type: none"> ○ non-commercial power generation ○ For powering vehicle
Advantage	<ul style="list-style-type: none"> • Higher performance • Pollution free 	<ul style="list-style-type: none"> • high efficiency • solid electrolytes cannot leak • no catalyst 	<ul style="list-style-type: none"> • Biofuels are cheap • Adoption of renewable energy sources • water treatment
Disadvantage	<ul style="list-style-type: none"> • Difficult to store and transport of highly flammable hydrogen. • Expensive Platinum catalysts 	<ul style="list-style-type: none"> • Solid electrolytes can crack, due to high operational temperature 	<ul style="list-style-type: none"> • operate well in mild conditions • Pure methanol cannot be used
Cell reaction	In page 23	In page 23	In page 23

Fuel Cell Applications or Fuel cells today

- Fuel cells have emerged as one of the most promising new power-generating source because of their:
 - simplicity, high efficiency and eco-friendly nature
 - non-interruption supply of electricity
 - Advantage for silent operation
 - Increased design flexibility
- Potential application of fuel cells ranges from systems of a few watts to megawatts.
- Fuel cell applications are classified as transportation, portable and stationary applications.

e) **Transportation-mobile applications**

Modern vehicle manufacturers, designed vehicle that works by using power produced by fuel cells.

- Light duty vehicles (LDVs), such as cars and vans
- Scooters and Motorcycles
- Loading Vehicles in airports i.e. baggage trucks
- Light Rail and trams
- Ferries and smaller boats
- Submarines
- Unmanned aerial vehicles (UAVs) and unmanned undersea vehicles (UUVs)

ii) **Remote Power Source (for Portable Electronic Equipment)**

Portable fuel cells are being developed in a wide range of sizes ranging from less than 5 W up to 500 kW. Portable fuel cells can be used as remote power generators in following fields.

- Telecommunication stations
- Weather stations
- Oceanic monitoring stations
- Rail-road crossing signals

iii) **Military (Portable applications)**

Fuel cells are especially suited for silent operations because of their low heat and no noise. Lower operating costs also apply

- Soldier portable power
- Field power
- Weapon systems
- Small vehicle propulsion
- Power source for border sensors

iv) **Stationary-which provide electricity but are not designed to be moved**

- Water pumping
- Schools and hospitals
- Lights and Communications

Solved Examples on Nernst Equation

P1. The Cu^{2+} ion concentration in a copper-silver electrochemical cell is 0.1M. If $E^\circ(\text{Ag}^+/\text{Ag}) = 0.8\text{V}$, $E^\circ(\text{Cu}^{2+}/\text{Cu}) = 0.34\text{V}$, and Cell potential (at 25°C) = 0.422V , find the silver ion concentration.

Here, the silver electrode acts as a cathode whereas the copper electrode serves as the anode.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.8\text{V} - 0.34\text{V} = 0.46\text{V}$$

Since the charge on the copper ion is +2 and the charge on the silver ion is +1, the balanced cell reaction is:



Since two electrons are transferred in the cell reaction, $n = 2$. Now, the Nernst equation for this electrochemical cell can be written as follows.

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0592/2) \times \log(0.1/[\text{Ag}^+]^2)$$

$$0.422\text{V} = 0.46 - 0.0296 \times (-1 - 2\log[\text{Ag}^+])$$

$$\text{Therefore, } -2\log[\text{Ag}^+] = 1.283 + 1 = 2.283$$

$$\text{Or, } \log[\text{Ag}^+] = -1.141$$

$$[\text{Ag}^+] = \text{antilog}(-1.141) = \mathbf{0.0722 \text{ M}}$$

P2. What is the Cell Potential of the electrochemical cell in Which the cell reaction is: $\text{Pb}^{2+} + \text{Cd} \rightarrow \text{Pb} + \text{Cd}^{2+}$; Given that $E^\circ_{\text{cell}} = 0.277$ volts, temperature = 25°C , $[\text{Cd}^{2+}] = 0.02\text{M}$, and $[\text{Pb}^{2+}] = 0.2\text{M}$.

Since the temperature is equal to 25°C , the Nernst equation can be written as follows;

$$E_{\text{cell}} = E^\circ_{\text{cell}} - (0.0592/n) \log_{10}Q$$

Two moles of electrons are transferred in the given reaction. $\text{Pb}^{2+} + \text{Cd} \rightarrow \text{Pb} + \text{Cd}^{2+}$,

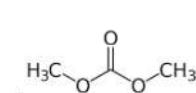
Therefore, $n = 2$. The reaction quotient (Q) is given by $[\text{Cd}^{2+}]/[\text{Pb}^{2+}] = (0.02\text{M})/(0.2\text{M}) = 0.1$.

The equation can now be rewritten as:

$$E_{\text{cell}} = 0.277 - (0.0592/2) \times \log_{10}(0.1) = 0.277 - (0.0296)(-1) = \mathbf{0.3066 \text{ Volts}}$$

Thus, the cell potential of this electrochemical cell at a temperature of 25°C is 0.3066 volts.

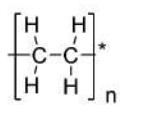
Structure of the compounds studied in this unit.....(Just for information)



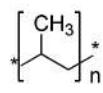
dimethylcarbonate



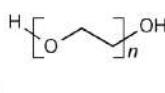
ethylene carbonate



polyethylenene



polypropylene



poly(ethylene oxide)

Compare primary Battery verses Secondary battery

PRIMARY BATTERIES	SECONDARY BATTERIES
These batteries are used once and discarded.	These batteries can be discharged and recharged multiple times
Ex:: galvanic cell, dry cell	Ex:: Ni-Cd storage battery, lithium ion batteries and lead-acid batteries
In this type, the cell reactions are irreversible. So when all the reactants are converted into product, no more electricity is produced and the batteries become dead	In this the material is present in one form during charging process and in during discharge process it turns into another form
In this battery operations involve true oxidation and reduction.	The fact is this battery operation does not actually involve true oxidation and reduction.
Energy densities are low. Can obtain max. of 1.5V	Energy densities are high. Can obtain min. 1.4V to max 4.4V, based on the name of the secondary battery
These are most commonly used in portable devices that have low current drain. Normally used in radios, hand lights etc.	They can be used widely; for example to power mobile phone, digital cameras, notebook computers, battery-powered electric vehicles etc.
can cause environmental pollution, because of their non-reusability	less environmentally damaging, because of their reusability
Low price, but need to replace time to time	Only initial expenditure, but maintenance free because of its 2-3 years of life time.

Compare Battery versus Fuel cell

Battery	Fuel cell
A fuel cell converts the stored chemical energy into electricity	A fuel cell converts the chemical energy of the fuels directly into electricity. $\text{Fuel} + \text{O}_2 \xrightarrow{\text{Catalyst}} \text{Oxidation products} + \text{electricity}$
a battery makes electricity from the energy it has stored inside the battery	fuel cell makes its electricity from fuel in an external fuel tank
a battery may run dead	a fuel cell will make electricity as long as fuel is supplied
Shows significant impact on the environment due to disposing or recycling batteries.	Replace the electricity source and often saves money over time and reduces the environmental impact of disposing or recycling batteries.
Used in portable toys, electronics for power supply	Used for commercial scale production and by astronauts
<i>Ex:</i> galvanic cell, dry cell (Primary battery) and Ni-Cd storage battery, lithium ion batteries and lead-acid batteries (Secondary battery).	<i>Ex:</i> <i>H₂-O₂ fuel cell (or) alkaline fuel cell</i> <i>Solid oxide fuel cells</i> <i>Methanol fuel cells</i>

Corrosion

Corrosion: Introduction, Definition, types of corrosion- wet (galvanic corrosion, concentration cell corrosion) and dry corrosion, Factors influencing corrosion, control of corrosion- sacrificial anodic protection, Impressed current cathodic protection, electroplating method (Nickel).

Metals and alloys are generally used as construction materials and in machineries. If the metal or alloy structures are not properly maintained they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. This destruction or deterioration of the metal or alloy surface is known as **corrosion**.

The corrosion is defined as "**The gradual destruction or deterioration of metals or alloys by the chemical or electro chemical reaction**".

The surface of almost all metals begins to decay more or less rapidly when exposed to corrosive environment such as gaseous atmosphere, water or reactive chemical environment. As a result of decay, the metals are converted to their oxides, hydroxides, carbonates, sulphides etc.

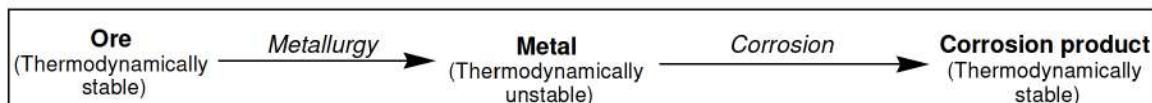
Examples:

- i) **Rusting of iron:** Formation of large red flakes and reddish brown powder ($\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$) on the surface of iron and the iron becomes weak.
- ii) **Corrosion of copper:** The formation of green film ($\text{CuCO}_3 + \text{Cu}(\text{OH})_2$) on the surface of copper when exposed to moist-air containing CO_2
- iii) **Corrosion of Aluminum:** Aluminum corrodes but it does not rust. Generally, aluminum oxide the corrosion product of aluminum is very hard material that actually protects the aluminum from further corrosion. Further, aluminum oxide appears as dull gray to powdery white in color.

(**Rust** is a term used to describe the **corrosion** of iron and iron alloys. **Corrosion** is a term that covers the destruction of any metal. In general, **corrosion** is the deterioration of a metal by **oxidation** or other chemical action)

Causes for corrosion:

- a) The corrosion is a process where "reverse of extraction of metals" occurs.



- b) The basic reason for corrosion is most of the metals naturally exists in impure state like ores or minerals. In general these ore or mineral is a stable form of metals, which is in combined form of metal oxides, metal chlorides, metal silicates, metal carbonates, metal sulphides etc.
- c) During the extraction of metals, these ores are reduced to pure metals by supplying considerable amounts of energy. Hence the isolated pure metals are present in excited state than their corresponding ores. As a result, every substance tries to get lower

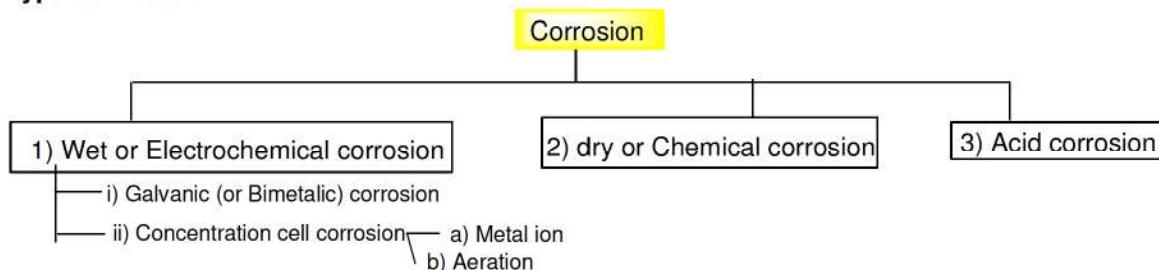
- energy state; because at lower energy state the metals are stable. So the pure form of a metal has the natural tendency to go back to their original state. i.e. Ores or minerals
- d) As a result when the metal is exposed to environment at conditions like dry gases, moisture and liquids etc, the metal surface reacts and form the thermodynamically more stable compounds of metals like oxides, chlorides, silicates, carbonates, sulphides etc. As a result of corrosion the loss of metal takes place.

Disadvantages / problem of corrosion/ consequences of corrosion:

The process of corrosion is slow and occurs only at surface of metals, but the losses are unpleasant due to the following facts.

- The valuable metallic properties like conductivity, malleability, ductility etc are lost due to corrosion.
- Poor in appearance
- Life span of the metallic parts of the machineries is reduced due to this corrosion. This leads to failure of machinery due to loss of useful properties of metals.
- Chance for explosion of engine.
- The plant may be shut down due to failure of machinery.
- Decrease in production rate and replacement of equipment is time and economy consuming.
- Contamination of product and release of toxic products from a corroded equipment
- The process of corrosion is very harmful and is responsible for the enormous wastage of metal in the form of its ores/minerals form.
- It is estimated that the amount of iron wasted by corrosion each year is about $\frac{1}{4}$ of its annual world production. The approximate estimation of loss of metal due to corrosion is few billion US dollars per annum all over the world. So corrosion is known as 'billion dollar thief'

Types of corrosion:



1) Wet (or) electrochemical Corrosion: (Indirect corrosion)

This wet corrosion occurs due to the following reasons

- a) Where a conducting liquid is in contact with metals or alloys
- b) Existence of separate anode and cathode between them the current flow through the conducting medium.

Wet corrosion can be explained by following two important ways.

- i) Galvanic corrosion ii) concentration cell corrosion

i) **Galvanic (or) Bimetallic corrosion**

- According to modern electrochemical theory, all the metals have a tendency to pass into solution of its salt.
- Based on Galvanic series when more than two metals are used in a structure, the metal with lowest reduction potentials becomes anode, as result the anode metal undergoes corrosion easily.

Examples:

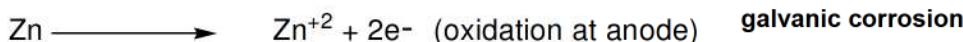
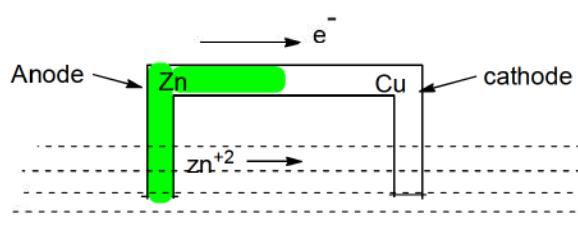
Metal	Zn	Fe	Cu	Ag	Pt
Reduction potential	-0.76 V	-0.44 V	+0.34 V	+0.80 V	+0.86 V

- When 'Zn' is in contact with 'Fe': 'Zn' corrodes faster than 'Fe' because 'Zn' is anode to 'Fe'.
- When 'Fe' is in contact with 'Cu': 'Fe' undergoes corrosion because 'Fe' acts as anode to 'Cu'.
- Similarly 'Cu' get corrode when it is connected to 'Ag' or 'Pt'. i.e. 'Cu' acts as anode when it is connected to 'Ag' or 'Pt'.
- Greater the difference in electrode potentials greater will be the corrosion.

Examples: The following observations can be made, when Zn couples with Fe and Cu separately. In Zn-Cu system Zn undergo rapid corrosion than in Zn-Fe system due to the greater difference in electrode potentials.

- The following chemical changes occur in galvanic corrosion.
- Oxidation takes place at anode; as a result metal ions are formed. Hence the corrosion always occurs at anode.
At anode: $M \text{ (metal)} \longrightarrow M^{n+} \text{ (metal ion)} + ne^-$
 M^{n+} = dissolves in solution and it can form compounds such as oxide
 - Reduction takes place at cathode. Generally, reduction reaction does not affect the cathode.

Ex: When two dissimilar metals are connected and jointly exposed to the corrosive environment, the metal possessing lower reduction potential becomes anode and undergoes corrosion.



galvanic corrosion

When 'Zn' and 'Cu' are connected and exposed to corroding environment (containing moisture). 'Zn' becomes anode due to lower reduction potential. 'Zn' undergoes oxidation and corroded whereas 'Cu' undergoes reduction and protected. The electrons flow from anode (Zn) to cathode (Cu)

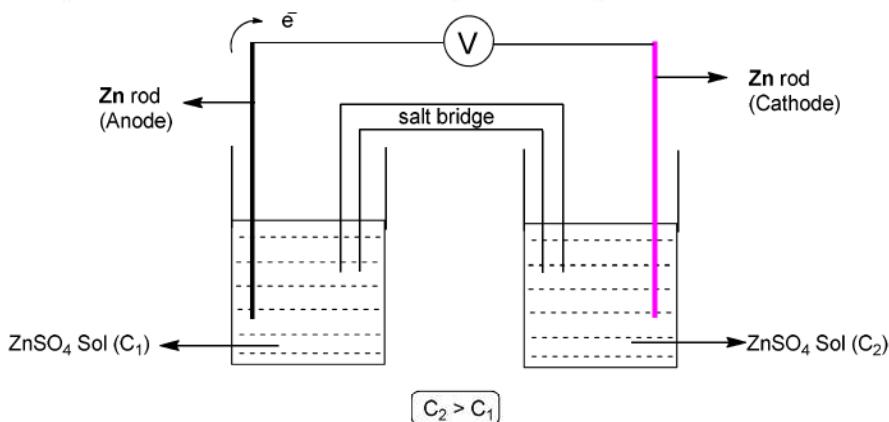
This reaction clearly indicates that corrosion occurs near anodic metal, while the cathodic metal (Cu) is protected.

ii) Concentration cell corrosion:

This type of corrosion is due to electrochemical attack on the metal surface, which is exposed to an electrolyte of varying concentration or of varying aeration.

a) Variation in metal ion concentration:

The difference in metal-ion concentrations arises due to the local temperature differences, or slow diffusion of metal-ions produced by corrosion and some other factors.



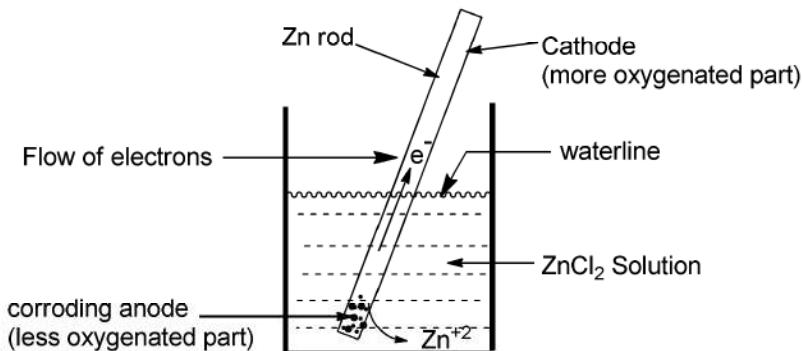
Explanation:

- i) When two plates of same metal dipped in a salt solution of same concentration and connected externally, no current flows, because both the plates have same potentials.
- ii) If the concentrations of the solutions around the metal electrodes are different then the metal which is at lower concentration go into solution. As result, the metal exposed to a solution of lower concentrations gives electrons hence become anode and dissolves. On the other hand the metal exposed to a solution of higher concentration becomes cathode as it receives electrons. As result EMF will generated.

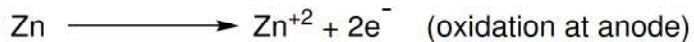
a) Variation in oxygen concentration: or Aeration corrosion:

Generally the aeration corrosion occurs because of difference in the concentration of O₂ levels. It is known that the O₂ deficient area serves as anode.

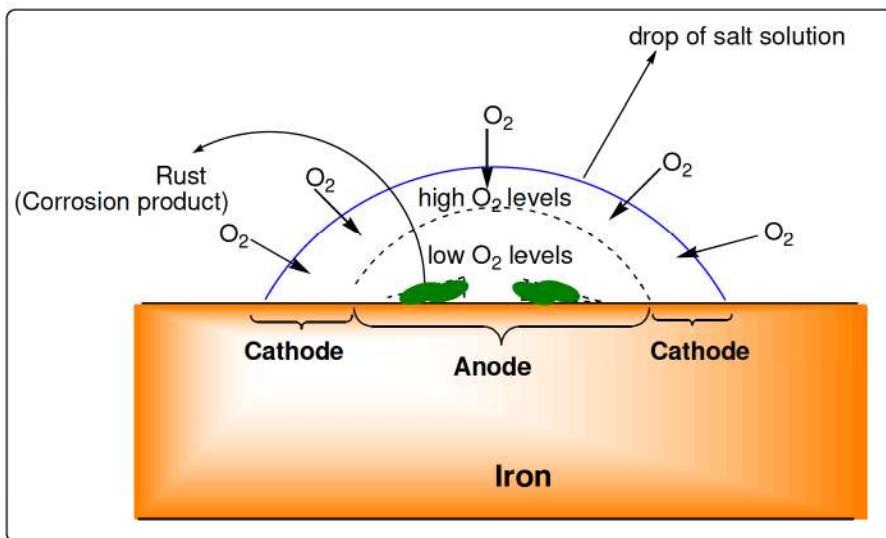
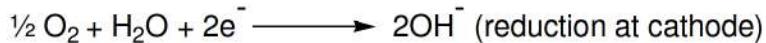
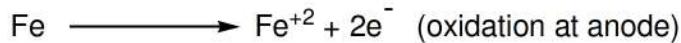
Case I: When one part of the metal is exposed to a different air concentration from the other part, causes a difference in potentials between these differently aerated areas. As a result, a differential in aeration of metal causes a flow of current, called 'differential current'. This leads to the corrosion of metals.



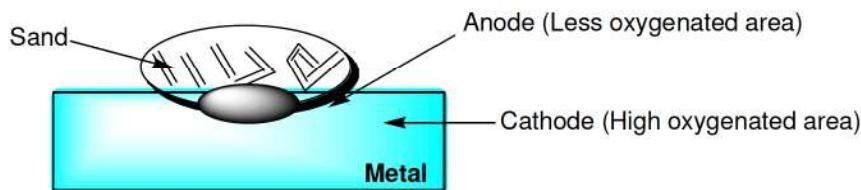
When a 'Zn' rode dipped in a dilute solution of ZnCl_2 and solution is not agitated properly, then the upper part of the 'Zn' rod i.e the portion adjacent to the waterline are more strongly aerated and hence become cathode and the 'Zn' rod immersed to depth have low oxygen levels, as a result this part becomes anode. So, a difference of potentials generated and this leads to a flow of current between the two differentially aerated areas of same metal. The system will act as concentration cell and the following chemical changes occur.



Case II: In the similar way, a drop of water on a piece of iron acts as an oxygen concentration cell. Area covered by droplets having low O_2 levels acts as anode and the area with high O_2 levels acts as cathode. As a result the corrosion occurs where the O_2 concentration is low. i.e. anode area.



Case III: Corrosion is accelerated due to the accumulation of rust or scale or sand or other contamination on the metal surface. Because they restrict the access of O₂ and establish an anode and the surrounding large parts become the cathode area and this phenomenon promotes the corrosion. i.e. corrosion starts just underneath the impurity.



2) Dry (or) Chemical corrosion:

Case I: According to this theory the corrosion of a metal is due to the direct chemical action of atmospheric gases like O₂, halogen, H₂S, oxides of S, N and fumes of chemicals on the metal surface.



Case II: An **amalgam** is an alloy of mercury with another metal. Liquid metal 'Hg' forms amalgam with other metals (Na, Zn, Au, Ag), thereby corrosion occurs, the notable exceptions being iron, platinum, tungsten, and tantalum.



3) Acid corrosion:

According to this type/theory the corrosion of a metal is due to the presence of acids surrounding the metal.



Write the differences between Dry corrosion and wet corrosion

	Dry corrosion	Wet corrosion
1	It <u>occurs</u> in dry condition.	It occurs in <u>wet</u> condition.
2	If the <u>corrosion</u> takes place due to direct chemical attack (in the absence of moisture), corrosion is known as dry corrosion.	If the corrosion takes place due to electrochemical attack in <u>presence</u> of <u>moisture</u> or a conducting medium, corrosion is known as wet corrosion
3	Explained by <u>absorption</u> mechanism	Explained by electrochemical mechanism
4	It occurs on both heterogeneous and <u>homogeneous</u> surfaces.	It occurs only on heterogeneous <u>metal</u> surfaces.

5	Corrosion is <u>uniform</u> .	Corrosion is not uniform.
6	It is a slow process.	It is a fast process.
7	Corrosion products accumulate at the place where corrosion occurs.	Corrosion takes place at anode but products accumulate near the <u>cathode</u> .
8	The metal oxidizes with the atmosphere alone.	Involving two processes, oxidation and reduction

Factors influencing corrosion:

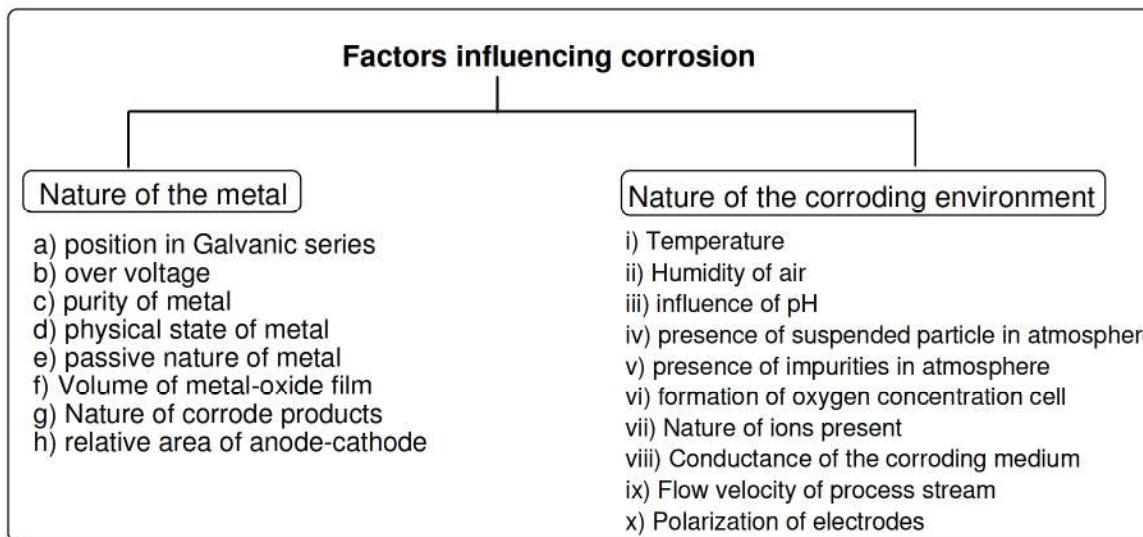
Corrosion is a natural phenomenon. The corrosion occurs because, metals have tendency to convert into its metallic compounds, such as an oxide, hydroxide, or sulfate by the attack of chemical or electrochemical action.

Following conditions must exist before corrosion can occur

- (1) Presence of a metal that will corrode (anode);
- (2) Presence of a dissimilar conductive material (cathode) which has less tendency to corrode;
- (3) Presence of a conductive liquid (electrolyte);
- (4) Electrical contact between the anode and cathode
- (5) Corrosive environment

Noble metals, such as gold and platinum, do not corrode since they are chemically uncombined in their natural state.

The following two factors influences the extent of corrosion I) Nature of the metal II) Nature of the environment



I) Nature of the metal: The following properties of metals are responsible for corrosion.

a) *Position of the metal in galvanic series*:

When two metals or alloys are in electrical contact, in presence of an electrolyte, the upper metal in the Galvanic series suffers corrosion, because it is more anodic. Greater is the

difference between the positions of two metals in Galvanic series, the faster is the corrosion.

b) *Oxidation:* _____

The difference between the equilibrium potential and actual potential is known as overvoltage.

Case: I. If overvoltage is less → more corrosion

Case: II. If overvoltage is more → less corrosion (need more voltage to corrode)

Ex: when a pure 'Zn' rod is placed in a dilute acid solution, it undergoes corrosion but the rate is quite slow because of its high hydrogen overvoltage (0.70V). However, the rate of corrosion can be enhanced by adding few drops of CuSO_4 , because some 'Cu' gets deposited on the 'Zn' metal forming minute cathode, where 'Cu' hydrogen overvoltage is only +0.33V. Such a decrease in the overvoltage of a corroding metal or alloy accelerates the corrosion.

c) *Purity of metal:*

If the metal is impure then, its rate of corrosion is more. This is because impurities act as "minute electrochemical cells" and the anodic parts gets corroded.

Ex: 'Zn' metal containing 'Fe or Pb' impurities undergoes rapid corrosion than pure form of 'Zn' metal.

d) *Physical appearance of metal:*

Physical state of metal like grain size, stress etc. affects the corrosion rate.

- i) Even in pure metal the stressed areas act as anode and undergo more corrosion.
- ii) Smaller the grain size of the metal or alloy, the greater will be its solubility and hence, greater will be its corrosion.

e) *Passive nature of metal:*

Metals like Ti, Al, Cr, Mg, Ni and Co show more corrosion resistance than expected from their position in the electrochemical series. These are called passive metals. This is due to formation of thin protective layer of oxide on metal surface. Moreover, this film is having a self healing nature. Thus, corrosion resistance of stainless steel is due to passivating character of chromium (Cr) present in it.

f) *Nature of surface film: or Volume of metal-oxide film:*

In aerated atmosphere all metals get covered with a thin surface film known as metal oxide film. The ratio of the volume of the metal oxide to the metal is known as '*specific volume ratio*'. Greater the specific volume ratio, lesser is the oxidative corrosion rate. The specific volume ratio of Ni, Cr, and W are 1.6, 2.0 and 3.6 respectively. Consequently, the rate of oxidation of tungsten (W) is least, even at elevated temperature.

g) *Nature of corrode products:*

Corrosion rate depends upon the nature of corrode product whether it is stable, unstable, porous etc.

Ex-1: 'PbSO₄' is an insoluble corrosion product formed when 'Pb' is placed in 'H₂SO₄' solution, then the formed corrode product (PbSO₄) stops the further corrosion.

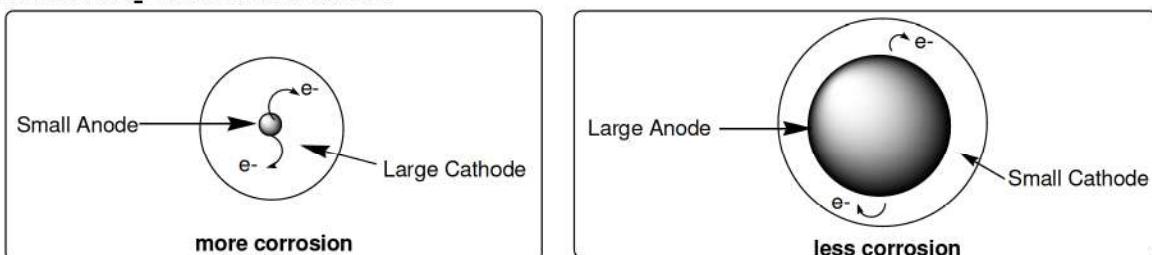
Ex-2: 'MoO₃' is a volatile corrosion product. This causes rapid and continuous corrosion.

Ex-3: The oxide layer formed, decomposes back into the metal and O₂. Thus Au, Ag, Pt do not undergo oxidation corrosion.

EX-4: A stable non-porous oxide layer can get adhered tightly to the parent metal surface. This type layer acts as protective coating and hence prevents the further corrosion.

Ex: oxide film on Al, Sn, Pb, Cu etc.

h) Relative area of Cathode and anode:



When a bigger cathode area covers a smaller anode area, severe corrosion is noted in the anode spot. This is called erosion. It is because large cathode area demands more electrons, to satisfy the requirement of cathode, smaller anodic area undergoes corrosion rapidly.

II) Nature of the corroding environment:

i) Temperature:

With increase of temperature of environment, the reaction as well as diffusion rate increases. Thereby corrosion rate is generally enhanced.

Case I: The 'evolution of hydrogen type corrosion' the H₂ evolved due to chemical reaction of acid on metal. Such type of corosions increases with rise of temperature because, the rate of chemical reactions increase with rise of temperature. According to theory of absolute reaction rate, the rate of reaction becomes double, for every 10 °C rise of temperature.

Case II: In case of 'absorption of oxygen type corrosion', rate of corrosion decreases with rise of temperature, because the O₂ (gases) content in the solvent decreases.

ii) Humidity (Moisture) of air:

More the moisture more is the rate of corrosion. Because

- The gases like SO₂, CO₂, NO₂, dissolves in moisture present in atmosphere promotes electrochemical attack
- The rain water not only gives moisture for electrochemical attack, but also washes away the oxide film on the metal surface and metal surface is further corroded.

iii) Influence of pH Value:

Generally, the rate of corrosion is more in acidic media (i.e. pH < 7) than the alkaline and neutral media .Ex: 'Zn' rapidly corroded, even in weakly acidic solutions such as HCO₃.

Amphoteric metals like Al, Zn, Pb etc dissolve in alkaline solution as complex ion.

- iv) *Presence of suspended particles in atmosphere:*
 - a) Presence of active salts like NaCl, $(\text{NH}_4)_2\text{SO}_4$ in the atmosphere absorbs moisture and acts strong electrolytes as results, increases the rate of corrosion.
 - b) Presence of in active particles like charcoal, absorb both SO_x and moisture from the atmosphere, as result the rate of corrosion increases.
- v) *Presence of impurities in atmosphere:*

Corrosion is more in the impure atmosphere.
Ex: Corrosion is more in industrial areas, due to the presence of gases like CO_2 , H_2S , SO_2 and fumes of HCl, H_2SO_4 etc. and near seashore area due to high humidity consists of salt traces.
- vi) *formation of oxygen concentration cell:*

By raising the content of O_2/air on the moist metal surface, the corrosion is promoted. Less O_2 concentration area becomes anodic center and high O_2 concentration area becomes cathode center, this leads to the formation of oxygen-concentration cell in which anode part suffers corrosion.
- vii) Nature of ions present:
 - a) Presence of anions like silicate (SiO_4^{4-}) in the medium leads to the formation of insoluble reaction products, which inhibit further corrosion
 - b) If Cl^- present in the medium, they destroy the protective and passive surface film, thereby exposing the fresh metal surface for further corrosion.
 - c) Presence of ammonium salts in the medium promotes the corrosion
 - d) Presence of even traces of copper or noble metal in mine water accelerates the corrosion of the iron pipes, used for carrying such water.
- viii) Conductance of the corroding medium:

The corrosion of underground (or) submerged structures depends on the conductance of the medium. Conductance of dry sandy soil is lower than those of clayey and mineralized soils. As a result, metallic structures, buried under clayey-soils experience severe damage than those under dry sandy-soils.
- ix) Flow velocity of process stream:

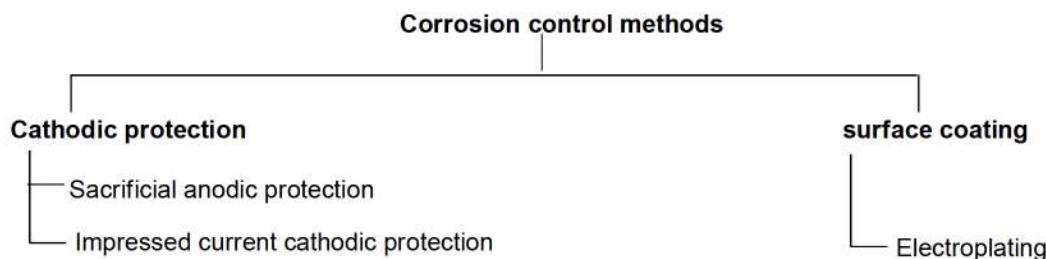
A metal that does not passivate in nature, with increase in flow velocity of the medium enhances diffusion rate, thereby increasing corrosion rate.
- x) Polarization of electrodes:

The potential difference between the anode and cathode is the driving force of an electrochemical corrosion process, but the corrosion rate is controlled by the current flow in the circuit. The extent of corrosion can be controlled by adding certain inorganic or organic substances called inhibitors to the corroding environment. The inhibitors

cause certain irreversible changes around the electrodes, which tend to oppose the direction of the corrosion current flow. This so called polarization of electrodes alters the potential of the cathode to less cathodic or more anodic and that of the anode to less anodic or more cathodic. As a result, of this the potential difference and current between anodic and cathodic areas decreases, thereby corrosion rate also decreases.

Corrosion control methods:

- The metallic structure to be protected is called 'base metal'.
- Corrosion is unnecessary process and this need to be controlled, to overcome the disadvantages due to corrosion.
- There are so many methods to overcome the corrosion and the most important are 1) cathodic protection, 2) surface coating



1) Cathodic Protection:

It can be defined as a method of protecting, metals and alloys from corrosion by making them completely cathodic and as a result, there is no site to act as anode. As a result there is no chance for corrosion.

This cathodic protection is divided into two types:

- i) Sacrificial anodic protection or cathodically protected
- ii) Impressed current cathodic protection

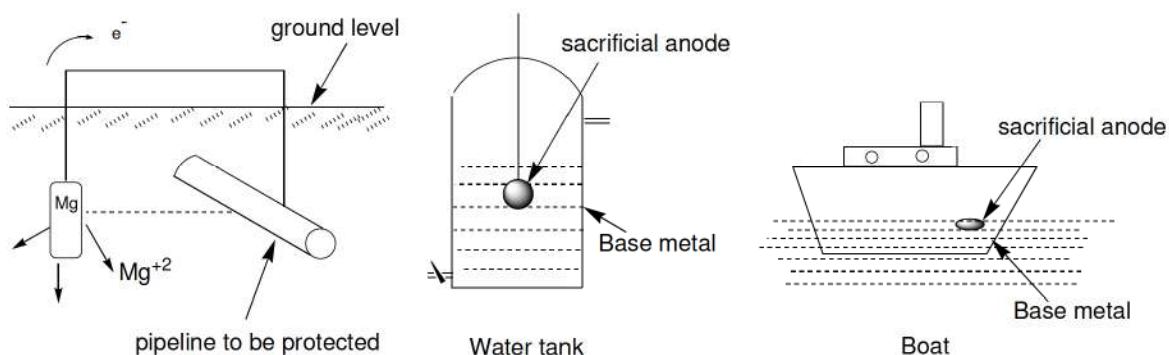
i) Sacrificial anodic protection: In this method 'base metal' is connected to more anodic metal through wire. The anodic metal undergoes corrosion slowly, while, the base metal is protected. The cored anode is called as sacrificial anode and it is replaced by a fresh one from time to time. Generally, 'Zn, Mg, Al' alloys are used as sacrificial anode. These protective or sacrificial anodes can be placed close to ground surface or at significant depth.

The protected facility is made to be a permanent cathode by use of cathodic protection devices (sacrificial anode). Thus, the facility is said to be "cathodically protected."

Applications of Sacrificial anode: sacrificial anode (cathodic protection) is used in many areas of industry.

- I) Protection of underground pipelines, and cables. Based on the galvanic series, a small piece of metal (anodic) is attached to the base metal. This anodic metal undergoes corrosion and is replaced from time to time.
- II) The formation of rusty water is prevented by insertion of 'Mg' sheet/rod into domestic water tanks.

- III) To protect marine structures and ship hull from marine corrosion. These are made of steel and connected to a "sacrificial anode" which undergoes corrosion.



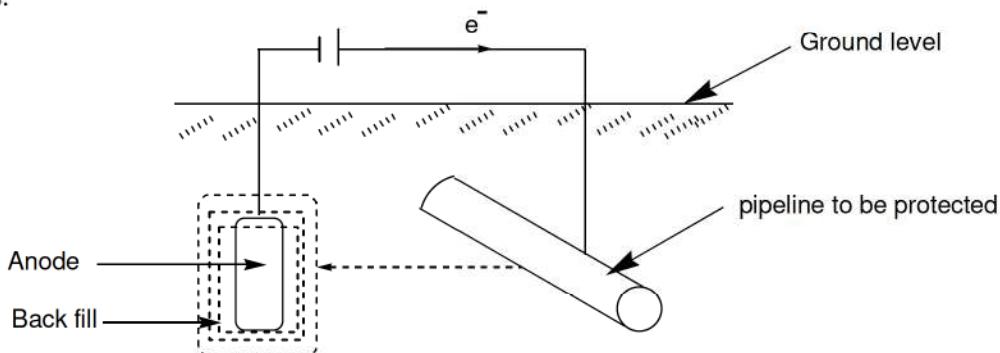
ii) Impressed current cathodic protection:

The flow of electrons during corrosion is called as *corrosion current* and the current which is taken from direct source (battery) is called *impressed current*.

In this method, the impressed current is applied in opposite direction to nullify the corrosion current. Thus the anodic corroding metal becomes cathode and protected from corrosion.

Generally, graphite, iron, Pt, steel etc are used as anode kept in a backfill composed of coke or gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), so as to increase the electrical contact with surrounding soil. Usually a sufficient direct current applied to anode connected to the metallic structure to be protected.

This kind of protection technique is, particularly useful for large structures for long-term operations.



This impressed current cathodic protection is applicable to i) open water box coolers ii) buried oil or water pipes, iii) marine pipes, iv) laid-ships v) transmission line towers etc.

2) Surface coating (or) protective coating:

Surface coatings provide a layer of protection on the surface of the metal for

- o 'Preventing it from rust/corrosion'
- o 'Enhancing its function'.

The most common example of surface coatings is **electroplating** (electrode deposition) and **galvanizing** of iron.

- a) Electroplating is "a process that uses electrical current to reduce dissolved metal cations, so that they form a metal coating on the surface of base metal (metal to be protected)".

The type of chemical reaction involved in electroplating is 'electrolysis'. Further, the 'Faraday's laws' govern the amount of metal deposited.

The purposes of electroplating

- | | |
|----------------------------------|---|
| (i) Good appearance | (ii) extra protection to articles |
| (iii) Special surface properties | (iv) To enhance the Engineering or mechanical properties. |

Applications of electroplating:

Electroplating is a most important and frequently used technique in industries to produce metallic coatings on both metals and non-metals.

- i) In metals the electroplating increases resistance to corrosion, protects from chemical attack, and to obtain special surface properties
- ii) In non-metals electroplating increases strength and decorates the surface of non-metals like plastics, wood, glass etc.

General procedure for electroplating:

- In this process base metal is made cathode and the pure metal is made anode or an inert material of good electrical conductivity is also used as anode.
- These electrodes were dipped in the salt solution of the coating metal, which acts as an electrolyte.
- If anode is made of graphite (inert material) the electrolytic salt is added continuously to maintain the proper coating metal ion concentration in the electrolyte bath.
- A direct current is passed through the electrolytic solution.
- In electroplating, the electrolytic solution gets dissociated into its respective cations, and the anions. The current in the solution is due to the flow of these ions. The anions move towards the anode, and the cations move towards the cathode. The cations are converted into atoms at the cathode and form a layer on it, called as electroplating. The process of electroplating is used for plating parts of vehicles with Nickel and Chromium, which protects them from corrosion
- Before electroplating, the oils, greases from the surface of the article to be electro plated are removed by using organic solvents. Later, this metal is subjected to acid pickling to remove any scales, oxides etc.
- The cleaned article is made cathode of the electrolytic cell. When direct current is passed, the coating metal ions migrate to the cathode and deposit on the base metal article in the form of a thin layer.

Factors affecting electroplating

The required conditions for brighter and smooth deposition of metal ions are:

- i) Cleaning of the article is essential for a strong adherent electroplating.
- ii) Concentration of the electrolyte is a major factor in electroplating. Low concentration of metal ions will produce uniform coherent metal deposition.

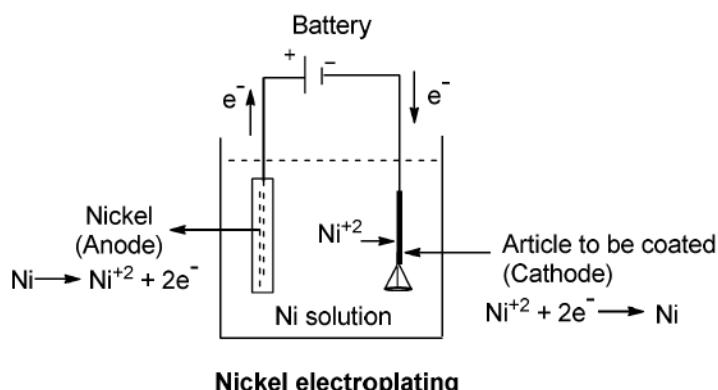
- iii) Thickness of the deposit should be minimized in order to get a strong adherent coating.
- iv) Additives such as glue and boric acid should be added to the electrolytic bath to get a strong adherent and smooth coating.
- v) The electrolyte selected should be highly soluble and should not undergo any chemical reactions with base metal and other materials during the process.
- vi) The pH of the electrolytic bath must be properly maintained to get the deposition effectively.
- vii) Optimum temperature should be maintained for uniform coating.

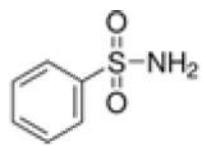
Nickel electroplating: The required conditions for the Nickel electroplating:

i)	Electrolyte bath composition	Nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$; 250 g/Lit) Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$; 45 g/Lit) Boric acid (H_3BO_3 ; 30 g/Lit)
ii)	Additives	Organic compounds (benzene sulphonamide, benzoic sulfilmine, benzopyrone)
iii)	pH of bath	4.5 (to avoid Ni(OH)_2 formation _____)
iv)	temperature	40 to 70 °C
v)	current	20-30 mA/cm ²
vi)	cathode	metal article to be plated
vii)	Anode	Ni pallets or Ni pieces in Titanium mesh

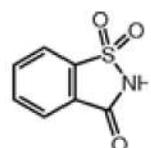
Uses of Nickel plating:

- o A thin layer of nickel is plated onto a metal object.
- o The nickel layer can be decorative, provide corrosion resistance, and wear resistance.
- o Normally, nickel plating is used as undercoat for chromium plating.

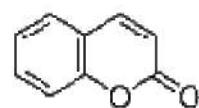




benzene sulphonamide



benzoic sulfilimine (saccharin)



benzopyrone (coumarin)

- ✓ This material gives you a basic information
- ✓ Refer text book for more details