

1.6 BATTERY TECHNOLOGY

1.6.1 Introduction

Can you imagine a world without batteries? The clock on your wall requires a battery for it to work. The watch on your wrist goes on a battery. The motor vehicle needs a battery for it to start and take you to your destination. Battery is the backbone of UPS to run your computer without interruption. After a days work, if you pick-up the remote control of the television, it is again the battery that helps you to change channels of the T.V. Cameras, laptop computers, cellular phones, key chain laser, heart pacemaker and children toys – they all require batteries. Batteries are used for so many different purposes and different applications require batteries with different properties. The battery required to start a car must be capable of delivering a large electrical current for a short period of time. The battery that powers a cardiac pacemaker must be small, rugged, leak proof, compact and capable of delivering a steady current for an extended period of time. In UPS systems, longer and consistent backup is needed. Batteries for hearing aids must be above all tiny. Batteries for torpedoes and submarines must be stable during storage and give high power for short times & certainly rechargeable. For a lap-top computer, a battery in the form of a flexible sheet distributed around the case is much preferred. Batteries remain an enormous industry with a turnover of billions of pounds worldwide.

1.6.2 Classification of commercial cells

Primary Cells: They are galvanic cells which produce electricity from chemicals that are sealed into it when it is made. This type of cells cannot be recharged as the cell reaction cannot be reversed efficiently by recharging. Once the cell reaction has reached equilibrium the cell must be discarded. No more electricity is generated and we say the battery is ‘dead’. These are also known as ‘throw – away’ batteries or irreversible batteries.

Eg: Dry cell, Lithium copper sulfide cell

Secondary cells: A secondary cell is rechargeable by passing current through it. In the charging process, an external source of electricity reverses the spontaneous cell reaction and restores a non- equilibrium mixture of reactants. After charging, the cell can be used for supplying current when required, as the reaction sinks toward equilibrium again. Thus as the secondary cell can be used through a large number of cycles of discharging and charging. Such cells are also known as rechargeable cells, storage cells, or accumulators.

Eg. Lead-acid batteries, Nickel-cadmium cell, Lithium- ion battery

1.6.2.1 Requirements of Primary Battery:

- Compact, lightweight and must be fabricated from easily available raw materials.
- Economic and have benign environmental properties
- Should have a high energy density, longer shelf life
- Provide constant voltage and should have a long discharge period

1.6.2.2 Requirements of Secondary Battery

- Long shelf-life in both charged & discharged conditions
- Longer cycle life and design life
- High power to weight ratio
- Short time for a recharge.
- High voltage & high energy density

1.6.2.3 Differences between Primary and Secondary batteries

Primary Batteries	Secondary Batteries
1. Cell reaction is irreversible	Cell reaction is reversible
2. They must be discarded after its active elements have been consumed	They may be recharged a number of times from an external d.c. source during its useful life
3. Have a relatively short shelf life	Have a very long shelf life
4. Function only as galvanic cells	Function as galvanic cells during discharge as & as electrolytic cells during the charging process.
5. They cannot be used as energy storage devices	They can be used as energy storage devices (e.g. solar/ thermal energy converted to electrical energy)
6. They cannot be recharged	They can be recharged.
e.g. Dry cell, Li-MnO ₂ battery	e.g. Lead acid battery, Ni-cd battery

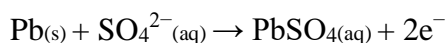
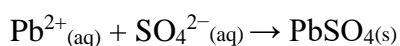
1.6.3 Lead Storage Battery (Lead Accumulator or Car Battery or The acid battery)

Construction: The electrodes are lead grids to maximize its surface area. The anode grid is filled with finely divided spongy lead (Pb) and the cathode grid is packed with lead dioxide (PbO₂). Both electrodes are submerged in a sulfuric acid solution (H₂SO₄) having a specific

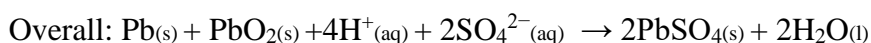
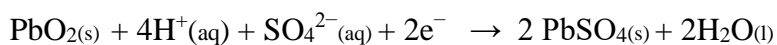
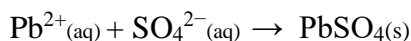
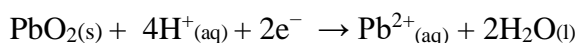
gravity of about 1.25 that acts as the electrolyte. Anode and cathode grids are separated by insulators like strips of wood, rubber or glass fiber. In car batteries, six cells are connected in series (anode to cathode) to produce a 12-volt battery. The battery is encased in a plastic container or hard vulcanized rubber vessel. The cell doesn't need to have a separate anode and cathode compartments because the oxidizing and reducing agents are both solids (PbO₂ & Pb) that are kept from coming in contact by the presence of insulating spacers between the grids. Both anode and cathode are immersed in a common electrolyte (i.e. cell without liquid junction). This is an example of a 'wet cell', because the electrolyte is an aqueous solution of sulphuric acid. The lead acid battery is very widely manufactured – 300 million units are made each year.

Working: Electrode reactions during discharging:

At the anode:



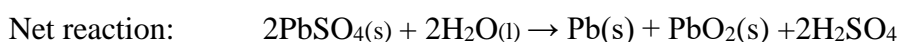
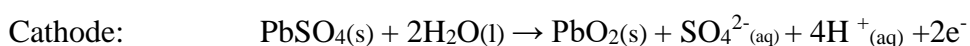
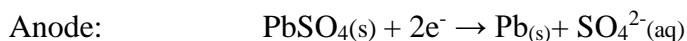
At the cathode:



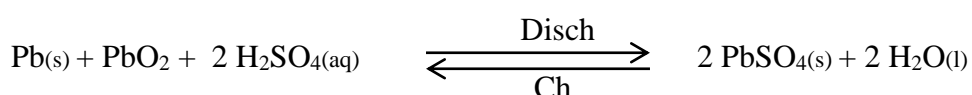
Explanation: At the anode, lead atoms lose two electrons (e⁻) and become positively charged lead ions (Pb²⁺). The lead ions combine with the sulfate ions (SO₄²⁻) in the sulfuric acid solution to produce lead sulfate (PbSO₄). At the cathode, lead dioxide gains electrons, releasing oxygen, which attaches to hydrogen ions (H⁺) to produce water (H₂O (l)) and lead ions. The lead ions react with sulfate ions to produce lead sulfate. As this reaction progresses, the flow of electrons creates an electric current. Lead sulfate adheres on each electrode and water increases. The concentration of sulfuric acid decreases and the amount of lead and lead dioxide decrease. When the reactants are depleted, the battery stops producing electricity. The reaction can be reversed by recharging the battery & the PbSO₄ formed during discharge remains adhered on

each electrode and is available at the site during recharging. The nominal voltage of each cell is about 2.1 V. The lead storage battery is designed to operate reversibly, so that it can be used for the storage of electrical energy. They are called storage batteries because their essential function is to store electrical energy. It is used to store energy in chemical form.

Reactions during Charging:



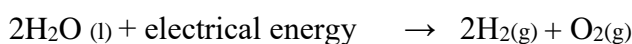
Recharging is possible because PbSO_4 formed during discharge adheres to the electrodes. By attaching an external power source to a battery (>2 volts), a current runs through the poles in the opposite direction from normal discharge. This changes the lead sulfate and water back into the original reactants, lead dioxide and sulfuric acid, i.e. the electrodes return to their former composition and the sulfuric acid is regenerated. Charging, therefore, produces a gradual increase in the sulfuric acid concentration. Since the level of charge on a storage battery is related to sulfuric acid concentration, the specific gravity of the H_2SO_4 solution is a measure of the operational condition of a battery. A charged battery at room temperature with its electrolyte at normal concentration supplies a potential difference of 2.1 to 2.2 V. The complete reaction cycle of a lead acid storage battery is as follows.



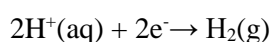
In an automobile, the energy necessary for recharging the battery is provided by the generator driven by the engine. As the external source forces electrons from one electrode to another, the PbSO_4 is converted to Pb at one electrode & to PbO_2 at the other.

Overcharging:

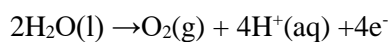
Electrolysis of water: The net reaction can be summarized by the equation.



No gases will be liberated on charging as long as lead ions are present in solution. If the electrolysis is permitted to proceed further, hydrogen gas is formed at the cathode and oxygen gas is evolved at the anode. The hydrogen ions are discharged at the cathode through the reaction



Sulphate ions are resistant to oxidation and are not discharged at the cathode. Water is oxidized at the anode in preference to SO_4^{2-}



Consequences: (i) Excessive charging may reduce the acid level and may damage the exposed electrode grids (ii) In extreme cases, there will be dangerous high-pressure build-up that can lead to a serious risk of explosion. In more normal circumstances, the older version of the battery needs to be ‘topped up’ from time to time.

Recent years have seen the introduction of “maintenance – free batteries” without a gas – release vent. Here the gassing is controlled by careful choice of the composition of the lead alloys used i.e. by using a Pb-Ca (0.1 %) as the anode which inhibits the electrolysis of water. Alternatively, some modern batteries contain a catalyst (e.g. a mixture of 98% ceria (cerium oxide) & 2% platinum) that combines the hydrogen and oxygen produced during discharge back into the water. Thus the battery retains its potency and requires no maintenance. Such batteries are sealed as there is no need to add water and this sealing prevents leakage of cell materials.

Applications: The many battery designs available for a wide variety of uses can be classified into three main categories. (a) Automotive (b) Industrial & (c) Consumer batteries.

The automotive type is used in cars and trucks, to provide a short burst of power for starting the engine. It is incorporated as an essential accessory into the starting circuit of internal combustion engines for starting, lighting & ignition (SLI). Units normally have nominal voltages of 12 V for LMVS and 24 V for HGVS. It is still playing a major role in transportation, powering literally millions of ICES in automobiles. The industrial batteries are used for heavy–duty applications such as motive and standby power. This class of batteries is used to operate electric trucks, submarines and mine locomotives. They also provide power for the air conditioning and lighting systems. It is used in the stationary back–up power applications such as telecommunication systems, because, the telephone network will continue to operate even in the event of a mains power failure. Such batteries are kept in hospital operating theaters, railway signal centres and other places where a power failure might be disastrous and is used to supply electrical power during emergencies. The consumer batteries are used in a emergency lighting systems, security and alarm systems, public address systems, power tools, UPS in computers, and small engine starting including electronic vehicles.

Advantages:

- A lead storage battery is highly efficient. The voltage efficiency of the cell is defined as follows.
- Voltage efficiency = $\frac{\text{average voltage during discharge}}{\text{average voltage during charge}}$

- The voltage efficiency of the lead – acid cell is about 80 %.
- The near reversibility is a consequence of the faster rate of the chemical reactions in the cell i.e. anode oxidizes easily and cathode reduces easily leading to an overall reaction with a high negative free energy change.
- A lead – acid battery provides a good service for several years. The number of recharges possible range from 300 to 1500, depending on the battery's design and conditions. The sealed lead-acid batteries can withstand up to 2000 – recharging. Time required for recharging is relatively low i.e. about 2-8 hours.
- The battery has low internal self – discharge.
- A typical car battery provides a voltage of 12 V. This is not a large voltage, but the battery can provide a large current. E.g. over 10 A, without being destroyed.

Disadvantages:

- If left unused in partially charged condition, it can be ruined in a short time by nucleation and the growth of relatively large PbSO_4 crystals, which are not easily reduced or oxidized by the charging current. This disaster is known as 'sulfation'.
- The lead acid battery has low energy storage to weight ratio i.e. its chief disadvantages is its great weight.(energy density $\sim 35 \text{ wh / kg}$)
- The cell potential decreases with a decrease in concentration of sulfuric acid. During the discharge process sulfuric acid is consumed and water is produced. So the solution of sulfuric acid in the cell becomes less concentrated. The state of charge of the cell can be judged by the concentration of sulfuric acid in the liquid and this is usually done with a simple device to measure the density of the liquid. The density of a healthy, fully charged battery is $\geq 1.25 \text{ g/mL}$.
- The battery is not efficient at a lower temperature. For a battery to function properly, the electrolyte must be fully conducting. There will be an increase in the viscosity of the electrolyte due to a decrease in the temperature. This leads to a decrease in the cell potential.
- Overcharging may damage the exposed electrodes and may also lead to an explosion in extreme cases. Sulfuric acid is highly corrosive liquid. In the event of an explosion, the electrolyte is sprayed on to the individual who is working on the battery. Therefore, safety goggles must be worn when working with these batteries.
- Lead is toxic and hence environmental & health problems arise due to careless disposal by consumers.

- The corrosion of the lead grid at the lead dioxide electrode is one of the primary causes of lead acid battery failure.

1.6.4 Nickel-Cadmium Cell

Construction: NiCad cell consists of a nickel wire gauze electrode grids. The anode grid consists of spongy cadmium metal and the cathode grid contains the nicked (III) compound NiO(OH) . The electrolyte is a concentrated solution of KOH . It is the electrolyte of choice because of its compatibility with the various electrodes, good conductivity and low freezing point temperature (about -30°C). Anode and cathode are separated by a very thin separator. The contents are encased as a sealed unit in a steel case.

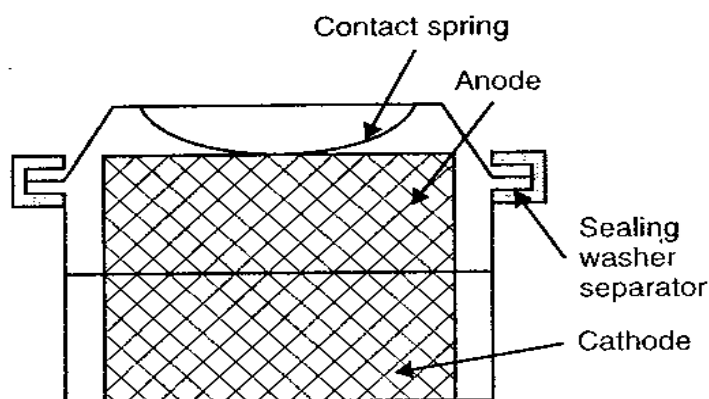
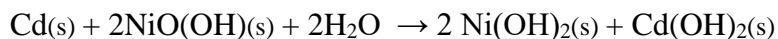
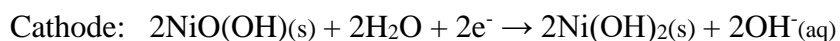
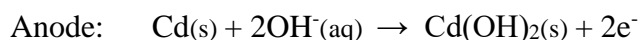


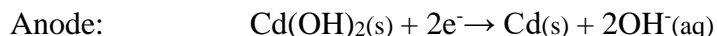
Figure 1.6.4 Schematic representation of NiCad cell

Working:

Discharging reactions

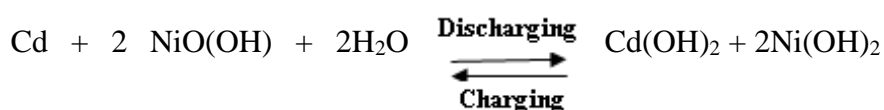


Charging reactions:



Explanation: At anode cadmium metal undergoes oxidation from 0 to +2, leaving behind two electrons for every atom oxidized, as the cell discharges. At cathode nickel is reduced from the +3 oxidation state (in nickel oxide hydroxide) to +2 (in nickel hydroxide). Note that OH^- is not used up as the cell is discharged. Therefore, there is no voltage drop through most of the useful

life of the battery as it discharges. The net reaction can take place until the active materials are exhausted. During charging process, the cadmium hydroxide is re-converted into cadmium and the nickelous hydroxide is reconverted to nickel oxide hydroxide. The overall chemical reaction of the Ni-Cd system may be represented as



The cell must be recharged by applying the correct dc charging voltage.

Applications: Nicad cells are available in standard sizes (AA, D, C, F etc.) for use in flash lights, photoflash units and portable electronic equipment such as radios, micro tape recorders, calculators, cordless phones, electronic shavers, drills & garden tools. It is also used in emergency lighting systems, alarm systems, personal audio equipment (walkman type cassette players), kitchen appliances and other battery powered small tools, toys & games.

Advantages:

- Ni-cad batteries can be recharged many times because the solid products of the electrode reactions adhere to the surface of the electrodes. Normally this battery can withstand up to 3000 – recharging (longer cycle life)
- They maintain nearly constant voltage level throughout their discharge. Note that there is no change in the electrolyte composition during the operation.
- It can be left unused for long periods of time at any state of charge without any appreciable damage (i.e. long shelf life).
- It can be encased as a sealed unit like the dry cell because gassing will not occur during nominal discharging or recharging.
- They possess a longer design life. It can be extended upto 30 years or more if maintained.
- They exhibit good performance ability at low temperatures.
- They can be used to produce large instantaneous currents as high as 1000-8000 A for one second.

Disadvantages:

- It poses an environmental pollution hazard due to careless disposal by consumers and produces health problems (decreases range from asthma to cancer) due to higher toxicity of metallic cadmium than lead.
- Cadmium is a heavy metal and its use increases the weight of batteries, particularly in larger versions. The energy density is approximately 40 Wh/kg.

- Cost of cadmium metal and hence the cost of construction of NiCad batteries is high. The overall capital cost of these batteries is roughly higher than that of lead storage batteries.
- The KOH electrolyte used is a corrosive hazardous chemical. It is a poison and if ingested attacks the throat and stomach linings. Eye contact can result in severe burns and blindness. Protective clothing and face shields or goggles should be worn while performing maintenance work.

1.6.5 Lithium ion cells

Lithium metal cannot be used safely in secondary batteries. Hence, various lithium compounds have been made, which are used in rechargeable batteries, commonly known as Lithium –Ion Cells. In these type of batteries, a lithiated metal oxide such as LiCoO_2 , LiV_2O_5 , LiMn_2O_4 etc is inserted into the cathode which consists of a layered graphite crystal. The electrolyte is normally LiPF_6 , but LiBF_4 can also be used as LiPF_6 is not corrosion resistant.

Construction:

The anode is a lithium-carbide intercalate (Li_xC_6). The cathode is a transition metal oxide MO_2 of variable oxidation state (MnO_2 , CoO_2 , NiO_2) which can intercalate lithium usually cobalt dioxide, CoO_2 is used. The electrolyte is usually inert polar dry ether or carbonate (diethyl carbonate or propylene carbonate), in which a conductivity salt such as LiPF_6 or LiBF_4 is dissolved.

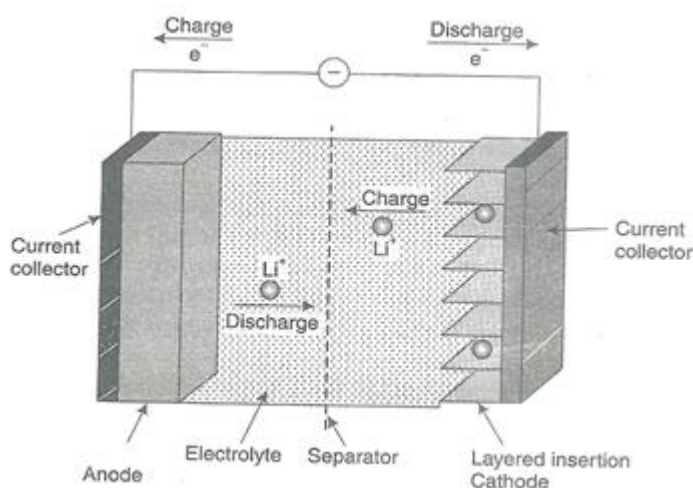


Figure 1.6.5 Schematic diagram of Rechargeable lithium ion battery

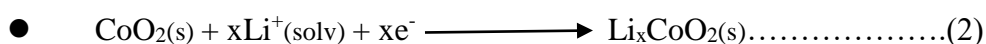
Working: Graphite has a layered structure and its electrochemically reduced in an aprotic organic electrolyte containing lithium salts and lithium is intercalated (or doped) between the layers of graphite to form Lithium-Graphite intercalated compound (GIC). Li-GIC undergoes oxidation leaving an electron.

At anode:

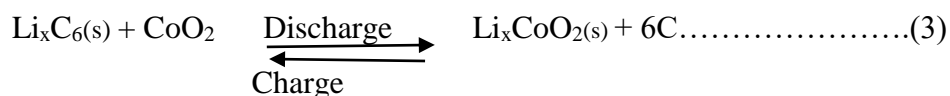


When a negative electrode is discharged, lithium is deintercalated (undoped) from lithiated graphite and lithium ions dissolve into the electrolyte. The lithium content in the LiCoO_2 electrode reversibly changes during charge and discharge as indicated in the following equation:

At cathode:



Net cell reaction:



Explanations: It is called as a lithium ion battery to emphasise that it contains no lithium metal. Both the electrodes are intercalation compounds. The electrode on the left serves as the anode when the cell discharges. It is a special intercalation compound consisting of a graphite host into which lithium ions have been electrochemically inserted between the carbon atom layers. The lithiated graphite is written as Li_xC_6 . During the discharge, the lithium ions are extracted by the half-reaction (1). The electrode that serves as cathode during discharge is normally cobalt dioxide. The reduction half reaction is cathode during discharge is normally cobalt dioxide. The reduction half reaction shown in eq.(2), where cobalt undergoes reduction from IV to III oxidation state. The overall reaction is shown in eq.(3). During discharge the Li^+ ions spontaneously migrate from the lithium graphite anode to the CoO_2 cathode enabling current to flow through the external circuit. When charged, cobalt ions are oxidized and lithium ions migrate into the graphite, when discharging the battery delivers energy to the external load and when charging it receives energy from a d.c. power source. The electrode that acts as an anode, during discharging becomes a cathode when its charging.

Applications:

- Lithium-ion batteries are most commonly used in applications where one or more of the advantages (size, weight or energy) outweigh the additional cost, such as mobile telephones and mobile computing devices.
- Lithium-ion-polymer batteries are used when the battery design matters in a particular application as different designs are possible (Cylindrical, jelly-roll design, flat rectangular).
- It is used in current-generation laptops, cellular phones, video-recorders.
- It is also used in portable CD players, televisions and implantable medical devices.

Advantages:

- Lithium-ion batteries were designed to overcome the safety problems associated with the highly reactive properties of Lithium metal.
- Long cycle life (400-1200 cycles).
- They are smaller, lighter and provide greater energy density than either nickel-cadmium or nickel-metal-hydride batteries
- They can be operated in a wide temperature range and can be recharged before they are fully charged.
- Typically designed to be recharged in the device rather than in an external charger.
- The average voltage of a Li-ion battery is equivalent to three Ni-Cd cells.

Disadvantages:

- Poor charge retention.
- The self discharge rate is about 10% per month.
- Its prices are high compared to other types of cells commonly used.

1.7 Fuel cells

A fuel cell is a galvanic cell of a special type in which chemical energy contained in a fuel – oxidant system is converted directly into electrical energy in a continuous electrochemical process. It is an energy conversion device or electricity producer. The fuel cell has two electrodes and an electrolyte like a primary cell. The reactants (i.e. fuel + oxidant) are constantly supplied from outside and the products are removed at the same rate as they are formed.

Cell: Fuel/ electrode/electrolyte/electrode/oxidant.

Anode: Fuel + oxygen ----->Oxidation products+ ne-

Cathode: Oxidant + ne⁻ ----->Reduction products

A fuel cell consists of fuel, electrodes, electrolyte, & oxidant. Fuel undergoes oxidation at the anode and oxidant gets reduced at the cathode. The cell can produce current as long as the reactants are supplied. Most fuel cells produce low voltages, commonly less than one volt, so a number of them are connected in series in “fuel batteries.”

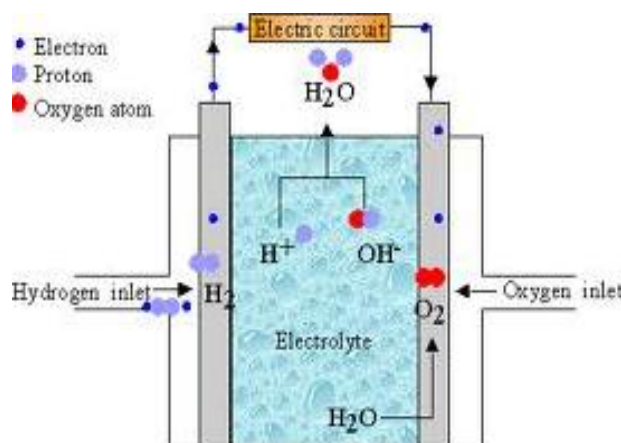


Figure 1.7 Fuel cell

Eg:- $\text{H}_2\text{-O}_2$ fuel cell, $\text{CH}_3\text{OH-O}_2$ fuel cell, Solid-oxide fuel cell, Molten carbonate fuel cell

1.7.1 Advantages of fuel cells

- High fuel to electricity conversion efficiency of 70-75 % while a thermal power plant converts 35-40% chemical energy of coal into electrical energy.
- Fuel cell products do not cause pollution problems such as noise pollution, chemical pollution and thermal pollution normally associated with conversional power plants.
- Fuel cell power plants can be located near the point of use electricity such as on an urban location, rather than at a remote place. So transmission and distribution loss (~30%) could be avoided.
- A fuel cell will produce a steady electric current as long as fresh reactants are available.

1.7.2 Classification of fuel cells

S. No.	Fuel cell type	Electrolyte used
1	Polymer electrolyte	Polymer membrane
2	Direct methanol	Polymer membrane
3.	Alkaline	Potassium hydroxide
4.	Phosphoric acid	Phosphoric acid
5.	Molten carbonate	Lithium/potassium carbonate
6.	Solid oxide	Yttria stabilized zirconia

1.7.3 Alkaline fuel cell (AFC)

Construction: Both electrodes are made up of porous carbon impregnated with finely-divided platinum. Potassium hydroxide is used as electrolyte is placed in the central compartment. The hydrogen gas is continuously supplied at the anode and pure oxygen gas is continuously supplied at the cathode from an external reservoir. The cell operates at about 80 °C and the

normal voltage is 1.10 V. At the anode, hydrogen is oxidized to the H^+ ions, which are neutralized by the OH^- ions of the electrolyte, forming water and electrons are released. At the cathode, oxygen and water take electrons to form hydroxide ions. The overall reaction is equivalent to the combustion of hydrogen. The only product discharge by the cell is water vapor that escapes through the exhaust point. Note that the gases H_2 and O_2 diffuse into the electrode pores and so does the electrolyte solution.

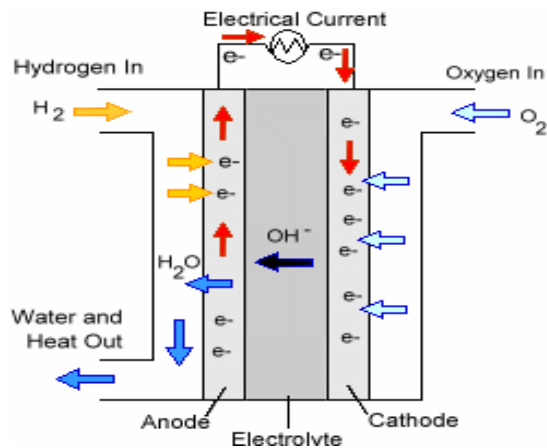
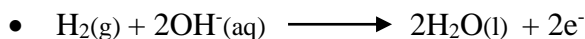


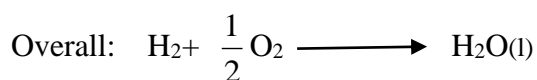
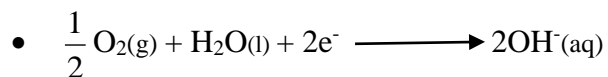
Figure 1.7.3 AFC

Working:

At Anode:



At Cathode:



Advantages: Desirable attributes of the AFC include its excellent performance on hydrogen (H_2) and oxygen (O_2) compared to other candidate fuel cells due to its active O_2 electrode kinetics and its flexibility to use a wide range of electro-catalysts.

Disadvantages:

- The sensitivity of the electrolyte to CO_2 requires the use of highly pure oxidant and fuel.
- As a consequence, the use of a reformer would require a highly effective CO and CO_2 removal system.

- If ambient air is used as the oxidant, the CO₂ in the air must be removed. While this is technically not challenging, it has a significant impact on the size and cost of the system.

Applications: AFC is widely used in US space programs to produce electrical energy and water onboard spacecraft.

1.7.4 Proton exchange membrane fuel cell (PEMFC)

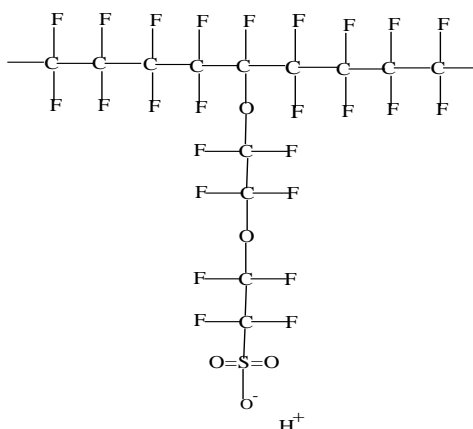
Polymer electrolyte membrane fuel cells – also called proton exchange membrane fuel cells – deliver high power density and offer the advantages of low weight and volume, compared to other fuel cells. PEM fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst. They need only hydrogen, oxygen from the air, and water to operate and do not require corrosive fluids like some fuel cells. Polymer electrolyte membrane fuel cells operate at relatively low temperatures, around 80 °C (176 °F).

Low temperature operation allows them to start quickly (less warm-up time) and results in less wear on system components, resulting in better durability. However, it requires that a noble-metal catalyst (typically platinum) be used to separate the hydrogen's electrons and protons, adding to system cost. The platinum catalyst is also extremely sensitive to CO poisoning, making it necessary to employ an additional reaction to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel. This also adds cost. Developers are currently exploring Pt/Ru catalysts that are more resistant to CO.

Role of Proton conducting membranes:

- The membrane function in two ways: It acts as the electrolyte which provides ionic communication between the anode and the cathode and also it serves as the separator for the two-reactant gases.
- Optimized proton and water transport properties of the membrane and proper water management are crucial for efficient fuel cell operation.

- Dehydration of the membrane reduces the proton conductivity and excess of water can lead to the flooding of the electrolyte. Both conditions result in poor performance.
- The absence of solution-phase electrolyte in PEF fuel cells, compared to alkaline and phosphoric acid fuel cells greatly reduces the complexity of the fuel and oxidant flow controls.
- Polymeric electrolyte is carbon dioxide tolerant.
- The most important breakthrough came with the development of perfluorinated membrane by DuPont. From 1966, the membrane requirements were best met by nafion family of perfluorinated ionomer membranes. Lifetimes over 60,000 hrs have been achieved at 353 K. Their general formula is



Construction:

Electrolyte:-Ion exchange polymeric membranes. This is an excellent insulator, but an excellent conductor of H⁺ ions. The material used, consists of a fluorocarbon polymer backbone, similar to Teflon, to which sulphonic acid groups are fixed to the polymer and cannot leak out, but the protons of these groups are free to migrate through the membrane.

Electrodes:- Typical gas diffusion electrodes, made up of porous C impregnated with Pt catalyst. Noble metal treated carbon fiber paper/cloth which is directly bonded to the polymer membrane at an elevated temperature and pressure (The catalytic electrode/membrane configuration is referred to as membrane electrodes assemble, MEA).

Fuel:- Hydrogen

Oxidant:- Air

Catalyst:-Platinum

Interconnect:- Carbon or metal

Operating temperature:- 40 – 80 °C.

Charge-carrier:- H^+

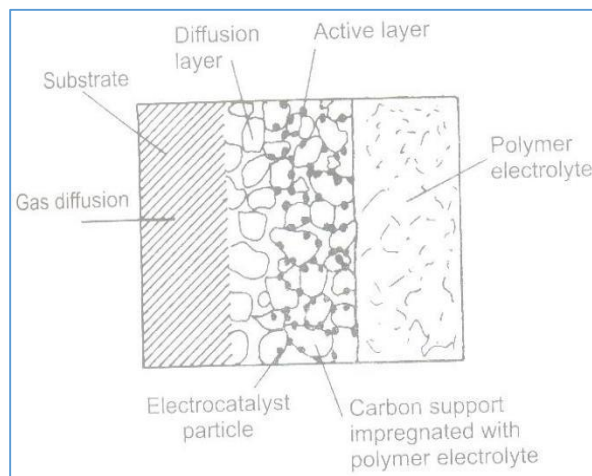


Fig.1.7.5.1 schematic of a typical PEMFC electrode, which displays three layers

- (i) A Teflonized substrate (typically, carbon cloth)
- (ii) A diffusion layer, generally formed by carbon particles of about 0.1 μm size with Teflon.

(iii) An active layer, where Pt catalyst grains are supported on carbon particles (Pt loading is usually 0.4 mg/cm² or less) with or without Teflon.

Cell reactions and Function of PEMFC:

PEM fuel cells operate at around 80 °C and practical efficiency of 60 %. Power output is in the range of 5-200 KW. They are ideal for transportation and portable power. Additional advantages are their high response, small size and low cost. A polymer electrolyte membrane fuel cell is unusual in that its electrolyte consists of a layer of solid polymer which allows protons to be transmitted from one fact to the other. Porous carbon is used as the anode and cathode of the PEMFC, as shown in Fig. It basically requires H₂ and O₂ as its inputs, though the oxidant may also be ambient air, and these gases must be humidified. It operates at a low temperature because of the limitations imposed by the thermal properties of the membrane itself. The operating temperatures are around 90°C and a Pt catalyst is used.

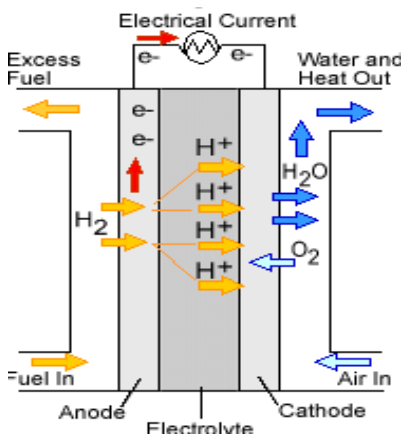
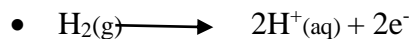
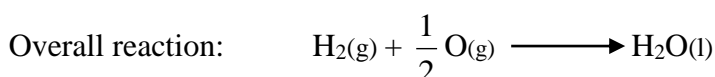
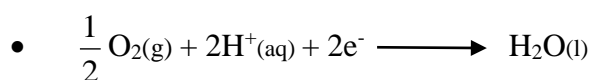


Fig.1.7.5.2 PEMFC

At anode:



At cathode



Applications:

- PEM fuel cells are used primarily for transportation applications and some stationary applications.
- Due to their fast startup time, low sensitivity to orientation, and favorable power-to-weight ratio, PEM fuel cells are particularly suitable for use in passenger vehicles, such as cars and buses.

Advantages:

- The PEMFC has a solid electrolyte which provides excellent resistance to gas crossover.
- The PEMFCs low operating temperature allows rapid start-up and, with the absence of corrosive cell constituents, the use of the exotic materials required in other fuel cell types, both in stack construction.
- PEMFCs are capable of high current densities of over 2 kW/l and 2 W/cm².

Disadvantages:

- The low and narrow operating temperature range makes thermal management difficult, especially at very high current densities, and makes it difficult to use the rejected heat for cogeneration.
- Optimized proton and water transport properties of the membrane and proper water management are crucial for efficient fuel cell operation. Dehydration of the membrane reduces the proton conductivity and excess water can lead to the flooding of the electrolyte. Both the conditions lead to poor performance.
- Perfluorinated membranes have a high cost.
- PEMFCs are quite sensitive to poisoning by trace levels of contaminants including CO, sulfur species and ammonia.

1.7.6 Differences between the fuel cell and galvanic cell:

Fuel Cell	Galvanic Cell
1. They do not store chemical energy	They store chemical energy
2. Reactants are fed from outside the cell continuously	The reactants from an integral part of its construction.
3. Need expensive noble metal catalysts & an optimum to an operative for their efficient functioning.	These special conditions are not required
4. Do not get discharged and no need of charging	Get-discharged when stored – up energy is exhausted.
5. Such cells never become dead as long as fresh reactants are available	Limited life span in use
6. Useful for long-term electricity generation.	Useful as portable power services.
7. Reaction products must be continuously removed	No such problem
8. No pollutants are generated (significant environmental benefits)	Pollutants are generated after their useful life
9. Produce power from fuels	They cannot generate electricity from fuels
10. Significantly higher power densities	Lower power density

1.8 Metal finishing

1.8.1 Introduction

Metal objects such as car components, kitchen utensils, juice cans, window frames, railings and so on which we see in everyday life will have undergone a surface modification, referred to as finishing. It covers a wide range of processes carried out to modify the surface properties of a metal. The process involves deposition of a layer of another metal or a polymer, conversion of a surface layer of atoms into oxide film or any other inorganic compound film or any process which can finally improve the surface characteristics. Metal finishing is done by electroplating, electroless plating, grinding wheels and honing, lapping and burnishing tools to obtain a smooth surface of a component with desired characteristics. Metal finishing is a process of electro deposition of an adherent metallic film of uniform thickness on the surface of the substrate for the purpose of modifying its surface properties.

The metal finishing techniques were originally introduced in the industry for improving the physical appearance of the metal objects by imbuing a decorative appeal. Since then a wide range of technological developments in the field was taken place for imparting additional desirable surface properties to the material other than their intrinsic properties to enhance the utility of the metal. Some of them are

- Improving resistance to corrosion
- Enhancing resistance to chemical attack, abrasion and wear
- Imparting thermal resistance and resistance to impact
- Improving thermal and electrical properties
- Increasing hardness, thermal and optical reflectivity to the surface
- Making the surface resistant for moisture attack

1.8.2 Electroplating

The techniques of metal finishing include electroplating of metals and alloys and Electroless plating of a modified surface. Electroplating is the process by which 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. It is primarily used for depositing a layer of material to bestow a desired property (e.g., abrasion and wear resistance, corrosion protection and aesthetic qualities) to a surface that otherwise lacks that property and sometimes to build up thickness on undersized parts. The common metals used for coating purpose are Zn, Cu, Ni, Cr, Ag, Au and Pt.

1.8.3 Theory of electroplating

Electroplating is the process of coating a metal on a substrate made up of another metal, alloy or non-metal by the process of electrolysis. The process used in electroplating is called electrodeposition and the principle is electrolysis. The electroplating device is an electrolytic cell in which two electrodes (anode and cathode) are dipped in an electrolytic solution. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. A rectifier supplies a direct current to the anode, oxidizing the metal atoms that comprise it and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they 'plate out' on to the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, ie equal to the current flowing through the circuit. In this

manner, the ions in the electrolyte bath are continuously replenished by the anode. Other electroplating processes may use an inert anode such as lead or graphite. In these techniques, ions of the metal to be plated must be periodically replenished to maintain proper coating metal ion concentration in the bath. The device used for electroplating is an electrolytic cell in the form of a tank having two electrodes immersed in the electrolyte solution. The schematic representation of various components of the electroplating unit is shown in Fig. 1.8.3.

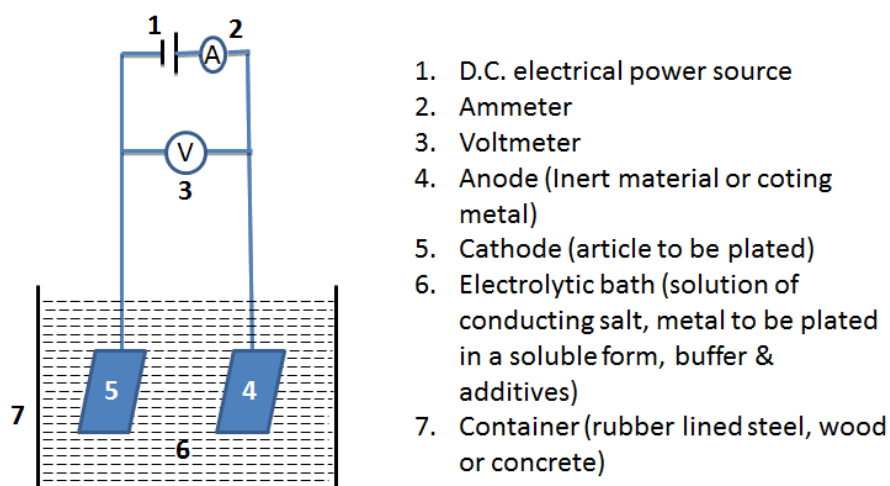
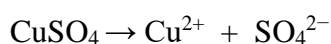


Fig. 1.8.3 Schematic of the electroplating bath

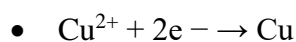
Essential components include:

- An electroplating bath containing a conducting salt and the metal to be plated in a soluble form as well as a buffer and additives.
- The article to be plated - electronically conducting cathode.
- The electronically conducting anode, the coating metal itself, or an inert material of good electrical conductance like graphite.
- An inert vessel to contain the above mentioned materials made up of either rubber lined steel, concrete or wood.

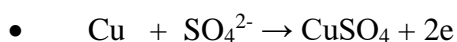
Suppose the anode is made of coating metal itself. During electrolysis, the concentration of the electrolytic bath remains unaltered, since the metal ions deposited from the bath are replenished continuously by the reaction of free anions with the anode metal. As an example, if the CuSO_4 solution is used as an electrolyte, it ionizes as



On passing current, Cu^{2+} ions go to the cathode and get deposited there.



The free SO_4^{2-} ions migrate to the copper anode and dissolve an equivalent amount of copper to form sulfate.



Thus there is a continuous replenishment of electrolytic salt during electrolysis. If however, the anode is made of some inert material like graphite, then electrolytic salt is added continuously in order to maintain proper coating metal ion concentration in the bath. Moreover the process of electroplating goes on nonstop, since the anode is not consumed and its replacement is not required. The process involves the passage of current and electrolysis of conducting media. Three important factors governing the electroplating process include decomposition potential (E_D), polarization and overvoltage.

1.8.3.1 Decomposition Potential (E_D):

When an electric current is passed through the electrolyte solution the electrolysis starts and the products formed, gather around the electrodes. Concentration in the vicinity of the electrodes changes and a back emf sets in. e.g., in the electrolysis of water, if a small voltage ($\sim 0.75\text{V}$) is applied between two platinum electrodes immersed in the 1M sulphuric acid solution, the electrolysis starts, proceeds to some extent and then decreases rapidly finally to stop. The reason for this observation is the initial passage of current causing release of a small amount of hydrogen and oxygen at the cathode and anode respectively. The gases are adsorbed at the surface of electrodes and the inactive platinum electrode is converted into active gas electrodes. This produces a back emf of the polarization current, which resists the emf of the battery or applied voltage. At potential below 1.7V the back emf counterbalance the effect of applied emf and the process of electrolysis is not sustained. If the applied voltage is slowly increased, there is a slight increase in the current until the applied voltage just exceeds the back emf (1.7 V), the current suddenly increases appreciably at that point. Thus, the minimum external potential or voltage, at which the electrolysis current begins to increase appreciably and continuous electrolysis sets in is known as decomposition potential of the electrolyte. It is equal to back emf.

Measurement of decomposition potential (E_D):

The schematic diagram for the determination of decomposition potential is shown in Fig.1.8.3.1a The electrolytic cell consists of two platinum electrodes (E_1 and E_2) dipped in the electrolytic solution. The applied voltage (V) is measured at different resistance and the corresponding current is measured with the help of milliammeter (M).

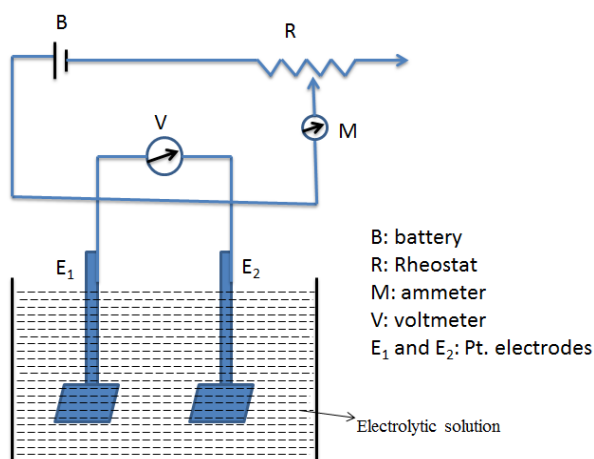


Fig. 1.8.3.1a Setup for measurement of decomposition potential

A series of readings for current passing through the electrolyte cell at corresponding applied voltage is recorded and a graph is plotted to measure the electrode potential. A graph between applied emf and the current density is shown in the following Fig.1.8.3.1b

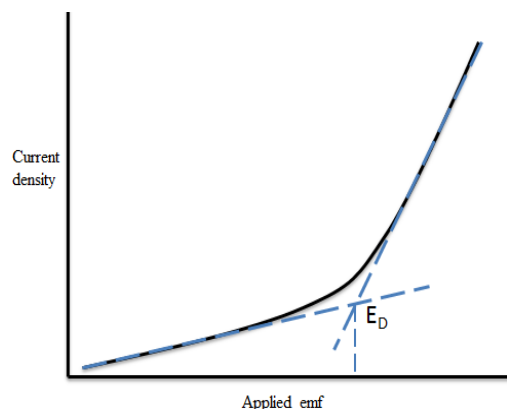


Fig. 1.8.3.1b A graph of external voltage applied vs current density

The linear portions of the graph are extended, until they intersect. Voltage corresponding to the point of intersection is the E_D of the electrolyte.

Factors influencing decomposition potential:

Decomposition potentials of different electrolytes are different. Even the E_D of an electrolyte is not a constant. It depends upon the following factors;

- Strength of the current flowing through the cell
- Chemical nature of the electrodes
- Physical nature of the electrodes
- Activity of the electrolyte
- Absolute temperature.

Use of decomposition potential values:

- Knowledge of E_D value enables the calculation of actual emf which is required for setting in continuous electrolytic processes, electroplating and electrorefining.
- It helps in predicting the sequence of discharge process to occur.
- Used in the separation of a mixture of metal ions from a solution by electrolysis.

1.8.3.2 Overvoltage

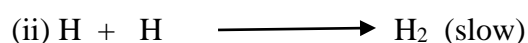
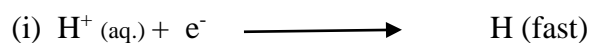
The decomposition potential of an electrolyte is approximately equal to the emf of the galvanic cell formed due to the discharge of products at the electrodes. The decomposition of an electrolyte is therefore expected to start as soon as applied potential reaches the value of reversible emf of the cell. This is true with respect to metal ions. But when products discharged at the electrodes are gases, then the actual decomposition potential is invariably much higher than its theoretical reversible electrode potential. The excess voltage is referred to as overvoltage (η) of the gas. It may occur at both the electrodes.

Overyoltage (η) is the difference between the actual applied emf to bring about continuous electrolysis and the theoretical emf needed for such electrolysis. For instance, the reversible potential of oxygen gas with smooth Pt electrode is 1.23 V. But actual gas evolution takes place at a potential of 1.68 V. The excess 0.45 V is the overvoltage of oxygen on smooth Pt surface. The following factors influence the overvoltage of an electrolyte;

- Nature of the electrode surface (or material)
- Current density and temperature
- Nature of the electrolyte

Overyoltage is believed to be a surface phenomenon at the electrodes. Of the many steps involved in gas evolution at electrodes, at least one is rather a slow process and requires energy. The extra energy is supplied by the applied voltage and this extra energy is related to overvoltage.

e.g., electrolysis of water



The step (ii) being slow, consumes energy and accounts for overvoltage. Hydrogen overvoltage is the measure of the tendency of hydrogen to be liberated at the cathode. Higher the value of overvoltage more difficult is the liberation of hydrogen on that metal.

1.8.3.3 Polarization

Since the electrolysis is a non spontaneous process, the minimum energy required to carry out such a process is equal to the free energy increase accompanying the change. However, in

irreversible conditions, the potential to be applied for electrolysis is higher than the reversible emf of the cell. A cell that requires excess voltage over the theoretical is said to be polarized and the phenomenon is referred to as polarization. Electrolytic processes occur at the electrodes of the cell. Polarization sets in the cell when the electrode processes become slow and irreversible. Thus polarization in the cell is due to polarization at the electrodes. Magnitude of overpotential is directly proportional to the extent of polarization. The observed polarizations are of two types.

- (a) Concentration polarization (b) Kinetic polarization

Concentration polarization:

An electrochemical reaction occurs only at the surface of the two electrodes. Reactant concentration decreases in the electrolyte adjacent to the electrode surface. The reactant species are transported to the electrode surface by processes like diffusion, migration and convection from the bulk of the solution. When the rate of transport is insufficient to match the rate of electrode reaction, current flowing through the cell drops. A higher potential than the theoretical value is required to maintain the current at the necessary level. This phenomenon is called concentration polarization. The steps involved in electrolytic processes are

- (i) Diffusion of reactant species towards the electrode and
- (ii) Diffusion of product away from the electrode, cause concentration polarization.

Concentration polarization can be eliminated or at least minimized by increasing the convection, by raising the temperature or mechanical agitation of the solution.

Kinetic or Activation polarization:

Activation polarization is caused when steps

- i) Adsorption of the reactant on the electrode
- ii) Charge transfer across the metal-solution interface and
- iii) Desorption of the product from the electrode become slow and need activation energy.

A higher potential than the theoretical value is to be applied to maintain current at the necessary level. It is not possible to eliminate or minimize kinetic polarization by any means. Activation polarization is normally very low, when metal deposition or metal dissolution is the electrode process. When the electrode process is a gas (H_2 and O_2) evolution, kinetic or activation polarization is usually very high.

Factors influencing polarization:

- Size and nature of the electrode

- Nature of ions accumulated on electrodes
- Electrolytic concentration
- Temperature
- Conductivity of electrolytic solution
- Stirring of electrolytic solution
- Use of depolarizer

Importance of polarization effect:

An impervious or non-porous film, contributes to the increase of polarization at an electrode. Considerable polarization effect can also be seen where loosely adhering and even porous films are formed. Such films either formed naturally (during manufacturing) or artificially (by the application of special coatings or products of corrosion) are important in determining the rate of corrosion of a metal or an alloy and also for the protection from corrosion.

1.8.4 Applications of electroplating

- *Plating for aesthetic appearance:*
- *Plating for protection*
- *For electroforming*
- *Plating on non-metals*

1.8.5 Characteristics of a good deposit

- The deposit should be bright and lustrous
- The deposit should be continuous, uniform, non porous and adhesive
- It should be hard and ductile
- It should be of fine grained nature

1.8.6 Factors influencing the nature of the deposit

There are several factors which affect the nature of an electro deposit.

(a) Current density

Higher the current density, more the deposition rate but will enforce the poor adhesion and loose and brittle plating quality. There is the possibility of a burnt and spongy deposit. Whereas low current density takes extra time to finish the job and is uneconomical. Therefore, optimum moderate current densities should be applied.

(b) Metal ion concentration

As the electroplating involves the discharge of free metal ions, the concentration of free metal ions plays an important role. If the concentration of metal ion is low the crystal size will be smaller and a fine adherent film may be coated. Thus the ideal situation is low free metal ion concentration in a concentrated solution of a metal compound which can be attained by addition of a compound with a common ion or by the formation of complex compound and ions. e.g., when copper is deposited from an electroplating bath containing copper sulphate solution, sulphuric acid is added to increase the concentration of sulphate ion. The concentration of cupric ions is reduced due to common ion effect.

(c) Temperature:

Generally, the solution to be deposited is used at room temperature. However, warm baths are used for increasing solubility of electrolyte and current density. The size of the crystals increases with increasing temperature and renders lower adherence. But on the other hand the solubility and metal dissociation increase at higher temperature leading to the higher conductance of the solution. Also, the mobility of ions increases at a higher temperature and decreases the viscosity of the electrolyte solution so that the cathode film is replenished at a faster rate. This increases the current density for a given voltage and reduces the tendency towards treeing. There are disadvantages also of using high temperatures. Since, the possibility of corrosion of equipment, decomposition of the organic addition agent and evolution of hydrogen gas at cathode would increase at a higher temperature. So the optimum range of temperature needs to be selected.

(d) pH of the electrolyte

The pH of the electrolyte solution should be properly maintained. The range of the pH varies for different types of the plating bath. If pH is more towards the acidic side the nature of the deposit will be affected adversely as the evolution of hydrogen gas is expected at cathode thereby forming a burnt deposit. If pH is more towards the basic side the plating is delayed, so uneven and thick deposit is obtained. Suitable buffers may be used for maintaining the appropriate pH.

(e) Presence of additives:

To obtain electroplate with desire qualities and specifications, additional substances called additives are added in small quantities to the electrolyte bath. These additives have the capacity to modify the structure, appearance and characteristics of the deposit. The different types of additives used are

(i) Complexing agents:

(ii) Brighteners:

(iii) *Levellers:*

(iv) *Wetting agents:*

(v) *Structure modifiers:*

(f) *Throwing power of the plating bath*

Throwing power is defined as the degree of uniformity of metal distribution or evenness of deposit thickness obtained on a cathode of irregular shape. If the distribution of the deposit is uniform throughout the surface of the article to be coated, the throwing power is considered good.

1.8.7 Methods of cleaning the metal surface

It is essential to clean the surface of base metal before the application of the electroplated coating. The common impurities found on the metal surface are grease, oil, oxide layer and other extraneous matters. The following methods are employed to clean the metal surfaces.

(iii) ***Physical (Solvent) cleaning:-*** Physical cleaning is done with the help of solvents to make the surface free from oil, grease, superficial dirt, and buffing, polishing and fatty substances. The commonly used solvents such as chlorinated hydrocarbons, xylene, toluene, aqueous cleaning agents are used with or without electric current. Solvent cleaning is made more effective by vapour degreasing. An organic volatile solvent like trichloroethene is heated and vapours are passed over the metal surface to be cleaned. The vapours condense on the surface and condensed liquid dissolves and washes away the oil, grease and other organic matter from the surface. The emulsifying agents are also added to the solvent to remove organic impurities from the surface of the metal.

(ii) ***Chemical (Alkali) Cleaning:*** It is used to remove the minute residue of soil and grease and for removal of tarnish and oxide film. The commonly used alkali cleaners consist of a number of alkalies, soap, chelating agents like Na_2O_3 , sodium phosphates, NaOH etc. Alkali cleaning is made more effective by passing current through a hot alkaline solution, with the article to be cleaned constituting the cathode. The evolution of H_2 at the cathode and O_2 at the anode, metal helps to dislodge the greasy substance. It is followed by thorough rinsing with water and then immersing in a very dilute solution of acids to remove traces of alkali after cleaning is completed.

(iii) ***Mechanical Cleaning:*** Involves removal of the oxide layer (tarnish), loose rust and other inorganic deposits from the surface to obtain better appearance, protection and optimum effects. This is done by hand cleaning with bristle brush and some abrasives like sand papers, polishing tools (grinding with grinding stone), scratch rubbing with chisel, knife, scrapers, wire brush or a abrasive stone or paper and detergent.

(iv) **Pickling:** The oxides sometimes cannot be removed by simple alkali or mechanical cleaning. The extraneous fragments like heavy scales of oxides, scratches and strains can be removed from the surface by dissolving in the acid solution. The acid pickling involves the removal of such oxides; rust or tarnish by immersing the material (except Al) in acid like dil. HCl or dil. H_2SO_4 or dil. HNO_3 . Pickling of Al is done in alkaline solution, whereas pickling of Cu, Ni or brass articles are accomplished in a solution of dil. HNO_3 or a mixture of dil. HNO_3 and dil. H_2SO_4 . Pickling is usually followed by polishing and buffing.

(v) **Electro polishing :-** In this method, the metal to be cleaned is made anode in a suitable solution. During the process, a surface layer of the metal gets dissolved along with the impurities. It also helps to remove minor surface irregularities. The most commonly used baths for electro polishing contain sulphuric acid, phosphoric acid, chromic acid, nitric acid etc. After the process, the metal is thoroughly rinsed with water, dried and used for electroplating.

1.8.8 Electroplating of chromium

Chromium plating is a finishing treatment utilizing the electrodeposition of a thin layer of chromium on a metal object. This layer can be decorative or corrosion protective to the base surface. The process of chromium plating includes degreasing to remove heavy soiling, manual cleaning to remove all residual traces of dirt and surface contamination and various pretreatments depending on the objectives of the coating. Different etching solutions such as hydrochloric, hydrofluoric, sulphuric acid and ferric chloride are used. Further, the treated base material is placed into the chrome plating bath for electroplating of desired thickness.

- Chromium coatings are generally thinner and have micro pores in it. As the thickness of the coating increases, cracks develop in the coatings. Hence, chromium coatings are always plated on nickel/copper undercoates. Ni gives protection and chromium gives a decorative finish.
- Chromium anodes are not used in electroplating of chromium on account of two difficulties. These electrodes become passive in acidic medium and they result in a black deposit.
- Chromium has higher electrode potential and can be easily coated on the iron to protect from rusting/corrosion
- The anode efficiency is nearly 100 % whereas cathode efficiency is at best around 20 %. It may be inferred that metal going into the solution is five times of the metal getting deposited, resulting in building up of excessive chromic acid concentration. This disturbs the ratio of Cr(III) to Cr(VI) and the conductivity of the bath and dull deposits called burnt

deposits are obtained. To avoid this, inert material is used as anode and chromium electrolyte in the bath.

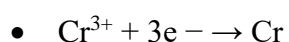
There are two types of chromium plating-Decorative coating and hard coating

Table 1.8.8 Comparison of decorative and hard coating of chromium

	Decorative coating	Hard coating
Bath composition	Chromic acid (250 g) + H ₂ SO ₄ (2.5 g) + Trivalent chromium (1g)	Chromic acid (250 g) + H ₂ SO ₄ (2.5 g) + Trivalent chromium (1 g)
Operating Temperature	45 – 55 °C	45 – 55 °C
Anode	Insoluble anodes like Pb – Pb : 6% Sb - Pb--7% Sn	Lead – lead : 6% Sb – Pb: 7% Sn
Cathode	Article to be coated	Article to be coated
Current density	145--430 A/ft ²	290--580 A/ft ²
Cathode efficiency	10 – 15	17 – 21
Applications	Decorative applications with corrosion resistance finish on cycles, automobiles, furniture, household fittings, aircraft, surgical and dental instruments.	Coating of industrial components like gauges, dies, cutting tools, piston rings and hydraulic rams.

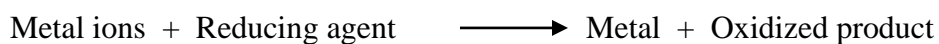
Working-

On passing current, Cr³⁺ ions go to the cathode and get deposited there.



1.8.9 Electroless plating

Electroless plating is a method of depositing a metal film on a substrate surface (conductor or non-conductor) from metal salt solution using a suitable reducing agent without using electrical energy. The reaction can be depicted as

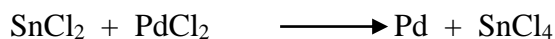


The method involves the deposition of metals such as Cu, Ag, Ni, Au or Pd on the surface of the base material by means of a reducing agent. Electroless plating results in a fine grained metal deposit that has similar finishing as that of traditional electrodeposit finishing. In industries, such process is used for plating on non-conductors like plastic, electroformed dies, hard memory disks, printed circuit boards (PCBs) or to obtain an extremely uniform plate. This technique is also used for the prevention of corrosion.

Process of electroless plating: The process of electroless plating involves the following steps:

(i) Preparation of active surface: This is the most important step and the surface is activated by any of the following ways.

- (a) etching – by acid treatment
- (b) electroplating with a thin layer of metal or insulators like plastic surfaces followed by heat treatment
- (c) Alternate treatment with SnCl_2 and PdCl_2 on the plastic surface



Pd is coated on plastic.

(ii) Preparation of plating bath:

- (a) Metal to be coated in the form of chloride or sulphate solution
- (b) Reducing agents like formaldehyde and sodium hypophosphate for reduction of metal ion to metal
- (c) Complexing agents like EDTA, tartrates, citrates to form metal complexes to prevent excess deposition
- (d) Stabilizers like thiourea, calcium ions to prevent decomposition of the bath and to impart stability to the solution
- (e) Exaltants (accelerators) like succinates, glycinate and fluorides to increase the rate of plating
- (f) Brighteners like thiosulphate to give a lustrous appearance
- (g) Buffers like boric acid to maintain the pH

(iii) Reduction step: Active surface is dipped in the bath and deposition is carried out. The plating is carried out in a series of tanks where the object is immersed to plate the desired metal. The rate of deposition is controlled by the amount of reducing agent present and the type of chelating agent used. The deposition rate is normally 12.5 – 25 μm , although, it has been done up to 650 μm in thickness.

Advantages of electroless plating

The following are main advantages of electroless plating

- More uniform coating on the surface of object whatever shape it may have. Even the objects having irregular shapes, holes, recesses, internal surfaces, valves or threaded parts get uniform deposit since it has better throwing power than electroplating.
- Electrical power and other accessories are not required.
- Coating is harder than regular plating and better wear resistance.
- Deposits have compatible wettability for oils, inherent lubricity and non-galling characteristics, unlike electrolytic nickel.
- Deposits are much superior to electroplated nickel and hard chrome, as they are less porous and provide better corrosion protection to steel substrates.
- Electroless plating of Ni on aluminum substrate enhances the solderability together with providing a non-magnetic under lay in magnetic components. The deposits are less porous and possess unique characteristic chemical, mechanical and magnetic properties.
- Additives or levelers are not required in the process nor the complex filtration method requirement.
- It is a simple process, so requires simple equipment.

Disadvantages of electroless plating

The main disadvantages of the process are the following;

- Due to speedy chemical renewal, cost of waste treatment is high.
- The frequency of dumping electroless bath is high as it is sensitive to contamination
- Costs per unit weight of the deposited metal are more.
- It needs pure chemicals.
- Chemical reductants are more expensive than electricity.
- Metal salts and reductant used in electroless plating solutions are thermodynamically not stable.
- Impurities or dust or colloidal matter (even if present in trace amount) promote the decomposition of bath components.

1.8.9.1 Electroless plating of Copper

It is an auto-catalytic reaction used to deposit a coating of copper on a substrate without the use of electrical energy. It is commonly used to plate plastic for decorative purposes and parts for engineering applications, particularly to render conductivity for electronic and printed circuit boards.

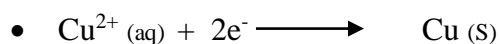
Reducing agents generally react with the plating bath, resulting in slow, deposition rates and poor deposit quality. It can be prevented by rejuvenating the bath at regular intervals. The bath solution undergoes spontaneous decomposition, resulting in an additional waste stream of copper and etching solution as copper built up on the tanks from the bath solution, must be stripped with an etchant such as sulphuric acid and hydrogen peroxide.

Electroless plating bath for copper includes;

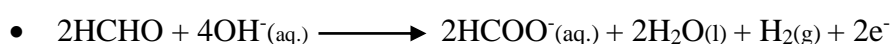
- Coating solution : CuSO_4 soln
- Reducing agent : HCHO
- Buffer: NaOH & Rochelle salt
- Complexing agent: EDTA di sodium salt
- Optimum pH: 11
- Optimum temperature: 25°C

The reactions involved at two electrodes are

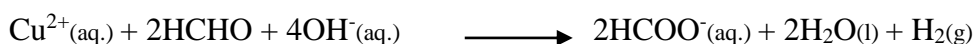
At cathode:



At anode:



Overall reaction:



Since Cu^{2+} ions and HCHO are consumed during the redox reaction, these are replenished periodically. The redox reaction involves consumption of hydroxyl ions and pH of the solution decreases as the reaction progresses. Hence addition of buffer is essential. Usual plating rate is $1\text{-}5\ \mu\text{m h}^{-1}$.

Applications of electroless plating:

- Electroless copper plating is widely used for metalizing printed circuit boards (PCBs)
 - It is used as a base coating for subsequent conventional electroplating
 - It is used for producing through hole connections and for decorative plating on plastics.
- When double sided PCBs are fabricated then holes are drilled for making electrical connections. These holes are plated by electroless plating.

1.8.10 Comparison of electroplating and electroless plating

Table 1.8.9 Comparison of electroplating and electroless plating

<i>Property</i>	<i>Electroplating</i>	<i>Electroless plating</i>
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Driving force	Electric current	Autocatalytic redox reaction
Anode reaction		
Cathode	Article to be plated	Article to be plated with a catalytic surface
Anode	Separate anode	Article to be plated
Reducing agent	Electrons bring about	Chemical reagents bring about reduction reaction
Anode reactant	M or H ₂ O	R, the reducing agent in solution
Nature of deposit	Pure metal or alloy	Usually metal contaminated with species derived from the redox reaction
Thickness limit (μm)	1 - 100	1 – 100
Applicability	Applicable to conductors only	Can be used for conductors and non-conductors
Throwing power	Less throwing power; cannot be used for irregular shapes and intricate parts	More throwing power and can be used for irregular and uneven shaped objects