

CELLS AND BATTERIES

On passing electric current through an electrolytic solution causes chemical reaction to take place. The reverse is also true i.e. Generation of electric current takes place by chemical reaction. Depending up on these two types of electrochemical processes there are two types of cells such as

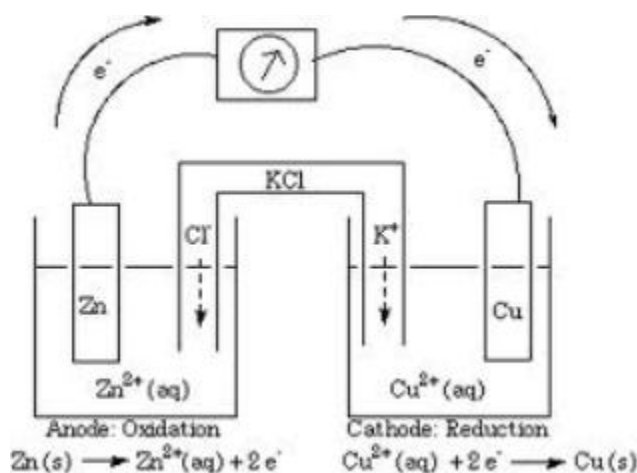
- 1) Electrolytic cell: is the cell that converts electrical energy into chemical energy.
- 2) Galvanic cell or Electrochemical Cell: is the cell that converts chemical energy into electrical energy.

Red-ox (Reduction-Oxidation) reactions are the basis for electrochemical cells. An electrochemical cell consists of two electrodes; each electrode is referred as '*Half Cell*' or '*Single Electrode*' connected by a metallic wire and electric current flows of as a result spontaneous red-ox reaction.

Difference between an electrolytic cell and a galvanic cell

| Electrochemical cell or Galvanic Cell | Electrolytic cell |
|--|---|
| A Galvanic cell converts chemical energy into electrical energy. | An electrolytic cell converts electrical energy into chemical energy. |
| The redox reaction is spontaneous and is responsible for the production of electrical energy. | The redox reaction is non spontaneous and electrical energy has to be supplied to initiate the reaction. |
| The two half-cells are set up in different containers being connected through the salt bridge or porous partition. | Both the electrodes are placed in a same container in the solution of molten electrolyte. |
| The anode is negative and cathode is the positive electrode. | The anode is positive and cathode is the negative electrode. |
| The electrons are supplied by the species being oxidized. They move from anode to the cathode in the external circuit. | The external battery supplies the electrons. They enter through the cathode and come out through the anode. |
| The electrodes are of different metal. | The electrodes may be of same metal or different metal. |

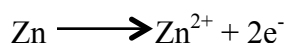
Galvanic Cell:



Construction and Working:

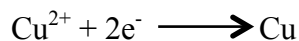
Galvanic cell (Daniel cell) consists of two containers, one of which contains zinc rod dipped in ZnSO_4 solution and in the other copper rod dipped in CuSO_4 solution. The zinc and copper rods are connected externally through ammeter and the solutions of the two containers are connected by an inverted U-tube, known as salt bridge. The tube is filled with either KCl or KNO_3 or NH_4NO_3 . On completing the circuit, the following reactions take place.

Oxidation reaction at anode:



- 1) Zinc starts to dissolve and goes into solution as Zn^{2+} .
- 2) ZnSO_4 solution becomes more concentrated with respect to Zn^{2+} ions.
- 3) The ammeter indicates the flow of electrons from zinc to copper rod.

Reduction reaction at cathode:



- 4) Copper ions deposited on copper rod.
- 5) CuSO_4 solution becomes richer with SO_4 ions.



The net red ox reaction is called electrochemical reaction and this is the cause for the production of electric current by the flow of $-^{\vee e}$ electricity from zinc to copper and the conventional current i.e., $+^{\vee e}$ electricity from copper to zinc. The net reaction is the sum of two electrode reactions. Each electrode reaction called as "*Half Cell Reaction* (oxidation half cell or reduction half cell).

To maintain the electro neutral Nity, $-^{\vee e}$ ions from salt bridge migrates to ZnSO_4 solution to neutralize excess of Zn^{+2} ions in oxidation half cell, similarly $+^{\vee e}$ ions from the salt bridge goes to reduction half cell to neutralize excess of SO_4^{-2} ions.

EMF (Electro motive force):

In a galvanic cell the electrons flow from electrode of higher potential (higher tendency to lose electrons then the other) to the electrode of lower potential. The electron transfer depends upon the potential difference between two electrodes. This potential difference is called EMF denoted by E_{cell} .

$$E_{\text{cell}} = E_C - E_A$$

If potential difference is large, the given number of electrons does large amount of electrical work.

If potential difference is small, the given number of electrons does less amount of electrical work.

Standard Electrode potential:

Is defined as the potential of an electrode when the electrode is in contact with a solution of 1M concentration, at 298 K and 1 atm pr. Standard electrode potential is denoted as E°

Nernst Equation:

Nernst derived a equation to establish relationship between electrode potential and concentration of metal ion.

Following equations:

$$1) E = E^\circ + \frac{0.05918}{n} \log \frac{[\text{species at cathode}]}{[\text{species at anode}]}$$

$$2) E = E^\circ + \frac{0.05918}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

Types of electrodes:

1) **Metal – metal ion electrode:** where a metal is in contact with its ionic solution.

Examples: Cu^{2+}/Cu , Zn/Zn^{2+} , Ag^{+}/Ag

2) **Gas electrode:** in which gas is in contact with an inert metal dipped in an ionic solution of the gas molecules.

Examples: Hydrogen electrode

3) **Metal-insoluble salt electrode:** in which metal is in contact with a solution containing the anion of the salt.

Examples: Calomel electrode, Ag/AgCl electrode

4) **Ion selective electrode:** Where a membrane is in contact with an ionic solution.

Examples: Glass electrode, solid state electrode

5) **Amalgam electrode:** metal amalgam contact with the solution of its metal ions.

Example: $\text{Hg-Pb}/\text{Pb}^{2+}$

6) **Oxidation reduction electrode:** when inert metal is in contact with the solution, the potential develops due to the presence of both oxidized and reduced species of the same metal.

Example: $\text{Pt}/\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{Pt}/\text{Sn}^{2+}/\text{Sn}^{4+}$

Reference electrode:

Reference electrode is the electrodes whose potentials are known and are used for determination of potentials of other electrodes.

Types of reference electrodes:

1) Primary reference electrode. Example- standard hydrogen electrode

2) Secondary reference electrode. Example- calomel electrode, silver- silver chloride electrode

Differences between Galvanic series and Electrochemical series:

| S.No | Electrochemical series | Galvanic series |
|-------------|---|--|
| 1 | This series was developed by studying the corrosion of metals and alloys in their salt solution of 1M concentration without any oxide film on them. | This series was developed by studying the corrosion of metals and alloys in unpolluted sea water without their oxide film. |
| 2 | The position of metal is fixed | The position of metal may shift |
| 3 | There is no information regarding position of alloys | The corrosion of alloys |
| 4 | The position of metal is permanently fixed | The position of metal when present in the form of alloy is different from that of pure metal. |
| 5 | This series predicts the relative displacement tendencies. | This series predicts the relative corrosion tendencies. |
| 6 | This series comprises of metals and non-metals | This series comprises of metals and alloys. |

BATTERY TECHNOLOGY

Introduction

- A battery is a portable energy source with three basic components-an anode (the negative part), a cathode (the positive part), and an electrolyte. As current is drawn from the battery, electrons start to flow from the anode through the electrolyte, to the cathode.
- A device enables the energy liberated in a chemical reaction to be converted directly into electricity.
- The term battery originally implied a group of cells in a series or parallel arrangement, but now it is either a single cell or group of cells.
- Examples: It ranges from small button cells used in electric watches to the lead acid batteries used for starting, lighting and ignition in vehicles with internal combustion engines.
- The batteries are of great importance based on the ability of some electrochemical systems to store electrical energy supplied by the external source. Such batteries may be used for emergency power supplies, for driving electric vehicles, etc.
- For the commercial exploitation, it is important that a battery should provide a higher energy, power density along with long shelf life, low cost and compatible rechargeable units.

Battery Components:

Cells are comprised of 4 essential components.

- The **Anode** is the negative or reducing electrode that releases **electrons** to the external circuit and oxidizes during an electrochemical reaction.
- The **Cathode** is the positive or oxidizing electrode that acquires electrons from the external circuit and is reduced during the electrochemical reaction.
- The **Electrolyte** is the medium that provides the *ion* transport mechanism between the cathode and anode of a cell. Electrolytes are often thought of as liquids, such as water or other solvents, with dissolved salts, *acids*, or *alkalis* that are required for *ionic conduction*. It should however be noted that many batteries including the conventional batteries contain solid electrolytes that act as ionic conductors at room temperature.
- The **Separator** is a permeable membrane placed between battery's anode and cathode. The main function of a separator is to keep the two electrodes apart to prevent electrical short circuits while also allowing the transport of ionic charge carriers that are needed to close the circuit during the passage of current in an electrochemical cell.

A separator generally consists of a polymeric membrane forming a microporous layer like Cellulose membrane, Poly olefins, Poly vinyl membranes, Cellophane or Nafion membranes etc. They are important to batteries because their structure and properties considerably affect the battery performance, including the batteries energy and power densities, cycle life, and safety.

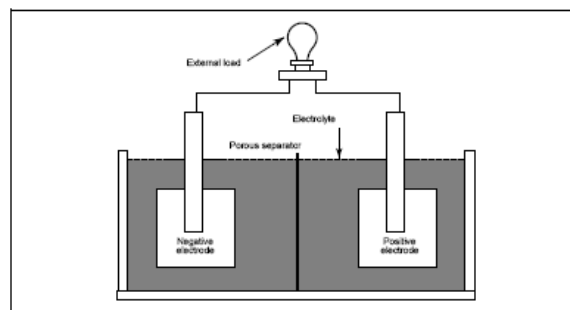


Figure 1. Major components of a cell.

Battery Characteristics:

- 1) Voltage
- 2) Capacity
- 3) Energy density
- 4) Power Density
- 5) % Energy Efficiency
- 6) Cycle Life
- 7) Electricity Storage Density
- 8) Shelf Life

Voltage

Voltage expresses differences in electric potential and magnitude of the available energy. The corresponding SI unit is Volts. The voltage between the two electrodes is denoted by $(V_C - V_A)$, can be directly measured by voltmeter.

$$E_{\text{cell}} = \{E_c - E_a\} - |\eta_a| - |\eta_c| - i \cdot r_{\text{cell}}$$

Here E_{cell} = Voltage of cell

E_c = Cathode electrode voltage

E_a = Anode electrode Voltage

$i \cdot r_{\text{cell}}$ = Internal resistance of the battery

To derive the maximum voltage from battery

- The difference in the electrode potentials must be high.
- The electrode reactions must be fast so as to minimize the over voltage.
- The internal resistance of the cell must be low.

The electrode systems should be such that the active mass at the positive electrode depletes readily and that at the negative electrode increases easily. This minimizes the over potential at anode and cathode.

The cell should be appropriately designed so as to minimize the internal resistance this can be achieved by keeping the electrodes close to each other and also by using an electrolyte of high conductivity. If the difference in the electrode potential is more, higher is the emf of the cell.

Capacity :

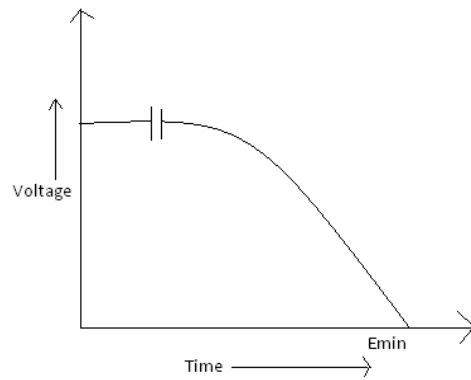
The energy stored in a battery is known as battery capacity.

Battery capacity is a measure of the charge stored by a battery, which is determined by the amount of electrical energy that the battery can deliver over for certain period and is measured in Ampere-hour (Ah).

The theoretical capacity may be calculated using faradays relation, $C = mnF/M$, (where m and M is weight and molar mass of the active material respectively, F is faraday, n is number of electrons transferred).

The variation of voltage during discharge is measured by plotting a graph of voltage vs. Time is the flatness of the curve. When the capacity of a battery falls below 60% to 80%, it should be discarded. The amount of the active materials actually consumed during discharge determines the capacity of the battery. The capacity also depends on the discharge conditions. It is measured by finding the time taken for the battery to reach a minimum voltage $E_{\text{cell}}^{\text{min}}$ for a fixed current discharge.

The length of the plot portion of the curve is a measure of the capacity of the battery, longer the plot portion better is the capacity.



Energy density:

Energy density is the ratio of the energy available from a battery to its mass or volume

$$\text{Energy density} = \frac{I \times t \times E_{\text{cell}}^{\text{min}}}{W}$$

Where i = fixed current

t = time taken to reach average voltage

$E_{\text{cell}}^{\text{min}}$ = Average voltage

W = mass of the battery

Energy density is determined by measuring the capacity and recording the average voltage and total mass of the battery.

Current:

Current is a measure of how many electrons are flowing through a conductor. Current is usually measured in amperes (A). And is the amount of charge flowing per second.

$$(\text{Current: } I = q / t, \text{ with units of } A = C \text{ s}^{-1})$$

Current flow over time is defined as ampere-hours, a product of the average current and the amount of time it flowed..

Energy efficiency:

Defined as the ratio of useful energy output to the total energy input.

$$\% \text{Energy efficiency} = \frac{\text{Energy released during discharge}}{\text{Energy required during recharge}} \times 100$$

Cycle life

Primary battery is non-rechargeable but secondary battery is rechargeable. The *Cycle Life* is a measure of how many charge and discharge cycles a battery can take before the battery is expected to collapse. The greater is the average depth of discharge, the shorter the cycle life.

Shelf-life

Shelf-life is the period of time a battery can be stored without significant deterioration. Aging is subject to storage temperature and state of charge. While primary batteries have a shelf life up to 10 years, lithium- based batteries are good for 2 to 3 years, nickel – based batteries are good for 5 years, etc.

Energy storage density: it is amount of energy stored in unit mass or unit volume of its active material of a battery.

Classification of Batteries:

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

Primary battery

Primary batteries are not rechargeable, and consequently are discharged then disposed off, 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. Generally primary batteries have a higher capacity and initial voltage than rechargeable batteries.

Example: Dry cell. Zn-MnO₂, lithium battery.

Secondary battery

Secondary (rechargeable) batteries can be recharged by applying a reverse current, as the electrochemical reaction is reversible. The original active materials at the two electrodes can be reconstituted chemically and structurally by the application of an electrical potential between the electrodes to “inject” energy. These batteries are able to discharge and recharge many times.

Example: Lead acid battery, Ni-Cd battery, lithium ion battery.

Reserve battery

A reserve battery is special purpose primary battery designed for emergency short service life and for long term storage. They are not rechargeable. The electrolyte is usually stored separately from the electrodes which remain in a dry inactive state and is activated only when required by assembling its internal parts.

Hence deterioration of the active materials during storage can be avoided and also eliminates the loss of capacity due to self discharge until the battery is put into use.

Example: Magnesium-water activated batteries, zinc-silver oxide batteries, etc.

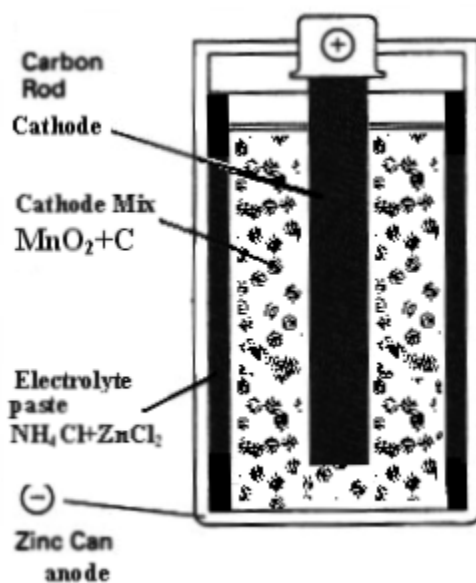
Difference between primary and secondary battery

| <i>Primary batteries</i> | <i>Secondary batteries</i> |
|---|--|
| Primary batteries are used only once | Secondary batteries can reused |
| Chemical reaction that supply current are irreversible. | Chemical reaction that supply current are readily reversed when current is supplied to battery |
| Cheap and initial cost is low | Costlier and initial cost is very high |
| Example: Dry cell | Example: lead acid battery |

Dry cell (Leclanche cell) or Zn-MnO_2 battery

Construction, working and applications of Zn-MnO_2

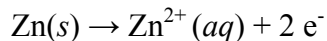
This is most familiar type of dry cell. The cell is packed in a zinc can that serves as both a container and negative terminal (anode). The positive terminal (cathode) is a carbon rod surrounded by a mixture of manganese dioxide and carbon powder, carbon powder is added to increase the electrical conductivity. The electrolyte used is a paste of zinc chloride and ammonium chloride dissolved in water. Starch is added to electrolyte to make it a thick paste. Zn-MnO_2 battery is the least expensive primary battery. Output voltage of a battery during discharge is 1.5 Volts.



Chemical reactions

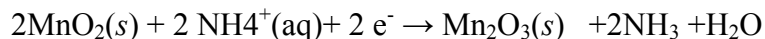
At anode

The zinc is oxidized according to the following half-equation.

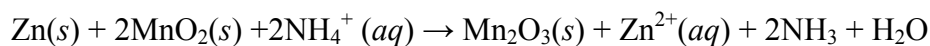


At cathode

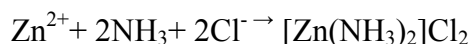
In this half-reaction, the manganese reduces from an oxidation state of (+4) to (+3).



Over all cell reaction



The NH_3 which is liberated from NH_4Cl reacts with Zn^{2+} to precipitate as $[\text{Zn}(\text{NH}_3)_2]\text{Cl}_2$



Advantages:

- Inexpensive
- Convenient
- Lightweight
- Available in variety of shapes and sizes

Disadvantages:

- Can be used only once.
- Low energy density
- Low energy efficiency
- Low-temperature performance

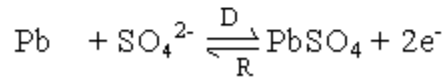
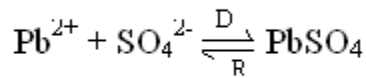
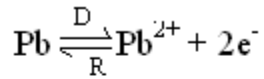
Applications:

- Used in Portable devices like toys, watches, calculators, flash lights etc.
- Used emergency Lighting purpose.

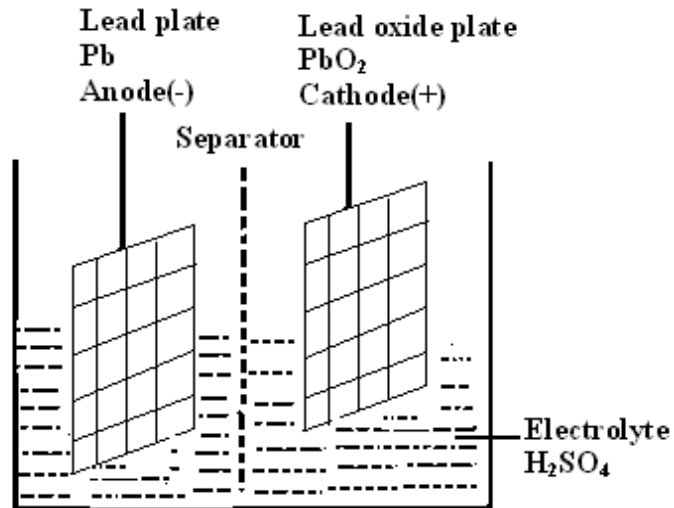
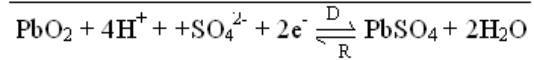
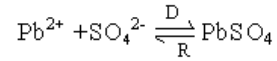
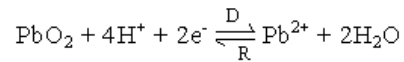
Lead Acid Batteries

A lead-acid battery is an electrical storage device that uses a reversible chemical reaction to store energy. It consists of lead grids as electrode materials, one lead grid coated with spongy lead acts as anode and the other coated with lead oxide acts as cathode. A porous partition separates the electrode pair and immersed in the electrolyte sulphuric acid (5M) solution. When electrodes connected to external circuit, the reactions take place to convert chemical energy into electrical energy and back again. Each electrode pair develops a potential of 2V. In order to obtain higher potential a number of electrode pairs are connected in series.

At anode



at cathode



During discharge, process sulphuric acid that consumed will form lead sulphate at the respective electrodes. However, sulphuric acid will regenerate during recharge processes and its original concentration restores. The specific gravity of sulphuric acid is 1.25g/cc.

Advantages:

- Low cost
- Good high and low-temperature operation

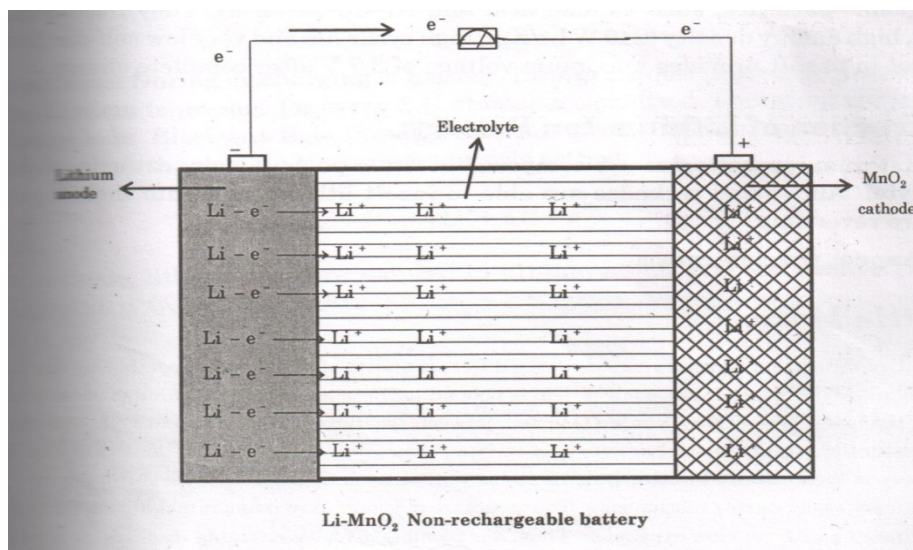
Disadvantages:

- Low cycle life
- Low energy density
- Poor charge retention

Uses:

- Car battery used to start engine
- Aircraft systems
- Standby power resources
- Emergency no-fail systems

LiMnO₂ battery

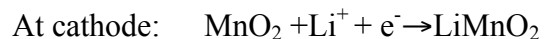


Construction:

- Lithium Manganese Dioxide cell, is a primary battery.
- Anode is Lithium metal (in the form of disc) and cathode is specially heat treated manganese dioxide (in the form of a pellet).
- The electrolyte is lithium halide like LiCl, LiBr, LiClO₄, LiAlCl₄ and LiCF₃SO₃ dissolved in mixture of organic solvent i.e Propylene carbonate and 1,2 dimethoxy ethane.
- Anode and cathode is separated by polypropylene separator. It provides an electrical contact between the two electrodes.

Working:

The half cell electrode reactions which are occurring during the discharge are



Formation of LiMnO₂ indicates that Li⁺ ion enters in to the MnO₂ crystal lattice. The Battery gives 4 volts and energy density of 230 wh/Kg.

Li-MnO₂ battery available in many configurations such as coin, cylindrical, prismatic, spherical and spirally wound etc.

Advantages

- High energy and power densities
- Higher and stable operating voltage (3.6V / 3.9V)
- Wider operating temperature range (-40⁰ C to + 85⁰ C)
- Outstanding storage capability (up to 10 Years)
- Ultimate safety
- Lowest self discharge (less than 1.5% per year)
- Good discharge performance.

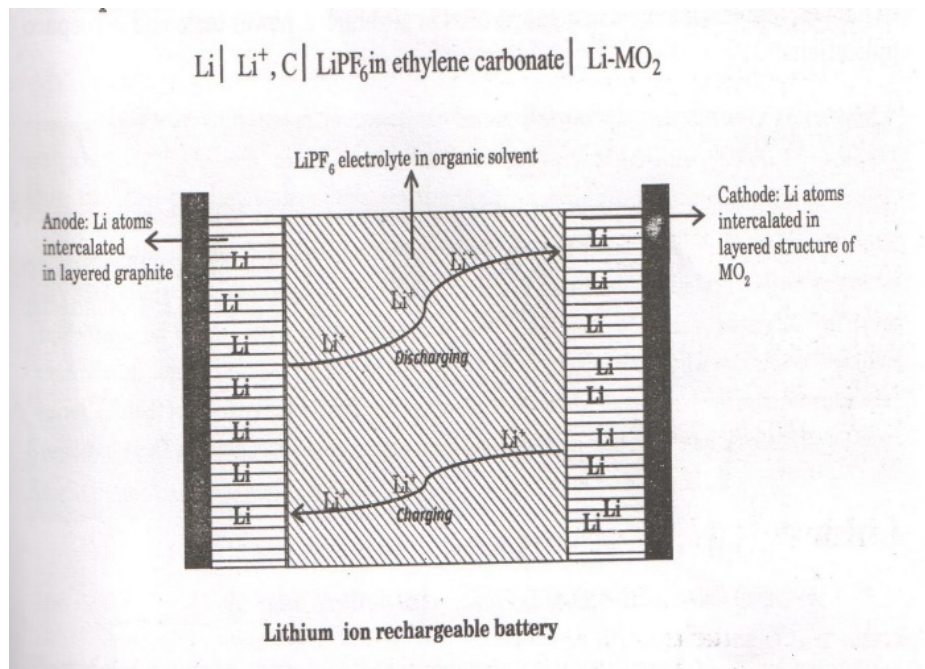
Limitations

- Aqueous electrolytes cannot be used in Lithium batteries, because of high reactivity of Li with water.

Applications:

Outdoor use (requiring a low temperature range) and for high-discharge devices, which include digital cameras, portable power tools, flashlights, walkie-talkies, portable televisions and video games etc.

Lithium ion Batteries:



CONSTRUCTION:

Lithium ion batteries are composed of three parts- Anode, cathode, and electrolyte. Anode cathodes are able to insert lithium ions in to their layered structure reversibly.

Anode – lithiated graphite

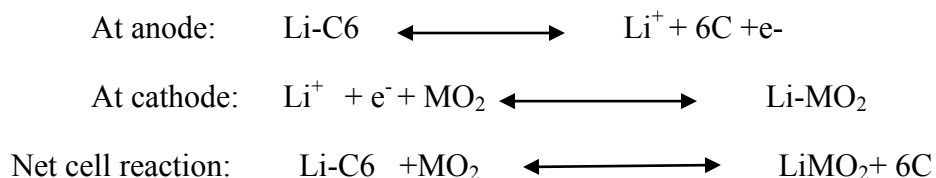
Cathode – lithiated transition metal oxide

Electrolyte – lithium salts are dissolved in organic solvents

Cell representation

Li/ Li⁺, C / LiPF₆ in organic solvent/ Li-MO₂

Electrode reactions are:



During discharging of battery, lithium atoms present in graphite layer (one lithium atom is present for every six carbon atom) are oxidized, liberating electrons and lithium ions. Electrons flow through the organic electrolyte towards cathode.

At cathode, lithium ions are reduced to lithium atoms and are inserted into the layered structure of metal oxide.

During charging of battery, lithium atoms present in layered structure of metal oxide are oxidized, liberating electrons and lithium ions. Electrons flow through external circuit and lithium ions flow through the organic electrolyte towards graphite carbon electrode.

At graphite electrode, lithium ions are reduced to lithium atoms and are inserted into the layered structure of graphite.

Advantages:

1. Low self discharge
2. High energy density
3. Higher cell potential

Disdvantages:

1. Low cycle life
2. Poor low temperature performance

Applications

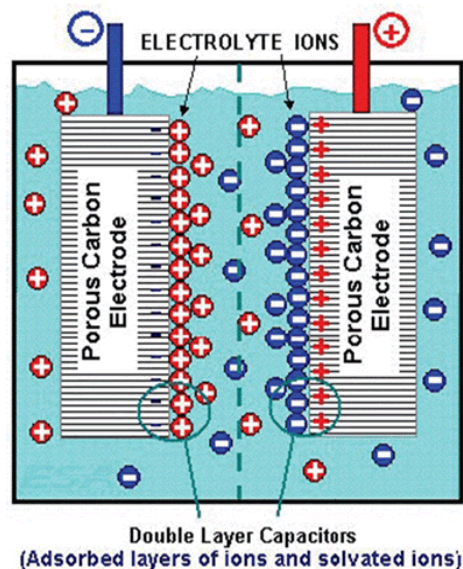
Used for electronic devices like cell phones, laptops and also in defense, electric vehicles power tools and aerospace applications.

Super capacitors:

Super capacitor or electrochemical double layer capacitor is an energy storage device similar to a capacitor but having a very high capacitance in a small package, high energy and power densities, high efficiency and large cycle life.

It consists of two electrodes in contact with an electrolyte. The electrodes are made with high effective surface materials, such as porous carbon, carbon nanotubes and certain conducting polymers. The average potential of the positive electrode attracts the negative ions in the electrolyte, while the potential of the negative electrode attracts the positive ions in the electrolyte. This results in the formation of electrical double layer at each electrode/electrolyte interface that allows the plates to store charge. The dielectric separator between the two electrodes prevents the charge from moving between the two electrodes.

The capacitance of these devices is proportional to the active electrode area, increases the electrode surface area will increase the capacitance, hence increasing the amount of energy that can be stores. Therefore, porous materials like activated carbon are used as electrode materials.



Advantages:

- Long cycle life
- Low cost per cycle
- Very high rate of charging and discharging
- High output power
- No chemical reactions involved
- No danger of over voltage

Disadvantages:

- High self discharge
- Cells have low voltage - serial connections are needed to get high voltage
- Low energy density
- Power is available only for a short duration

Uses:

- In electronic devices (MP3 player, AM/FM radios, cell phone)
- In digital cameras
- In flash lights
- In portable media players

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.

Fuel cell: Fuel cell is a galvanic cell in which chemical energy of conventional fuel oxidant system is converted directly into electrical energy by means of electrochemical process. A fuel cell may be represented as,

Fuel Cell representation: Fuel / electrode / electrolyte /electrode /oxidant

In these aspects fuel cells differ from conventional electrochemical cells

Difference between Battery and fuel cells

| S.No | Battery | Fuel cells |
|------|---|--|
| 1 | Chemical Energy may be stored | Do not store chemical energy |
| 2 | Charging is needed | No need of charging |
| 3 | Energy efficiency is limited | Energy efficiency is high |
| 4 | Reactants are not continuously supplied | Reactants are continuously supplied and products are continuously removed. |
| 5 | Presence of harmful waste products | Absence of harmful waste products |
| 6 | It produces the DC for limited period at high cost. | It produces the DC for long periods at low cost. |

Advantages of fuel cells:

- Power output is high.
- Do not pollute the atmosphere
- Electrical energy can be obtained continuously.
- No movable parts hence it is free from wear and tear
- Recharging is not required

Classification of fuel cells based on operating temperature and type of electrolyte used

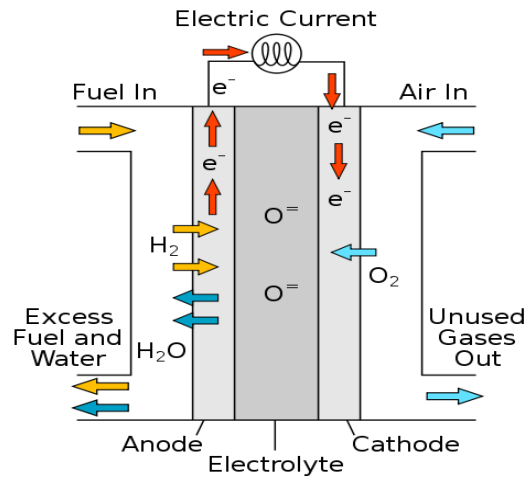
1. **Low temperature fuel cell (below 100⁰C) - water** based electrolytes are used like KOH, NaOH
2. **Medium temperature fuel cell (100⁰C-600⁰C) –molten salts** are used like H₃PO₄
3. **High temperature fuel cell (650⁰C-1000⁰C) – ceramic based** electrolytes are used

SOLID OXIDE FUEL CELL

A solid oxide fuel cell (SOFC) is an electrochemical conversion device that produces electricity directly from oxidizing a fuel. Fuel cells are characterized by their electrolyte material; the SOFC has a solid oxide or ceramic, electrolyte. Advantages of this class of fuel cells include high efficiency, long-term stability, fuel flexibility, low emissions, and relatively low cost. The

largest disadvantage is the high operating temperature which results in longer start-up times and mechanical and chemical compatibility issues.

Construction



A solid oxide fuel cell is made up of four layers, three of which are ceramics (hence the name). A single cell consisting of these four layers stacked together is typically only a few millimeters thick. Hundreds of these cells are then connected in series to form what most people refer to as an "SOFC stack". The ceramics used in SOFCs do not become electrically and ionically active until they reach very high temperature and as a consequence the stacks have to run at temperatures ranging from 500 to 1,000 °C. Reduction of oxygen into oxygen ions occurs at the cathode. These ions can then diffuse through the solid oxide electrolyte to the anode where they can electrochemically oxidize the fuel. In this reaction, a water byproduct is given off as well as two electrons. These electrons then flow through an external circuit where they can do work. The cycle then repeats as those electrons enter the cathode material again.

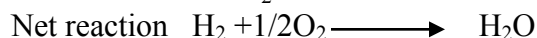
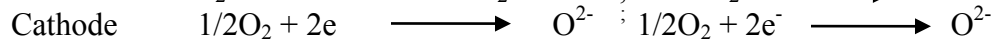
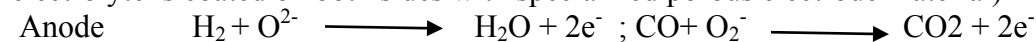
The fuel may be H_2 or CO or mixture of both. It uses an electrolyte in solid form- solid oxide to make it conducting, it is doped appropriately. As the oxidant is oxygen, the solid electrolyte helps in the conduction of oxide ions (O^{2-}) through the vacant sites in the electrolyte.

Anode: Porous Co-ZrO₂ or Ni-ZrO₂

Cathode: Porous strontium doped LaMnO₃

Electrolyte: Solid-non Porous metal oxide (ZrO₂ doped with Y₂O₃)

The anode, cathode and electrolyte are made from ceramic substances (the hard ceramic electrolyte is coated on both sides with specialized porous electrode material)



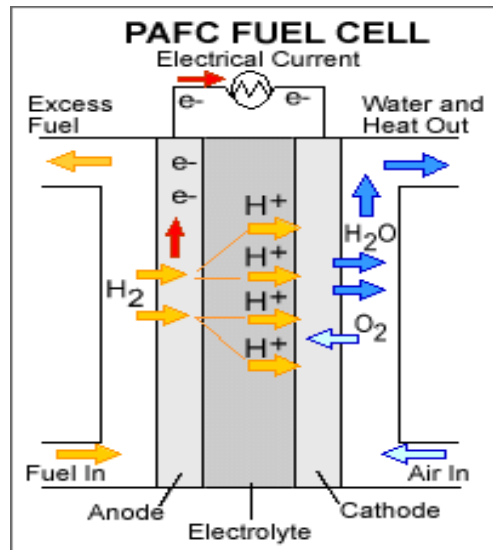
At high operating temperature oxygen ions are formed at the cathode. When a fuel gas containing H_2 is passed over the anode the oxygen migrates through the crystal lattice to oxidize the fuel. Electrons generated at the anode move out through an external circuit creating electricity.

Advantages:

1. The reaction rate at the operating temperature is quite high, so no noble metal catalyst is required.
2. Carbon monoxide does not poison the electrodes
3. Because of solid electrolyte is less corrosive.
4. During the operation it gives large quantity of heat which can be used for space heating, water heating etc. and also for in locomotives.

Applications:

1. Used for producing light and heat for large buildings.
2. Used in stationary power generations, hospitals etc.

2. PHOSPHORIC ACID FUEL CELL

Phosphoric acid fuel cells (PAFC) are a type of fuel cell that uses liquid phosphoric acid as an electrolyte. Phosphoric Acid Fuel Cells (PAFC) were the first fuel cells to be commercialized. Developed in the mid-1960s and field-tested since the 1970s, they have improved significantly in stability, performance, and cost. Such characteristics have made the PAFC a good candidate for early stationary applications.

Phosphoric acid fuel cells use liquid phosphoric acid as the electrolyte and operate at about 200°C. One of the main advantages to this type of fuel cell, besides the nearly 85% cogeneration efficiency, is that it can use impure hydrogen as fuel. PAFCs can tolerate a CO concentration of about 1.5 percent, which broadens the choice of fuels they can use. If gasoline is used, the sulfur must be removed. The electrodes are made of carbon paper coated with a finely dispersed platinum catalyst, which make them expensive to manufacture. However, reduction in fabrication costs also represent an opportunity for cost reduction. Cost reductions to manufacture

phosphoric acid fuel cells can be addressed by new research and development (R&D) in the areas of:

1. Reductions in platinum loadings
2. Reductions in the cost of fabricating separator plates and electrolyte reservoir plates
3. Increases in power density through the reduction or elimination of that portion of the cell polarization caused by anion adsorption

At an operating range of 150 to 200 °C, the expelled water can be converted to steam for air and water heating. At lower temperatures phosphoric acid is a poor ionic conductor, and CO poisoning of the Pt electro-catalyst in the anode becomes severe. Phosphoric acid fuel cells have been used for stationary applications with a combined heat and power (CHP) efficiency of about 80% and the operating temperature still low enough to allow the use of common construction materials and proving considerable design flexibility for thermal management. This type of fuel cell is used in stationary power generators with output in the 100 kW to 400 kW range to power many commercial premises around the world, and they are also finding application in large vehicles such as buses.

Reactions:

At anode: $\text{H}_2 \longrightarrow 2\text{H}^+ + 2\text{e}^-$

At cathode: $\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{H}_2\text{O}$

Net cell reaction: $\text{H}_2 + \frac{1}{2} \text{O}_2 \longrightarrow \text{H}_2\text{O}$

Advantages:

1. Phosphoric acid polymerizes to pyrophoric acid ($\text{H}_4\text{P}_2\text{O}_7$) at 150 °C which has higher conductivity and efficiency of fuel.
2. Long proven life (10,000-50,000 hrs)

Limitations:

1. Very expensive since Pt used as catalyst.
2. Large size and weight.

Applications:

1. Used for producing light and heat for large buildings.
2. Used in stationary power generation, used for large vehicles to produce power.

SOLAR ENERGY

The Devices which convert solar energy into useful electric energy are called Photovoltaic cells.

Importance of Photovoltaic cells:

- Photovoltaic cells provide power for spacecraft and satellites.
- They provide ecofriendly environment.
- Used as energy back up for telecommunication equipment and solar home systems.
- It can be used for large scale electricity generation as substitute for conventional fuels

Advantages

:

- The fuel source is infinite.
- Very much ecofriendly.
- Operating costs are low, because no fuel is required.
- Stable towards corrosion problems.

Disadvantages:

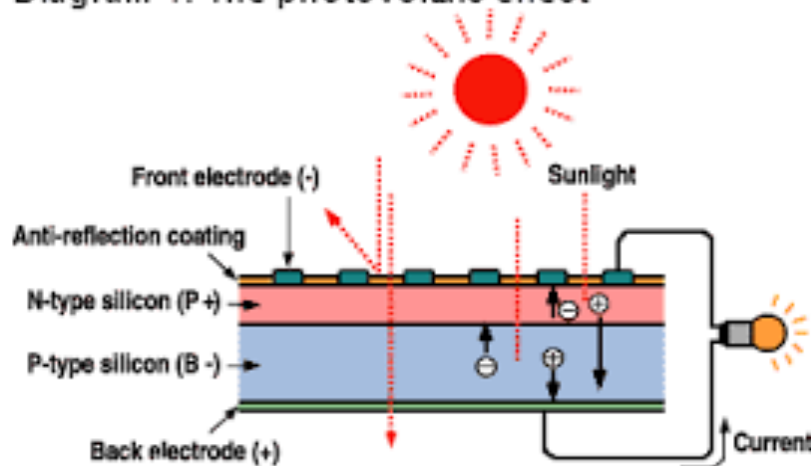
- Energy can be produced only during day time.
- High installation costs.

Construction and Working of Photovoltaic cells

A typical semiconductor photovoltaic cell is composed of p-type and n-type silicon, which forms a p-n junction (diode).

The construction of a solar cell (photovoltaic cell) is as shown below;

Diagram 1. The photovoltaic effect



The solar cells consist of p-n junction formed by the n-type and p-type semiconductors which interacts with light and produce electricity. Since the refractive index of silicon is very high, it is

coated upon by antireflective layer of either Silicon nitride or Titanium dioxide of several nanometer thickness using Plasma enhanced chemical vapour deposition (PECVD) technique. The front side surface of semiconductor is provided with a metallic conductor in the form of grids and the rear side surface is also coated by a noble metal for electrical contact as shown above.

When light of suitable frequency ($E = h\nu$) enters into the semiconductor, the p-n junction breaks down forming free electron (-) and hole pairs (+). Thus the solar energy is converted into electrical energy and stored and used for various applications.

Physical and chemical properties of silicon

Silicon is a semiconductor which belongs to IV A group element with valence 4. Silicon exhibits both physical and chemical properties.

Physical properties:

- Silicon has forbidden gap of 1.2eV.
- At normal pressure silicon exhibits Cubic structure and at 15GPa it becomes bcc.
- Silicon contracts on heating and on cooling expand.
- Silicon has high refractive index.

Chemical properties:

Since Silicon exhibits tetra valency it gives following reactions.

- It reacts with Oxygen to give silicon dioxide (SiO_2)
- Silicon reacts with Hydrogen to produce silane, which is used for the production of amorphous silicon.
- It combines with Chlorine and forms Chlorosilanes. It also reacts with Carbon to form Siliconcarbide, which is an excellent abrasive.

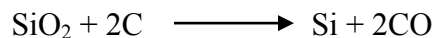
Production of Solar grade silicon:

The process of production of solar grade silicon is called Carbothermic reduction of silica and the different steps involved are;

1. Reduction of Silica by carbon.
2. Refining of crude silicon.
3. Production of Silicon hydride.
4. Decomposition of silicon hydride to semiconductor grade silicon.

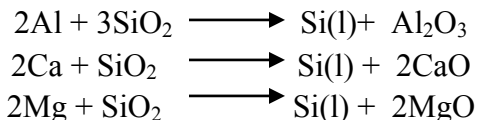
Reduction of Silica by carbon:

In this process a furnace is used which consists of a crucible filled with quartz along with electrodes. When an electric arc is struck between the two electrodes, the quartz (SiO_2) undergoes reduction to crude Silicon as follows,



Refining of crude silicon:

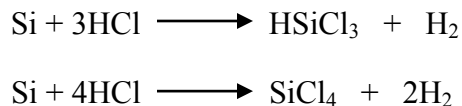
The silicon obtained above contains Al, Ca, and Mg as impurities which are removed as slag by treating the molten crude silicon with oxygen and silica flux and the reactions are as follow,



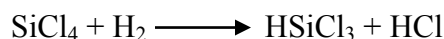
The silicon obtained above is called metallurgical grade silicon of purity 98.5% which is further processed to get semiconductor grade silicon.

Production of Silicon hydride:

The metallurgical grade silicon obtained above is treated with dry HCl gas at 300⁰C which yields trichlorosilane and a small amount of tetrachlorosilane. This mixture is distilled to get pure trichlorosilane.



The SiCl₄ is reduced to trichlorosilane by hydrogen at 1000⁰C in a reactor,

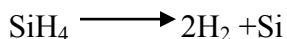


The trichlorosilane is further fed into fixed bed columns filled with the catalyst quaternary ammonium ion exchange resins.



The products obtained above are isolated by distillation. Trichlorosilane and tetrachlorosilane are recycled in a hydrogenation reactor.

Finally the SiH_4 is distilled and pyrolysed to polysilicon onto a heated silicon seed rods taken in a metal bell-jar reactor.



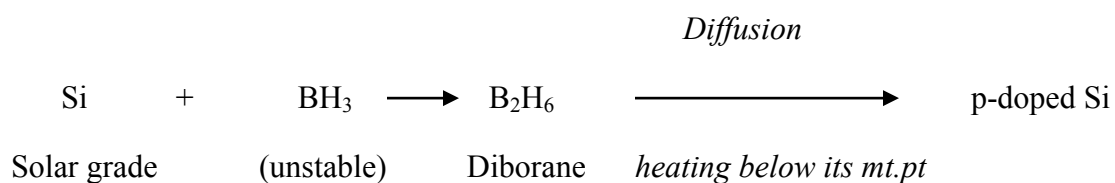
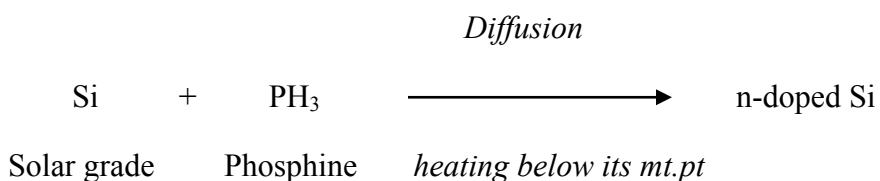
Doping of Silicon

The process of adding suitable impurities (dopants) into the structure of semiconductor is called doping.

Doping is carried out at the crystal formation stage, by adding known amount of suitable dopant into the melt of the intrinsic semiconductor. There are several methods of doping, one such method is *Diffusion technique*.

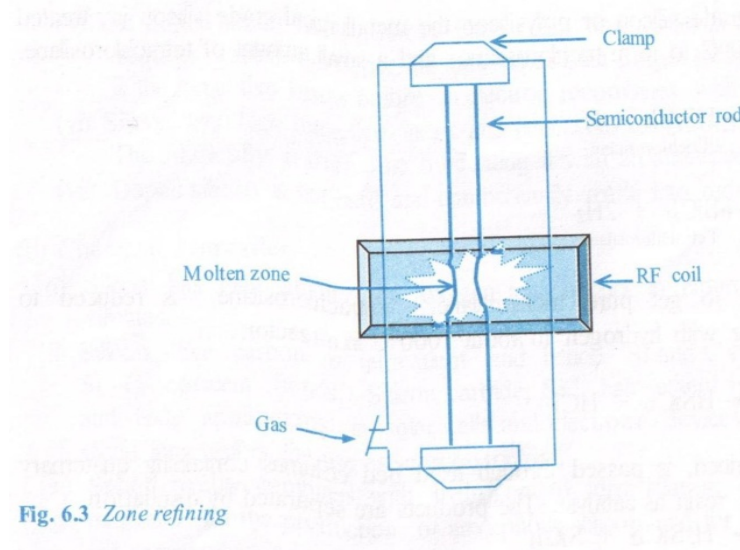
Diffusion Technique:

In this technique some region of crystal lattice of semiconductor is incorporated with dopant atoms by the diffusion without actually melting it. The reactions during the synthesis of n-type and p-type semiconductors are;



Zone Refining:

High purity silicon is required for the semiconductor industry and the need levels cannot be reached by chemical methods alone. Zone refining techniques used for purification of silicon of 99.999999 purity.

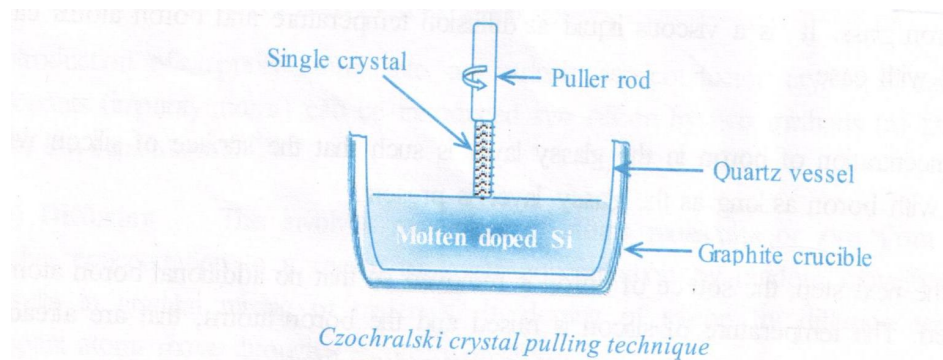


The principle of zone refining is that when a solid is melted, the impurities tend to concentrate in the molten zone.

A vertical zone refiner is used in the purification of silicon. A rod of silicon to be purified is clamped as shown in the above fig. and is heated by a RF coil to the melting point of silicon in the presence of argon gas. The heater is moved very slowly from top to bottom. This is said to be one zone pass. Impurities move with molten part of the material as the RF coil moves down. Pure silicon solidifies at the upper portion.

When the process is complete, the bottom portion where the impurities are concentrated is removed. The rod is subjected to several zone passes to get ultra pure silicon.

Czochralski methods - crystal pulling technique:

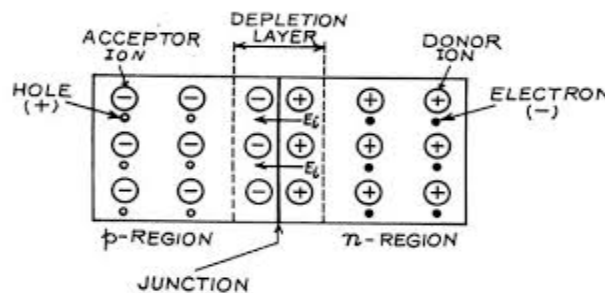


In the method polycrystalline silicon mixed with calculated amount of dopant is taken in a quartz vessel placed in a graphite crucible. The crucible is heated using a RF power source in

an inert atmosphere of argon. When the material melts, the temperature is lowered so that it is kept at the melting point of the material. A single crystal of silicon is attached to the tip of a puller rod and is lowered into the molten material so that it just touches the surface of the material. The rod is slowly rotated at a speed of about 100 rpm and simultaneously pulled out at a rate of 1.5-5cm/hr. as the melt is pulled out, it solidifies and as the same orientation and crystal structure as the seed.

Opposite type of impurity is diffused into the single crystal to form semiconductor diode or p-n junction.

p-n junction diode formation



P-n junctions are formed by joining *n*-type and *p*-type semiconductor materials, as shown above. Since the *n*-type region has a high electron concentration and the *p*-type a high hole concentration, electrons diffuse from the *n*-type side to the *p*-type side. Similarly, holes flow by diffusion from the *p*-type side to the *n*-type side. If the electrons and holes were not charged, this diffusion process would continue until the concentration of electrons and holes on the two sides were the same, as happens if two gasses come into contact with each other. However, in a *p-n* junction, when the electrons and holes move to the other side of the junction, they leave behind exposed charges on dopant atom sites, which are fixed in the crystal lattice and are unable to move. On the *n*-type side, positive ion cores are exposed. On the *p*-type side, negative ion cores are exposed. An electric field \hat{E} forms between the positive ion cores in the *n*-type material and negative ion cores in the *p*-type material. This region is called the "depletion region". The depletion region at the junction acts as a barrier for further diffusion. This results in a barrier potential across the junction which prevents the further diffusion of electrons and holes across the junction. Only when an energy exceeding the barrier potential is applied, the material starts conducting.

Expected Model Questions:

- 1). Write the differences between galvanic cell and electrolytic cell?
- 2). Describe the various components of a battery with neat diagram?
- 3). Explain the following battery characteristics?
 - a). Voltage b). Energy density c). capacity d). % energy efficiency e). cycle life f). shelf life
 - g). Electricity storage density
- 4). Define battery? Describe its classification with suitable example?
- 5). What are primary batteries? Explain construction and working of dry cell and Li-MnO₂ battery?
- 6). What are secondary batteries? Explain construction and working of lead acid battery and Lithium ion battery?
- 7). What are super capacitors and describe the working of super capacitor with advantages and disadvantages?
- 8). What are fuel cells? Give classification of fuel cell based on electrolyte and Temperature?
- 9). Give Differences between fuel cells and battery?
- 10). Explain the construction, working, advantages, applications and limitations of solid oxide fuel Cell?
- 11). Explain the construction, working, advantages, applications and limitations of phosphoric acid fuel cell?
- 12). Give physical and chemical properties of silicon?
- 13). Construction, working and applications of photo voltaic cell or solar cell?
- 14). Explain the production of single crystal semiconductor by crystal pulling technique (Czochralski method)?
- 15). How the semiconductor grade silicon is purified by zone refining method.
- 16). What are antireflective coatings? Give example.

