

Program/ Course	:	B.E – Science and Humanities
Course Name	:	Engineering Chemistry
Course Code	:	18CHE12
Year / Semester	:	2019/I Sem
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Module 1

Electro chemistry and energy storage systems

Thermodynamic functions ;

Thermodynamic is a branch of physical chemistry deals with the quantitative relation between heat and mechanical energy.

Energy : Energy is a quantitative property that must be transferred to an object in order to perform work or to heat the object, energy is a conserved quantity

Helmholtz free energy : it is a thermodynamic function defined to measure the useful work obtained from a closed system, it is denoted as A and is defined as

$$A = E - TS$$

E,T and S are state functions of the system

Gibb's free energy : It is thermodynamic function which is related to enthalpy and entropy as $G = H - TS$

Entropy : Entropy is the quantity that whether a chemical reaction or a physical change can occur spontaneously in an isolated system or not, change in entropy from one state to another is denoted by $S = S_{\text{final}} - S_{\text{initial}}$

Derivation Of Nernst equation :

Nernst equation gives the relationship between the electrode potential concentration of the species and was derived by a well known scientist Nernst, it was derived by taking well known thermodynamic considerations

Consider a reversible equation



The decrease in free energy is given by Vant hoffs reaction isotherm

$$\Delta G = \Delta G^{\circ} + RT \ln k$$

ΔG = Gibbs free energy

ΔG° = Standard gibbs free energy

R = Gas constant

T = Temperature

k = equilibrium constant

decrease in free energy represents the maximum work done

$$\text{i.e., } -\Delta G = W_{\max}$$

where n is the total number of electrons flowing from anode to cathode and the total amount of

energy available per coulomb

$$\text{i.e., } W_{\max} = nFE$$

$$\text{therefore } \Delta G = -nFE$$

$$\Delta G^\circ = -nFE^\circ$$

$$k = \frac{\text{concentration of products}}{\text{concentration of reactants}}$$

Substitute all these values in equation 1 we get,

$$-nFE = -nFE^\circ + RT \ln \frac{[\text{Mn}^+]}{[\text{M}]}$$

Divide the whole equation by $-nf$ we get,

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Mn}^+]}{[\text{M}]}$$

$$\text{or}$$

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{Mn}^+]}{[\text{M}]}$$

Convert from \ln to \log we get

$$E = E^\circ + \frac{2.303RT}{nF} \log \frac{[\text{Mn}^+]}{[\text{M}]}$$

when the concentration of $[\text{M}] = 1$, we get

$$E = E^\circ + \frac{2.303RT}{nF} \log \frac{[\text{Mn}^+]}{1}$$

at 298K, when we substitute the values of $R = 8.314$, $F = 96500$, we get

$$E = E^\circ + \frac{0.0591}{n} \log \frac{[\text{Mn}^+]}{1}$$

is the required Nernst equation for single electrode potential

Reference electrodes :

Reference electrodes are the electrodes with reference to which the electrode potential of other electrodes can be calculated, they are of two types

1. Primary reference electrodes
2. Secondary reference electrodes

Secondary reference electrodes

These are the electrodes having constant and reproducible potential and are used to determine the electrode potential of any unknown electrodes

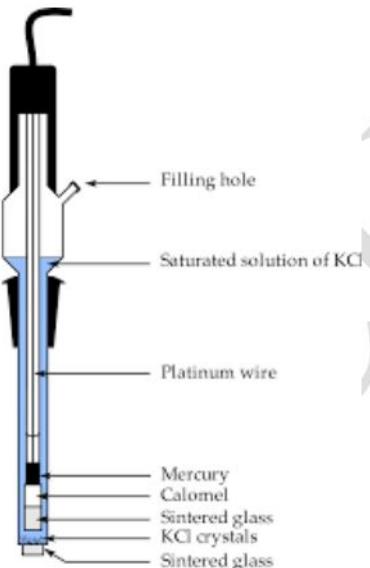
Eg : 1. Calomel electrode , Silver silver chloride electrode

Construction and working of Calomel electrode

- It consists of mercury at the bottom of the tube
- Mercury is covered with a paste of mercury + mercurous chloride (calomel)
- KCl solution is introduced into the tube through the side tube
- A platinum wire inserted up to the bottom serves for external electrical contacts
- The electrode is coupled with any other electrode through the salt bridge
- Calomel electrode acts as both anode as well as cathode depending on the nature of the other electrode
- When the electrode acts as anode the cell reactions are

$$\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \longrightarrow 2\text{Hg} + 2\text{Cl}^-$$
- When the electrode acts as cathode the cell reactions are

$$2\text{Hg} + 2\text{Cl}^- \longrightarrow \text{Hg}_2\text{Cl}_2 + 2\text{e}^-$$



- Overall cell reaction is written as

$$2\text{Hg} + 2\text{Cl}^- \rightleftharpoons \text{Hg}_2\text{Cl}_2 + 2\text{e}^-$$
- The electrode potential of the calomel electrode is given by

$$E = E^\circ + \frac{0.0591}{n} \log [\text{Cl}^-]^2$$
- It is clear from the above equation that the potential of calomel electrode depends on the concentration of chloride ions
- For 0.1N, 1N and saturated KCl the potentials are found to be 0.33, 0.28 and 0.2422 respectively

Advantages

- Easy to construct
- Potential does not vary with the Variation of temperature

Applications

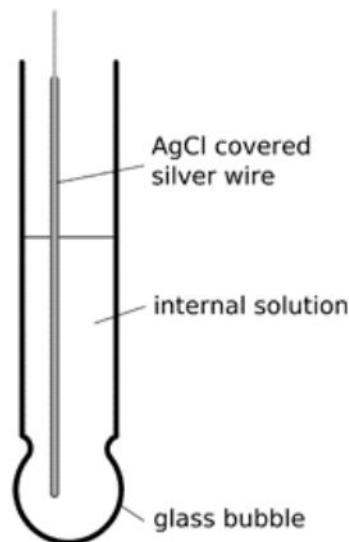
- Used to determine potential and pH when combined with platinum and glass electrodes respectively

Ion selective electrodes : are the electrodes which responds to a particular ions in a

mixture of ions, Different types of membranes available are

1. Solid state membrane
2. Liquid membrane
3. Heterogeneous membrane
4. Glass membrane

Construction and working of glass electrode



- Glass electrode consists of a long glass tube with a glass membrane bulb at the bottom, glass membrane is made up of 72% SiO₂, 22 % Na₂O, 6%CaO and the thickness varies from 0.03 – 0.1 mm, Ag/AgCl or calomel electrode is used as an internal reference electrode
 - When the glass electrode is working the Na⁺ ions from glass membrane are replaced by the H⁺ ions from the solution.
- Gl. H⁺ + Na⁺ → Gl. Na⁺ + H⁺
- Glass electrode is represented as Ag/AgCl/HCl/Glass

Determination of pH of a solution by using a glass electrode

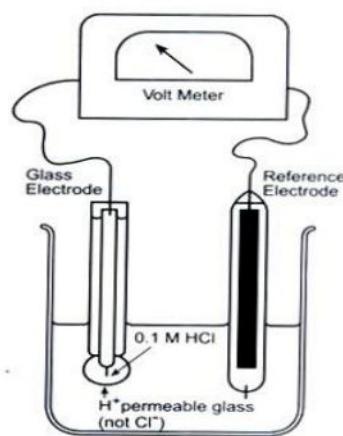


Fig. 2.1: Schematic diagram of pH meter

- Glass electrode is coupled with secondary reference electrode like calomel or silver silver chloride electrodes and are connected to a pH meter, the electrodes are dipped in the solution for which the pH has to be determined

- Here the electrode reaction is assumed to be the reduction of H^+ ions, by knowing the potentials of glass and reference electrodes the pH of the solution can be calculated

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

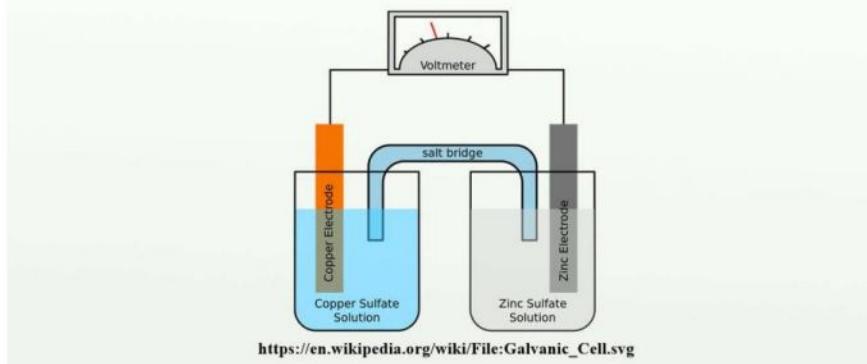
$$E_{Glass} - E_{SRE}$$

$$E_G = E_G^o - 0.0591PH$$

$$E_G = E_G^o - 0.0591PH - E_{SRE}$$

Therefore PH = $\frac{E_G^o - E_{SRE} - E_{cell}}{0.0591}$
--

Concentration cell



Concentration cell : | two electrodes made up of same metal are dipped in the solution of its own electrolyte but of different concentrations forms a cells called as concentration cell.

Flow of electrons is seen until the concentration is different once the concentration becomes constant there is no more flow of electrons and hence no current.

The above concentration cell consists of two electrodes made up of Zn are dipped in the solution of $ZnSO_4$ but of different concentrations, until the concentrations are different the flow of electrons are seen once the concentrations become equal there is no more flow of electrons and hence no current

The cell reactions are



When $C_1 = C_2$, $emf = 0$

The potential of concentration cell is given by the Nernst equation

$$E = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

where $C_2 > C_1$

CLASSIFICATION OF BATTERIES:

Batteries are classified as primary (non-rechargeable), secondary (rechargeable) and reserve (inactive until activated):

Primary batteries

Primary batteries are not rechargeable, and consequently are discharged then disposed of, in which the electrolyte is not a liquid but a paste or similar. Cell is operated until the active components in the electrodes are exhausted. Once all the active components are utilized they do not have any further electrical use. Generally primary batteries have a higher capacity and initial voltage than rechargeable batteries.

Example : Dry cell. Zn-MnO₂, Li – MnO₂ batteries

Secondary batteries

Secondary batteries are also called storage cells, because they can be recharged and reused until the shelf life and cycle life of the battery are good, here the cell reactions are reversible and the batteries are recharged by applying direct current in the opposite side of the discharge current,

Example: Lead acid battery, Ni MH battery, Ni-Cd battery

Reserve battery

A reserve battery is a special purpose primary battery designed for emergency short service life and for long term storage. They are not rechargeable. Here any one of the active components are stored separately and are incorporated into the battery when required, generally electrolyte is usually stored separately or in case of aqueous batteries water is stored separately from the electrodes which remain in a dry inactive state and is activated only when required by assembling its internal parts and by adding water

Eg : Ag₂O activated by water battery, Mg activated by water battery

NICKEL-METAL HYDRIDE BATTERY (NI-MH)

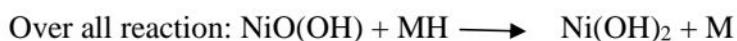
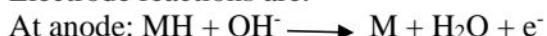
Nickel metal hydride (metal hydride is a binary compound formed by the union of hydrogen and other elements) batteries are similar to Ni-Cd battery, but are less toxic and offer higher capacities. Ni-MH batteries have a high self-discharge rate and are relatively expensive to purchase.

Construction:

- In a Ni-MH cell, a hydrogen storage metal alloy behaves as anode and nickel oxy hydroxide cathode.
- At cathode (a highly porous substrate) nickel oxy hydroxide is impregnated.
- The electrolyte is an aqueous potassium hydroxide solution.

- Synthetic non-woven material used as a separator that separates the two electrodes and behaves as a medium for absorbing the electrolyte.

Electrode reactions are:



- The open circuit voltage is 1.35V.
- During recharging of the battery the above cell reaction is reversed.

Advantages

- Higher capacity
- Long shelf life
- Simple storage and transportation
- Environmentally friendly

Disadvantages:

- Limited service life
- Limited discharge current
- High self-discharge
- High maintenance

Uses:

- Cellular phones
- Emergency
- Power tools
- Portable electric vehicles

Lithium ion battery

Construction:

- A lithium-ion rechargeable battery consists of a spiral structure with 4 layers.
- A positive electrode activated by cobalt acid lithium, a negative electrode activated by special carbon, and separator are put together in a whirl pattern and stored in the case.
- It also incorporates a variety of safety protection systems such as a gas discharge valve, which helps prevent the battery from exploding by releasing internal gas pressure if it exceeds the design limit.

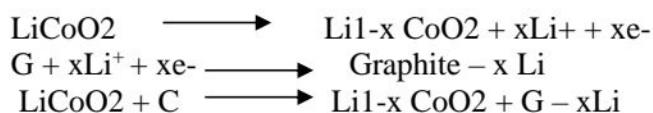
Working:

- The lithium ion battery makes use of lithium cobalt oxide (which has superior cycling properties at high voltages) as the positive electrode and a highly-crystallized specialty carbon as the negative electrode.

- It uses an organic solvent, optimized for the specialty carbon, as the electrolytic fluid.

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- The chemical reactions for charge and discharge are as shown below:



Discharge

- The principle behind the chemical reaction in the lithium ion battery is one where the lithium in the positive electrode lithium cobalt oxide material is ionized during charge, and moves from layer to layer in the negative electrode.
- During discharge, the ions move to the positive electrode and return to the original compound.

Advantages

- High Energy Density
- High Voltage
- No Memory Effect
- Flat Discharge Voltage
- The Functions of the Safety Circuits (typical functions)
- Long shelf life
- Simple storage and transportation
- Environmentally friendly

Disadvantages:

- Limited service life
- Limited discharge current
- High self-discharge
- High maintenance

Uses:

- Cellular phones.
- Portable CD player.
- Note PC
- DVC/DSC/DVD/Portable LCD TV etc.
- MD player.
- Semiconductor-driven audio etc.
- Portable electric vehicles

MODULE - II
CORROSION & METAL FINISHING

Corrosion

Corrosion is defined as natural tendency of metal to undergo destruction or dissolution by chemical or electrochemical reactions.

There are mainly two types of corrosion, they are:

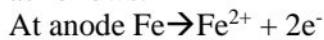
1. Dry Corrosion (or) Chemical corrosion
2. Wet corrosion (or) Electro chemical corrosion

Electrochemical theory of corrosion:

Let us consider a strip of iron and copper in contact with each other in an aqueous medium.

This forms a galvanic cell and flow of electrons takes place between the two metals. Copper acts as cathode.

Metal which acts as anode undergoes corrosion and the other metal which acts as cathode. Electrochemical reactions which occur at anode and cathode are as follows:



At cathode reduction of either H^+ or water takes place and the reactions are as follows:

Case 1: In presence of Oxygen.

- a. Acidic media. $4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$
- b. Basic/Neutral media. $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-$

Case 2: Absence of Oxygen

- a. Acidic media. $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
- b. Basic/Neutral media. $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2 \uparrow$

Ferrous ions formed at anode react with hydroxyl ions formed at cathode to produce the corrosion product which settles between the electrodes. $\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe}(\text{OH})_2$
 $3\text{Fe}(\text{OH})_2 + 1/2\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 \cdot 3\text{H}_2\text{O}$

Rust (Corrosion Product)

Different types of corrosion [Electrochemical or wet corrosion]

1. Differential metal corrosion
2. Differential aeration corrosion
3. Stress corrosion

1.Differential metal corrosion:

This type of corrosion occurs due to the difference in the electrode potential of metals on combining two different metals.

When the two different metals are in contact with each other metal which lies high in electrochemical series acts as anode and undergo corrosion.

Whereas metal which lies in the lower electrochemical series acts as cathode and is unaffected.

- Eg: (i)Steel screws in brass or bronze equipment
(ii)Lead- Tin Solder around copper wire
(iii) Steel pipe connected to Cu plumbing

Explanation:

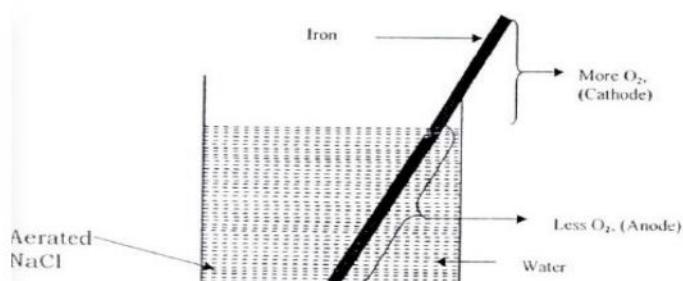
Let us consider iron and copper in contact with each other in a corrosion media. Since the iron lies high in electrochemical series than the copper iron acts as anode and undergoes corrosion protecting the copper.

In order to prevent differential metal corrosion both nut and bolt can be made with the metal.

2 Differential Aeration corrosion: When a metal is exposed to different oxygen or electrolyte concentration it form galvanic cell or oxygen concentration cell. Here part of metal which is exposed to less oxygen concentration acts as anode and undergoes corrosion. The other part of metal which is exposed to higher oxygen concentration acts as cathode and is protected.

There are mainly two types of differential aeration corrosion:

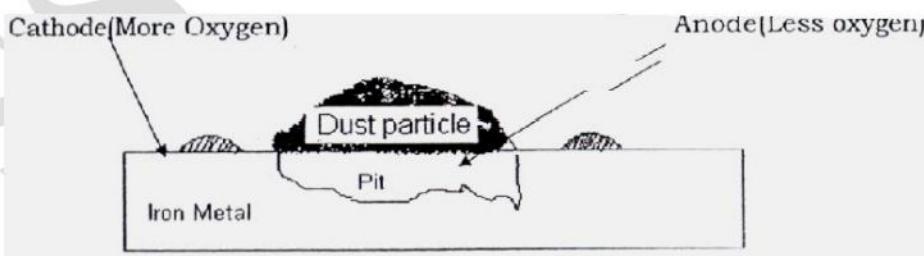
1. Waterline Corrosion



Let us consider iron rod dipped in an electrolyte or water. Part of metal or iron rod con tact with less oxygen concentration acts as anode and undergoes corrosion. Other part of metal above water line which is ion contact with higher oxygen concentration acts as cathode and is unaffected.

Eg: Ship sailing on water, Steel water tank.

2. Pitting Corrosion :



Deposition of impurities like dust, sand, drop of oil or water on metal surface induces pitting corrosion. Part of metal covered by the impurities is in contact with less oxygen concentration compared to other part of metal. Due to this uneven oxygen concentration oxygen concentration cell is formed. The part of metal below the impurity which is in contact with less oxygen concentration acts as anode and undergoes protecting the other part of the metal. Corrosion starts just beneath dust particles resulting in formation of small hole known as

pit. Since this type of corrosion results in formation of pit it is known as pitting corrosion. Once the pit is formed rate of corrosion increases.

Eg: Less aerated areas of machinery.

Factors affecting rate of corrosion:

1. Relative areas of anode and cathode

2. Corrosion product
 3. pH
 4. Temperature
 5. Nature of Metal
 6. Conductivity
1. Relative areas of Anode and Cathode:

Smaller the anodic area larger the cathodic area, rate of corrosion is high. This is because demand of electrons by larger cathodic area can be met only by smaller anodic area by undergoing corrosion.

Eg: Tinning

Large the anodic area, smaller the cathodic rate of corrosion is less. This is because presence of more number of electrons from anodic area cannot be accommodated in smaller cathodic area.

Eg: Galvanisation

2. Nature of Corrosion product:

If the corrosion product formed is highly soluble, porous and unstable. Then, rate of corrosion is very high Eg: It occurs in Fe, Mg, Zn etc.

If corrosion product formed is highly insoluble, non porous and stable rate of corrosion is less. Then it forms a protective layer over the surface of the metal. This protective layer acts as a barrier between metal and corrosive media thereby preventing corrosion.

Eg: Al, Ni, Cr, W, Ti etc.

(According to pilling bed worth rule higher the specific volume lower will be the rate of corrosion.

Specific Volume= Volume of metal oxide / volume of metal

W=3.6 ,Cr=2.0,Ni=1.6, Al=2.6)

3. pH

- Rate of corrosion in acid media is greater compared to basic media. Media.
- Iron undergoes severe corrosion when pH is less than 3 and is more when dissolved oxygen is absent, due to continuous evolution of O₂
- When pH is greater than 10 rate of corrosion decreases rapidly due to formation of protective layer of ferrous hydroxide [Fe(OH)₂] on the surface of metal.
- Thus, formed Fe(OH)₂ acts as a barrier between metal and corrosive media hence, rate of corrosion decreases.
- Between pH 3 and 10 the presence of oxygen is essential for corrosion of iron.

4. Temperature

- Rate of corrosion is directly proportional to temperature. It implies that as temperature increases corrosion rate also increases.
- As there is rise in temperature conduction of aqueous medium increases.
- This results in diffusion of electrode from anode to cathode.
- Hence, rate of corrosion increases with increases in temperature.
- In case of passive metals, rise in temperature decreases passive range and increases rate of corrosion.

5. Nature of Metal:

- Metal which lie high in electrochemical series are more reactive than metals which lie low in electrochemical series.
- Metals which lie high in electrochemical series are more susceptible to undergo corrosion.



- Tendency of metals to undergo corrosion decreases as we go down the series.

Eg: Active metals like Li, K, Zn are more susceptible to corrosion compared to copper, silver, gold and platinum.

- When two dissimilar metals are in contact with each other metals with higher negative potential act anode and the other metal with low negative electrode potential acts as cathode.
- Higher the difference in potential between two metals, the rate of corrosion is high.

Eg: Zinc undergoes more corrosion when it is in contact with copper than it is in contact with iron.

6. Conductivity:

- Presence of conductivity species in corrosive medium increases the corrosive rate.
- Corrosion is an electrochemical phenomenon which involves transfer of electrons.

Rate of wet corrosion is greater than dry corrosion.

Eg: Iron undergoes severe corrosion when it is in contact with marine water than it is in contact with river water or oxygen.

Corrosion Control:

Corrosion can be controlled by following methods:

1. Metallic coating
2. Inorganic coating
3. Cathodic protection

1. Metallic coating:

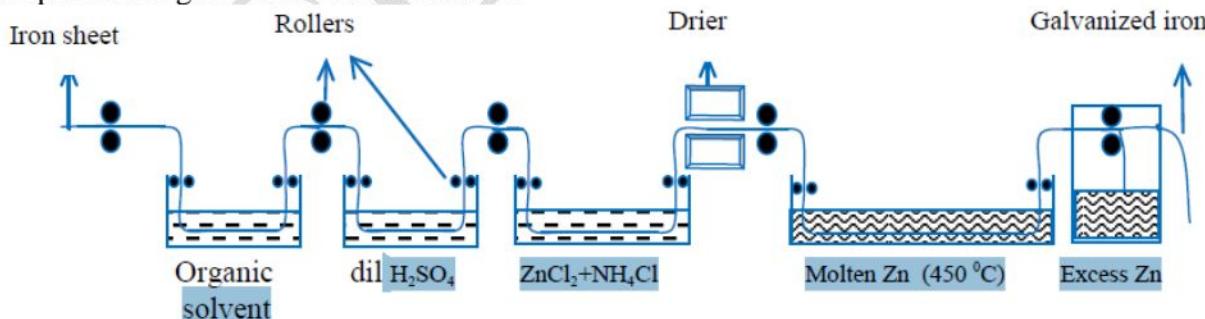
Deposition of metallic layer on the surface of base metal (metal to be protected from corrosion) is known as metallic coating. There are mainly two examples of metallic coating. They are:

1. Galvanization
2. Tinning

1. Galvanization:

- The process of coating of zinc on surface of iron is known as galvanization.
- Galvanization is an example of anodic coating. The process of galvanization can be diagrammatically represented as follows:

The process of galvanization is as follows:



- Article to be galvanized is cleaned with organic solvent to remove oil, grease if present on the surface.
- Rust and other oxides are removed by treating it with dil. H_2SO_4 .
- Finally the cleaned article is dipped in molten zinc containing ammonium chloride [NH_4Cl].
- NH_4Cl prevents oxidation of zinc and acts as an accelerator. Excess of is removed by passing the articles between two rollers. Then the articles are cooled down to room temperature.
- Galvanization is safe and efficient. This is due to the factor according to which rate of corrosion is less if anodic area is large and cathodic area is small.

Applications:

Used in protecting roofing sheets, wires, pipes, nails, bolts, buckets etc.

Used in electrical appliances.

Inorganic Coating:

1. These are also known as non-metallic coatings.
2. Here surface layer of base metal is converted into a compound which forms a barrier between the base metal & corrosive atmosphere by chemical or electrochemical reactions

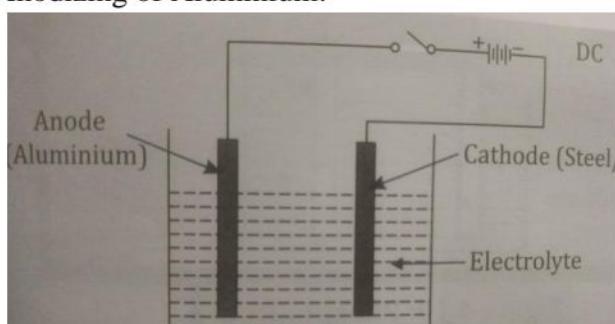
There are two types of inorganic coatings:

- a. Phosphating
- b. Anodising

Anodizing:

The process of increasing thickness of oxide layer on passive metals artificially in acid medium is known as anodizing.

Anodizing of Aluminium:



Aluminium articles to be anodized are degreased thoroughly, washed dried and subjected to anodizing as follows:

Anode- Aluminium

Cathode- Graphite

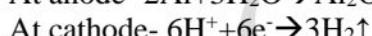
Electrolyte- Sulphuric Acid or chromic acid

Voltage- 40 volts

Temperature- 35° C

Current density- 10-20 mA/cm²

Reactions occurring during anodizing of Aluminium are:



Anodizing of Aluminium is carried by passing DC in acid medium in which the metal is suspended. Oxide layer is formed due to progressive oxidation of metal. This oxide layer acts as a barrier between metal and corrosive environment thereby preventing corrosion of base metal.

The coating found is slightly porous so it is sealed by dipping in hot water. Thickness of film can be controlled by adjusting current and bath solution.

Applications:

Used in window frame, computer hardware and home appliances.

Used in satellites. Due to minimum maintenance used in roofs, curtains, staircase, escalator etc. Used for office partitions, cabins etc.

Cathodic Protection:

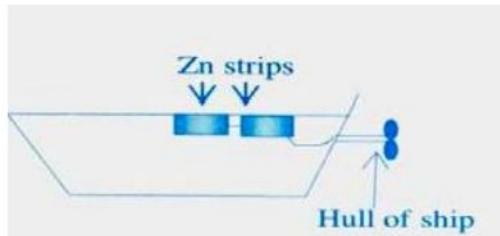
Corrosion of specimen occurs due to flow of electrons from anode to cathode. The technique of protecting a specimen from corrosion by providing electrons from an external source or converting anodic sites to cathodic sites is known as cathodic protection. There are two types of cathodic protection, they are:



1. Sacrificial anodic method
2. Impressed voltage method

1. Sacrificial Anodic Method:

- Here metal to be protected from corrosion is converted into cathode by connecting it to a metal which is anodic to it.
- The base metals are usually Fe, Cu & brass.
- Metals like Zn and Mg which are more active than iron are used to supply electrons to the specimen thereby converting the anodic sites to cathodic sites.
- Since anode undergoes corrosion protecting the specimen is called sacrificial anodic method.
- The sacrificial anodes are replaced by new ones.
- This method is used to protect ships, pipelines etc.



Eg: In case of ship Mg hull is connected to base of the ship which acts as sacrificial anode and prevents corrosion of base of the ship.

Advantages:

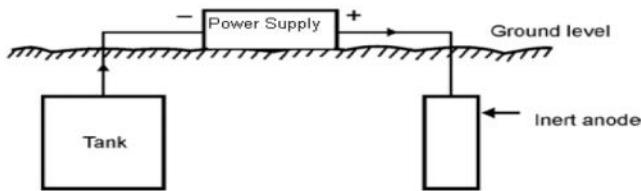
- Low installation cost
- Low maintenance
- Simple method

Disadvantages:

Involves recurring expenditure for replacement of sacrificial anodes.

2. Impressed Voltage Method:

- It is a method of protecting base metal by applying current larger than corrosion current. In this method electrons for protection are supplied from DC power source.
- Metal to be protected is made as cathode by connecting to external power supply as shown in the figure:



- Anode is inert metal like graphite.
- The metal structure being cathode doesn't undergo corrosion.
- Hence, remains unaffected.
- This technique is used to protect water tanks, oil tanks, oil pipelines etc.

Advantages:

- Low maintenance
- One installation can protect large area of metal

Disadvantages:

Impressed current should be uniform or else localized corrosion occurs.

METAL FINISHING

The process carried out to modify surface properties of metals, alloys, plastics etc by depositing a layer of other metal, polymer or forming oxide layer is called Metal Finishing

Metal Finishing is a surface phenomenon

The Technological importance of metal finishing are

- To provide Corrosion resistance
- To give decorative surface
- To provide / improve thermal & electrical conductivity
- To improve hardness
- To impart optical reflectivity
- To impart thermal resistance
- To improve hardness
- To impart wear resistance
- To impart abrasion resistance

Metal finishing is done by

- Electroplating
- Electroless plating
- Hot dipping
- Electro phoretic painting

Electroplating

- Here a metal is deposited on a base metal (metal which takes coating /to be coated)by passing DC through an electrolytic solution containing soluble salts of the metal
- Electroplating consists of a electrolytic cell in which anode & cathode are dipped in an electrolyte
- Cathode always being a base metal

There are 3 important principles governing Electroplating & they are

Polarization

Decomposition potential

Over Voltage

Polarization

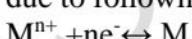
Definition: Polarization is defined as “The decrease in electrode potential due to inadequate supply of metal ions from bulk of the solution to the vicinity of the electrode.”

Explanation: Polarization is related to an electrode in an electrochemical cell. The Electrode potential of a cell is determined by the following Nernst equation

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

Where $[M^{n+}]$ is the concentration of metal ions surrounding the electrode at equilibrium

When current flows, the metal ion concentration in the vicinity of the electrode decreases due to following reaction



As a result of above reaction there will be decrease in electrode potential. When ions from bulk of the solution diffuse towards the electrode equilibrium is reestablished.If diffusion is slow(diffusion of metal ion from bulk of solution to vicinity of electrode) the electrode is said to be polarized & the process is known as polarization

Disadvantages Of Polarization

Polarized galvanic cell develops potential smaller than predicted

In an electrolytic cell, polarization needs to use more negative potential than required

Polarization can be minimized by

Increasing the temperature

Increasing rate of stirring

Addition of de-polarizers such as Nitric acid & Chromic acid



Making electrode surface rough
Using large electrode surface

Decomposition Potential

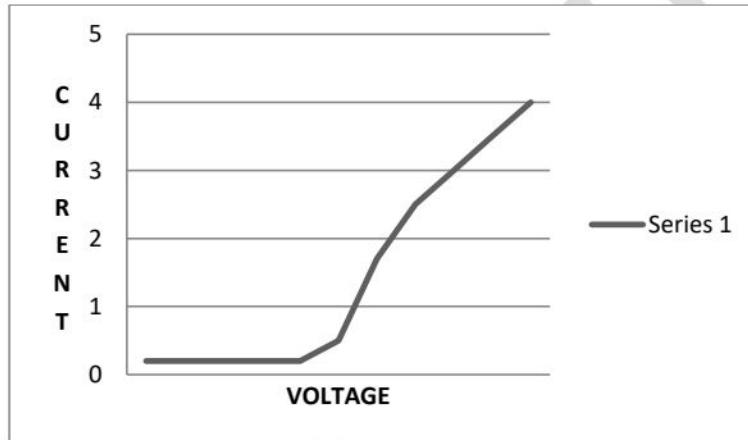
During electrolysis process, the products accumulate on electrode surface causing change in concentration around the electrodes.

This develops a potential which opposes the applied voltage, which is known as Back EMF

Definition: Decomposition Potential is defined as “The minimum external voltage which is applied greater than back emf in order to bring about continuous electrolysis”

Explanation: Let us consider electrolysis of an dilute acid or base using Platinum electrodes

When an voltage is applied, at once electrolysis starts & stops very soon, this is because back emf exceeds applied voltage(due to liberation of H₂ & O₂ at electrodes). Now electrolysis starts only if applied voltage is increased greater than back emf. That additional voltage greater than emf is known as Decomposition Potential. Above explanation can be graphically represented as



OVER VOLTAGE

Definition: “The voltage that has to be applied greater than theoretically determined decomposition potential in order to maintain continuous electrolysis”

Explanation: For carrying out continuous electrolysis process the applied voltage should be greater than back emf. It is observed in few cases that electrolysis does not occur unless potential greater than theoretically determined decomposition potential is applied.

Ex: For electrolysis of dil.Sulphuric acid the required potential is 1.7V, but theoretically determined potential is 1.23V, therefore over voltage is 0.4V

Factors affecting Over Voltage are

Temperature

Current

Electrode potential

Rate of stirring

Chromium Electroplating

Usually in Ni under coating is given for articles before Chromium (Cr) plating Cr plating is done by electrolyte consumption method. There are 2 types of Cr plating, Hard & decorative Cr plating, the process of plating is as follows

Electrode reactions are



	Decorative Chromium	Hard Chromium
Anode	Insoluble anodes like- Pb-Sn coated with PbO ₂	Insoluble anodes like- Pb-Sn coated with PbO ₂
Cathode	Object to be plated	Object to be plated
Bath composition	100:1 Chromic acid & H ₂ SO ₄	100:1 Chromic acid & H ₂ SO ₄
Current density(mA/cm ²)	100-200	215-430
Current efficiency	8-12%	10-15%
p ^H	2-4	2-4
Temperature	45-55°C	43-66°C
Applications	Good decorative finish on automobiles, surgical & optical instruments	Used in industrial & engineering applications

Cr anodes are not used in Cr

electroplating because, Cr anodes passivates strongly in acidic media, Cr anode on dissolution gives rise Cr³⁺ to which leads to black deposits. Cr as high negative electrode potential. Anodic efficiency is 100% whereas cathodic efficiency is 10-20%

Electroless plating

Definition: “The process of depositing a metal on a catalytically active substrate using reducing agent, without using electricity is known as electro less plating”

It can be represented as



Ex: Electrolessplating of Cu, Ni etc.

Advantages of electrolessplating

Use of electricity is eliminated

Semiconductors, insulators, glass & plastic can also be plated

Small parts of machineries can be plated uniformly & no levelers are required

Electroless bath solutions have better throwing power

Electroless coatings are harder

Distinction between Electroplating & Electrolessplating

	Electroplating	Electrolessplating
Driving force	Current	Auto catalytic redox reaction
Anode	Separate anode	Catalytically active surface of substrate

Cathode	Object to be plated	Object to be plated
Reducing agent	Electrons	Chemical agents
Throwing power	Less	High
Applicability	Only conductors	Conductors & non conductors

Electrolessplating Of Copper

The surface to be plated is cleaned to remove oil & grease

If substrate is insulator it is activated by dipping it in SnCl_2 & PdCl_2

Electrolessplating of Cu is as follows

Electrode or Substrate : Catalytically active metal surface

Source of metal: CuSO_4

Reducing agent: HCHO (Formaldehyde)

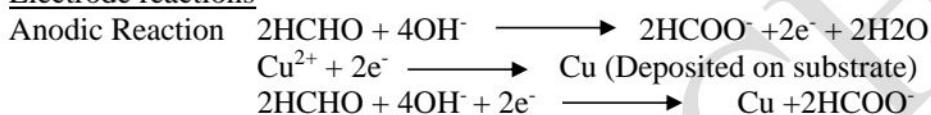
Complexing agent: EDTA

Buffer : NaOH

Temperature: 25°C

p^{H} : 11

Electrode reactions



Applications:

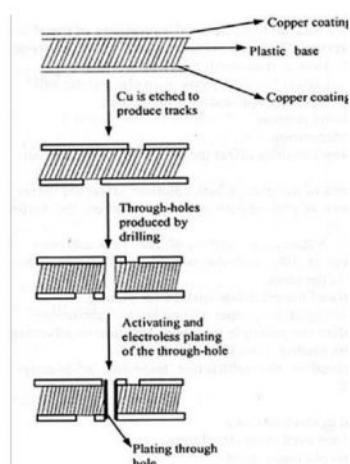
Used in manufacture of PCB's

Used in plating insulators

In producing through hole connections

Manufacture of Double Sided PCB With Cu

- The base object in manufacturing PCB is plastic material/epoxy/GRP
- The catalytically active surface is first coated with copper on both sides of plastic / glass(PCB)
- The circuit/ track is printed using a photoresist & rest of Cu is etched away by ammonia
- More no.of components are packed in small space by making double sided tracks
- The connection between both sides of PCB is made by drilling hole & Electrolessplating of Cu through holes
- Various steps involved are shown diagrammatically as follows



Electroless plating of Nickel :

The metallic surface to be plated is degreased and by using organic solvents or by using hot alkali treatment followed by pickling to remove scales and hardly adhered impurities. Non metallic objects are activated by dipping in SnCl_2 and then PdCl_2

Composition of plating bath :

Electrolyte solution : NiCl_2

Reducing agent : Hypophosphite

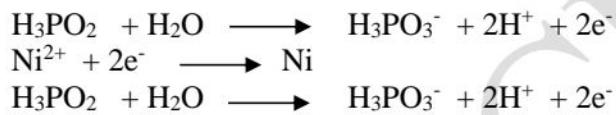
Buffer : Acetate buffer

pH : 4 – 5

Complexing agent : Sodium succinate

Temperature : 45 – 60°C

Cathode : article to be plated (pretreated)



Both the cell reactions takes place on the surface of substrate itself, as there is a liberation of H^+ ions the pH tends to decrease hence to maintain the required pH suitable buffers are used

Module III

Chemical fuels and solar energy

Chemical fuels are defined as “substance which contains Carbon and Hydrogen as its main constituents and produce significant amount of heat and light .



Example:-wood, coal, charcoal, petrol, diesel, kerosene

Classification of fuels.

Fuels are mainly classified into two types :-

1) Based on physical state, These are further classified into:-

a. Solids.

Eg: wood,coal,charcoal,peat,lignite,bituminous etc.

b. Liquids.

Eg: petrol,diesel,kerosene.

c. Gaseous. Eg,LPG, CNG, biogass,etc.

2) Based on occurrence

There are two types:-

- Primary fuels: All naturally occurring fuels are known as primary fuels.
Example:-wood,coal,crude petroleum oil ,natural gas.
- Secondary fuels : The products of primary fuels which can be used as fuels are known as secondary fuels.

Example: charcoal,petrol,diesel,kerosene,LPG,CNG, etc.

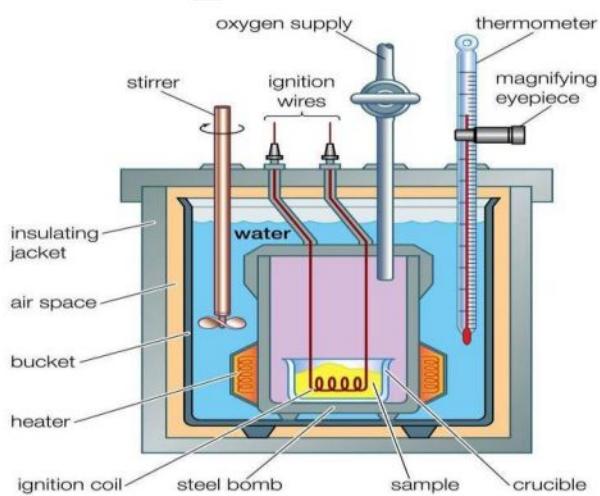
The performance of the fuel is measured by its calorific valueCalorific value. It is defined as “the amount of heat liberated when a unit mass of fuel is completely burnt in excess of air or oxygen.”

These are mainly of two types:-

1. Gross calorific value(GCV): It is defined as “amount of heat liberated when a unit mass of fuel is completely burnt in excess of air or oxygen and the products of combustion are cooled to room temperature.
2. Net calorific value(NCV): It is defined as “amount of heat liberated when a unit mass of fuel is completely burnt in excess of air or oxygen and the products of combustion are let out into atmosphere.

Determination of calorific value of solid or liquid fuel using Bomb Calorimeter

Construction and working



Bomb Calorimeter consists of platinum or ceramic crucible in which fuel sample is placed, Crucible is placed in well insulated stainless steel vessel known as Bomb. Bomb is equipped with oxygen valve and electric ignition system. Bomb is placed in a well insulated copper vessel known as calorimeter, which contains known weight of water, stirrer and thermometer. Initial temperature of water is noted down.Fuel is ignited using electric ignition system and liberated heat is absorbed by the surrounding water.Final temperature is noted down.

Raise in temperature is calculated by knowing mass of fuel sample taken, weight of calorimeter and other accessories. Calorific value can be calculated as follows:-



Observation and calculations; Mass of fuel = m kg

Weight of water taken in calorimeter = w₁ kg

Water equivalent of calorimeter = w₂ kg

Total water equivalent = (w₁ + w₂) kg

Initial temperature = t₁ °C

Final temperature = t₂ °C

Amount of heat(Q) liberated by m kg of fuel = Amount of heat absorbed by water and other accessories

$$GCV = \frac{(t_2 - t_1)(w_1 + w_2) \times 4.187}{m}$$

NCV = GCV – latent heat of condensation/steam

$$NCV = GCV - 0.09 \times \% \text{ of H}_2 \times 587 \times 4.187 \text{ KJ/kg}$$

Knocking of petrol or gasoline

compression ratio increases efficiency of engine also increases.

Beyond certain combustion ratio explosive combustion of fuel air mixture which results in Thermal shock wave.

These waves hit the inner walls of Engine and Piston producing rattling noise known as Knocking.

Thus knocking of petrol is defined as “Production of rattling sound as a result of Explosive combustion of fuel air mixture due to increasing Compression ratio”.

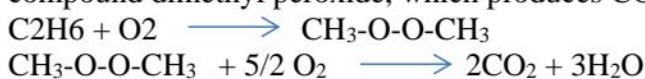
Mechanism of Knocking

Knocking occurs due to explosive combustion of fuel air mixture.

Here chain reaction proceeds at faster rate and produces unstable gasses instead of CO₂ and H₂O. These gasses hit or knock the inner walls of piston or Engine producing a rattling noise known as Knocking.

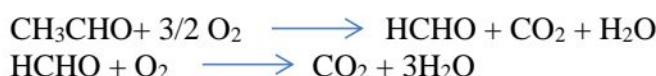
Efficiency of the IC engine increases with the increase in compression ratio, compression ratio is the ratio of the cylinder volume at suction stroke to that of compression stroke. Beyond certain combustion ratio explosive combustion (incomplete combustion) of fuel air mixture occurs which results in production of rattling noise referred to as knocking. Thus knocking of petrol is defined as “Production of rattling sound as a result of Explosive combustion of fuel air mixture beyond a particular compression ratio”.

Mechanism of Knocking : Knocking occurs due to explosive combustion of fuel air mixture. Under normal conditions : when the fuel burns with air or oxygen produces an unstable compound dimethyl peroxide, which produces CO₂ and H₂O



Under Explosive condition : Here chain reaction proceeds at faster rate, the fuel burns with air or oxygen instead of producing CO₂ and H₂O and produces number of gases like formaldehyde, acetaldehyde etc., which hits the walls of the engine and piston producing a rattling noise referred to as knocking





III Effects :

1. Reduces efficiency of the engine
2. Increases power consumption
3. Due to the rattling noise journey becomes unpleasant
4. Damages the mechanical parts of the engine

Antiknocking Agents

Knocking property of petrol can be decreased by adding certain chemical substances known as. Commonly used Antiknocking agents are Tetraethyl lead(TEL) and Tetra methyl lead(TML) and mixed Tetraethylmethyle lead during combustion TEL forms lead and lead oxide(Pb and Pbo) free radicals. These species acts as free radical chain inhibitors and prevent propagation of exposures combustion their by minimizing Knocking. The fuel which doesnot contain lead or leaded components are referred to as unleaded petrol

Power alcohols

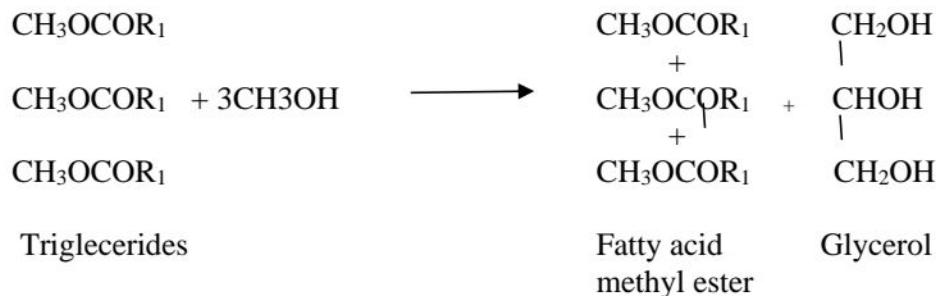
- a) when ethanol is mixed with petrol and is used as fuel is known as power alcohol.
- b) Nearly 25% of ethanol is mixed with petrol to get power alcohol.
- c) Alcohol and petrol are two immiscible liquids and hence blending agents such as C_6H_6 , ether, etc. are added.

Advantages of power alcohols

- a. Octane rating of power alcohol is high.
- b. It has less knocking tendency.
- c. Alcohol promotes more complete combustion.
- d. Power output of alcohol is high compared to gasoline or petrol.
- e. Alcohol present absorbs moisture if in present in petrol.

Bio Diesel

It is a source of energy obtained from renewable sources of plant origin. It is produced from vegetable oil (soybean, corn, sunflower, safflower, cotton seeds, rice bran etc.,). It can be used as an alternative fuel to diesel in automobiles. The oils are triglyceride esters of fatty acids. Biodiesel is obtained from transesterification of these oils with Metanol in presence of NaOH & a catalyst at 60°C . Transesterification is alcoholysis of the triglyceride oil in the presence of a base. The result mixture of monoalkyl esters of fatty acids is referred to as biodiesel. Biodiesel is obtained as follows.



Where $R_1, R_2 & R_3$ are long chain fatty acids. Thus obtained biodiesel is separated from glycerol.

Advantages

It burns more efficiently than petroleum diesel

Cetane number of biodiesel is greater than normal diesel

It is 100% free from Sulphur compounds

40-50% reduction in CO_2 emission & 60% reduction in particulate matter , CO

Applications

It can be used in normal engine without much modification in engine hardware.

Addition of 20% of biodiesel (B20) to petroleum diesel brings down emission of pollutants to a greater extent

FUEL CELLS

These are galvanic cells in which electrical energy is obtained by the combustion of fuels. Here, the fuels are supplied from outside and do not form integral part of the cell. These do not store energy. Electrical energy can be obtained continuously as long as the fuels are supplied and the products are removed simultaneously. In these aspects fuel cells differ from conventional electrochemical cells

Advantages of fuel cells:

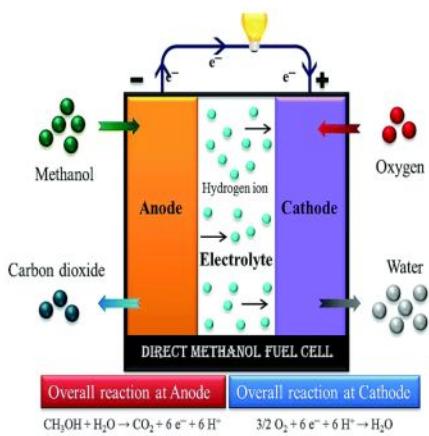
- Power output is high.
- Do not pollute the atmosphere
- Electrical energy can be obtained continuously

Difference between conventional batteries and fuel cells



	Conventional batteries	Fuel cells
1	Secondary batteries are rechargeable	Fuel cells are not rechargeable
2	Anodic, Cathodic components, electrolyte, separator forms the integrals parts of the batteries	There's a continuous movement of fuel and oxidant in and out of the cell
3		
4		

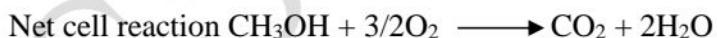
Methanol – oxygen fuel cell



- It consists of anodic and cathodic compartments.
- Both the compartments contain platinum electrode.
- Methanol containing H_2SO_4 is passed through anodic compartment.
- Oxygen is passed through cathodic compartment.
- Electrolyte consists of sulphuric acid.
- A membrane is provided which prevents the diffusion of methanol into the cathode.

Reactions:

- At anode: $\text{CH}_3\text{OH} + \text{H}_2\text{O} \longrightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^-$
- At cathode: $\frac{3}{2}\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \longrightarrow 3\text{H}_2\text{O}$



Advantages:

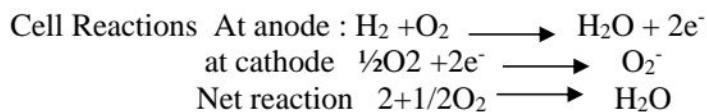
- Methanol has low carbon content
- The OH^- group is easily oxidisable
- Methanol is highly soluble in water and cheaply available

Uses: in military applications.

Solid oxide fuel cells (SOFCs)

These cells operate at temperature 650 to 1000°C anode is porous electrode coated with Co, and ZrO₂, cathode contains LaMnO₃ doped with Stroncium, electrolyte used is solid oxide such as ZrO₂ and Y₂O₃, the fuel used to H₂ or CO.

Working :



Applications: used where large amount of heat is required

Solar Energy

Photovoltaic Cells

Light is composed of tiny packets of energy called photons. Photons may have different masses and carry varying amounts of energy. When a photon strikes an atom, it can interact with the electrons, the photon's energy (E =hv) is absorbed and exited the electron from the metal surface. The excited electrons flow through the external circuit against the current and produce electrical energy. The metal surface is used for absorption of solar radiation is called solar cell or photovoltaic cell.

A solar cell is a semiconductor device that converts photons from the sun into electricity.

Importance of photovoltaic cells:

Solar energy, being unlimited and renewable source.

PV cells do not require recharging and produce electrical energy as long as sunlight is available.

During conversion of solar energy into electrical energy does not pose any pollution problem. Eco friendly.

There is no moving parts in PV cells, hence there is no problem of wear and tear.

PV cells generate electrical energy at ambient temperature.

Photovoltaic cell can also used as roof integrated systems, preventing over heating in the summer.

The raw material silicon used for PV cells is abundantly available.

These are effectively used in transportation systems.

They can be conveniently used for all domestic electrical appliances

Used in traffic lightings, calculators, watches

Used in electronically operated agricultural machines and has enormous application in space industry as it is the sole provider of energy for the spacecraft and is now also being used for



producing solar sails, another efficient spacecraft

Construction & Working of PV cell

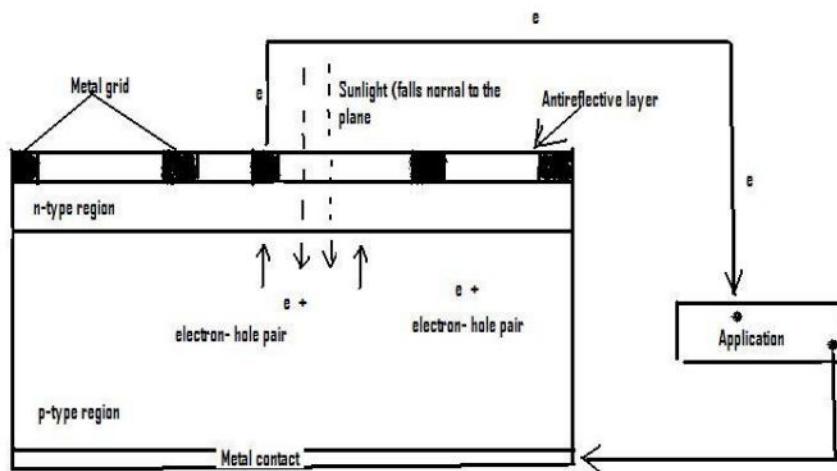
Photovoltaic cells consists of a p-n junction diode made from silicon semiconductor. It has two electrical contacts; one is a metallic grid over n-type and second is a layer of silver metal at the back of p-type semiconductor. An antireflective layer (silicon nitride or TiO_2) is coated in between the metal grids to prevent reflection of solar light. When sunlight with their photons carrying energy $E = h\nu$ falls on p-n diode, an electron –hole pair is generated

These ejected electrons drift & get collected at n-side of p-n junction. Since p-n junction allows only one way movement of electrons, these electrons must flow through the external circuit to recombine with holes present in p-side of semiconductor.

This movement of electrons from n-side to p side through the external circuit generates an electric current.

The solar cell is a very small in size, regardless of size, a typical silicon PV cell produces about 0.5 – 0.6 volt DC.

The current out put of a PV cell depends on its efficiency and size, and in proportional the intensity of sunlight striking the surface of the cell.



Advantages Of PV Cells

They are Eco-friendly.

They do not corrode

They do not contain any moving parts

Recharging is not required

Its economical

Disadvantages

Not available during night. (Complicated to store the energy)

Very expensive and installation cost is very high.

PV cells generate only DC current.

Unavailable during monsoon.

Usage of cadmium in certain types of cells

Production of Solar grade silicon by Union Carbide Process

Solar Grade Si is obtained by 2 steps I Manufacture of Metallurgical Grade Si

II Conversion Of Metallurgical Grade Si in Solar Grade Si

Step I: Manufacture of Metallurgical Grade Si

Silica(SiO_2) is reduced to silicon (Si) by heating it with carbon in an electric arc furnace and heated to $1500\text{-}2000^\circ\text{C}$.



Silicon obtained above is treated with air and fresh silica as a flux to remove the impurities Al, Mg and Ca



Oxides of Al, Mg and Ca form insoluble slag with excess of silica which is separated from molten silica. And silica obtained above is called metallurgical grade Si (98 %)

StepII: Conversion Of Metallurgical Grade Si in Solar Grade Si Solar grade is obtained in following steps

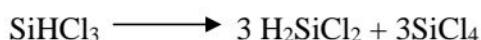
1. Metallurgical grade silicon is refined by heating it with anhydrous HCl at 300°C to obtain trichlorosilane and tetrachlorosilane



2. Trichlorosilane is separated by distillation and tetrachlorosilane is converted into trichlorosilane by hydrogenating in a reactorat 1000°C

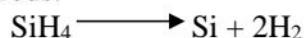


3. Trichlorosilane is converted into silane by passing through fixed bed columns containing quaternary ammonium ion exchange resin as catalyst. Silane obtained in each step is removed by distillation.



Tetrachlorsilane and trichlorosilane obtained in the above steps are again passed through reactor and fixed bed columns respectively and finally converted to silane.

Pyrolysis: Silane obtained in the above step is subjected to pyrolysis in a reactor at high temperature. In pyrolysis reactor, pure silicon rods are used for heating . Si formed by decomposition of silane gets deposited over these pure Si rods.



Si thus obtained is known as Solar Grade Silicon & can be further purified by zone refining.