

ELECTROCHEMISTRY AND BATTERY TECHNOLOGY**Introduction**

Electrochemistry is the branch of chemistry, which deals with the interaction of matter and electrical energy i.e., producing electrical energy from chemical reaction (spontaneous process) or bringing out chemical reactions by applying electrical energy (non spontaneous process). Depending upon the reactions the cells are classified into two.

- 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.

Single electrode potential

It is defined as the potential developed at the interface between electrode and electrolyte when an electrode is in contact with a solution of its own ions. It is denoted as E.

Standard Electrode potential

It is defined as the potential developed when an electrode is in contact with its own ionic solution of 1M concentration, at 298 K and 1 atm pressure. It is denoted as E° .

Nernst equation:

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

Due to the power output from an electrochemical cell, the free energy decreases i.e.

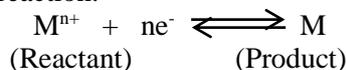
$$-\Delta G = nFE \quad (\text{or}) \quad \Delta G = -nFE$$

Under standard conditions the free energy ΔG is given by the equation

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

E° is a constant called standard reduction potential.

Consider a reduction reaction.



For spontaneous reaction, the change in the free energy depends on the concentration of reacting species.

$$\Delta G = \Delta G^\circ + RT \ln K_c \quad \longrightarrow (1)$$

$$\text{Where } K_c = \frac{[\text{Product}]}{[\text{Reactant}]}$$

Substituting the value for K_c in (1) we get

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$\text{Therefore, } \Delta G = \Delta G^\circ + RT \ln \frac{[M]}{[M^{n+}]} \quad \longrightarrow (2)$$

Substitute for ΔG and ΔG° in eqn (2)

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

Under standard conditions $[M] = 1$

$$\text{Hence, } -nFE = -nFE^\circ + RT \ln \frac{[1]}{[M^{n+}]} \quad \longrightarrow (3)$$

Dividing eq (3) by $-nF$ we get

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[1]}{[M^{n+}]}$$

Converting ln to log and solving for log we get.

$$E = E^\circ + \frac{2.303RT}{nF} \log [Mn^+] \longrightarrow (4)$$

Substituting for RT and F in eqn (4) we get

$$E = E^\circ + \frac{0.05918}{n} \log [Mn^+] \longrightarrow (5)$$

Types of electrode

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: Standard Hydrogen Electrode.
3. Metal-insoluble salt electrode: In which metal is in contact with a metal salt and places in the 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

Reference electrode

Reference electrode is that its potentials is known and is used for determination of potential of other electrodes.

Types of reference electrodes

Primary reference electrode

The electrode whose potential is fixed as zero at all temperature and pressure is known as primary reference electrode. Example: Standard hydrogen electrode (SHE).

Limitations of primary reference electrode

1. Difficulty in setting up of the electrode.
2. Difficult to maintain one atm pressure of H_2 gas uniformly for a long time..
3. Platinum foil is poisoned easily by the adsorption of impurity in the solution.
4. The equilibrium between H^+ ions and hydrogen gas gets disturbed due to adsorption of impurities.
5. The hydrogen electrode cannot be used in the presence of oxidizing agents. (As H_2 gas is a reducing agent and it reacts with oxidizing agent)

Secondary reference electrode

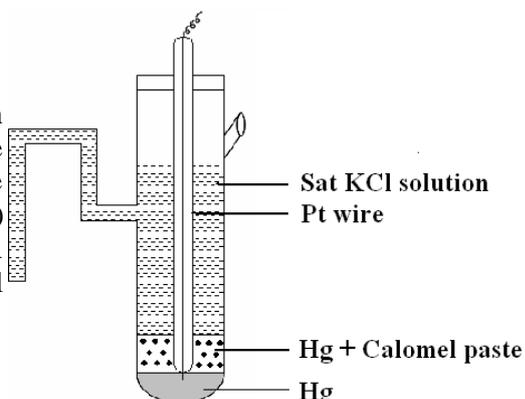
The Electrode whose potential with respect to SHE is known are called as secondary reference electrode. These electrodes commonly used to find out the potential of other electrode.

Calomel Electrode

Construction:

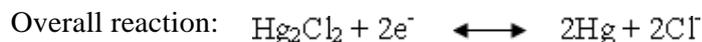
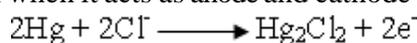
Calomel electrode consists of long glass tube with two openings on either side. One at the top to fill sat KCl solution and the other side tube for connecting to the salt bridge. Mercury is placed at the bottom which is covered with a layer of Hg and Hg_2Cl_2 (calomel) paste. The remaining portion is filled with saturated KCl solution. A platinum wire is dipped into the mercury to provide external electrical contact. The calomel electrode is represented as

$Cl^-/Hg_2Cl_2/Hg$



Working:

Calomel electrode behaves as anode or cathode depending upon the nature of other electrode. The half-cell reaction when it acts as anode and cathode is given below.



Applying Nernst equation,

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Hg}]^2[\text{Cl}^-]^2}{[\text{Hg}_2\text{Cl}_2]}$$

$$E = E^\circ - 0.0591 \frac{\log[\text{Cl}^-]^2}{n}$$

The calomel electrode potential is depends on the concentration of chloride ions in KCl. If the concentration of chloride ions increases, the potential decreases and vice versa. (The potential of calomel is inversely proportional to the concentration of chloride ions)

The potential of calomel electrode is measured with respect to SHE and it depends on concentration of KCl solution used.

Conc. KCl	0.1N	1N	Saturated KCl
Potential (V)	0.334V	0.281V	0.242V

Applications:

- Used to determine the potential of the other electrodes.
- It is commonly used as reference electrode in all potentiometric determinations.
- Electrode potential is reproducible.

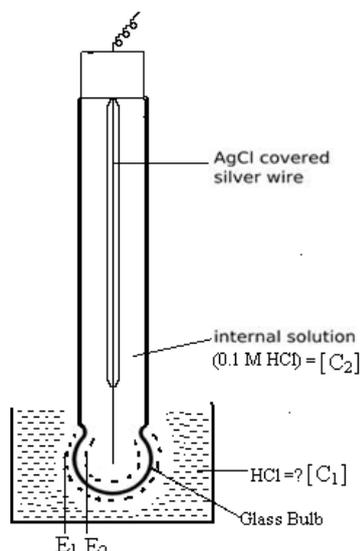
Ion-selective electrode

The electrode, which responds to a specific ion in a mixture by ignoring other ions, is known as ion selective electrode. It consists of a thin membrane in contact with ion solution.

Glass Electrode

This electrode works on the principle that when a thin, low resistivity glass membrane is in contact with a solution containing H^+ ions, a potential develops across the membrane and the solution. Potential developed depends on the concentration of hydrogen ions in the solution.

Representation: $\text{Ag} / \text{AgCl} / \text{HCl} (0.1\text{M}) / \text{Glass} / \text{unknown solution}$



Construction & working:

It consists of a long glass tube with a thin walled glass bulb at the bottom containing 0.1 M HCl. Ag/AgCl electrode placed in to the solution to provide electrical contact. The glass tube is sealed at the top to maintain the concentration of H^+ ions. The electrode than is dipped in unknown solution of other concentration. The potential develops across the membrane by the exchange of H^+ ions with the composition of glass. Then the potential is known as glass electrode potential (E_g). When the concentration of H^+ ions on either side is same the potential developed across the membrane is called standard glass electrode potential (E_g^0).

The potential developed is calculated by applying Nernst equation

$$E_g = E_g^0 - \frac{0.0591}{n} \log[H^+], \text{ where } \log[H^+] = -p^H \text{ \& } n = 1$$

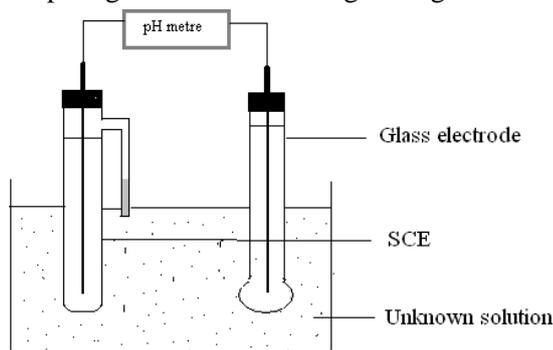
Replace for $\log[H^+]$ in above equation, we get

$$E_g = E_g^0 + 0.0591p^H$$

Determination of pH of a Solution using Glass Electrode

The potential of a glass electrode depends on the concentration of H^+ ions. In order to find out the pH of a solution, the glass electrode is placed in the solution and it is coupled with calomel electrode to form electrochemical cell. The cell assembly is represented as

$Hg/Hg_2Cl_2/Cl^- // \text{solution of unknown pH} / \text{glass}/0.1 \text{ M HCl} / AgCl / Ag$



The emf of a cell is determined by using voltmeter. The emf of the complete cell is given by.

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

$$\therefore E_{cell} = E_{calomel} - E_{glass} \rightarrow 1$$

Substitute for E_g in eq(1)

$$\therefore E_{cell} = E_{cal} - (E_{glass}^0 + 0.0591pH) \rightarrow 2$$

$$E_{cell} = E_{cal} - E_{glass}^0 - 0.0591pH \rightarrow 3$$

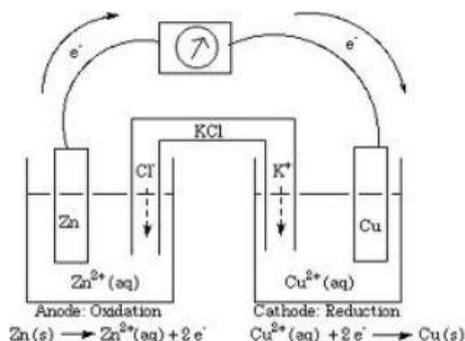
rearrange eq 3, we get

$$0.0591pH = E_{cal} - E_{glass}^0 - E_{cell}$$

$$\therefore pH = \frac{E_{cal} - E_{glass}^0 - E_{cell}}{0.0591}$$

Electrochemical cell

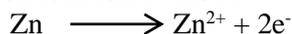
An electrochemical cell is a device in which a redox reaction is utilized to produce electrical energy. The electrochemical cell is also commonly known as voltaic cell. The practical application of electrochemical cell is denial cell.



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:
- $$Cu^{2+} + 2e^- \longrightarrow Cu$$
- 4) Copper ions deposited on copper rod.
 - 5) $CuSO_4$ solution becomes richer with SO_4 ions.
- Net reaction: $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

The net redox reaction is called electrochemical reaction and this is the cause for the production of electric current by the flow of negative electricity from zinc to copper and the conventional current i.e., positive 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 neutrality, $-ve$ ions from salt bridge migrates to $ZnSO_4$ solution to neutralize excess of Zn^{+2} ions in oxidation half cell, similarly $+ve$ ions from the salt bridge goes to reduction half cell to neutralize excess of SO_4^{-2} ions.

EMF (Electro motive force):

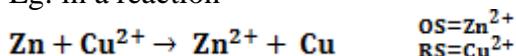
In galvanic cell the potential difference between the two electrodes causes the flow of current from one electrode (higher potential) to the other (lower potential), is called the electromotive force (emf) of the cell. This potential difference is called EMF, denoted by E_{cell} .

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

$$E_{cell} = E_{cell}^0 - \frac{2.303RT}{nF} \log Q$$

Where, $E^0 = E_{Cathode}^0 - E_{Anode}^0$ & $Q = \frac{[OS]}{[RS]}$ OS=Oxidises form of Species
RS=Reduced form of Species

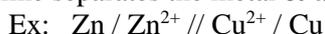
Eg: in a reaction



Cell notation and Sign convention

The conventions employed in the representation of electrochemical cell are as follows:

The oxidation half-cell is written on left hand side and reduction half cell is written on right hand side. A single vertical line separates the metal & an electrolyte and two vertical lines between them represent salt bridge.



Fuel cell

"Fuel cells are galvanic cells which converts chemical energy of the fuels into electrical energy through catalyzed redox reactions with elimination of minimum harmful biproducts".

Fuel is represented as

Fuel / electrode / electrolyte / electrode / oxidant

At anode, fuel undergoes oxidation, when battery discharge potential, the following reactions takes place at respective electrodes.

Fuel \longrightarrow oxidized product + ne

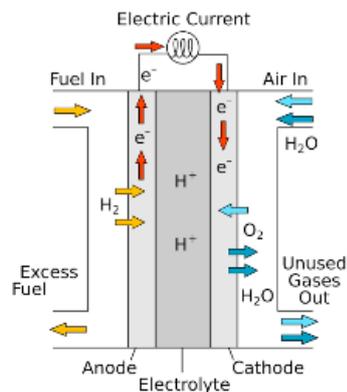
At cathode, oxidant is reduced, oxidant + ne \longrightarrow reduced product

Advantages of fuel cells

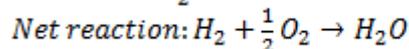
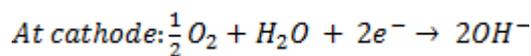
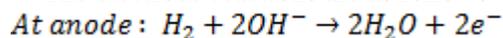
1. Do not pollute the atmosphere
2. Electrical energy can be obtained continuously.
3. Fuel cell provides high quality of DC power.
4. Fuel cells have a higher efficiency than diesel or gas engines.

Hydrogen-Oxygen fuel cell

Hydrogen-Oxygen fuel cell is a simplest type of alkaline fuel cell. The device consists of two electrodes (anode and cathode). The electrodes are porous graphite impregnated with Pt-Ru-Co or Pt-Ru-Ni catalyst. Solution of KOH or NaOH is placed between two electrodes to serve as electrolyte. The battery works at about 75 °C. Hydrogen gas (fuel) and oxygen is supplied continuously at the anode and cathode respectively. Gas diffuses slowly through the electrodes. In presence of catalyst, at anode hydrogen undergoes oxidation to form hydrogen ions and electrons. Further, the electrons released travels through external circuit. At cathode oxygen combines with electrons forming hydroxyl ions. The water is removed continuously from the cell to maintain electrolyte concentration.



The electrode reactions are as follows

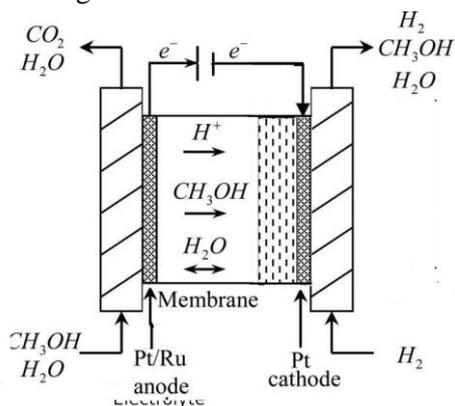


Application:

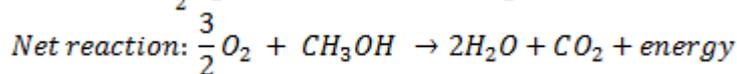
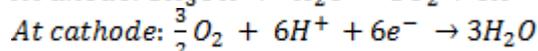
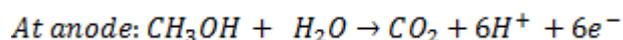
- Used in space vehicles, submarines, military applications, etc.,

Methanol-Oxygen fuel cell

In this fuel cell methanol is used as fuel and oxygen as oxidant to generate electric current. The fuel cell consists of two electrodes (anode and cathode). Anode consists of porous nickel electrode impregnated with Pt/Ru catalyst. Porous nickel electrode impregnated with silver catalyst constitute cathode. Wet sulphuric acid solution is placed between two electrodes to serve as electrolyte. The methanol (fuel) is supplied at anode and oxygen gas is supplied at cathode. The anode and cathode is separated by sulphonic acid polymer membrane. The membrane allows the conduction of proton between the electrodes and avoids the diffusion of methanol towards cathode. In presence of catalyst, at anode methanol undergoes oxidation to form hydrogen ions, carbon dioxide and electrons. Further, the electrons released travels through external circuit. At cathode oxygen combines with electrons forming water. The water is removed continuously from the cell to maintain electrolyte concentration.



The electrode reactions are as follows



Application:

- Used in military applications
- Large-scale power productions.

Battery Technology

A battery is a portable energy source with three basic components- anode (the negative part), cathode (the positive part), and electrolyte.

A battery is a device consisting of two or more galvanic cells connected in series or parallel, which convert chemical energy into electrical energy through redox reactions.

Classification of Batteries

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

Primary battery

Primary batteries are those which are constructed by joining two or more galvanic cells in series or parallel. They produce electrical energy as long as the active materials are present. These are not rechargeable batteries and are to be discarded after the use.

Example: Dry cell. Zn-MnO₂, Ag₂O-Zn battery

Secondary battery

Secondary batteries are those which are constructed by joining two or more galvanic cells in series or parallel. They produce electrical energy at the expense of free energy of active materials. After discharge, the active materials can be restored back at respective electrodes on recharging. The recharging of the battery is done by passing current through it in the opposite direction of the discharge is known as secondary battery.

Example: Lead acid battery, NiMH battery, Ni-Cd battery the battery can be recharged and

Reserve battery

The reserve batteries are also called as high current batteries, in which active materials are isolated from electrolyte due to their reactivity and are brought into contact whenever high potential is required for application..

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

Characteristics of a battery

Cell potential / Voltage

The cell potential or voltage of the battery is determined theoretically, $E_{\text{cell}} = (E_C - E_A) - \eta_A - \eta_C - iR_{\text{cell}}$

Where E_C & E_A are reduction potential of cathode and anode, η_A & η_C are over potential at the anode and cathode and iR_{cell} is the internal resistance.

To attain the maximum cell potential or voltage from the battery, difference in the standard electrode potential must be high, the electrode reaction must be fast to minimize the over potential and internal resistance must be low.

Current

Current is *“the measure of the rate of flow of charges in a battery”*.

To attain the maximum current from the battery, difference in the standard electrode potential must be high, the electrode reaction must be fast to minimize the over potential and internal resistance must be low.

Capacity

Capacity of the battery is *“The total amount of electricity that is produced from a battery until the failure of battery is called capacity of the battery. Capacity of the battery is expressed in Ampere hours (Ah).”*

The capacity is determined by faradays relation, $C = WnF/M$, where W and M is weight and mass of the active material respectively and n is the number of moles of the electro active material.

Electrical storage density

Electrical storage density is *“the Amount of electrical energy stored per unit weight of the battery.”* The weight of the battery includes mass of the electrolyte, current collector and other elements. Lighter the weight of the elements leads to high storage density.

Energy density

Energy efficiency is *“the amount of energy available from the battery to its mass”*. It is given by

$$\text{Energy Density} = \frac{IEt}{w}$$

Where “I” is the current drawn from the battery at fixed voltage “E” from time duration “t” and “w” is the weight of the battery

Energy efficiency

It is the ratio of energy released on discharge to the energy required on recharge. Higher the efficiency, very good is the battery.

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

Energy required during recharge

Cycle life

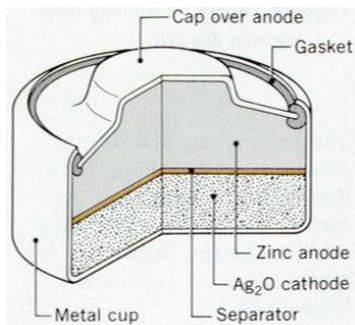
Cycle life of the battery is “The total number of discharge and recharge cycles that are possible before the failure of the battery”. It is applicable only to secondary battery, higher the cycle life, better is the battery life.

Shelf-life

Shelf life of the battery is “The duration of storage of a battery without self discharge is known as shelf life of a battery”. It referred to storage duration of battery. If shelf life is high, better is the battery.

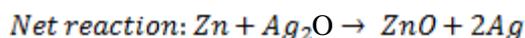
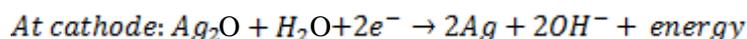
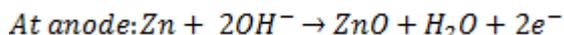
Silver oxide-Zinc battery**Construction:**

Silver oxide zinc battery is a primary cell available in small size as button cell. The cathode is generally composed of monovalent silver oxide with added graphite to improve conductivity. The anode is zinc powder mixed with a gelling agent dissolved in KOH alkaline electrolyte. The anode and cathode are separated by a combination of layers of plastic membrane, cellophane (thin transparent sheet made of cellulose) and absorbent fibers like rayon or nylon. The two are taken in nickel-plated steel cup. The anode is covered with a sheet at the top made up of laminated layers of copper, tin, steel and nickel. An insulating gasket prevents contact between the two.

**Working:**

The cell reaction involves the oxidation of Zinc metal at the anode to produce positively charged Zinc ions (Zn^{2+}) and electrons (e^-). Zn^{2+} ions go into the electrolyte to form stable ZnO . Electrons travel through the external circuit and arrive at the cathode where monovalent silver ions reduces to silver liberating energy.

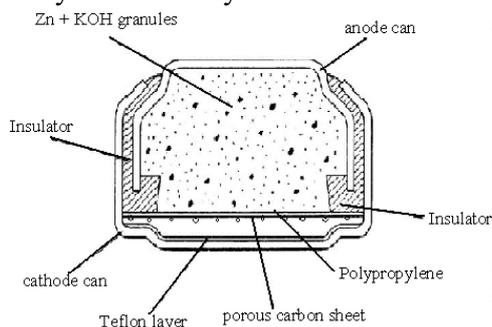
During discharge the following reaction takes place

**Applications**

Used in electronic watches, cameras, hearing aid instruments, etc.,.

Zinc-air battery

It is a type of metal air battery which uses oxygen directly from atmosphere to produce energy. The battery is commonly known as “zinc-air” cell.

**Construction:**

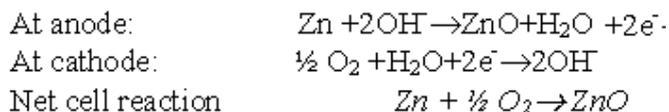
It consists of nickel-plated steel cans acting as anode and cathode. The anodic can is filled with zinc powder and 30% KOH electrolyte in the form of granules with a gelling agent. The cathode is made up of nickel plated steel mesh coated by carbon sheet impregnated with MnO_2 (to increase the conductivity of cathode). Multiple air holes punched at the bottom to provide air access to the cell. The sheet is laminated with Teflon layer (to diffuse the oxygen faster to cathode side) on one side. The anodic and cathodic compartments are separated by polypropylene separator.

Working:

During discharging Zinc undergo oxidation at anode giving electrons. The moist air at the cathode reduces to hydroxyl ions taking up the electrons.

When the battery discharge, the following reactions takes place at respective electrodes.

Reactions:



The output voltage is 1.45 Volts.

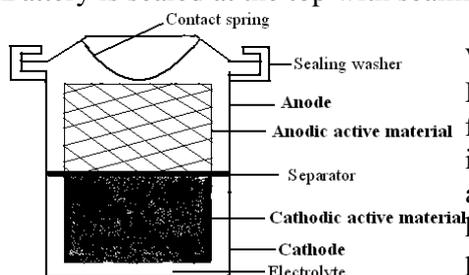
Application:

- Used in hearing aids,
- In telecommunication devices such as pagers and wireless headsets
- In medical devices such as patient monitors, recorders, nerve & muscle stimulators and drug infusion pumps.

Nickel-metal hydride battery (Ni-MH)

Construction:

In a Ni-MH battery the electrodes are made up of nickel wire gauge. Anode is pasted with hydrogen storage alloy in the form of metal hydride (VH_2) and cathode is impregnated with nickel oxy hydroxide as active material. Many positive and negative electrodes are connected with each in parallel and are soaked in aqueous KOH electrolyte solution taken in steel container. The electrodes are separated using polypropylene separator. Battery is sealed at the top with sealing washer.

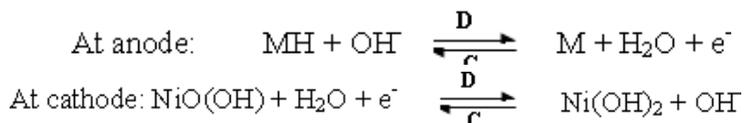


Working:

During discharging the cell reaction involves the oxidation of hydrogen from the metal hydride at anode to produce positively charged hydrogen ions (H^+) and electrons (e^-). Electrons travel through the external circuit and arrive at the cathode where nickel oxy hydroxide reduces to nickel hydroxide. When discharge is complete, the battery is charged by passing current from the external source to restore the components at the respective electrodes.

When battery is discharging /charging, the following reactions take place at respective electrodes.

Reactions:



The output voltage is 1.35V.



Applications:

- Used in Cellular phones and laptops
- In Emergency lights and Power tools
- In electric vehicles

Lithium battery

There are two types of lithium-based batteries available.

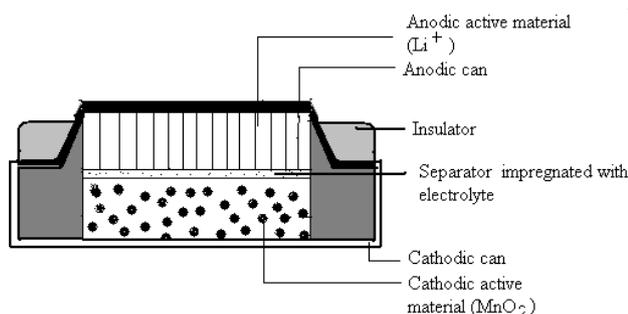
1. Lithium batteries
2. Lithium-ion batteries

In lithium batteries, a pure lithium metallic element is used as anode. These types of batteries are not rechargeable.

LiMnO₂ battery

Construction:

Lithium Manganese Dioxide battery is a primary battery constructed by connecting many number of anode and cathode in series. The anode is pure lithium and cathode is heat treated manganese dioxide taken in the form of a pellet. The anode is placed in stainless cap and cathode in stainless steel can. The electrodes are separated using polypropylene separator impregnated with the electrolyte. The electrolyte is lithium halide dissolved in polypropylene carbonate which provides an electrical contact between the two electrodes. The terminals of anode and cathode are insulated using rubber.

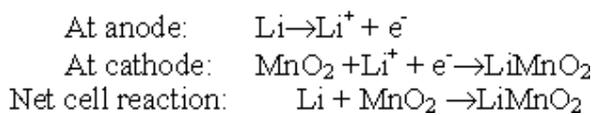


Working:

The cell reaction involves the oxidation of lithium metal at the anode to produce positively charged lithium ions (Li⁺) and electrons (e⁻). Li⁺ ions go into solution and diffuse through the electrolyte and separator to the cathode. Electrons travel through the external circuit and arrive at the cathode where MnO₂, Li⁺ ions and electrons combine. Accepting the electron the Mn in MnO₂ reduces from the tetravalent to the trivalent state and Li⁺ diffuses into host to form LiMnO₂ which remains in the cathode.

When battery is discharging, the following reactions take place at respective electrodes.

Reactions:



The output voltage is 3.0V.

Application:

- Outdoor use (requiring a low temperature range)
- In high-discharge devices, which include digital cameras, electric watches, hearing aids, walkie-talkies, portable televisions, handheld video games, etc

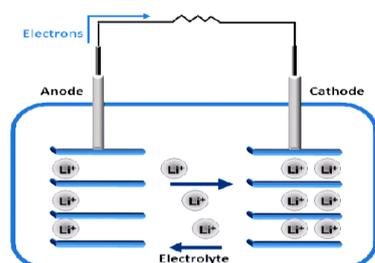
Lithium-ion battery

In lithium-ion battery (Li-ion battery) the lithium ions (electrons) move from the negative electrode (anode) to the positive electrode (cathode) during discharge and back when charging.

Construction:

Li-ion battery is a secondary battery constructed by connecting many number of anode and cathode in series. Anode is made up of carbon material with a copper foil as current collector. Cathode is made up of lithium metal oxide with aluminum foil as current collector. The Common cathode material is Lithium Cobalt Oxide, Lithium Manganese Oxide or Lithium Iron Phosphate. Electrolyte is made of lithium salts dissolved in organic solvent (LiPF₆, LiBF₄ or LiClO₄ in an organic solvent, such as ether,). The electrodes are separated with polypropylene and placed in electrolyte taken in container.

The most common lithium-ion batteries have an anode of carbon (C) and a cathode of lithium cobalt oxide (LiCoO₂).

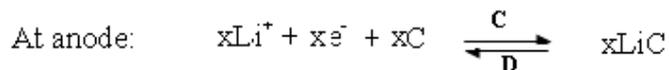
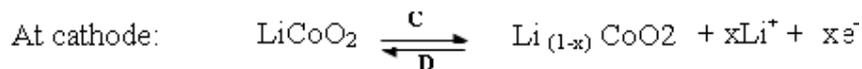


Working:

During discharge, the lithium ions are detached from the anode and travel through the electrolyte to the cathode. This releases the electrons which flow through an external wire, providing the electric current. At cathode Li ions reduces and form LiCoO_2 .

During charging and discharging the following reactions takes place

Reactions:



When the cathode becomes full of lithium ions, the reaction stops and the battery is flat. Then the battery is recharged. The external electric charge that we apply pushes the lithium ions back into the anode from the cathode.

During discharging and charging the following reactions takes place

Application:

- The Li-ion batteries are used in mobile phones, cameras, calculators, LCD TVs, pagers, to operate laptop computers and aerospace application