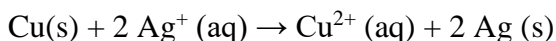


UNIT- III: Electrochemistry and Water technology

Overview of Fundamentals of Electrochemistry - Concentration Cells – Batteries: Dry Cell - Ni-Cd cells - Ni-Metal hydride cells- Li cells - Zinc – air cells. Fuel cells: Hydrogen Oxygen fuel cells – Methanol Oxygen fuel cells

Overview of Fundamentals of Electrochemistry:

- Electrochemistry is defined as the branch of chemistry that examines the phenomena resulting from combined chemical and electrical effects. Electron transfer reactions are oxidation-reduction or redox reactions.
- In electrochemistry, the following two conversions are discussed.
 - Conversion of electrical energy into chemical energy.
 - Conversion of chemical energy into electrical energy.
- **Oxidation** (Reducing agent): loss of electrons (or) increase in oxidation number (or) increase in oxygen (or) decrease in hydrogen.
- **Reduction** (Oxidizing agent): gain of electrons (or) decrease in oxidation number (or) decrease in oxygen (or) increase in hydrogen.
- Direct redox reaction: Oxidizing and reducing agents in direct contact.



- Indirect redox reaction: A battery functions by transferring electrons through an external wire from the reducing agent to the oxidizing agent.



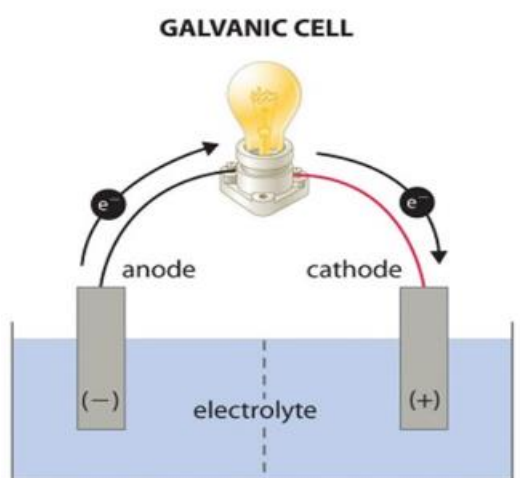
Electrolytes: A solution that contains ions and conducts electricity in the fused state or in the aqueous solution or as a solution in any other solvent is known as electrolyte. Ex; fused salts like KCl, NaCl, aqueous solutions like KOH, NaOH

Non-electrolytes: Chemical substances that do not permit the passage of current through them either in the fused state or in the aqueous solution or in any other solution form is known as non-electrolyte. Ex: Urea, benzene, sugar

An electrochemical cell is a device capable of either generating electrical energy from chemical reactions or using electrical energy to cause chemical reactions.

Types of electrochemical cells: Electrochemical cells are of two types.

- **Galvanic or Voltaic cells:** Chemical reactions that result in the production of electrical energy. Galvanic cells convert chemical energy into electrical energy. The energy conversion is achieved by spontaneous redox reactions producing a flow of electrons. Batteries are voltaic cells.
- **Electrolytic cells:** Reactions in which chemical changes occur on the passage of an electrical current. Electrolytic cells are driven by an external source of electrical energy. A flow of electrons drives non-spontaneous redox reactions.

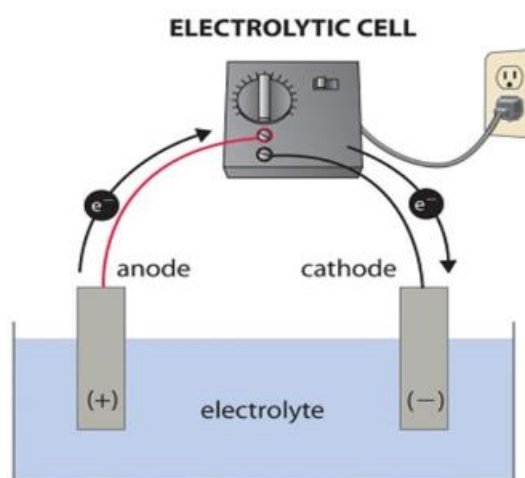


Energy released by spontaneous redox reaction is converted to electrical energy.

Oxidation half-reaction: $Y \rightarrow Y^+ + e^-$

Reduction half-reaction: $Z^+ + e^- \rightarrow Z$

Overall cell reaction: $Y + Z \rightarrow Y^+ + Z^-$



Electrical energy is used to drive nonspontaneous redox reaction.

Oxidation half-reaction: $Z^- \rightarrow Z + e^-$

Reduction half-reaction: $Y^+ + e^- \rightarrow Y$

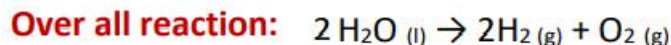
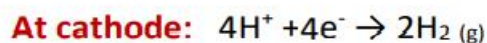
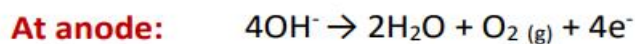
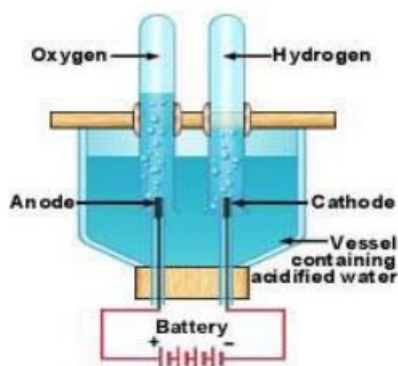
Overall cell reaction: $Y^+ + Z^- \rightarrow Y + Z$

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 reaction at the anode is oxidation and that at the cathode is reduction.	The anode is positive and cathode is the negative electrode. The reaction at the anode is oxidation and that at the cathode is reduction.
The electrons are supplied by the species getting 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.

Electrolytic cell: An electrolytic cell is often used to decompose chemical compounds, in a process called electrolysis. Ex: Decomposition of water into hydrogen and oxygen.

The electrolyte provides the medium for the exchange of electrons between the cathode and the anode. Pure water is however a very poor conductor of electricity and one has to add dilute sulphuric acid in order to have a significant current flow. Hydrogen gas is evolved at the cathode, and oxygen at the anode. The ratio, by volume of hydrogen to oxygen, is exactly 2:1.

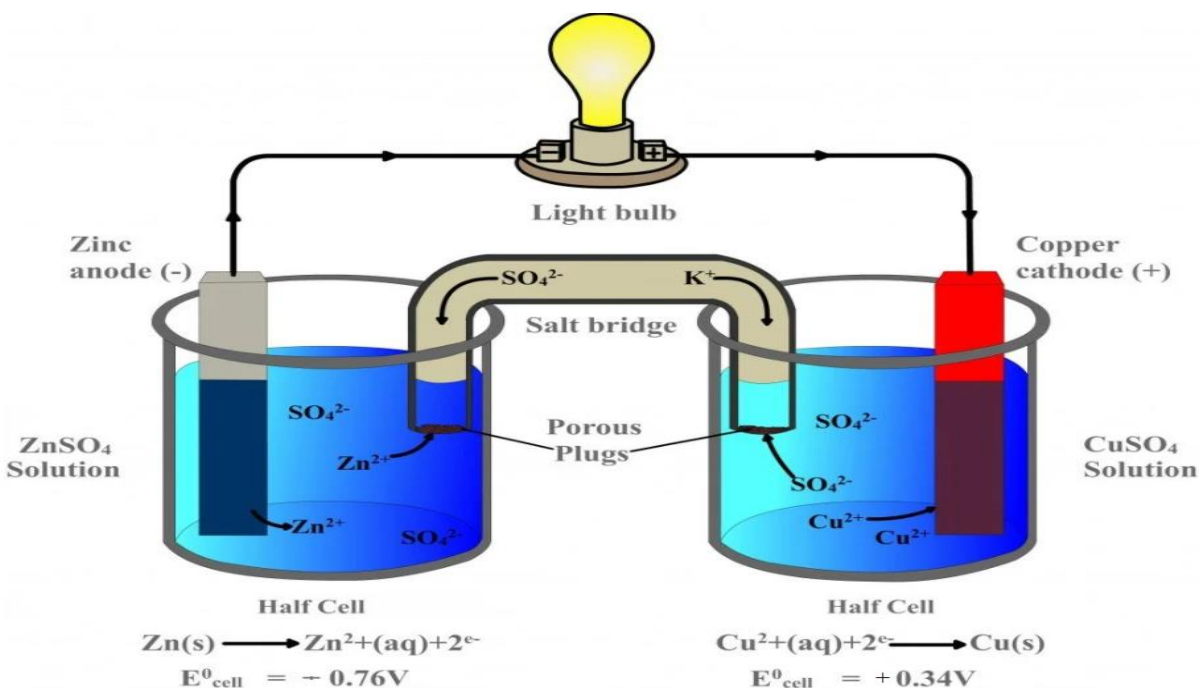
The overall reactions are:



Galvanic cell:

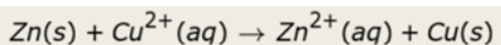
An electrochemical cell that converts the chemical energy of spontaneous redox reactions into electrical energy is known as a galvanic cell or a voltaic cell. The operation of a galvanic (or voltaic) cell is opposite to that of an electrolytic cell.

Ex: Reaction between aqueous solutions of zinc (Zn) and copper (Cu):



$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{right}} - E_{\text{left}} \\ E_{\text{cell}} &= .34 - (-.76) \\ &= 1.10 \text{ V} \end{aligned}$$

The oxidation half reaction takes place at zinc electrode (anode) and the reduction half reaction at copper electrode (cathode). There is a flow of current in the external circuit from anode to cathode. To maintain electronic neutrality, the zinc ions at the anode start moving towards the cathode internally and the sulphate ions at the cathode start moving towards the anode internally with the help of salt bridge. Thus, at anode, oxidation of zinc electrode occurs and at cathode, reduction of copper ions takes place. The overall reaction is:



Electrochemical series: A series which shown an increasing order of standard reduction potential values of electrode is called Electrochemical series.

To determine an oxidation potentials from a reduction table, just take the opposite sign of the Reduction.

Standard reduction potentials at 298 K:		
Electrode	Electrode reactions	E ⁰ volts
Li ⁺ Li	Li ⁺ (aq) + e ⁻ → Li(s)	- 3.05
K ⁺ K	K ⁺ (aq) + e ⁻ → K(s)	- 2.93
Mg ²⁺ Mg	Mg ²⁺ (aq) + 2e ⁻ → Mg(s)	- 2.37
Al ³⁺ Al	Al ³⁺ (aq) + 3e ⁻ → Al(s)	- 1.66
Zn ²⁺ Zn	Zn ²⁺ (aq) + 2e ⁻ → Zn(s)	- 0.76
Fe ²⁺ Fe	Fe ²⁺ (aq) + 2e ⁻ → Fe(s)	- 0.44
Cd ²⁺ Cd	Cd ²⁺ (aq) + 2e ⁻ → Cd(s)	- 0.40
Ni ²⁺ Ni	Ni ²⁺ (aq) + 2e ⁻ → Ni(s)	- 0.25
Pb ²⁺ Pb	Pb ²⁺ (aq) + 2e ⁻ → Pb(s)	- 0.13
Pt, H ⁺ H	2H ⁺ (aq) + 2e ⁻ → H ₂ (s)	0.00
Cd ²⁺ Cu	Cu ²⁺ (aq) + 2e ⁻ → Cu(s)	+ 0.34
I ₂ / I ⁻	I ₂ (s) + 2e ⁻ → 2 I ⁻ (aq)	+ 0.54
Fe ³⁺ Fe ²⁺	Fe ³⁺ (aq) + 3e ⁻ → Fe ²⁺ (aq)	+ 0.77
Hg ₂ ²⁺ Hg	Hg ₂ ²⁺ (aq) + 2e ⁻ → Hg(l)	+ 0.79
Ag ⁺ Ag	Ag ⁺ (aq) + e ⁻ → Ag(s)	+ 0.80
Br ₂ Br ⁻	Br ₂ (aq) + 2e ⁻ → 2 Br ⁻ (aq)	+ 1.08
Pt, Cl ₂ Cl ⁻	Cl ₂ (aq) + 2e ⁻ → 2 Cl ⁻ (s)	+ 1.36
Au ³⁺ Au	Au ³⁺ (aq) + 3e ⁻ → Au(s)	+ 1.50
F ⁻ F ₂ Pt	F ₂ + 2e ⁻ → 2F ⁻	+ 2.87

- The electrode at which oxidation occurs with respect to standard hydrogen electrode has –ve reduction potential, i.e., the electron accepting tendency of the metal electrode is lesser than that of standard hydrogen electrode. These electrodes shows lesser tendency towards reduction than the tendency of H⁺ ions for reduction.
- The electrode at which reduction occurs with respect to standard hydrogen electrode has +ve reduction potential, i.e., the electron accepting tendency of the electrode is more than that of a standard hydrogen electrode. These electrodes shows greater tendency towards reduction than the tendency of H⁺ ions for reduction.

- Reactive metals are placed on top (e.g., Li) and they have a great tendency to get oxidized. Non-reactive metals like Ag and Au are placed at the bottom.
- The elements (or) metals which are present above hydrogen in ECS liberates H₂ from acids.

Example:



Concentration Cells:

Concentration cell is a special kind of electrochemical cell where EMF arises due to the difference in concentration of electrolyte or electrode of two half cells. Ions are transferred from more concentrated solution to less concentrated solution directly or indirectly. Along with ions, electrons also move which causes the current flow. EMF of this cell depends upon the difference of concentration of the species involved.

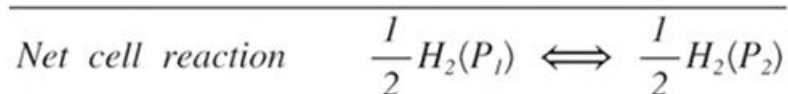
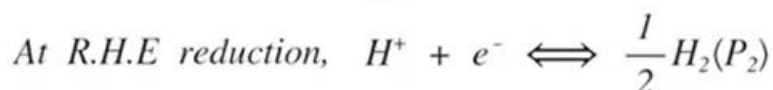
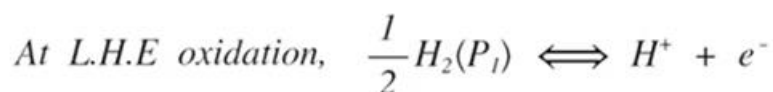
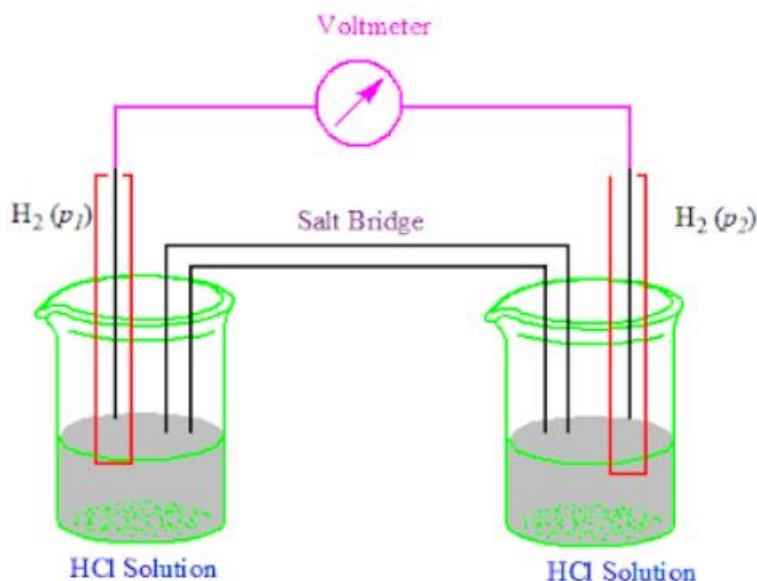
Types of concentration cells: Concentration cells can be classified into two types:

(i) Electrode concentration cells:

Concentration cell having like electrode of different concentration/pressure immersed in the electrolytic solution of same concentration.

Two hydrogen electrodes at unequal gas pressure immersed in the same solution of hydrogen ions constitute an electrode-concentration cell.

The potential difference is developed between two like electrodes at different concentrations dipped in the same solution of the electrolyte.



The Nernst equation for the above cell may be written as

$$E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln \left(\frac{P_2}{P_1} \right)^{1/2}$$

$$E_{cell} = E_{cell}^0 - \frac{2.303RT}{F} \log \left(\frac{P_2}{P_1} \right)^{1/2} \quad (n=1)$$

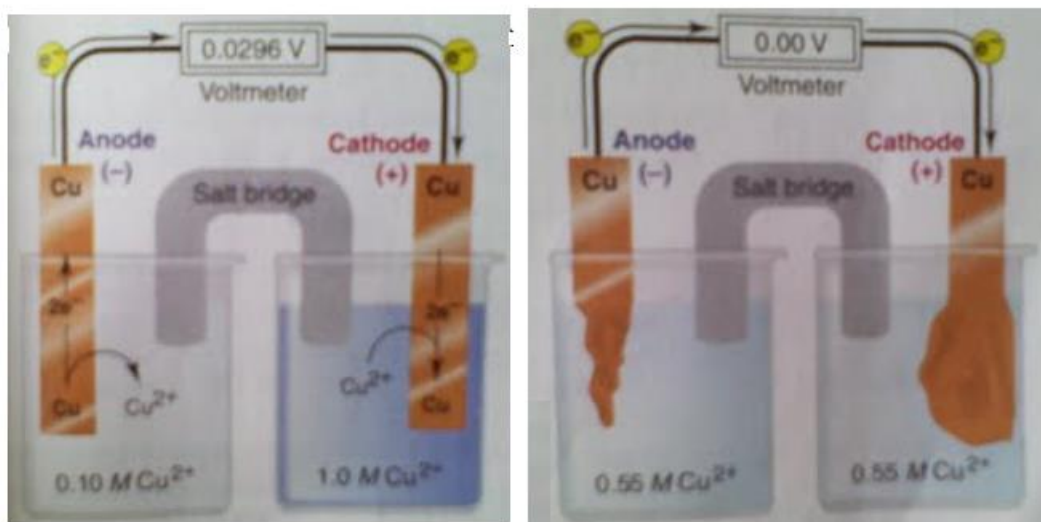
$$E_{cell} = - \frac{0.0591}{2} \log \left(\frac{P_2}{P_1} \right) \quad E_{cell}^0 = 0$$

$$E_{cell} = \frac{0.0591}{2} \log \left(\frac{P_1}{P_2} \right)$$

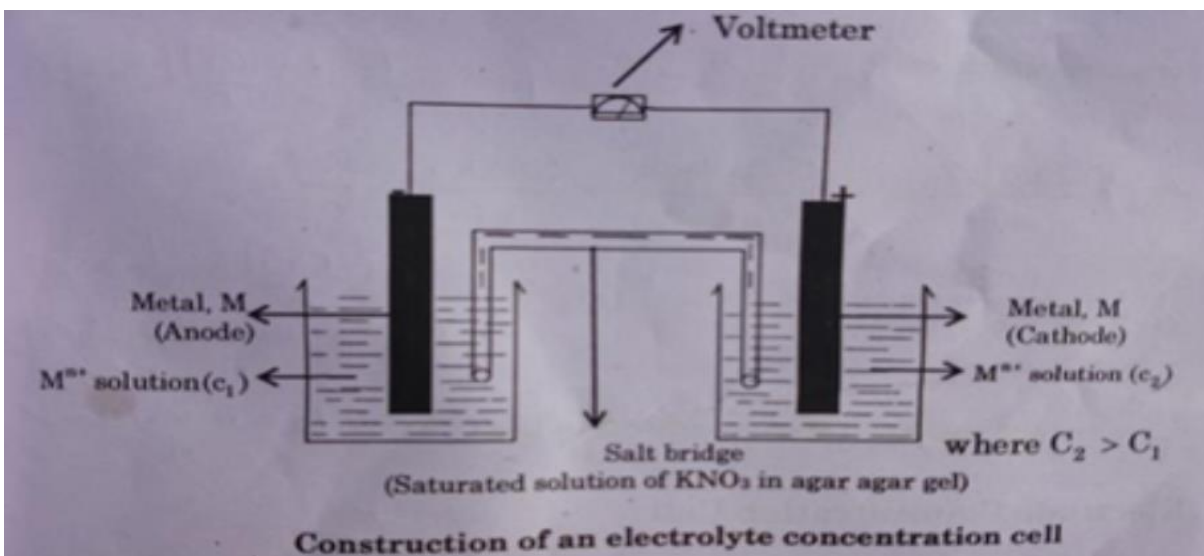
Electrolyte concentration cells:

These cells consist of same electrodes immersed in the solutions of the same electrolytes but with varying concentrations.

In the half cell with dilute electrolyte (anode), the Cu atoms in the electrode give up electrons and become Cu^{2+} ions, which enter the solution and make it more concentrated. The electrons released at the anode flow to the cathode compartment.



In the half cell with concentrated electrolyte (cathode), the Cu^{2+} ions in the solution pick up electrons and become Cu atoms, which deposit on the electrode, so the solution becomes less concentrated. When the solutions reach equilibrium, no more work can be done.



Metal immersed in dilute solution will have lower potential and it is taken as anode, whereas, metal immersed in concentrated solution will have higher potential and is taken as cathode.

The Nernst equation for electrolyte concentration cell is:

$$E_{\text{cell}} = E_{\text{ca}} - E_{\text{an}}$$

$$E_{\text{ca}} = E^0 + \frac{0.0591}{n} \log [C_2]$$

$$E_{\text{an}} = E^0 + \frac{0.0591}{n} \log [C_1]$$

$$E_{\text{cell}} = E^0 + \frac{0.0591}{n} \log [C_2] - (E^0 + \frac{0.0591}{n} \log [C_1])$$

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

Electrolyte concentration cells are of two types

- Concentration cells without transference
- Concentration cells with transference

Battery: A number of cells connected in series forms a battery. Which converts chemical energy into electrical energy. In today's life batteries play an important part as many household and industrial applications use batteries as their power source. Unfortunately, there is no single battery technology available on the market today. There are a variety of batteries in use, each with its own advantages and disadvantages.





Primary cells (Irreversible): In these the redox reaction occurs only once and cannot be reversed irrespective of the amount of external EMF. The active materials may not return to the original forms. These are also called as single-use or throw away batteries because they have to be discarded after they run empty as they cannot be recharged for reuse. Primary batteries can produce current immediately on assembly. These are most commonly used in portable devices.

Ex: Silver-Oxide cells, Lithium cells, alkaline cells, Carbon-Zinc (Heavy-duty), Zinc-Air cells etc.

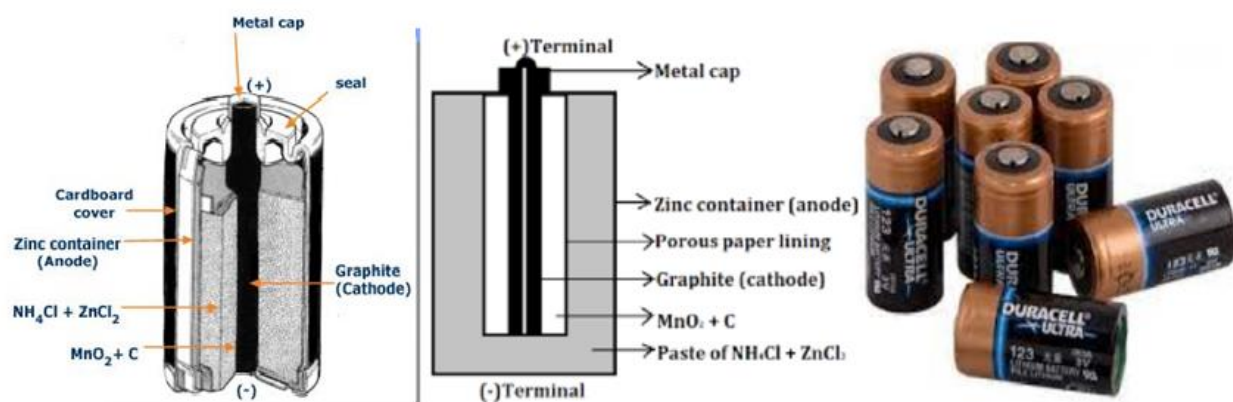


Secondary cells (Reversible): These can be recharged by passing current and can be used again and again. This charging and discharging can happen many times depending on the battery type. Mostly called rechargeable batteries. These cells can be recharged by applying electric current which reverses the chemical reactions that occur during its use. Devices to supply the appropriate current are called chargers or rechargers.

Ex: Lead-Acid, Ni-Cd, Ni-Metal hydride, Lithium-ion, Rechargeable alkaline battery etc.

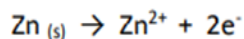


Dry/Leclanche Cell:

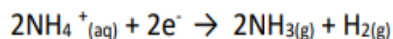


It is a Leclanche cell where the zinc vessel acts as negative electrode (anode) and the carbon rod acts as positive terminal (cathode). The space between the electrodes is filled with mixture of NH_4Cl and ZnCl_2 . The graphite rod is surrounded by carbon and manganese dioxide is used as electrolyte. The zinc vessel is lined with a blotting paper and top of the cell is sealed.

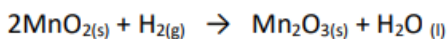
The anode half-reaction is as follows:



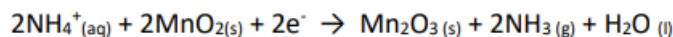
The paste of ammonium chloride reacts according to the following half-reaction:



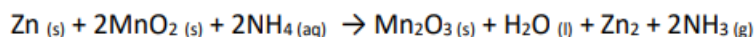
The manganese (IV) oxide in the cell removes the hydrogen produced by the ammonium chloride, according to the following reaction:



The combined result of these two reactions takes place at the cathode. Adding these two reactions together, we get:



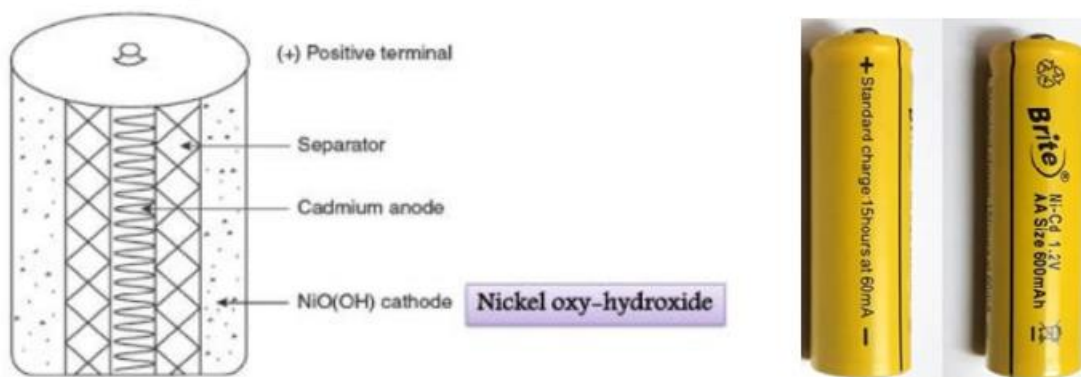
Therefore, the overall equation for the cell is:



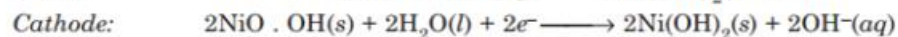
The potential for the above reaction is 1.50 V. It does not have a long life because the acidic NH_4Cl corrodes the Zinc container.

Ni-Cd cells:

In Ni-Cd cells, nickel oxide hydroxide and metallic cadmium act as electrodes. Alkaline KOH solution is used as electrolyte. These cell offer good life cycle and good performance at low temperature. Normal cell voltage is 1.2 V.



These battery is constructed of cadmium anode and a paste of $\text{NiO}(\text{OH})(\text{s})$ cathode. The cell reaction is



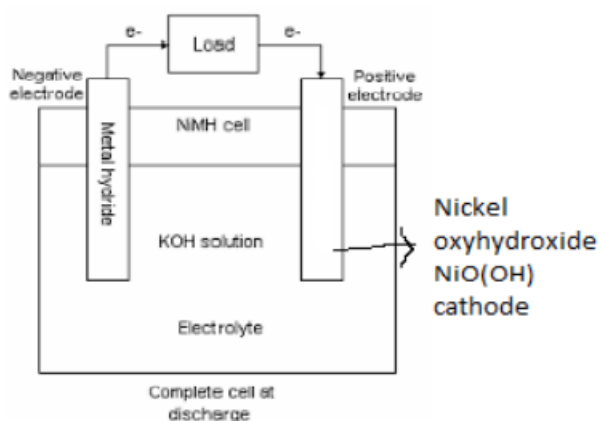
This type of battery is rechargeable. The main advantage of this battery is that, it undergoes no deterioration as no gases are produced during charging and discharging.

Uses: It is used in calculators, electronic flash units, toys, aircraft starting batteries, electric vehicles and standby power supply.

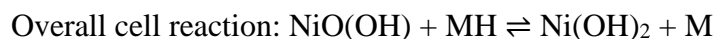
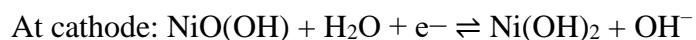
Ni-Metal hydride cells:

These are an extension of the old fashioned Ni-Cd batteries. Normal cell voltage is 2.0V. They exhibit good high current capability and have a long cycle life. The self-discharge rate is approximately 10% per month. In these cells, no toxic cadmium but contain a large amount of nickel oxides which are human carcinogens and should be recycled.

Ni-Metal hydride cells:



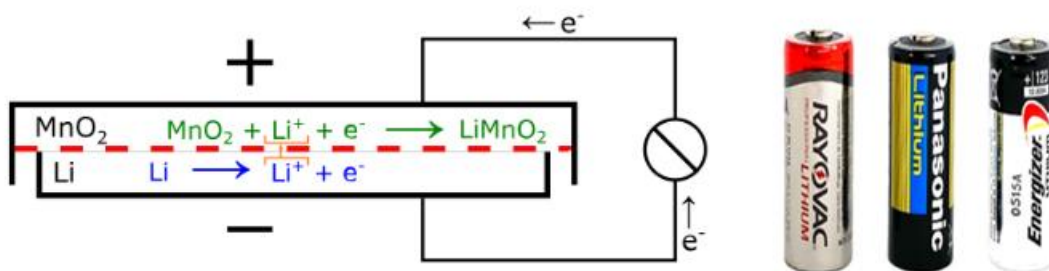
In Nickel-metal hydride cell, metal hydride vessel (MH) acts as an anode and nickel oxyhydroxide rod (NiO(OH)) acts as a cathode. The alkaline potassium hydroxide (KOH) electrolyte separates the two electrodes. Nickel-Metal hydride cell is a secondary cell which can be rechargeable. Reactions at electrodes are:



Uses: It is used in digital cameras, cell phones, portable video games, portable bluetooth devices.

Li cells:

Lithium batteries are primary batteries that have metallic lithium as an anode and manganese dioxide (MnO_2) as cathode. Lithium perchlorate in organic solvent used as an electrolyte which separates the two electrodes.



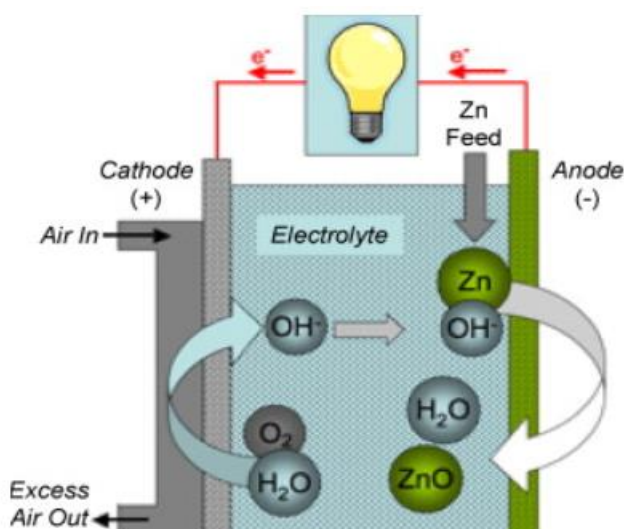
Lithium cells generally have voltages of between 1.5 and 3.7 V. Lithium batteries offer longer life due to their high charge density, which can balance the higher initial cost.

Lithium primary batteries are found in a range of sizes, from small button cells to large size. Small lithium cells are commonly used in small, portable electronic devices like watches, digital cameras, calculators and remote car locks. Larger lithium cells are found in many medical, defense, and industrial applications.

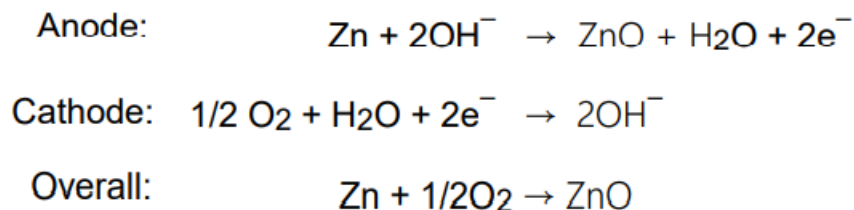
Zinc – air cells:

Zinc–air batteries are metal–air batteries powered by oxidizing zinc with oxygen from the air. Zinc pellets are added from the top of the cell which oxidized at the anode and oxygen supplied into the chamber get reduced at the cathode. LiOH , NaOH , and KOH are the common electrolytes for Zn–air batteries. Normal cell voltage is 1.59 V.

They have a very long run time because they store only the anode material inside the cell and use the oxygen from the ambient air as a cathode.



The chemical equations for the zinc–air cell are:



Uses: Power sources for hearing aids, medical devices, and pagers.

Fuel cells:

Fuel cells are devices which convert the energy produced during the combustion of fuels like H_2 , CO , and CH_4 directly into electrical energy.

Hydrogen-Oxygen fuel cells: The most successful fuel cell is the H_2 - O_2 fuel cell. Hydrogen fuel cells combine hydrogen and oxygen, creating pure water as exhaust. It was used in the Apollo space programme and the water produced used as drinking water for the astronauts.

(The Apollo programme was designed to land humans on the Moon and bring them safely back to Earth).

Principle:

- The combustion reaction like $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$ is an exothermic redox reaction and can be used to produce electricity.
- The reactants of this fuel cell can be continuously supplied from outside, hence this type of galvanic cell can be used to supply electrical energy for a very long period.

Construction:

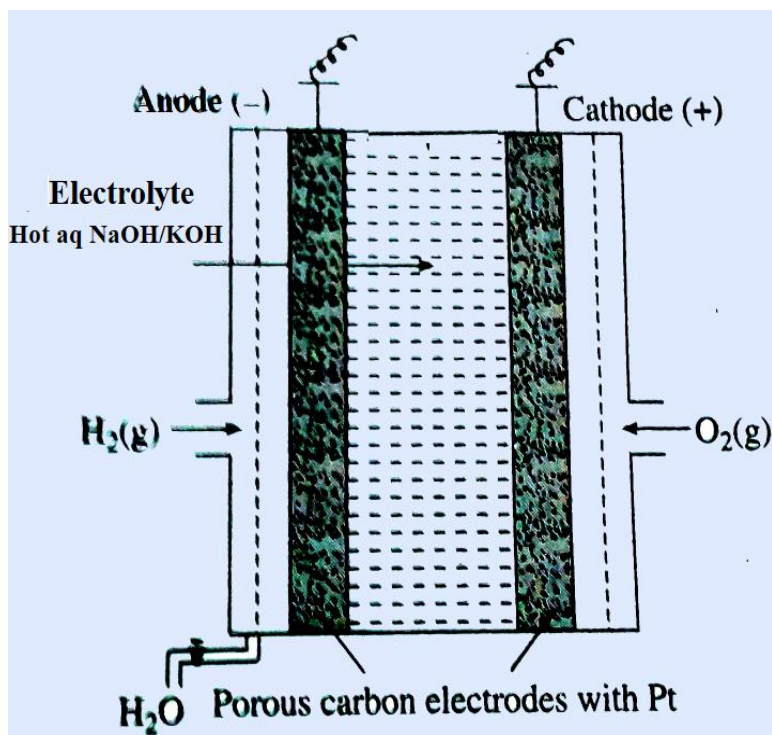
- The fuel cell has porous carbon electrodes with suitable catalyst since combustion of hydrogen is a slow reaction.
- Anode and cathode consists of porous carbon rods impregnated with finely divided platinum which acts as a catalyst for the reactions.
- The electrolyte used is hot aqueous KOH solution in which porous anode and cathode carbon rods are immersed.
- H_2 is continuously bubbled through anode while O_2 gas is bubbled through cathode.

○ Cell reactions:

At anode: $2\text{H}_2(\text{g}) + 4\text{OH}^-(\text{aq}) \rightarrow 4\text{H}_2\text{O}(\text{l}) + 4\text{e}^-$

At cathode: $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$

Net cell reaction: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$



Advantages:

- The cell reactions do not cause any pollution.
- The efficiency of this cell is about 70% highest as compared to ordinary galvanic cells.

Industrial applications of hydrogen fuel cells:

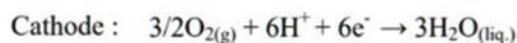
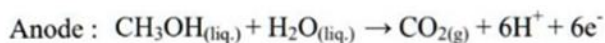
- Buses: Hydrogen power is being considered for other public transportation applications, including hydrogen fuel cell buses. Several major cities including Chicago, London, and Beijing have experimented with hydrogen powered buses.
- Trains: Hydrogen fuel cell trains have now appeared in Germany, and other models are expected to come to Great Britain, France, Italy, Japan, South Korea, and the United States.
- Personal vehicles: The major auto manufacturers are developing hydrogen fuel cell electric vehicles (HFCEVs) for personal use. Notable models include the Toyota Mirai, Honda Clarity,

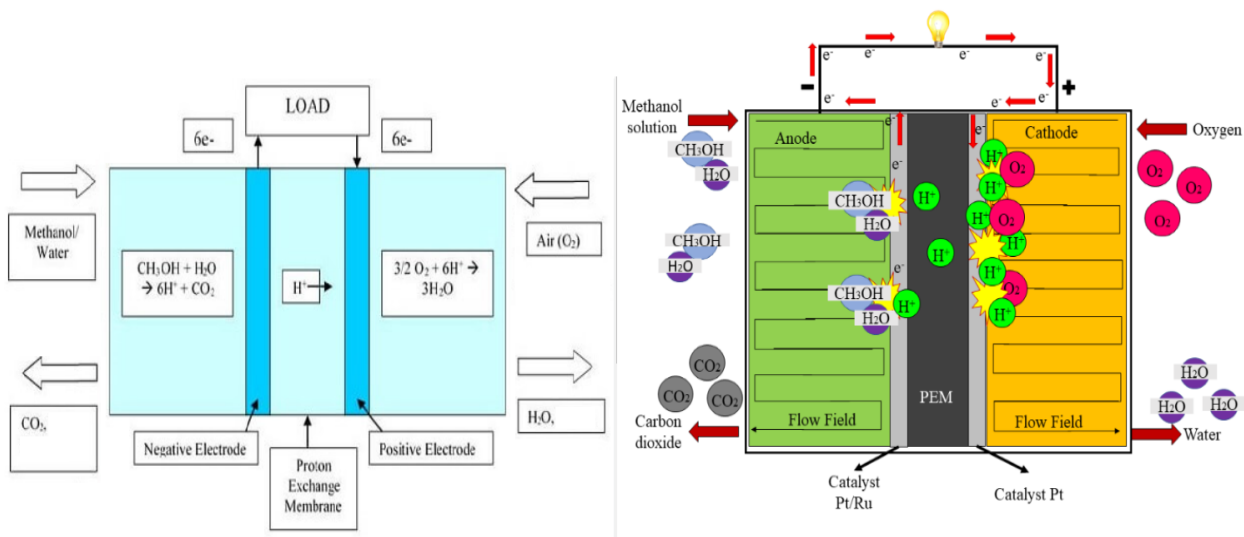
Hyundai Nexo, and BMW I Hydrogen Next. Companies like Nikola, Hyundai, Toyota, Kenworth are building hydrogen powered semi-trucks and vans.

- Planes: Several experimental projects have explored application of hydrogen fuel cells in aerospace.
- Hydrogen fuel cells were developed by NASA to provide electricity for rockets and shuttles in space.
- Unmanned arial vehicles (UAVs): Applications of UAVs (i.e. drones) are significantly limited by the power and range provided by traditional batteries. Both military and private industry plan to overcome these challenges with hydrogen fuel cells that claim up to three times the range of battery-based systems.
- Boats and Submarines: Hydrogen fuel cells have found their way into a number of marine applications.

Methanol-Oxygen fuel cells:

- The methanol-oxygen fuel cell has two porous carbon electrodes. Anode is coated with platinum catalyst and cathode is saturated with silver catalyst. The electrolyte is aq. H_2SO_4 .
- The proton exchange chamber (PEM) separates the two electrodes.
- In this cell, methanol and water are fed at anode while oxygen is fed at cathode.
- The oxidation of methanol at the anode forms carbon dioxide and release electrons.
- Water is consumed at the anode and is produced at the cathode.
- Protons (H^+) are transported across the proton exchange membrane from anode to cathode where they are consumed. Oxygen gets reduced at the cathode.
- The released electrons at the anode transfer to cathode through the circuit producing electricity.





Advantages:

- Low cost
- Simple design
- Large availability
- Easy handling

Methanol-oxygen fuel cell can produce a small amount of power over a long period of time. This makes them ideal for smaller vehicles such as forklifts & tuggers and consumer goods such as mobile phones, digital cameras or laptops. Also used in space vehicles and military since they have low noise and no toxic effluents.