UNIT – III

ELECTROCHEMICAL CELLS and CORROSION

Syllabus:

Electrode potential, Nernst's equation, Electrochemical cells, EMF of an electrochemical cell. Reference electrodes – Standard Hydrogen Electrode (SHE), Calomel Electrode.
***Batteries**:* Introduction, Types of batteries, Ni-Cd battery, lithium ion battery. Applications.
Fuel cells: Definition, $H_2 – O_2$ Fuel cell, Phosphoric acid fuel cells, proton exchange membrane fuel cells, solid oxide fuel cells. Applications of fuel cells.
Corrosion: Introduction, Definition, Types of corrosion, galvanic corrosion, concentration cell corrosion, control of corrosion – Electroplating method.

Redox reactions:

Oxidation - the process which involves loss of electrons by a substance.
Reduction - the process which involves gain of electrons by a substance.
Redox reaction - The reaction in which both oxidation and reduction takes place.

OIL	RIG
Oxidation **I**s **L**oss	**R**eduction **I**s **G**ain

Oxidizing agent - The reactant which is an electron acceptor.

Reducing agent - The other reactant which is an electron donor.

It is quite apparent that if a substance loses electrons, some other substance must be involved in the reaction to accept these electrons. On the other hand, if a substance accepts electrons, some other substance must be involved in the reaction to supply these electrons. In other words oxidation and reduction must go side by side.

Examples:

1. If we place zinc metal in a copper sulphate, immediate precipitation of Cu takes place.

In this change, the zinc atom is oxidised to zinc ion, since it loses electrons; while the copper ion is reduced to copper atom, since it gains electrons.

$$\text{(a) } Zn(s) \text{------}\rightarrow Zn^{2+}(aq) + 2e^- \qquad \text{(oxidation)}$$

$$\text{(b) } Cu^{2+}(aq) + 2e^- \text{---------}\rightarrow Cu(s) \qquad \text{(reduction)}$$

The overall reaction, obtained by adding (a) and (b), is called Redox reaction.

$$Zn(s) + Cu^{2+}(aq) \text{---------}\rightarrow Zn^{2+}(aq) + Cu(s) \qquad \text{(Redox)}$$

2. Redox reaction of dichromate ions with ferrous ions in presence of acid.

In this change, the ferrous ion is oxidised to ferric ion, since it loses electrons; while the chromium (+6) in the dichromate ion is reduced to chromium (+3) ion, since it gains electrons.

(a) $(Cr_2O_7)^{2-} + 14\ H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7\ H_2O$ (reduction)

(b) $6\ Fe^{2+} \longrightarrow 6\ Fe^{3+} + 6e^-$ (oxidation)

$(Cr_2O_7)^{2-} + 6\ Fe^{2+} + 14\ H^+ \longrightarrow 2Cr^{3+} + 6\ Fe^{3+} + 7\ H_2O$ (Redox)

Electrochemical cells:

"An electrochemical cell is a device in which a redox reaction is utilized to get electrical energy".

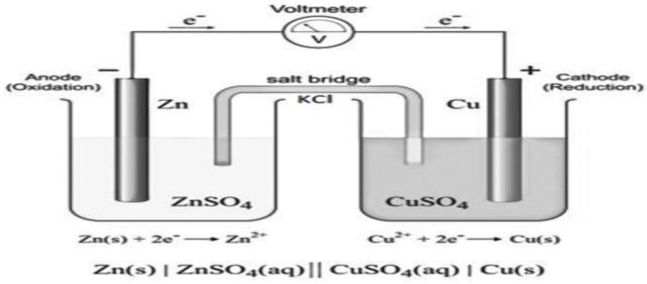
Here, chemical energy is converted into electrical energy.

An electrochemical cell is also commonly referred to as Voltaic cell or Galvanic cell. The electrode where the oxidation occurs, is called ***anode***; while the electrode where reduction occurs, is called ***cathode***. The practical application of an electrochemical cell is Daniel cell.

$$E = E_0 + nFRT\ ln\ [M^{n+}]$$
$$E = E_0 + nF2.303RT\ \log[M^{n+}]$$

Construction and working of Galvaniccell:

It consists of a copper rod dipped in $CuSO_4$ solution, which is separated by a salt bridge from a solution of $ZnSO_4$ in which a zinc rod is dipped.When the two electrodes are connected, the flow
of electric current takes place and oxidation occurs at anodeand reduc tion occurs at cathode.



i.e., Zn metal passes into the solution as Zn^{+2} ions liberating two electrons (oxidation).

$Zn\ (s)\ Zn^{2+} + 2e^-$ of electric current takes place and oxidation occurs at anodeand reduc tion occurs at cathode.

The liberated electrons move through the voltmeter and then pass through the Copper rod. Then Cu^{+2} ions accepts $2e^-$ and are discharged as copper metal at copper electrode (reduction).

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

Cell reaction can be represented as

$$Zn(s) + Cu^{+2}\ Zn^{+2} + Cu(s)$$

The flow of electrons in the cell is from anode to cathode (Zn electrode to Cu electrode). But flow of current in the cell is from cathode to anode. The SO_4^{2-} ions move from cathode to anode through the salt bridge. This completes the circuit of the cell. The e.m.f. of the cell is 1.1 volts.

Here the salt bridge is used to maintain the electrical neutrality between the electrolytic solutions, internally.

IUPAC representation of a Cell:

$$Zn/ZnSO_4 \,||\, CuSO_4/Cu \text{ (or)}$$

$$Zn/Zn^{2+} \,||\, Cu^{2+}/Cu$$

IUPAC representation of a galvanic cell:

1. Anode is written on the left-hand side; while cathode is written on the right-hand side.
2. The electrode on the left is written by writing the metal first and then electrolyte. The two are separated by a vertical line or a semicolon.
3. The cathode of the cell is written on the right-hand side. In this case, the electrolyte is represented first and the metal thereafter. The two are separated by a vertical line or semicolon.
4. A salt bridge is indicated by two vertical lines, separating the two half-cells.

EMF of an electrochemical cell:

"The difference of potential, which causes a current to flow from the electrode of higher potential to the electrode of lower potential, is called the electromotive force (e.m.f.) of the cell". It is expressed in volts. Mathematically, the e.m.f. of an electrochemical cell is the algebraic sum of the single electrode potential. It can readily be calculated from the reduction half-cell potentials, using the following relationship.

Where,

E_{cell} = e.m.f. of cell;

$E_{cathode}$ = reduction potential of cathode;

and E_{anode} = reduction potential of anode.

We can also take, $E_{cell} = E_{right} - E_{left}$

It should be remembered that a positive value of E_{cell} indicates that the cell reaction is feasible. If however, it comes out to be negative, the cell reaction is not feasible and in actual operation of the cell, the electrodes will have to be reversed in order to bring about cell reaction.

Measurement of EMF of an electrochemical cell:

EMF can be measured in two ways.

1. Nernst's equation for a cell reaction to calculate E_{cell}:

Where

$$E0_{cell} = E0_{cathode} - E0_{anode}$$

For the Daniel cell reaction,

$$Zn(s) + Cu^{+2}\ Zn^{+2} + Cu(s)$$

The Nernst's can be written as:

$$E_{cell} = (Eo_{Cu^{2+}/Cu} - E_{0\ Zn^{2+}/Zn}) + RT/nF\ 2.303 \log[Cu^{2+}][Zn^{2+}]$$

Here n = number of electrons = 2.

2. Measurement of EMF of electrochemical cell by potentiometer:

The e.m.f. cannot be determined accurately by connecting directly a volt meter between the two electrodes, because during such a measurement, a part of the cell current is drawn, thereby causing a change in the emf,

$$E_{cell} = E_{cathode} - E_{anode}$$

$$E_{cell} = E^{0}_{cell} - nF\,2.303RT \log[\text{reactants}][\,products]$$

Electrode potential (E):

A metal consists of metal ions, with the valence electrons that bind them together. When a strip of this metal M is placed in a solution of its ions M^{n+}, a metal - metal ion electrode is obtained. The possible processes that can occur at the electrodes are:

(a) A metal atom on the electrode M may lose n electrons to the electrode, and enter the solution as M^{n+}, (i.e., the metal atom is oxidised).

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

(b) A metal ion M^{n+} collides with the electrode, gains n electrons and gets converted into a metal atom M(i.e., the metal ion is reduced).

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

The above processes affect the electrodes as follows:

If the metal has relatively high tendency to get oxidized, its atoms will lose electrons readily and form M^{n+} ions, which go into the solution. The electrons lost from the electrode get accumulated on the metal electrode and the electrode acquires a slight negative charge with respect to the solution. After some time, an equilibrium is established as:

$$\underset{\text{Electrode}}{M(s)} \rightleftharpoons \underset{\text{Solution}}{M^{n+}(aq)} + \underset{\text{(on electrode)}}{ne^{-}}$$

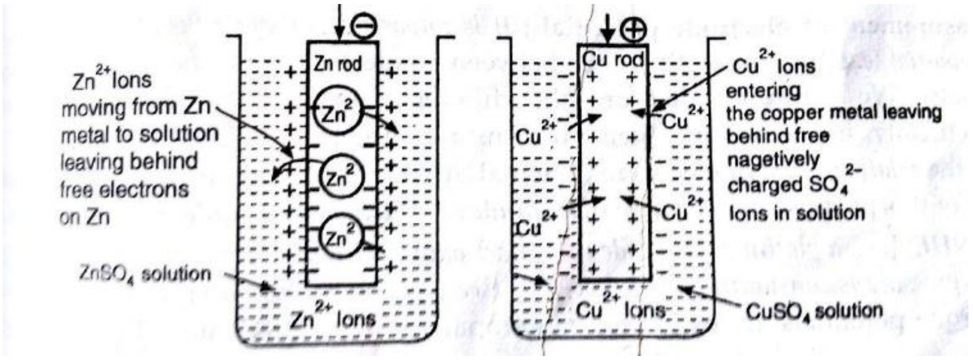
Such an equilibrium results in separation of charges (negative on the electrode with respect to the solution).

Similarly, if the metal ions have relatively greater tendency to get reduced due to electron deficiency, they will take electrons from the electrode. As a result, separation of charges occurs and a net positive charge will be developed on the electrode with respect to the solution.

Example:

(a) Zinc rod dipped in $ZnSO_4$ solution.

(b) Copper rod dipped in $CuSO_4$ solution.



Oxidation Reduction

Thus, a short layer of positive ions or negative ions is formed around the metal. This layer is called Helmholtz electrical double layer. A difference of potential is, consequently setup between the metal and the solution. At equilibrium, the potential difference between the metal and solution becomes a constant value. The equilibrium potential difference so established, is called the "electrode potential" of the metal.

Definition of Electrode potential:

The measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt is called its "*Electrode potential*".

The tendency of an electrode to lose electrons is a direct measure of its tendency to get oxidised; and this tendency is called *Oxidation potential*.

The tendency of an electrode to gain electrons is a direct measure of its tendency to get reduced; and this tendency is known as *Reduction potential*.

It is quite obvious that the value of reduction potential is negative of its oxidation potential and vice versa.Thus, if oxidation potential of an electrode is +X volt, then its reduction potential will have a value of –X volt.

Standard electrode potential (E0):

It is the potential developed when the pure metal is in contact with its ions at one molar concentration at a temperature of 25_{o}C or 298 K.

Example: When a Zn rod of any length is dipped in 1M $ZnSO_4$ solution, standard electrode is formed and the potential developed is called standard zinc electrode potential (E_0).

In case of a gas electrode, the standard electrode potential (E_o) is defined as the potential developed at the interface of the gas and solution containing its own ions when an equilibrium is established between the gas at a pressure of 1 atm (760 mm of Hg) and the ions in solution of unit concentration.

The General Nernst Equation

The general Nernst equation correlates the Gibb's Free Energy ΔG and the EMF of a chemical system known as the galvanic cell. For the reaction

a A + b B = c C + d D

and

$$Q = \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

It has been shown that

$\Delta G = \Delta G^\circ + R\ T \ln Q$

and

$\Delta G = -\ n\ F \Delta E.$

Therefore

$-\ n\ F\ \Delta E = -\ n\ F\ \Delta E^\circ + R\ T \ln Q$

where R, T, Q and F are the gas constant (8.314 J mol^{-1} K^{-1}), temperature (in K), reaction quotient, and Faraday constant (96485 C) respectively. Thus, we have

$$\Delta E = \Delta E^\circ - \frac{R\ T}{n\ F} \ln \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

This is known as the **Nernst equation**. The equation allows us to calculate the cell potential of any galvanic cell for any concentrations. Some examples are given in the next section to illustrate its application.

It is interesting to note the relationship between equilibrium and the Gibb's free energy at this point. When a system is at **equilibrium**, $\Delta E = 0$, and $Q_{\text{eq}} = K$. Therefore, we have,

$$\Delta E^\circ = \frac{R\ T}{n\ F} \ln \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}, \qquad \textbf{(for equilibrium concentrations)}$$

Thus, the equilibrium constant and ΔE° are related.

The Nernst Equation at 298 K

At any specific temperature, the Nernst equation derived above can be reduced into a simple form. For example, at the standard condition of 298 K (25°), the Nernst equation becomes

$$\Delta E = \Delta E^\circ - \frac{0.0592\ \mathrm{V}}{n} \log \frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}$$

Please note that log is the logrithm function based 10, and ln, the natural logrithm function.

For the cell

$Zn\ |\ Zn^{2+}\ ||\ H^+\ |\ H_2\ |\ Pt$

we have a net chemical reaction of

$Zn(s) + 2\ H^+ = Zn^{2+} + H_2(g)$

and the standard cell potential $\Delta E^\circ = 0.763$.

If the concentrations of the ions are not 1.0 M, and the H_2 pressure is not 1.0 atm, then the cell potential ΔE may be calculated using the Nernst equation:

$$\Delta E = \Delta E^\circ - \frac{0.0592\ \mathrm{V}}{n} \log \frac{P(H_2)\ [Zn^{2+}]}{[H^+]^2}$$

with $n = 2$ in this case, because the reaction involves 2 electrons. The numerical value is 0.0592 only when T = 298 K. This constant is temperature dependent. Note that the reactivity of the solid Zn is taken as 1. If the H_2 pressure is 1 atm, the term $P(H_2)$ may also be omitted. The expression for the argument of the log function follows the same rules as those for the expression of equilibrium constants and reaction quotients.

Indeed, the argument for the log function is the expression for the equilibrium constant K, or reaction quotient Q.

When a cell is at equilibrium, $\Delta E = 0.00$ and the expression becomes an equilibrium constant K, which bears the following relationship:

$$\log K = \frac{n\ \Delta E^\circ}{0.0592}$$

where $\Delta E°$ is the difference of standard potentials of the half cells involved. A battery containing any voltage is not at equilibrium.

The Nernst equation also indicates that you can build a battery simply by using the same material for both cells, but by using different concentrations. Cells of this type are called **concentration cells**.

Batteries

Definition:

“An electrochemical cell or combination of electrochemical cells connected in series, that can be used as a source of direct current at a constant voltage is called Battery”.

Batteries are classified as follows,

i) Primary battery
ii) Secondary battery
iii) Fuel cell or Flow battery

Primary battery: *(non-rechargeable)*

Primary battery is a cell in which the cell reaction is not reversible. Thus, once the chemical reaction takes place to release the electrical energy, the cell gets exhausted. Then battery become dead. These are nonrechargeable type.

Example: Dry cell, mercury cell etc.

Secondary battery: *(rechargeable)*

Secondary battery is a cell in which the cell reaction is reversible, by passing direct current in opposite direction. Thus, these are rechargeable cells, used through a large number of cycles of discharging and charging.

Example: Lead-acid battery, Nickel-Cadmium battery, Lithium batteries etc.

$$\text{pH} = 0.0591 \cdot 0.2422 \ {}_{cell}E$$

Fuel cell or Flow battery:

Fuel cell is the cell in which materials (reactants, products and electrolytes) pass through the battery. When the reactants are exhausted, new chemicals replace them. Here chemical energy of fuel is converted into the electrical energy.

Example: Hydrogen-oxygen fuel cell, methyl-oxygen fuel cell etc.

1) Ni- Cd battery:

This battery consists of a cadmium anode and a cathode composed of a paste of NiO(OH). These electrodes are immersed in the solution of KOH (electrolyte).

Working:

When the nickel battery operates, Cd is oxidized to Cd^{+2} ions at anode and the insoluble $Cd(OH)_2$ is formed. NiO(OH) is reduced to Ni^{+2} ions which further combines with OH^- ions to form $Ni(OH)_2$. It produces about 1.4 V. The following cell reactions occur (during discharging).

At anode $Cd (s) + 2OH^- (aq)\ Cd(OH)_2 (s) + 2e^-$
At cathode $2NiO(OH) (s) + 2H_2O + 2e^-\ 2Ni(OH)_2 (s) + 2OH$
Net reaction $Cd (s) + 2NiO(OH) (s) + 2H_2O\ Cd(OH)_2 + 2 Ni(OH)_2$

The reaction can be readily reversed by passing the current in opposite direction, because the products, $Cd(OH)_2$ and $Ni(OH)_2$, adhere to the electrode surfaces.

Reactions during recharging:

At cathode $Cd(OH)_2 (s) + 2e^-\ Cd (s) + 2OH^- (aq)$
At anode $2Ni(OH)_2 (s) + 2OH^-\ 2NiO(OH) (s) + 2H_2O + 2e^-$
Net reaction $Cd(OH)_2 + 2 Ni(OH)_2\ Cd (s) + 2NiO(OH) (s) + 2H_2O$

It may be noted that during discharging process cell acts as voltaic cell (chemical energy is converted to electrical energy), during recharging it acts as an electrolytic cell (electrical energy is converted to chemical energy).

Advantages of Ni-Cd battery:

1. It is portable and rechargeable cell having voltage about 1.4 V.
2. It has longer life than lead-acid battery.
3. Since no gaseous products are formed during discharging and recharging, this cell can be sealed.
4. It can be left for long periods of time without any appreciable deterioration.

Applications:

1. It is used in electronic calculators.
2. It is used in electronic flash units.
3. It is used in transistors and cordless electronic shavers.

2) Lithium batteries:

Lithium cells most popularly used cells, which are available in various configurations. These cells have following advantages.

1. These are light in weight.
2. High energy density
3. More cycle life.

Lithium has the most negative standard reduction potential (-3.05 V) of any metal, so it has lot of appeal as an anodic material. Furthermore, lithium is a very light metal, correspondingly lithium employed cell is light in weight.

Lithium batteries fall into two categories:
(a) Solid Lithium cells (primary batteries)
(b) Lithium ion cells (secondary batteries)

(a) <u>Solid lithium Batteries:</u>

One of the most common lithium primary cell is the lithium manganese dioxide battery. This cell uses a solid lithium anode and a cathode made of heat treated MnO_2.

The electrolyte is a mixture of propylene carbonate and dimethyoxy ethane containing dissolved salt such as $LiClO_4$.Propylene carbonate, Dimethoxy ethane

The cell reactions are as follows:

$Li\ Li^{+}$-----------> $+\ e^{-}$ (anode)

$MnO_2 + Li^{+} + e^{-}$ ---------->$MnO_2(Li)$ (cathode) (Mn^{+4} to Mn^{+3})

$Li + MnO_2$------------> $MnO_2(Li$ (net cell reaction)

This cell produces a voltage of about 3.4 V which is more than twice that of alkaline dry cell, and because of the light weight of lithium, it produces more than twice as much energy for a given weight.

Applications:

These cells are used in applications that require a higher current drain or energy pulses (photoflash). $H_2CCHOCOOH_3C$

(b) Lithium ion Batteries (rechargeable):

These cells do not contain metallic lithium. But they contain lithium ions. In fact, the cell's operation does not actually involve true oxidation and reduction. But it uses the transport of Li^{+} ions through the electrolyte from one electrode to the other, accompanied by the transport of electrons through the external circuit to maintain charge balance.

Initial charging:

It was discovered that Li^{+} ions are able to slip between two layers of atom in certain crystals such as graphite and $LiCoO_2$. When the cell is constructed, it is in its uncharged state with no Li^{+} ions between the layers of carbon atoms in the graphite. While the cell is initial charging, Li^{+} ions leave $LiCoO_2$ and travel through the electrolyte (usually $LiPF_6$) to the graphite (C_6).

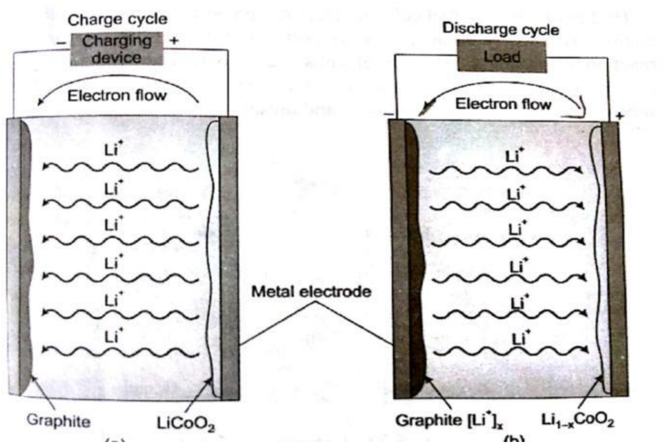
$$LiCoO_2 + \text{graphite } (C_6)\ Li_{1-x}CoO_2 + Li_xC_6$$

Discharging:

When the cell spontaneously discharges to provide electrical power, Li^{+} ions move back through the electrolyte to the Lithium cobalt oxide, while the electrons move through external circuit from the graphite electrode to the cobalt oxide electrode. If we represent amount of Li^{+} ions transferring by 'y', then the discharge reaction is represented as,

$$Li_{1-x}\ CoO_2 + Li_xC_6\ Li_{1-x+y}\ CoO_2 + Li_{x-y}C_6$$

Thus, the charging and discharging cycle simply sweep Li^{+} ions back and forth between two electrodes with electrons flowing through external circuit to keep the charge balance.



Applications:

1. Used as power suppliers in portable electronics, telecommunications, personal computerssuch as cell phones, and laptops.
2. For transportation-in electric bikes and electric cars which runs with electricity.

Fuel cells

Introduction:

We know that galvanic cells involve oxidation-reduction reaction. A workable cell forces the electrons that leave the substance being oxidized through an external conductor before they are received by the oxidizing agent. We also know that all ordinary combustion reactions are redox reactions. However, when a fuel is burned, the electron exchange take place only when the atoms of the oxidising agent (oxygen or air) come in direct contact with the atoms of the substance being oxidised (the fuel). The energy is released principally as heat. In a fuel cell, electrical energy is obtained without combustion from oxygen and a gas that can be oxidized.

The galvanic cells can only produce electrical energy for a limited time because the electrode reactants are eventually depleted. Fuel cells are electrochemical cells in which electrode reactants are supplied continuously and are able to operate without theoretical limit as long as the supply of reactants is maintained. This makes fuel cell an attractive source of power where long-term generation of electrical energy is needed. Fuel cell converts the chemical energy of the fuels directly to electricity.

Definition of Fuel cell:

An electrochemical cell in which, reactants are supplied continuously from an external source, and chemical energy of the fuel is directly converted into electricity, is called Fuel cell.

A large number of these cells are stacked together to make a battery, called fuel cell battery or fuel battery. The essential process in a fuel cell is;

Fuel + Oxygen Oxidation products + Electricity

Fuels in fuel cell are gases or liquids like H_2, CH_4, methanol etc. Oxygen acts as an oxidant.

Fuel cell Battery

- Open system
- Anode and cathode are gases in contact with a platinum catalyst.
- Reactants are externally supplied,

no recharging required.

- Closed system
- Anode and cathode are metals.
- Reactants are internally consumed,

need periodic recharging.

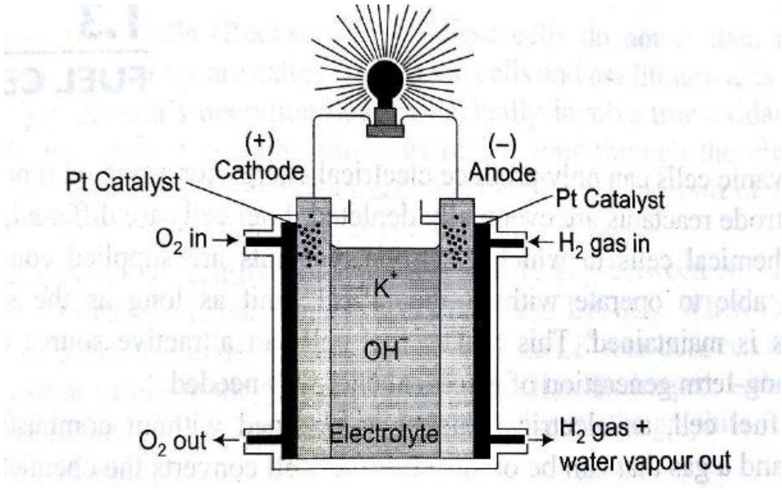
Types of fuel cells:

There are different types of fuel cells, differentiated by the type of electrolyte separating the hydrogen from the oxygen. The types of fuel cells are

1. Alkaline Fuel cells
2. Molten Carbonate Fuel cells (out of syllabus)
3. Phosphoric Acid Fuel cells
4. Proton Exchange Membrane Fuel cells
5. Solid Oxide Fuel cells

1) Alkaline fuel cells (AFCs) (or) Hydrogen- Oxygen fuel cell:

One of the simplest and successful fuel cell is hydrogen-oxygen fuel cell. It consists of an electrolyte, a hot concentrated solution of KOH in the centre compartment, and KOH is in contact with two porous carbon electrodes that contain catalyst (platinum) to facilitate the electrode reactions. Gaseous hydrogen and oxygen under pressure are circulated so as to come in contact with the electrodes.



The electrode reactions are as follows;

$2\ H_2(g) + 4\ OH^-(aq)\ 4\ H_2O + 4\ e^-$ (at anode)

$O_2(g) + 2\ H_2O + 4\ e^-\ 4\ OH^-(aq)$ (at cathode)

$2\ H_2(g) + O_2(g)\ 2\ H_2O$ net cell reaction

The standard EMF of the cell is 1.23 V. Generally, large number of these cells are connected in series to make a fuel battery.

Advantages:

1. These fuel cells are an attractive alternative to gasoline powered engine, because these are pollution free and the only product of the reaction is harmless water.
2. These are highly efficient (75%), converting as much as (75% of) available energy to useful work compared to the efficiency of gasoline and diesel engines (25-30%).
3. The fuel (hydrogen) and electrolyte material are available in plenty and inexhaustible unlike fossil Fuels.

Applications:

1. Hydrogen-oxygen fuel cells are used as auxiliary energy source in space vehicles, submarines, or military vehicles.
2. The weight of fuel battery is about 250 kg which is enough for 15 days in space.
3. In case of hydrogen-oxygen fuel cells, the product of water process to be a valuable source of fresh 55+water to the astronauts.

2) Proton Exchange Membrane Fuel Cells (PEMFCs):

In these fuel cells, “a polymer membrane, which is an electronic insulator, but an excellent conductor of hydrogen ions” is used as electrolyte. It consists of a fluorocarbon backbone, similar to Teflon, to which sulfonic acid groups are attached.

Ex: Nafion

The acid groups are fixed to the polymer and cannot leak out, but the protons on these acid groups are free to migrate through the membrane. The use of solid polymer electrolyte eliminates the corrosion and safety concerns associated with liquid electrolyte fuel cells. Its low operating temperature provides instant start-up. The anode and cathode are prepared by applying a small amount of platinum black to the surface of a graphitised paper. The electrolyte is then sandwiched between the anode and cathode, and the three components are sealed together under heat and pressure to produce a single “Membrane Electrode Assembly” (MEA). This MEA is the heart of the fuel cell which is less than one millimetre thick(Nafion).

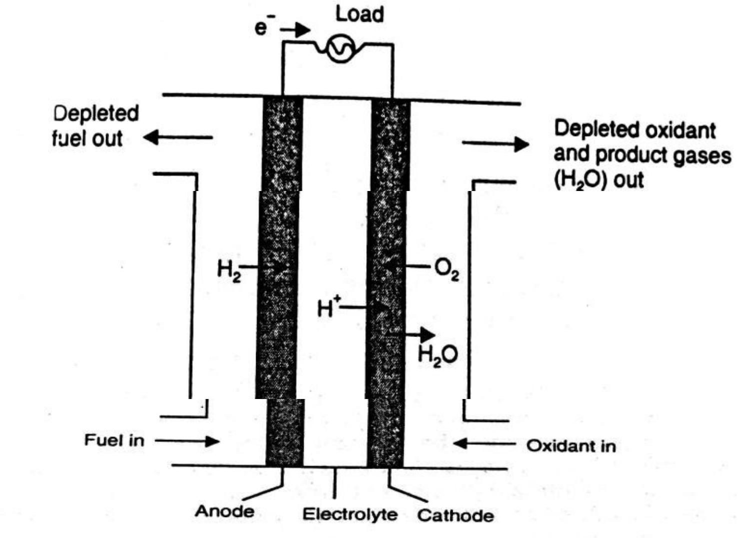
Working:

Hydrogen from the fuel gas is consumed at the anode, yielding electrons to the anode producing hydrogen ions, which enter the electrolyte. At the cathode, oxygen combines with electrons and hydrogen ions to produce water. The water does not dissolve in the electrolyte and is rejected from the back of the cathode. As the PEMFs are operating about 80^0C, the water is produced in liquid state.

At anode: $H_2 \rightarrow 2H^+ + 2e^-$

At cathode: $(1/2)O_2 + 2H^+ + 2e^- \rightarrow H_2O$

Net Reaction: $H_2 + (1/2)\ O_2 \rightarrow H_2O$



3) Solid Oxide Fuel Cells (SOFCs):

Solid oxide fuel cells work at very high temperatures, the highest of all the fuel cell types at around 800ºC to 1,000°C. They can have efficiencies of over 60% when converting fuel to electricity; if the heat they produced is also harnessed; their overall efficiency in converting fuel to energy can be over 80%.

"SOFCs use a solid ceramic electrolyte, such as zirconium oxide stabilised with yttrium oxide (or calcium oxide), instead of a liquid or membrane".

Working:

At high operating temperatures, oxygen ions are formed at the "air electrode" (cathode). When a fuel gas containing hydrogen is passed over the "Fuel electrode" (anode), the oxygen ions migrate through the crystal lattice to oxidise the fuel. Electrons generated at the anode move out through an external circuit, creating electricity. In this cell water gas ($CO + H_2$) is used as the fuel.

Anode reaction:

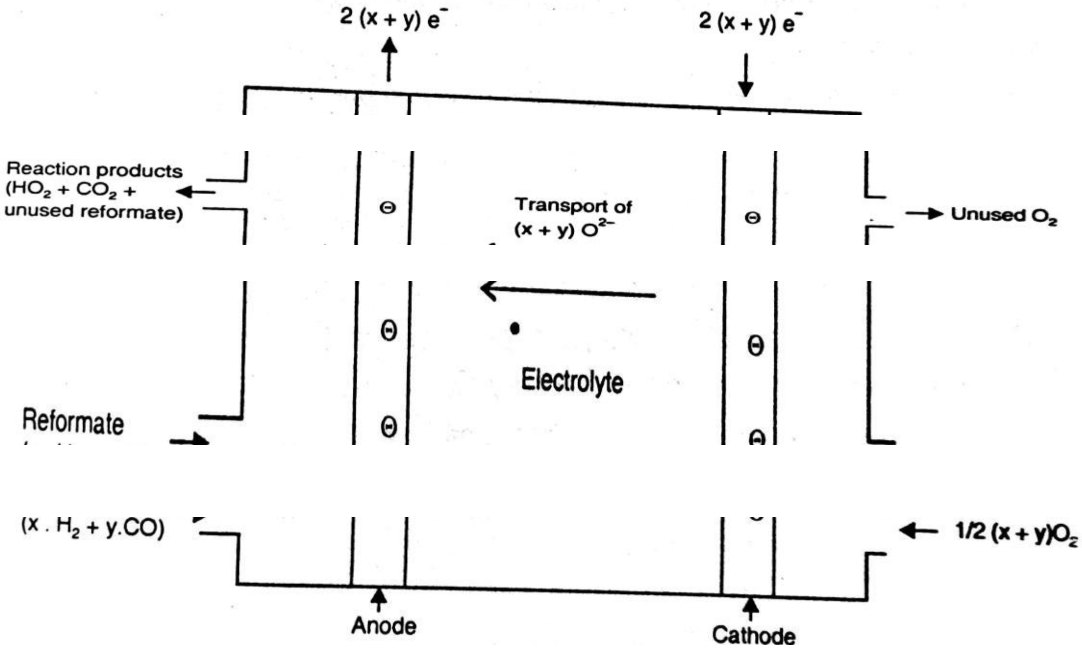
$$x\,H_2 + y\,CO + (x+y)\,O^{2-}\;\; x\,H_2O + y\,CO_2 + 2(x+y)\,e^-$$

Cathodic reaction:

$$\tfrac{1}{2}(x+y)\,O_2 + 2\,(x+y)\,e^-\;\; (x+y)\,O^{2-}$$

Net Reaction:

$$x\,H_2 + y\,CO + \tfrac{1}{2}(x+y)\,O_2\;\; x\,H_2O + y\,CO_2$$



There are two different SOFC geometries of SOFC: planar, tubular.

- In the planar design, components are assembled in flat stacks where the air and hydrogen traditionallyflow though the unit via channels built in to the anode and cathode.
- In the tubular design, air is supplied to the inside of an extended solid oxide tube (which is sealed at one end) while fuel flows round the outside of the tube. The tube itself forms the cathode and the cell components are constructed in layers around the tube.

Advantages:

- Their high operating temperature means that fuels can be reformed within the fuel cell itself, eliminating the need for external reforming and allowing the units to be used with a variety of hydrocarbon fuels.
- They are also relatively resistant to small quantities of sulphur in the fuel, compared to other types of fuel cell, and can hence be used with coal gas.
- A further advantage of the high operating temperature is that the reaction kinetics are improved, removing the need for a metal catalyst.

Disadvantages:

- Due to the high temperature: these cells take longer to start up and reach operating temperature, they must be constructed of robust, heat-resistant materials, and they must be shielded to prevent heat loss.
- While solid electrolytes cannot leak, they can crack.

- Design Cost & choice of material.

Applications:

- Suitable for decentralized electricity production
- While the major application of SOFCs are seen in stationary plants, auxiliary power units in
- Transportation vehicles
- On-board power for aircraft
- Power packs- small enough to be carried by soldier.

Corrosion

Introduction:

Most metals (except noble metals such as Au, Pt, etc) exist in nature in combined forms as their oxides, carbonates, hydroxyl carbonates, sulphides, chlorides and silicates. These are reduced to their metallic states from their ores, during their extraction processes. During extraction of metals, considerable amounts of energy is required. Consequently, isolated pure metals can be regarded as in excited state (higher energy state) than their corresponding ores, and they have a natural tendency to revert back to combined state (lower energystate). Hence, when metals are put into use, in various forms, they are exposed to environment (such as dry gases, moisture, liquids, etc), the exposed metal surfaces begin to decay (i.e. conversion to more stable metal compounds) more or less rapidly, when they come in contact with surroundings. In other words destruction or deterioration of the metal starts at the surface. This type of metallic destruction may be due to direct chemical attack (by the environment) or electrochemical attack (i.e, similar to reactions in a Daniel cell).

REACTION:

Definition of corrosion:

"Any process of deterioration or destruction of a metal or alloy, through an unwanted chemical or electrochemical attack by its environment, starting at its surface, is called corrosion".

Thus, corrosion is a process of "reverse of extraction of metals".

Examples:

1. Rusting or iron, when exposed to the atmospheric conditions. During this, a layer of reddish scale and powder of oxide (Fe_2O_3) is formed, and the iron becomes weak.
2. Formation of green film of basic carbonate [$CuCO_3 + Cu(OH)_2$] on the surface of copper, when exposed to moist-air containing carbon dioxide.

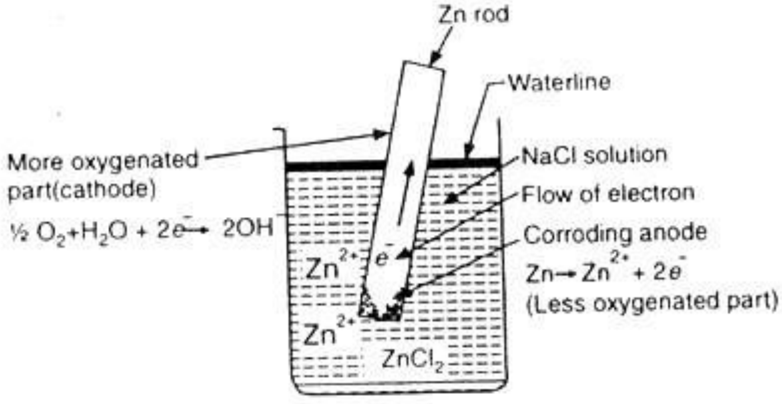
Concentration cell corrosion:

This type of corrosion is due to electrochemical attack on the metal surface, exposed to an electrolyte of varying concentrations or of varying aeration. The most common type of concentration cell corrosion is Differential aeration corrosion. It occurs when one part of metal is exposed to a different air concentration from the other part. This causes a difference in potential between differently aerated areas. It has been found experimentally that "pooroxygenated parts are *anodic*". Consequently, a differential aeration of metal causes a flow of current, called differential current. It accounts for the corrosion of metals, partially immersed in a solution, just below the water line.

Explanation:

If a metal (say Zn) is partially immersed in a dilute solution of a neutral salt (say NaCl) and the solution is not agitated properly, then, the parts above and closely adjacent to the waterline are more strongly aerated, because of easy access of oxygen and hence, become *cathodic*. On the other hand, parts immersed to greater depth, which have less access of oxygen, show a smaller oxygen concentration and thus, become *anodic*. So, a difference of potential is created, which causes the flow of current between the two differentially-aerated areas of the same metal.

Zinc will dissolve at the anodic area, and oxygen will take up electrons at the cathodic area to form hydroxyl ions.



Differential aeration corrosion

$$Zn \text{----------}> Zn^{2+} + 2e^-$$

$$1/2\ O_2 + H_2O + 2e^- \text{----------}> 2OH^-$$

The circuit is completed by migration of ions, through the electrolyte, and flow of electrons through the metal, from anode to cathode. In a similar way, iron corrodes under drops of water (or salt solution). Areas covered by droplets, having low access of oxygen, become anodic with respect to the other areas, which are freely exposed to air .

From the above, it is clear that oxygen concentration cell increases corrosion, but it occurs where the oxygen concentration is lower.

General facts about the differential aeration (concentration cell corrosion) corrosion:

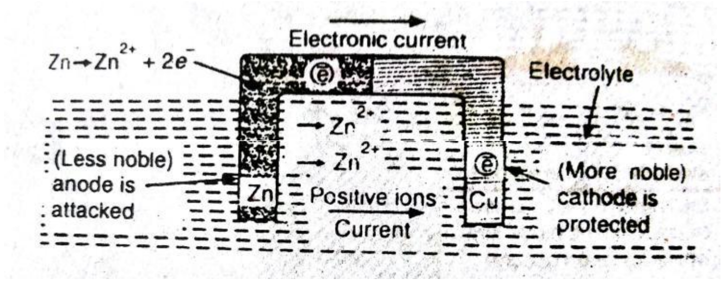
(i) Corrosion may be accelerated in apparently inaccessible places, because the oxygen deficient areas serve as anode and, therefore, cracks or crevices serve as foci for corrosion.

(ii) Corrosion is accelerated under accumulation of dirt, sand, scale or other, contamination. This is because accumulation of rust or scale or sand etc. restricts the oxygen and establishes an anode to promote still greater accumulation. The result is localized corrosion, due to non-uniform conditions.

(iii) Metals exposed to aqueous media, corrode under blocks of wood or pieces of glass, which screen that portion of metal from oxygen access. The differential aeration type of corrosion is a localized attack on some oxygen deficient areas, resulting in characteristics localized pitting. This arrack becomes more intensified with the time, because the corrosion products accumulate around a small anodic area, thereby making inaccessibility of that part more effective.

Galvanic corrosion (or bimetallic corrosion):

When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series (which is having low E_0 value) undergoes corrosion. This type of corrosion, is called “galvanic corrosion”.



Explanation:

When zinc and copper are connected and exposed to corroding environment, zinc (higher in electrochemical series) acts as anode and is going to corrode; whereas copper (lower in electrochemical series or nobler) acts as cathode.

Mechanism:

In acidic solution, the corrosion occurs by the hydrogen evolution process; while in neutral or slight alkaline solution, oxygen absorption occurs. The electron-current flows from the anodic metal i.e. Zn to the cathodic metal (Cu). Thus, it is evident that the corrosion occurs at the anodic metal; while the cathodic part is protected from attack.

$$Zn\ Zn_{+2} + 2e_{-}\ \text{(oxidation)}$$

Examples for galvanic corrosion:

1. Steel screws in a brass marine hardware.
2. Lead-antimony solder around copper wire.
3. A steel propeller shaft in bronze bearing.
4. Steel pipe connected to copper plumbing

Types of corrosion:

1. Dry corrosion (Chemical corrosion).
2. Wet corrosion (Electro chemical corrosion).

2)Wet corrosion:

According to electrochemical theory, corrosion of metals occurs due to the following changes, when they are exposed to the environment.

1) A large number of minute galvanic cells are formed which acts as anodic and cathodic areas.
2) At anode the metal undergoes oxidation and electrons are liberated which migrates towards cathodic region
3) Oxygen of the atmosphere undergoes reduction at cathodic area in the presence of moisture forming hydroxyl ions at the cathode

***Anodic reactions**:* At anode the metal undergoes oxidation-liberating electrons

$$\underset{\text{Metal}}{M} \xrightarrow{\qquad\qquad} \underset{\text{Metal ions}}{M^{n+}} + ne^{-}$$

Ex: when iron is exposed to the environment it undergoes oxidation as

$$Fe \xrightarrow{\qquad\qquad} Fe^{2+} + 2e^{-}$$

***Cathodic reactions**:* The electrons released at anode migrates to the cathodic area and reduces oxygen to hydroxyl ions.

The different cathodic reactions are,

a) ***In acidic medium:*** In acidic medium and in the absence of oxygen, hydrogen ions are reduced to hydrogen gas

$$2H^{+} + 2e \longrightarrow H_2$$

b) ***In alkaline and in the absence of O_2:*** If the solution is alkaline and in the absence of oxygen the cathodic reaction is,

$$2\ H_2O + 2e^{-} \longrightarrow 2OH^{-} + H_2$$

c) ***In neutral and aerated medium:*** when the solution is neutral and aerated, hydroxyl ions are formed as follows.

$$2\ H_2O + O_2 + 4e^{-} \longrightarrow 4OH^{-}$$

d) ***Formation of corrosion product:*** The hydroxyl ions migrate towards anode and reacts with metal ions (M^{n+} ions) and forms corrosion product. In the case of iron OH- reacts with Fe^{2+} ions and forms an insoluble hydrated ferric oxide known as brown rust.

$$2Fe^{++} + 4OH^{-} \text{-------}\rightarrow \longrightarrow 2Fe\ (OH)_2$$

$$2Fe\ (OH)_2 + O_2 + 2H_2O\text{-------}\rightarrow 2\ (Fe_2O_3 .\ 3H_2O)\text{ rust.}$$

Galvanic series:

In the electrochemical series, a metal high in the series is more anodic and undergoes corrosion faster than themetal below it. For example, Li (–3.05V) corrodes faster than Mg (–2.36V), Zn (–0.76V) corrodes faster than Fe (–0.44V), Fe corrodes faster than Sn (–0.14V), Cu (0.34V) corrodes faster than Ag (0.80V) and so on.

However, some exceptions to this generalization are known.

Examples:

1. Ti (– 1.63V) (above Ag in the electrochemical series) is less reactive than Ag (0.80V).
2. In Zn-Al couple, Zn (–0.76V) (below Al in the electrochemical series) is corroded; while Al (–1.66V)acts cathodic and is protected.These observations, exactly opposite to that predicted by the electrochemical series, are due to the fact that metals like Ti and Al develop, strongly adhering oxide layers on their surfaces, thereby making their effective electrode potential more positive (or less negative).

From the above, it is clear that electrochemical series does not account for the corrosion of all metals and alloys. Consequently, a more practical series, called *galvanic series* have been prepared by studying the corrosion of metals and alloys in a given environment like sea-water. Thus, galvanic series give real and useful information for studying the corrosion of metals and alloys.

Factors affecting the corrosion (Metal and Environment):

The main important factors, which affect on the rate of corrosion, are

a) Nature of the metal and
b) Nature of the environment

Nature of the metal:

i) *Nature of corrosion product:*

If the nature of corrosion product forms, a protective layer on the metal surface, it prevents the further corrosion of metal .If the corrosion product is thin, invisible and doesn't form a protective layer it leads to further corrosion of metal.

Example: In oxidizing environment metals like Al, Cr, Ti etc. forms protective metal oxide films on their surfaces which prevents further corrosion .Metals like Zn,Fe ,Mg ,etc .do not form protective layer and are readily under goes corrosion .Therefore the rate of corrosion depends on the nature of corrosion product.

ii) Electrode Potential of anode and cathode:

The rate of corrosion increases if the potential difference between anode and cathode is high and vice versa. When two different metal with large electrode potential difference (SRP values) under goes very fast corrosion

Example: The potential difference between copper and iron is 0.78 V. The potential difference between iron and tin is 0.3 V. In these two cases iron undergoes fast corrosion when it is in contact with copper than when it is in contact with tin.

iii) Anodic to cathodic areas:

If a metal has small anodic and large cathodic area the rate of corrosion increases and vice versa. This is because when anode is small the electrons liberated during oxidation are completely consumed on large cathodic surface for the reduction reactions and rate of corrosion increases.

b) *Nature of the environment:*

i) Temperature: Increases in temperature results in an increase in the conductance of the aqueous medium and rate of corrosion also increases and vice versa.

ii) PH: In general at lower PH value the rate of corrosion is more at higher pH value (more than pH = 10) the rate of corrosion ceases due to the formation of protective coating of hydrous oxides on the metal. Corrosion rate is maximum between PH 3 and 10 in presence of oxygen

Control of corrosion:

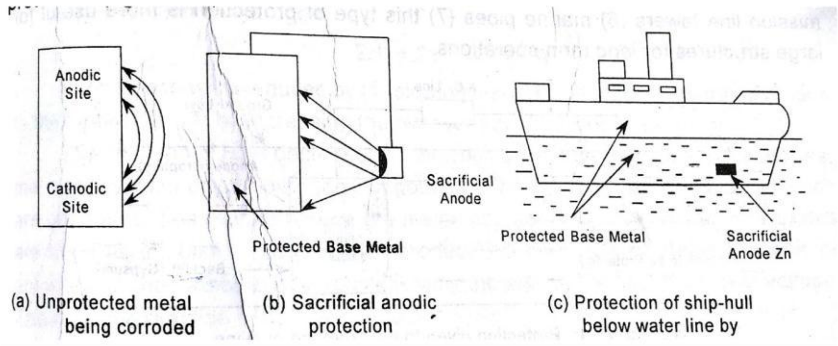
Cathodic protection (Sacrificial anodic protection)

Cathodic protection: (Sacrificial anodic protection):

It is a method of protecting metals and alloys from corrosion by making them completely The metallic structure to be protected called 'base metal' is connected to more anodic metal through a wire. The anodic metal undergoes corrosion slowly, while the base metal is protected. The corroded anode is called sacrificial anode, and it is replaced by a fresh one. The commonly used anodic metals are magnesium, aluminium and their alloys.

Application:

To protect marine structures and ship-hulls, which are made of steel are connected to a sacrificial anode, which undergoes corrosion leaving the base metal protected.



(a) Unprotected metal being corroded (b) Sacrificial anodic protection (c) Protection of ship-hull below water line by

Electroplating (or electrodeposition):

Definition:

The process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution, containing the soluble salt of the coating metal is called “electroplating”.

Objectives of electroplating:

(1) ***On metals:***

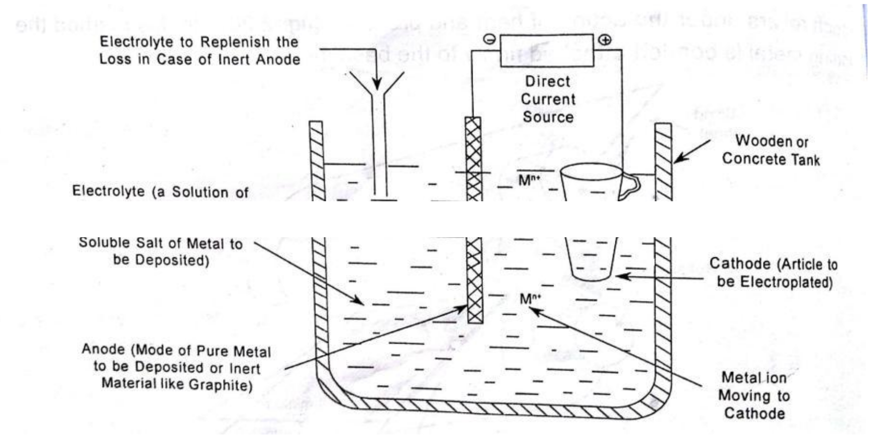
i) To increase the resistance to corrosion of the plated metal.
ii) To increase the resistance to chemical attack and wear resistance.
iii) To improve physical appearance and hardness.
iv) To improve the surface properties.
v) To increase the decorative and commercial values of the metal.

(2) ***On non-metals:***

i) For increasing strength.
ii) For preservation and decoration of the surfaces of non-metals like plastics and wood.
iii) For making the surface conductive by utilization of light-weight plastics.

Process:

In this process the base metal is made cathode and the coating metal is made anode or an inert material of good electrical conductivity is also used as anode. A direct current is passed through the electrolytic solution. If anode is made of graphite, the electrolytic salt is added continuously to maintain the proper coating metal ion concentration in the electrolyte bath.



The article to be electroplated is subjected to solvent cleaning by trichloroethylene to remove oil, greases etc. Then it is subjected to acid pickling with dil HCl or dil H_2SO_4 to remove any scales, oxides etc. The cleaned article is made cathode of the electrolytic cell and the anode can be made of the pure coating metal or graphite.The electrodes were dipped in the salt solution of the coating metal, which acts as an electrolyte. 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. For brighter and smooth deposits, conditions like low temperature, medium current density, and low metal ion concentration are used.

For example for electroplating of nickel on iron article, the following conditions are maintained.

1. Electrolytic bath solution : nickel sulphate, nickel chloride and boric acid.
2. pH maintained : 4.0 by boric acid buffer.
3. Operating temperature : 40-70^{0}C
4. Current density : 20-30 mA/cm^2
5. Additive agent : Saccharin/coumarin derivatives.
6. Cathode : metal article to be plated.
7. Anode : nickel pellets/pieces taken in a titanium mesh basket.

Applications:

- Electroplating is a most important and frequently used technique in industries to produce metallic coating. Both metals and non-metals can be electroplated.
- In metals the electroplating increases resistance to corrosion, chemical attack, hardness, wear resistance, and surface properties.
- In non-metals electroplating increases strength and decorates the surface of non-metals like plastic.