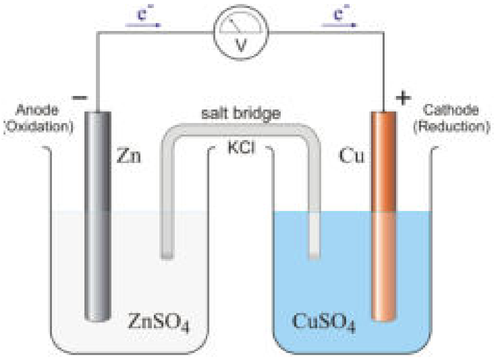
ELECTROCHEMISTRY

Introduction: Electrochemistry is defined as the branch of chemistry which deals with inter-conversion of chemical energy to electrical energy and vice versa. For example, in a battery, chemical energy is converted to electrical energy whereas in electroplating / electrolysis electrical energy is converted to chemical energy.

Chemical energy is converted into electrical energy by Galvanic cell. These cells are known as electrochemical cells or voltaic cells. The best example of galvanic cell is Daniel cell. This cell is formed by combination of two half cells. One is oxidation half cell or anodic half cell and other one is reduction half cell or catholic half cell. The oxidation half cell consists of 'Zn' electrode dipped in $ZnSO_4$ solution and reduction half cell consists of 'Cu" electrode dipped in $CuSO_4$ solution. Both the half cells are externally connected by metallic wire and internally connected by 'salt bridge'. Salt bridge is a U shaped tube containing solution of $K2SO_4$, KNO_3, KCl or NH_4NO_3 in agar-agar gel contained porous site. It maintains the electrical neutrality between two solutions.



The following reactions take place in the cell.

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

$$\text{At cathode: } Cu^{2+} + 2e^- \rightarrow Cu$$

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Presentation of galvanic cell: $Zn|Zn^{2+}$ (C1) || $Cu2^{+}$ (C2)|Cu

Single electrode potential: If a metal is in contact with solution of its own ions, the metal either gains electrons or loses electrons. The tendency of an electrode to lose or gain electrons when it is in contact with its own ions in the solution is called electrode potential. The tendency to gain electrons is called "reduction potential". Similarly, the tendency to lose electrons is called "oxidation potential". Oxidation and reduction potentials of an electrode have same magnitude but opposite sign.

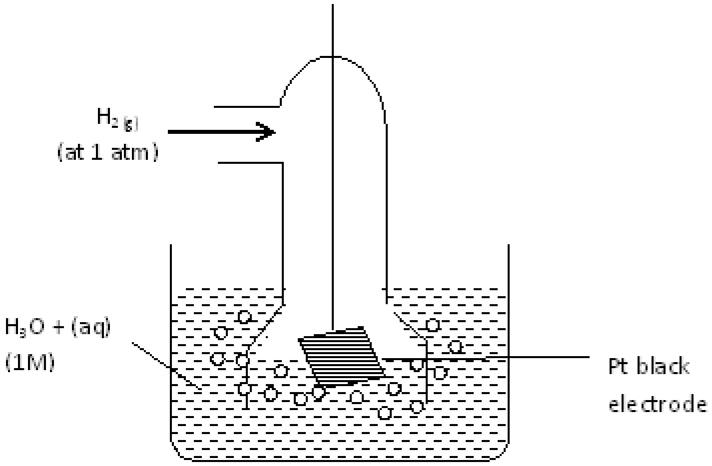
EMF of electrochemical cell: The difference between potentials of the two half cells is known as e.m.f. Ecell = ER – EL (Both are reduction potentials)

Standard electrode potential: The tendency of an electrode to lose or gain electrons when it is in contact with the solution of its own ions of unit molar concentration (in case of gas electrode 1 atm pressure) at 25^0C is called standard electrode potential.

Measurement of electrode potential: It is impossible to measure the absolute value of a single electrode potential. We can only measure the difference between two electrodes potentiometrically by combining them to form a complete cell. By arbitrarily fixing potential of one electrode as zero, it is possible to assign numerical values to potentials of various electrodes. Ex: "Standard Hydrogen Electrode": Pt, H_2(g) (1 atm), H^+ (aq) (C=1M). All other single electrode potentials measured with respect to SHE are referred to as potentials on the hydrogen scale.

REFERENCE ELECTRODES

Normal Hydrogen Electrode: Hydrogen electrode is the primary standard electrode. It consists of a small Platinum strip coated with Platinum black as to adsorb H_2 gas. Platinum is welded to the Pt strip and sealed in a glass tube as to make contact with the outer circuit. The Platinum strip and glass tube is surrounded by an outer glass tube which has an inlet for H_2 gas at top and a no. of holes at the base for the escape of excess of H_2 gas. The Platinum strip placed in an acid solution which has H^+ ions of 1M concentration. Pure hydrogen gas passed through the inlet at 1 atmospheric pressure. A part of gas is adsorbed and the rest escapes through holes. This gives equilibrium between the adsorbed H^2 and H^+ ions in the solution. The temperature of the cell is maintained at 25 ^{0}C. By international agreement the H_2 electrode is assigned a potential of 0.0 volts. The electrode represented as Pt, H2 (g) / H+ (aq). Hydrogen electrode can acts as anode or cathode w.r.to the other electrode to which it is connected.

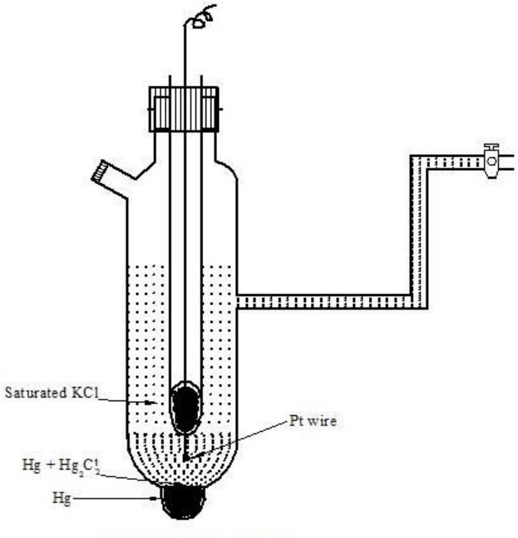


Anode: Oxidation: H_2 (g) → $2H^+ + 2e^-$(Eele = 0.0V)

Cathode: Reduction: $2H^+ + 2e^-$ → H2 (g) (Eele = 0.0V)

Calomel electrode: It consists of mercury at the bottom over which a paste of mercury-mercurous chloride is placed. A solution of potassium chloride is then placed over the paste. A platinum wire sealed in a glass tube helps in making the electrical contact. The electrode is connected with the help of the side tube on the left through a salt bridge with the other electrode to make a complete cell. The electrode is represented as Pt, Hg/ Hg_2Cl_2, $Cl^-_{(aq)}$. The potential of the calomel electrode depends upon the concentration of the potassium chloride solution. If potassium chloride solution is saturated, the electrode is known as saturated calomel electrode

(SCE). If the potassium chloride solution is 1N, the electrode is known as normal calomel electrode (NCE). For 0.1N potassium chloride solution, the electrode is referred to as decinormal calomel electrode (DNCE).



Standard Calomel Electrode

Calomel electrode acts as either anode or cathode w.r.to the other electrode connected to it. If it acts as anode, it involves oxidation:

$$2Hg \rightarrow Hg_2^{2+} + 2e^-$$
$$Hg_2^{2+} + 2Cl^- \rightarrow Hg_2Cl_2$$

$$2Hg + 2Cl- \rightarrow Hg2Cl2 + 2e-$$

Oxidation half reaction, which results in fall of concentration of Cl^- ions, if it acts as cathode, it involves reduction

$$Hg_2Cl_2 \rightarrow Hg_2^{2+} + 2Cl^-$$
$$Hg_2^{2+} + 2e^- \rightarrow 2Hg$$

$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$$

Reduction half reaction, which results increase in concentration of Cl^- ions

NERNST EQUATION

Derivation of Nernst equation: Nernst found that the single electrode potential varies with the change in concentration of ions and temperature and hence the EMF of the cell also varies. He derived a mathematical relationship between the standard electrode potential, temperature and the concentration of ions. This relationship is known as the Nernst equation.

Consider the redox reaction: $M^{n+} + ne^- \leftrightarrow M$

In the above reversible reaction the free energy change (G) and its equilibrium constant (K) are related by the following equation which is popularly known as Van't Hoff reaction isotherm.

$$\Delta G = RT \ln K + RT\ln \frac{\text{Product}}{\text{Reactant}}$$

$$\Delta G = \Delta G^0 + RT\ln \frac{\text{Product}}{\text{Reactant}}$$

Where, ΔG^0 is the standard free energy change.

The free energy change is equivalent to the electrical energy –nFE

Where n = valency

F = Faraday (96500 coloumbs)

E = Electrode potential

R = 8.314 Joules K^{-1} $mole^{-1}$ (Gas constant)

T = Temperature (K)

$$-nFE = -nFE^0 + RT\ln([M])/([M^{n+}]) \text{ (Concentration of M is unity)}$$

$$-nFE = -nFE^0 - RT\ln [M^{n+}]$$

$$= -nFE^0 - RT2.303 \log_{10} [Mn+]$$

Dividing the equation by – nF

$$E = E^0 + 2.303RT/\, nF \log_{10} [Mn+]$$

Put the values of R, T and F then

$$2.303RT/nF = 0.0591/n$$

$$\frac{2.303RT}{nF} = \frac{0.0591}{n}$$

$$\boxed{E = E^0 + \frac{0.0591}{n} \log_{10} [M^{n+}]}$$

BATTERIES

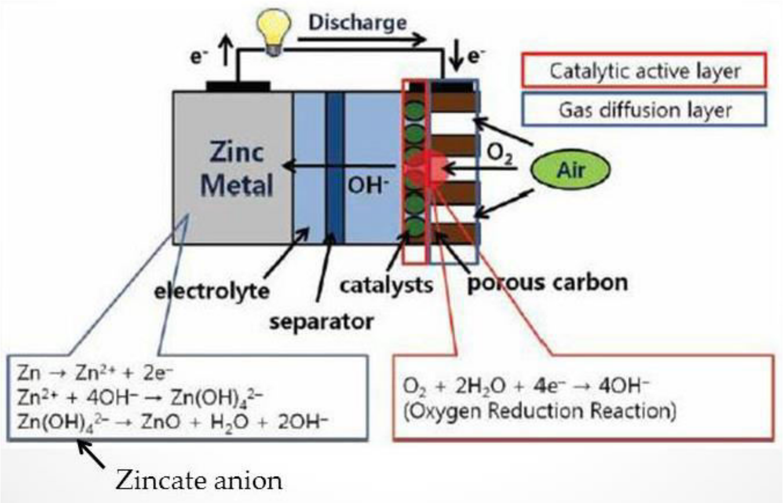
Battery: Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at a constant voltage. A device which converts chemical energy to electrical energy is called battery a term usually applied to a group of two or more electric cells, connected together electrically in series. Batteries are commercial electrochemical cells. These are two types (a) primary cells and (b) secondary cells.

Primary batteries: These are irreversibly (within limits of practicality) transform chemical energy to electrical energy. When the initial supply of reactants is exhausted, energy cannot be readily restored to the battery by electrical means.

Secondary batteries: It can be recharged; in which cell reaction can be reversed by passing direct electric current in opposite direction. Thus, a secondary battery may be used through a large number of cycles of discharging and discharging.

Differences between primary cell (Non-Rechargeable Battery) and Secondary cell (Non rechargeable battery

Zinc-Air Battery: Zinc–air battery is a primary battery, means they are non-rechargeable. Lose granulated Zinc acts as anode and porous carbon plate acts as cathode. The electrolyte used in this battery is NaOH/KOH. The cathode is activated by MnO_2. Two electrodes are separated using a gasket or a separator for insulation. The whole assembly is enclosed in a glass or ebonite container which contains gas permeable Teflon layer. The Teflon layer is hydrophobic, which allows only oxygen and prevents allowing moisture. During discharge, a mass of zinc particles forms a porous anode, which is saturated with an electrolyte. Oxygen from the air reacts at the cathode and forms hydroxyl ions zinc oxide by releasing electrons to travel to the cathode. The water and hydroxyl from the anode are recycled at the cathode, so the water is not consumed.



At anode: $Zn + 2\,OH^- \rightarrow ZnO + H_2O + 2e^-$

At Cathode: $\frac{1}{2}\,O_2 + H_2O + 2e^- \rightarrow 2OH^-$

$$Zn + \frac{1}{2}\,O_2 \rightarrow ZnO$$

Advantages:

- Primary batteries have higher energy density than rechargeable secondary cells.
- High specific energy, long storage times (low self-discharge), and instant readiness give primary batteries a unique advantage over other power sources.
- They are usually the best choice for low-drain applications. They can be carried to remote locations and used instantly, even after long storage; they are also readily available and environmentally friendly when disposed.

Disadvantages:

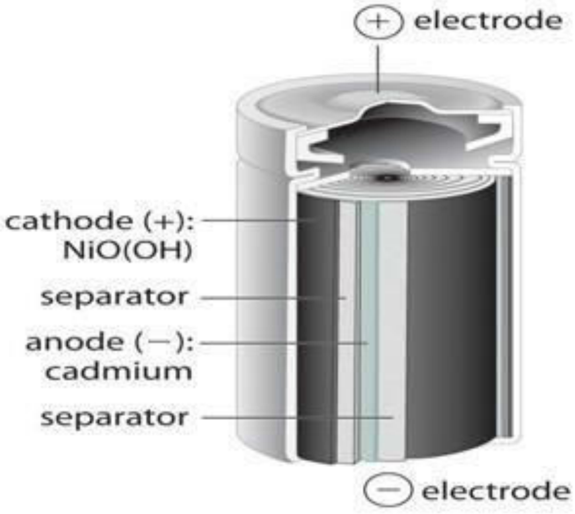
- They are non-rechargeable.
- They are less environment friendly batteries.
- Zinc-air batteries have limited power output, which is mainly due to the inadequate performance of air electrodes.

- The performance and operation of these batteries are depends on ambient conditions such as humidity and temperature.

Applications:

- Used as power source in hearing aids
- Used in electronic pagers
- Used in military radio receivers
- Used in voice transmitters

Ni-Cadmium Battery: The Nickel Cadmium batteries have the advantage of being recharged many times and possess a relatively constant potential during discharge and have more electrical and physical with standing capacity. This battery uses nickel oxide for cathode, a cadmium compound for anode and potassium hydroxide solution as its electrolyte.



Chemical reactions during Discharge process:

At the anode electrode: $Cd+2OH^- \xrightarrow{} Cd(OH)_2+2e^-$

At the cathode electrode: $2NiOOH+2H_2O+2e^- \xrightarrow{} 2Ni(OH)_2+2OH^-$

Overall reaction: $Cd+2NiOOH+2H_2O \xrightarrow{} Cd(OH)_2+2Ni(OH)_2$

Chemical reactions during recharge process:

At the anode electrode: $Cd(OH)_2+2e^- \longrightarrow Cd+2OH^-$

At the cathode electrode: $2Ni(OH)_2+2OH^- \longrightarrow 2NiOOH+2H_2O+2e^-$

Overall reaction: $Cd(OH)_2+2Ni(OH)_2 \longrightarrow Cd+2NiOOH+2H_2O$

Advantages:

- Delivers high current out put
- It tolerates over charging
- It with stands up to 500 cycles of charging

Disadvantages:

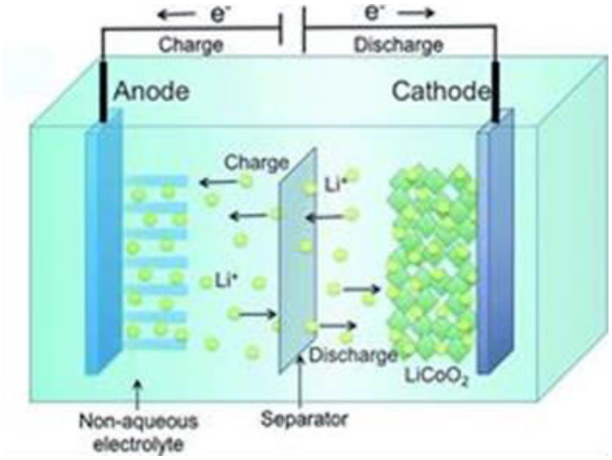
- Cadmium is not an eco-friendly material
- Less tolerance towards temperature as compared to other batteries.

Applications:

- Sealed Ni–Cd cells may be used individually, or assembled into battery packs containing two or more cells.
- Small cells are used for portable electronics and toys (such as solar garden lights), often using cells manufactured in the same sizes as primary cells.
- Miniature button cells are sometimes used in photographic equipment, hand-held lamps (flashlight or torch), computer-memory standby, toys, and novelties.

Li-Ion Cell: This cell does not contain metallic lithium hence they called as lithium ion cells and use lithium ions instead. In this cell transport of Li^+ ions through the electrolyte from one electrode to other electrode takes place through the external circuit to maintain charge balance. In this battery lithium ions interchanged between two layers of graphite and $LiCoO_2$. When the cell is in charging Lithium ions leaves $LiCoO_2$ and travel through the electrolyte to the graphite

(C6) and when the cell is discharges to provide power Li^+ ions moved back through the electrolyte to the cobalt oxide while the electrons move through the external circuit from the graphite electrode to the cobalt oxide electrode.



Anodic and Cathodic Reactions:

At Cathode:

$$LiCoO_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_{1-x}CoO_2 + xLi^+$$

At Anode:

$$C + xLi^+ \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_xC$$

The charging and discharging cycle is simple migration of Li+ ions from one electrode to another electrode with flow of electrons through the external circuit.

Advantages:

- High energy density
- Lower self-discharge compared to other rechargeable batteries.
- Low Maintenance cost
- Good load characteristics
- Variety types available

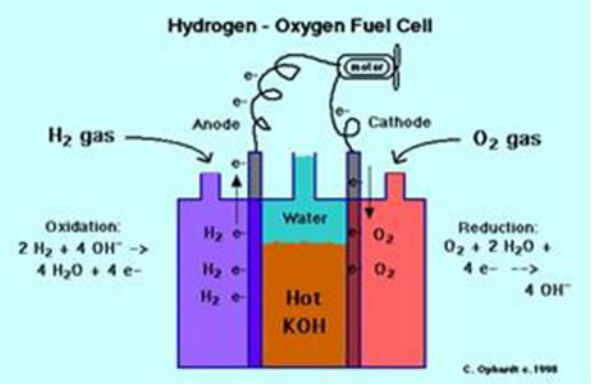
Disadvantages:

- Requires protection circuit to maintain voltage and current within safe limits.
- Subject to aging, even if not in use - storage in a cool place at 40% charge reduces the aging effect.
- Transportation restrictions - shipment of larger quantities may be subject to regulatory control. This restriction does not apply to personal carry-on batteries.
- Expensive to manufacture - about 40 percent higher in cost than nickel-cadmium.
- Not fully mature - metals and chemicals are changing on a continuing basis

Applications:

- Pacemakers, defibrillators, watches, meters, cameras, calculators, portable, cell phones, Laptops, low-power use.

Hydrogen-Oxygen Fuel: The cell consists of three compartments separated by a porous electrode. Hydrogen gas is introduced into one compartment and oxygen gas is fed into another compartment. These gases then diffuse slowly through the electrodes and react with anelectrolyte that is in the central compartment. The electrodes are made of porous carbon and the electrolyte is a resin containing concentrated aqueous sodium hydroxide solution (25%). Hydrogen is oxidized at anode and oxygen is reduced at cathode. The overall cell reaction produces water. The reactions which occur are:



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

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

Overall: $2H_2 (g) + O_2 (g) \rightarrow 2H_2O(l)$

Applications and advantages:

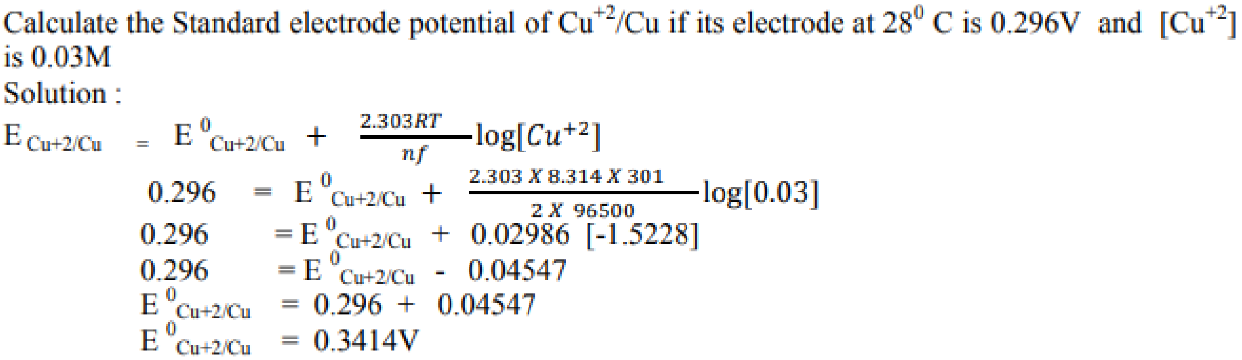
- These types of cells are used in space-crafts.
- Fuel cells are efficient and pollution free.
- These types of cells are used in sub – marines or other military vehicles.
- The weight of the fuel battery sufficient for 15 days in space is approximately 250kg.
- In case of hydrogen-oxygen fuel cells, the produced water is a valuable source of fresh water by astronauts.

Disadvantages:

- Hydrogen Energy is Expensive.
- Storage Complications. ...
- It's Not the Safest Source of Energy. ...
- It is Dependent on Fossil fuels. ...
- Hydrogen Energy Cannot Sustain the Population.

Problems on Nernest's Equation:

1.



Calculate the Standard electrode potential of Cu^{+2}/Cu if its electrode at 28^0 C is 0.296V and $[Cu^{+2}]$ is 0.03M

Solution :

$$E_{Cu+2/Cu} = E^0_{Cu+2/Cu} + \frac{2.303RT}{nf}\log[Cu^{+2}]$$

$$0.296 = E^0_{Cu+2/Cu} + \frac{2.303 \times 8.314 \times 301}{2 \times 96500}\log[0.03]$$

$$0.296 = E^0_{Cu+2/Cu} + 0.02986\ [-1.5228]$$

$$0.296 = E^0_{Cu+2/Cu} - 0.04547$$

$$E^0_{Cu+2/Cu} = 0.296 + 0.04547$$

$$E^0_{Cu+2/Cu} = 0.3414V$$

2.

Calculate the Standard electrode potential of Cu^{+2}/Cu if its electrode at 25^0 C is 0.296V and $[Cu^{+2}]$ is 0.015M

Solution:

Given, E=0.296V $[M^{n+}]$=0.015M n=2

$$E = E^0 + \frac{0.0591}{n}\log[M^{n+}]$$

$$E_{Cu+2/Cu} = E^0_{Cu+2/Cu} + \frac{0.0591}{n}\log[Cu^{+2}]$$

$$0.296 = E^0_{Cu+2/Cu} + \frac{0.0591}{2}\log[0.015]$$

$$0.296 = E^0_{Cu+2/Cu} + 0.0295[-1.8239]$$

$$0.296 = E^0_{Cu+2/Cu} - 0.0538$$

$$E^0_{Cu+2/Cu} = 0.296 + 0.0538$$

$$E^0_{Cu+2/Cu} = 0.3498V$$

CORROSION

Introduction: Any process of deterioration or destruction and consequent loss of a solid metallic material, through in chemical or electro chemical attack by its environment, starting at its surface is called corrosion. Thus, corrosion is reverse of extraction of metals or metallurgy.

$$\text{Metal} \quad + \quad \text{oxide} \underset{\text{Metallurgy}}{\overset{\text{Corrosion}}{\rightleftharpoons}} \text{Metal oxide}$$

(Higher Energy) (Lower Energy)

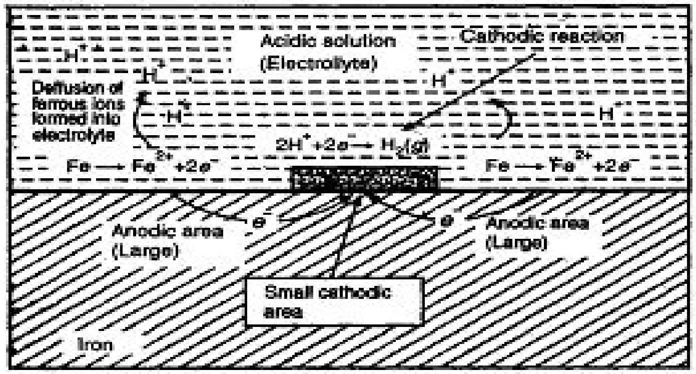
Examples:

1. The most familiar example of corrosion is rusting of iron ($Fe_2O_3 .3H_2O$)
2. Formation of green film of basic carbonate on the surface of copper [$CuCO_3 + Cu(OH)_2$]

Electrochemical Theory of Corrosion

Electrochemical corrosion involves flow of electron-current between the anodic and cathodic. The anodic reaction involves in dissolution of metal as corresponding metallic ions the liberation of free electrons. A cathode reaction consumes electrons with either by two ways:

1. Evolution of Hydrogen Type Corrosion (In acidic environments):



. Mechanism of wet corrosion by hydrogen evolution.

Considering metal like Fe, the anodic reaction is dissolution of iron as ferrous ions with the liberation of electrons. Thus, this type of corrosion causes "displacement of hydrogen ions from the acidic solution by metal ions." Consequently, all metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution.

At Anode: $Fe \longrightarrow Fe^{2+} + 2e^-$ ---------------------------- (Oxidation)

At cathode**:** $2H^+ + 2e^- \longrightarrow H_2$ ---------------------------- (Reduction)

$\frac{1}{2} O_2 + 2e^- + H_2O \longrightarrow 2 OH^-$

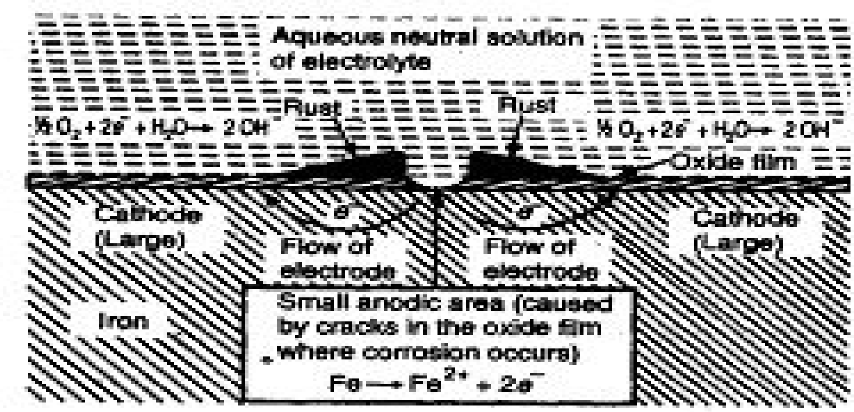
$Fe^{2+} + 2 OH^- \longrightarrow Fe(OH)_2$

$4 Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4 Fe(OH)_3$

$2 Fe(OH)_3 \longrightarrow Fe_2O_3.xH_2O$ (Yellow rust) + $(3-x) H_2O$ (Or)

$3 Fe(OH)_2 + \frac{1}{2} O_2 \longrightarrow Fe_3O_4$ (Black rust) + $3H_2O$

2. Absorption of Oxygen Type Corrosion (In neutral aqueous solution):



Mechanism of wet corrosion by oxygen absorption.

The surface of iron is, usually coated with at thin film of iron oxide. However, if this iron oxide film develops some cracks, anodic areas are created on the surface; while the well-metal parts act as cathodes. It follows that the anodic areas are small surface parts; while nearly the rest of the surface of the metal forms large cathodes.

At Anode: $Fe \longrightarrow Fe^{2+} + 2e^-$ ------- (Oxidation)

At cathode: $\frac{1}{2} O_2 + 2e^- + H_2O \longrightarrow 2 OH^-$

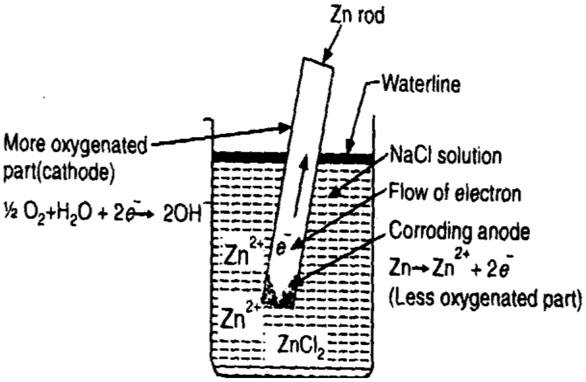
$Fe^{2+} + 2 OH^- \longrightarrow Fe(OH)_2$

$4\ Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4\ Fe(OH)_3$

$2\ Fe(OH)_3 \longrightarrow Fe_2O_3.xH_2O$ (Yellow rust) $+ (3-x)\ H_2O$ (Or)

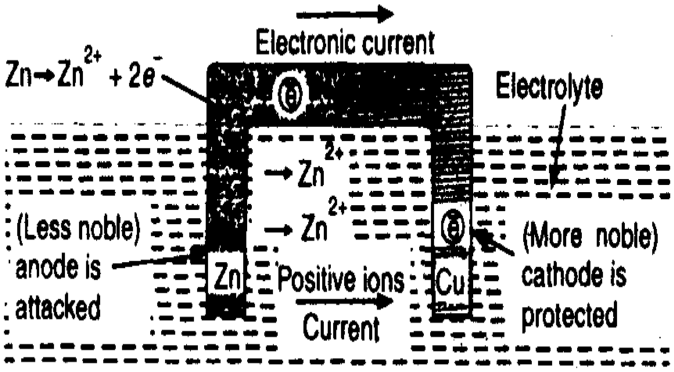
$3\ Fe(OH)2+½\ O_2 \longrightarrow Fe_3O_4$ (Black rust) $+ 3H_2O$

Differential Aeration Corrosion:



The most common type of concentration cell corrosion occurs when one part of metal is exposed to a different air con cent ration from the other part. This causes a difference in potential between differently aerated areas. It has been found experimentally that "poor-oxygenated parts are anodic". Consequently, a differential aeration of metal causes a flow of current, called the differential current.

Galvanic Cell Corrosion:



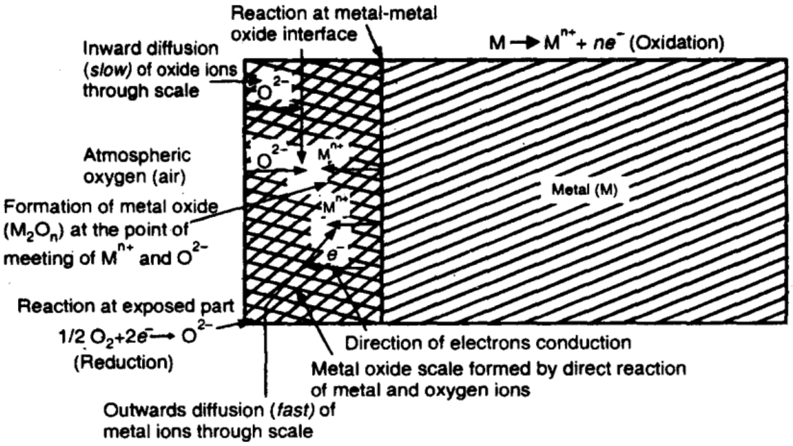
When two dissimilar metals (e.g., zinc and copper) are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called "galvanic corrosion". In the above example, zinc (higher in electrochemical series) forms the anode and is attacked and gets dissolved; whereas copper (lower in electrochemical series or nobler) acts as cathode.

Mechanism of Corrosion: The mechanism of corrosion classify as two types

Metal Oxide Formation by Dry Electrochemical Corrosion

This type of corrosion occurs mainly through the direct chemical action of environment/atmospheric gases such as-oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid with metal surfaces immediate proximity.

Dry Corrosion: It is brought about by the direct action of oxygen on metals usually in the absence of moisture. Alkali metals (Li, Na, K, Rb, etc.) and alkaline-earths (Be, Ca, Sr, etc.) are even rapidly oxidized at low temperatures. At high temperatures, almost all (except Ag, Au, and Pt) are oxidized.



$$M \longrightarrow M^{2+} + 2e^-$$
$$\tfrac{1}{2} O_2 + 2e^- \longrightarrow O^{2-}$$

$$M + \tfrac{1}{2} O_2 \rightarrow MO$$

Mechanism: Oxidation occurs first at the surface of the metal and the resulting metal scale forms a barrier that tends to restrict further oxidation. For oxidation to continue either metal must diffuse outwards through the scale to the surface or the oxygen must diffuse inwards through the scale to the underlying metal. Both transfers occur, but the outward diffusion metal is generally much more rapid than the inward diffusion of oxygen, since the metal ion appreciably smaller than the oxygen ion and consequently of much higher mobility. Nature of the oxide formed plays an important part in oxidation corrosion process. A layer is called film, when its thickness is less than about 300 Ǻ and its called scale, when its thickness exceeds this value. The following types of films are there:

1. Stable:

- A stable layer is fine grained in structure and can get adhered tightly to the parent metal surface.
- Hence, such a layer can be of impermeable nature. Such a film behaves as protective coating in nature thereby protecting the surface.
- The oxide films on Al, Sn, Pb and Cuetc are stable film.

2. Unstable:

- The oxide layer formed decomposes back into the metal and oxygen.
- Metal oxide $\rightleftharpoons$ Metal + Oxygen.
- Ag, Au and Pt metals form unstable film.
- The film is unstable therefore do not undergo oxidation corrosion in these metals.

3. Volatile:

- The oxide layer volatilizes as soon as it is formed.
- Thereby leaving the original metal surface exposed for further attack.
- This cause rapid and continuous corrosion, leading to excessive corrosion.
- Molybdenum oxide (MoO_3) is volatile.
- $2Mo + 3O_2 \longrightarrow 2MoO_3$ (Volatile)

4. Porous:

- Having pores or cracks in the film or scale.
- In such a case, the atmospheric oxygen has entrée to the original surface of metal through the pores or cracks of the film.
- Thereby the corrosion continues till the entire metal is completely converted into its oxide.
- Alkali, alkaline earth metals and iron form porous films.

Pilling-Bedworth's Ratio

It states that an oxide layer is compact, non-porous as well as protective preventing corrosion if the volume of metallic oxide is equal to or greater in volume to the metal surface. The alkali metals like Li, Na, K and alkaline earth metals like Mg and metals like Fe produce oxide film whose volume is less than the volume of the metal and as a result oxygen can diffuse through the pores of the film producing oxide films continuously. This principle also explained according to specific volume ratio.

$$\text{Specific Volume Ratio} = \frac{\text{Volume of Metal Oxide}}{\text{Volume of Metal}}$$

- Smaller the specific volume ratio greater the corrosion.
- Volume of oxide $\geq$ volume of metal, thus non-porous film and protective film.
- Volume of oxide $<$ volume of metal, thus porous film and non protective film.

Factors Affecting Rate of Corrosion: The rate and extent of corrosion, depends on the following factors:

1. Depending on Nature of the metal

- **Position in galvanic series:** When two metals or alloys are in electrical contact, in presence of an electrolyte, the more active metal (or higher up in the series) undergo corrosion. The rate of corrosion depends upon the difference in their positions, and greater is the difference the faster is the corrosion of the anodic metal.

- **Relative areas of the anodic and cathodic parts:** When two dissimilar metals or alloys are in contact, the corrosion of the anodic part is directly proportional to the ratio of areas of the cathodic part and the anodic part.

$$\text{Corrosion} \propto \frac{\text{Area of cathode}}{\text{Area of anode}}$$

- **Purity of metal:** Impurities in a metal, generally, and form Minute or tiny electrochemical cells and the anodic parts get corroded. For example, zinc metal containing impurity (such as Pb or Fe) undergoes corrosion of zinc, due to the formation of local electrochemical cells.
- **Physical state of metal:** The rate of corrosion is influenced by physical state of the metal .The smaller the grain-size of the metal or alloy, the greater will be its solubility and hence, greater will be its corrosion.
- **Nature of surface film**: The ratio of the volumes of the metal oxide to the metal is known as a "specific volume ratio**."** Greater the specific volume ratio, lesser is the oxidation corrosion rate. According to Pilling- bedworth rule the volume of oxide film is greater than metal from which metal oxide formed, then the film is protective.
- **Solubility of corrosion products:** In electrochemical corrosion, if the corrosion product is soluble in the corroding medium, then corrosion proceeds at a faster rate. On the contrary, if the corrosion product is insoluble in the medium or thereby suppressing further corrosion.
- **Volatility of corrosion products:** If the corrosion product is volatile (MoO_3), it volatilizes as soon as it is formed, thereby leaving the underlying metal surface ex posed for flirt her attack. This causes rapid and continuous corrosion.

- **Passivity of metal:** Metals like Ti, Al, Cr and Ni are passive they exhibit much higher corrosion resistance, due to the formation of highly protective on the metal. Moreover the film is self healing nature. Thus corrosion resistance of stainless steel is due to passive character of Cr.

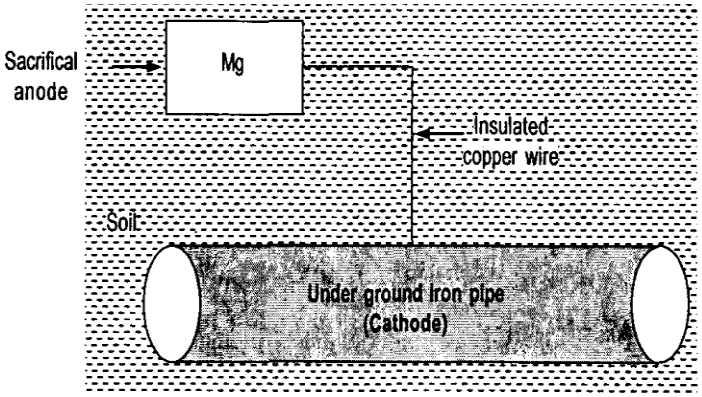
2. Depending on Nature of the environment

- **Temperature:** With increase of temperature of environment, the reaction as well as diffusion rate increase, thereby corrosion rate is generally enhanced.
- **Humidity of air:** "Critical humidity" is defined as the relative humidity above which the atmospheric corrosion rate of metal increases sharply. The reason why corrosion of a metal becomes foster in humid atmosphere is that gases ($CO_{2,}$ O2, etc.) and vapors, present in atmosphere furnish water to the electrolyte, essential for setting up an electrochemical corrosion cell.
- **Presence of impurities in atmosphere:** Atmosphere, in the vicinity of industrial areas, contains corrosive gases like $CO_{2,}$ H_2SO_4 and fumes of HCI, H_2 etc. in presence of these gases, the acidity of the liquid, adjacent to the metal surfaces, increases and its electrical conductivity also increases. This consequently, results in an increase of corrosion.
- **Influence of pH:** Generally, acidic media (i.e., pH <7) are more corrosive than alkaline and neutral media.
- **Nature of ions present:** Presence of anions like silicate in the medium leads to the formation of insoluble reaction products (e.g., silica gel), which inhibit further corrosion. On the other hand, chloride ions, if present in the medium, destroy the protective and passive surface film.

Cathodic Protection:

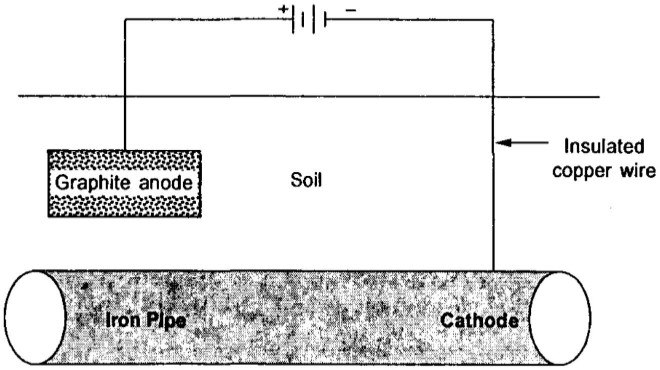
The principle involved in this method is to force the metal to be protected to behave like a cathode, thereby corrosion does not occur. There are two types of cathodic protections.

Sacrificial Anodic Protection Method:



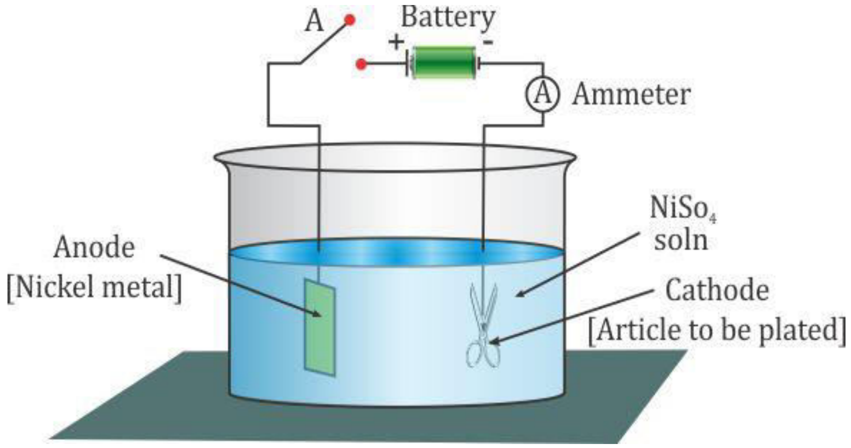
In this protection method, the metallic structure (to be protected) is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly; while the parent structure (cathodic) is protected. The more active metal so-employed is called **"sacrificial anode"**. The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anodes are magnesium, zinc, aluminum and their alloys. Important applications of sacrificial anodic method include protection of buried pipelines, underground cables; marine structures, ship-hulls, water-tanks, piers, etc.

Impressed current cathodic protection:



In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode. Usually, the impressed current is derived from a direct current source (like battery or rectifier on a.c. line) with an insoluble anode (like graphite, high silica iron, scrap iron, stainless steel or platinum). This type of cathodic protection has been applied to open water-box coolers, water-tanks, buried oil or water pipes, condensers, transmission line towers, marine pier, laid-up ships, etc.

Electroplating:



- It is a process in which coating metal Nickel is deposited on the base metal Iron (Scissors) by passing direct current through an electrolytic solution containing the $NiSO_4$ salt.
- The base metal Iron (Scissors) is first subjected to acid pickling to remove any scales, oxides etc.
- The base metal Iron (Scissors) is made as cathode of the electrolytic cell and the coating metal Nickel rod is made as anode.
- Nickel rod and Scissors are dipped in the electrolyte solution which contains the Nickel metal ions to be deposited on the Scissors. When a direct current is passed from an external source, the Nickel metal ions migrate towards cathode and get deposited over the surface of Scissors in the form of a thin layer.
- Low temperature, medium current density, low metal ion concentration conditions are maintained for better electro-plating.

Electroless plating: The method of deposition of a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electrical energy is called electroless plating. This process is also called chemical plating or autocatalytic plating. The metallic ions (M^+) are reduced to the metal with the help of reducing agents. When the metal (M) is formed, it gets plated over a catalytic surface.

$$2HCHO + 2OH^- \rightarrow 3H_2 \text{ (gas)} + 2CO_2 + 2e^-$$
$$Cu^{2+} + 2e^- \rightarrow Cu \text{ (metal)}.$$

Pretreatment and activation of surface:

The surface is treated to remove grease and other impurities. In case of insulators, the surface is activated by dipping in stannous chloride and then in palladium chloride. The surface is dried. Then the electroless-plating is done under the following conditions.

Plating bath:

Bath: Copper sulphate ($CuSO_4$) 12 g per litre

Reducing agent: Formaldehyde (HCHO) 8 g per litre

Buffer: NaOH 15 g/litre & Rochelle salt 14 g/litre

Complexing agent: EDTA 20 g /litre

pH: 11.0 and Temperature: 25 ^{0}C