Unit III: ELECTROCHEMICAL CELLS, STORAGE DEVICES AND SENSORS

Electrode potential, Electrochemical cell, EMF of an electrochemical cell
Batteries: Introduction, types of Batteries-Primary battery-dry cell, secondary battery- Lead-acid batteries, Lithium-ion batteries, Lithium- Polymer batteries, Applications of batteries.
Fuel Cells: Definition, H_2–O_2 fuel cell, solid oxide fuel cell, applications of fuel cells.
Sensors: Introduction, Types of Sensors, electrochemical sensors, applications

1) *Introduction:*

- Electric current is a flow of electrons generated by a battery, when the circuit is completed. The substance which allows the electric current to pass through it is called a conductor. Ex all metals, graphite, and aq. Solutions of electrolytes.
- The conductors are of two types. Metalic conductors and electrolytic conductors

Metallic conductance	Electrolytic conductance
Conductance is due to migration of electrons.	Migration of ions to different electrodes takes place in molten salts (or) electrolytic solution
It does not result in any chemical change.	It involves the decomposition of the conductor.
It decreases with increase in temperature.	It increases with increase in temperature.
It does not involve the transfer of any matter.	It involves the transfer of matter.

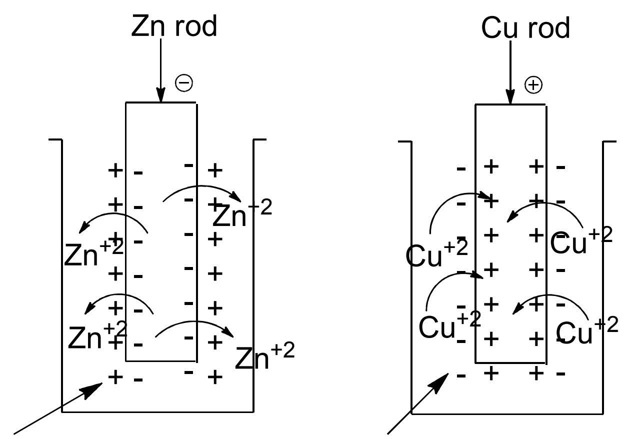
2) Electrode potential

***Electrode potential*:** It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with its own salt solution of a unit molar concentration at 25 ^{0}C (298 K).

When a metal rod is dipped in its salt solution (electrolyte), the metal atom tends either to lose electrons (oxidation) or to accept electrons (reduction).In this process, there develops a potential between the metal atom and its corresponding ion called the electrode potential.

Oxidation**:** $M \longrightarrow M^{n+} + ne^-$[oxidation potential]

Reduction**:**$M^{n+} + ne^- \longrightarrow M$[Reduction potential]



ZnSO$_4$ Solution (**Fig-1**) CuSO$_4$ Solution (**Fig-2**)

In Oxidation, a metal (M) is in contact with a solution of its own salt, the +ve ions in the metal come into the solution, leaving behind an equivalent number of electrons on the metal. As a result metal acquires a –ve charges, ex; Zn rod dipped in $ZnSO_4$ solution (Fig-1).

Similarly in reduction, the positive charge density is more on the surface of metal with respect to the solution. ex: Cu rod dipped in $CuSO_4$ solution (Fig-2).

Because of these –ve or +ve charges developed on the metal attracts the +ve or –ve charged free ions in the solution. Due to this attraction, the +ve and –ve ions remain quite close to the metal to form a layer like. This layer is called *Helmholtz electrical double layer*. As a result, a potential difference develops between metal and the solution, known as **electrode potential**.

There is a dynamic equilibrium between metal and metal ion and the potential difference between these two is called the **electrode potential** **or** the **equilibrium potential**. It is measured in volts. The potential difference for oxidation reaction is called the oxidation potential and that of reduction is called the reduction potential.

For any system, its oxidation and reduction potentials are numerically same with the opposite sign, i.e. if the oxidation potential of the electrode is +X volts, then its reduction potential will be –X volts.

The electrode potential of an electrode at a given temperature depends upon the concentration of the ions in the surrounding solution.

If the concentration of the ions is unity at 25 ^{0}C (298 K), the potential of the electrode is termed as *the* ***standard electrode potential*** (E^0).

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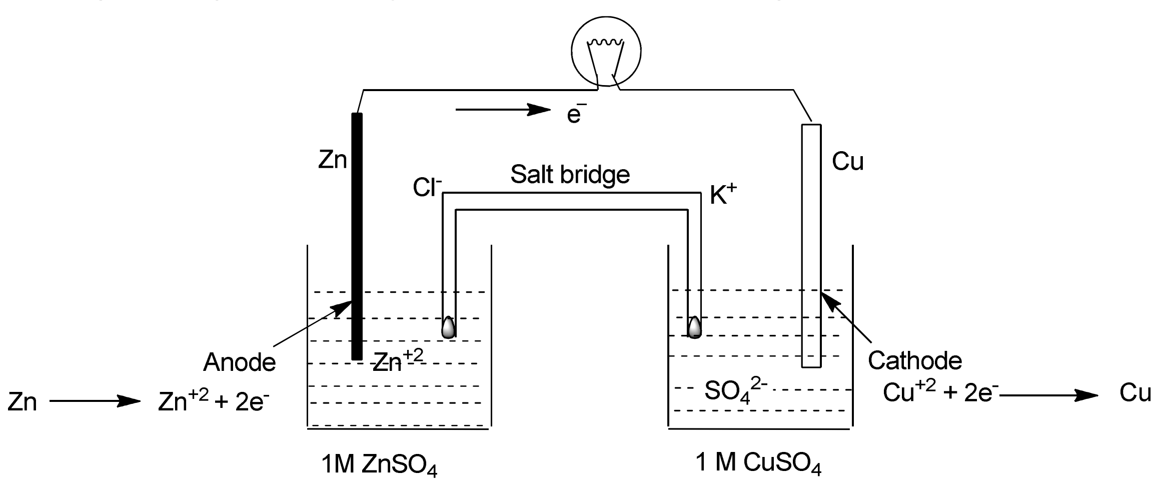
3) Electrochemical cell (***galvanic cell***)*: An electrochemical cell is a device in which redox reaction is utilized to get electrical energy. The electrode where oxidation occurs is called anode; while the electrode where reduction occurs is called cathode.*

An electrochemical cell can be created by placing metallic electrodes into an electrolyte. This phenomenon generates an electric current by a chemical reaction.



Galvanic cell (Denial cell)

A simple electrochemical cell can be made from zinc and copper metals with solutions of their sulfates. As a result, electrons can be transferred from the zinc to the copper through an electrically conducting.The flow of current is due to the difference in electrode potentials of both the electrodes. Each electrode and electolyte may consider as a half cell. The two electrolyte solutions are separated by a 'slat bridge'.

The electrode showing oxidation reaction is called as anode and the reduction reaction is called as cathode. The flow of electron will be externally from anode to cathode and internally from cathode to anode through the salt bridge.

A galvanic cell (Daniel cell) obtained by coupling Zinc half-cell and copper half-cell through a slat bridge.

The tendency of Zn to form Zn^{+2} is greater than the tendency of Zn^{+2} to get deposited as Zn and hence, Zn metal acquires a -ve charge. On the other hand the tendency of Cu^{+2} to get deposited as Cu is more and hence copper electrode becomes +vely charged. Because of the polarization of the electrodes, the flow of the current becomes slow after using them for a long time. This can be overcome by using a salt bridge.

A zinc or a copper galvanic cell can be represented as **$Zn/ZnSO_4$ || $CuSO_4/Cu$**. The double bar shows salt bridge, i.e. electrolyte–electrolyte junction.

The electrode reactions in galvanic cell (Denial cell) are

$$Zn_{(S)} \longrightarrow Zn^{+2}(aq) + 2e^- \quad \text{(anodic half-cell)}$$

$$Cu^{+2}(aq) + 2e^- \longrightarrow Cu(S) \quad \text{(cathodic half-cell)}$$

$$Zn_{(S)} + Cu^{+2}(aq) \longrightarrow Zn^{+2}(aq) + Cu(S) \quad \text{(Redox)}$$

Salt Bridge and its Significance:

(i) Salt bridge is U – shaped glass tube filled with agar–agar (plant gel) mixed with an electrolyte like KCl, KNO_3, NH_4NO_3 etc.

(ii) The electrolytes of the two half-cells should be inert and should not react chemically with each other.

(iii) The cation as well as anion of the electrolyte should have same ionic mobility and almost same transport number, viz. KCl, KNO_3, NH_4NO_3 etc.

EMF (**electro-motive force**)

*T*he cell electromotive force or cell EMF is the *net voltage between the oxidation and reduction half-reactions taking place between two redox half-reactions*. The EMF of the cell (E_{cell}) is measured with the potentiometer.

The difference in potential, causes a current to flow from the electrode of higher potential to lower potential (i.e. a difference in potential that tends to give rise to an electric current), **is called the electromotive force** of the cell and expressed in volts.

$$E_{cell} = E_{right} - E_{left}$$

Or

$$E_{cell} = E_{Cathode} - E_{Anode}$$

$$E_{cell} = \text{EMF of cell}$$

E_{right}= reduction potential of right hand side electrode (reduction) [Cathode]

E_{left}= reduction potential of left hand side electrode (oxidation) [Anode]

If $E^o_{cell} > 0$ i.e. +ve then cell reaction is spontaneous

$E^o_{cell} < 0$ i.e. –ve then cell reaction is not feasible.

$E^o_{cell} = 0$ cell stops working

Ex: Zn/Zn^{+2} is the anodic oxidation

$Zn \longrightarrow Zn^{+2} + 2e^-$ (anodic half-cell) $E^o_{Zn|Zn^{2+}} = +0.76$ v

$2H^+ + 2e^- \longrightarrow H_2$ (cathodic half-cell) $E^o_{SHE} = +0.00$ v

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$Zn + 2H^+ \longrightarrow Zn^{+2} + H_2$ $E^o_{cell} = ?$

Note: The cell EMF calculated using standard reduction potentials.

$$E^0_{cell} = E^0_{SHE} - E^0_{Zn^{2+}|Zn} = +0.00 - (-0.76) = +0.76 \text{ v}$$

Because the voltage (EMF) is positive, the reaction is spontaneous and Zn will generate $H_{2(g)}$ when added to an acid solution (but not water).

Batteries

The era of using fossil fuels as the main source of energy has been fading in our modern society. The development of various energy harvest, conversion, and storage technologies reduces the human impact on the environment, meanwhile, enriches our lives from all aspects.

An electric **battery** is a device consisting of one or more electrochemical cells that convert stored chemical energy into electrical energy.

Each battery consists of a three parts; i) negative electrode material, ii) positive electrode material, iii) electrolyte that allows ions to move between the electrodes. Terminals of electrodes allow current to flow out of the battery to perform work.

Unfortunately there is no single battery technology available on the market today that can be considered as “The Solution” for all classes of portable battery operated devices. There are a variety of batteries in use, each with its own advantages and disadvantages.

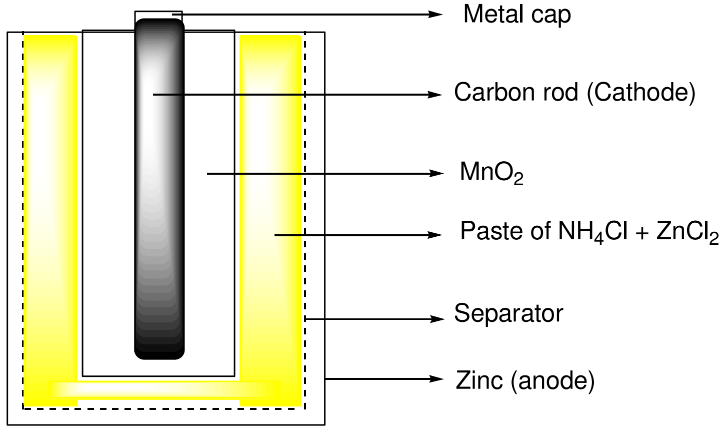
Batteries are divided into following types, based on their recharging capacity.

I) **Primary battery** (single-use or "disposable") - batteries are used once and discarded. eg: galvanic cell, dry cell, alkali metal sulphide batteries

II) **Secondary battery** (rechargeable batteries) - can be discharged and recharged multiple times; eg: Ni-Cd storage battery, lithium ion batteries and lead-acid batteries.

I) Primary battery-(Primary cell**):-** in this type, the cell reactions are irreversible. So when all the reactants are converted into product, no more electricity is produced and the batteries become dead. **Ex:** galvanic cell, dry cell, alkali metal sulphide batteries

Dry cell or Laclanche cell (or) Zinc-Carbon Dry-Cell / Battery



Dry cell

The zinc-carbon dry cell is made up of an outer zinc container, which acts as the anode. The cathode is a central carbon rod, surrounded by electrolyte paste. Electrolyte paste is a mixture of carbon, NH_4Cl, $ZnCl_2$, MnO_2 (manganese (IV) oxide) and with only enough moisture to allow current to flow. A fibrous fabric separates the two electrodes, and a metal cap in the center of the cell conducts electricity to the outside circuit.

Chemical reactions occur in every part of the battery, converts the chemical energy into electrical energy. These reactions can be described as follows.

The anode (oxidation) half reaction: **$Zn\ (s) \longrightarrow Zn^{+2} + 2e^-$ ----------(eq-1)**

The cathode (reduction) half reaction: The MnO_2 reduces to Mn_2O_3(Manganese trioxide)(eq-2). An acid-base reaction between OH^- and NH_4^+ leads to form the NH_3, Formation of ammonia may disrupt the current flow (eq-3). This is prevented by the reaction between $NH_3(g)$ and $ZnCl_2$ (eq-4).

$$2MnO_2\ (s) + H_2O\ (l) + 2e^- \longrightarrow Mn_2O_3\ (s) + 2OH^-\ (aq) \quad \text{(eq-2)}$$

$$2NH_4^+\ (aq) + 2OH^-\ (aq) \longrightarrow 2NH_3\ (g) + 2H_2O\ (l) \quad \text{(eq-3)}$$

$$2NH_3(g) + ZnCl_2(s) \longrightarrow [Zn(NH_3)_2Cl_2] \quad \text{(eq-4)}$$

$$2MnO_2 + 2NH_4^+\ (aq) + ZnCl_2 + 2e^- \longrightarrow Mn_2O_3\ (s) + H_2O\ (l) + [Zn(NH_3)_2Cl_2] \quad \text{(eq-5)}$$

Net cell reaction(eq-6) obtained by combining the eq-1 and eq-5:

$$Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) + ZnCl_2(aq) \longrightarrow Zn^{+2} + Mn_2O_3(s) + 2H_2O(l) + [Zn(NH_3)_2Cl_2] \quad \text{(eq-6)}$$

Advantages of dry cell:

- Unlike wet cell, dry cell can operate in any orientation without spilling, as it contains no free liquid. This versatility makes it suitable for portable equipment.
- The dry-cell battery allowed for a major advance in battery safety and portability

Disadvantages of dry cell:

- When current is drawn rapidly from battery, products build up on the electrodes causes drop in voltage.
- Due the acidic nature of NH_4Cl, zinc metal dissolves slowly, as result the cell run down slowly.

II) Secondary battery: is called as rechargeable battery or storage battery and is a type of energy accumulator. They can be recharged by applying electric current, which reverses the chemical reactions that occur during its use. These batteries are designed for repeated use just by recharging them. Ex: lithium ion, lead–acid etc. Secondary battery consists of several different combinations of chemicals: nickel cadmium (NiCd), nickel metal hydride (NiMH), lithium ion (Li-ion), and lithium ion polymer (Li-ion polymer), lead–acid etc.

Lithium battery **(Rechargeable Li-battery)**:

Lithium shows highest reduction potential (-3.05 V) than any metal, so it produces high voltage. Further, lithium is a very light metal, as results the Lithium batteries are light in weight.

Ex: Lithium-ion batteries, Lithium- Polymer batteries

Li-ion batteries:

These Li-ion batteries do not contain metallic lithium and in these batteries the conductivity is due to the transport of Li^+ ions through the electrolyte from one electrode to another and accompanied by the transport of electrons through the external circuit to maintain charge balance. They named as 'Li-ion batteries' since they uses lithium ions.

Li-ion battery consists of four parts namely, Cathode, Anode, electrolyte and separator. Li-ion battery consists of positive electrode (Cathode), negative electrode (Anode), electrolyte and separator

a) *Anode*: finely divided Graphite adhere well to the copper foil
b) *Cathode*: Layered Lithium Metal Oxide, e.g. Lithium Cobalt Oxide ($LiCoO_2$) adheres well to the aluminium foil. But in latest batteries lithium iron phosphate (Li $FePO_4$) is in use.
c) *Electrolyte*: Lithiumhexafluorophosphate ($LiPF_6$) salt, dissolved in organic solvent mixture dimethylcarbonate, ethylene carbonate. Since water reacts with lithium, only non-aqueous electrolytes are used.
d) *Separator* is a micro-porous film of polyethylene (PE) or polypropylene (PP). It prevent the electrodes from touching each other directly, and allows only the ions and not the electrode particles to migrate from one side to the other

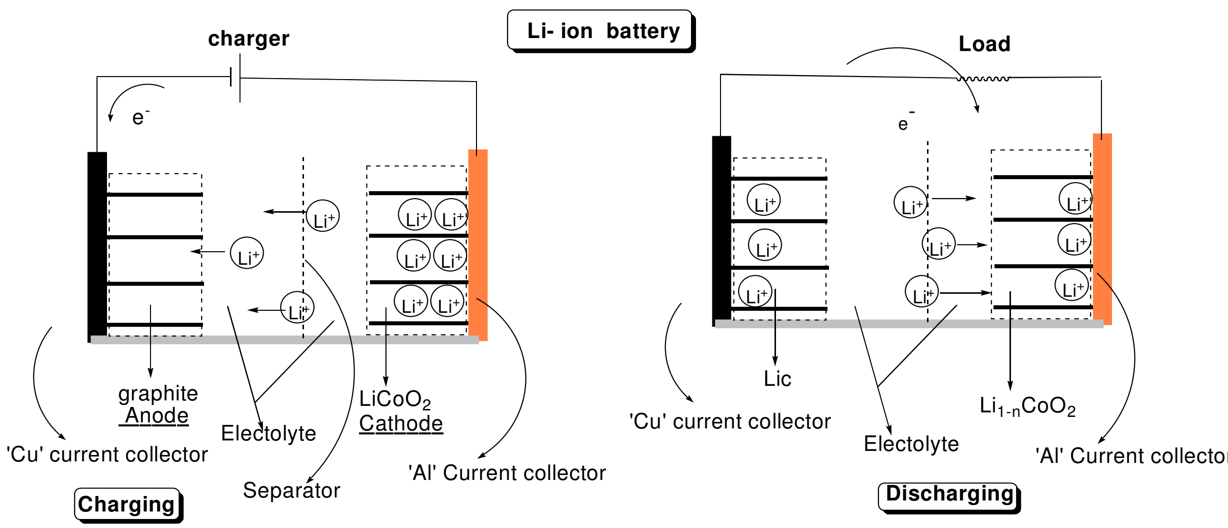
Working: When the lithium ion battery is constructed, it is in its uncharged state and no Li^+ions between the graphite layers. When battery is charged, Lithium ions move from $LiCoO_2$ to the graphite (C_g) through the electrolyte materials and remains there. In this process, battery stores energy. When the battery is discharging, the lithium ions move back across the electrolyte to the $LiCoO_2$ electrode, producing the energy.

$$LiCoO_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_{1-n}CoO_2 + nLi^+ + ne^- \quad \text{(The positive electrode (cathode) half-reaction)}$$

$$C_g + nLi^+ + ne^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_nC \quad \text{(The negative electrode (anode) half-reaction)}$$

$$LiCoO_2 + C_g \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_{1-n}CoO_2 + Li_nC \quad \text{(Net cell reaction in Li-ion batteries)}$$

Where n = 1 to 6



The fact is this battery operation does not actually involve true oxidation and reduction. In both cases, electrons flow through the external circuit to carry the charges. The electrons do not flow through the electrolyte, because as per electrons concerned it acts as an insulator. But Li^+ ions can move easily in between these electrodes through electrolyte material due to the layer structure of both graphite and $LiCoO_2$.The movement of Li^+ ions through the electrolyte and electrons through external circuit are interconnected processes.

<u>The overall reaction has its limits</u>**:**

Overcharge leads to the synthesis of cobalt (IV) oxide, as evidenced by x-ray diffraction

$$LiCoO_2 \xrightarrow{\text{over charge}} Li^+ + CoO_2 + e^-$$

Over discharge leads to the production of lithium oxide and cobaltous oxide as evidenced by x-ray diffraction studies

$$LiCoO_2 + Li^+ + e^- \xrightarrow{\text{over discharge}} Li_2O + CoO$$

<u>Applications of Li-ion batteries</u>**:**

i) these Li-ion batteries are used in high-performance devices

ii) Used as power suppliers in portable electronics such as cell phones digital cameras, personal computers and in telecommunications.

iii) For Transportation - in eclectic bikes and eclectic cars which runs with electricity

Advantages of Li-ion batteries**:**

a) Energy densities are high.
b) Voltages are high, with average operating voltages at 3.6 V, these are approximately three times the cutoff voltage of Ni-Cd battery.
c) *Lithium-ion (Li-ion)* batteries are less environmentally damaging than batteries containing heavy metals such as cadmium and mercury
d) Charge / discharge cycles characteristics are excellent.
e) Self-discharge is minimal when the battery is fully charged. (@ 3.3 % of its capacity in three months compared to8% loss per month for Ni-Cd batteries)

Disadvantages of Li-ion batteries**:**

- They start degrading as soon as they leave the factory. Their life time is only two or three years from the date of manufacture whether it is in use or not.
- They are extremely sensitive to high temperatures. Heat causes lithium-ion battery packs to degrade much faster than they under normal conditions.
- If the lithium-ion batteries are completely discharged, it is ruined.
- If a lithium-ion battery pack fails, it will burst into flame.

Lithium- Polymer batteries/cell (or) lithium-ion polymer battery/cell

A lithium polymer battery is a rechargeable battery with lithium-ion technology in a pouch format. These batteries are abbreviated variously as LiPo, LiP, Li-poly etc. The nominal cell voltage of a LiP cell depends on its chemistry from about 2.7-3.0 V (discharged) to about 4.2-4.4 V (fully charged).

In chemistry point of view, they are the same as the "Li-ion" batteries, **The primary difference is that instead of using lithium hexafluorophosphate ($LiPF_6$) salt, dissolved in organic solvents mixture dimethylcarbonate, ethylene carbonate, these battery uses a solid polymer electrolyte (SPE) such as poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA) or poly(vinylidene fluoride) (PVdF) or a high molecular weight poly(trimethylene carbonate) (PTMC).** The main advantage with this SPE is even a small fraction (5%) by weight is enough for binding the active particles together to maintain good conductivity, and help make the slurry mix adhere well to the copper and aluminum foils that compose the current collectors of the battery cell. Moreover, they do not participate in the electrochemical reactions.

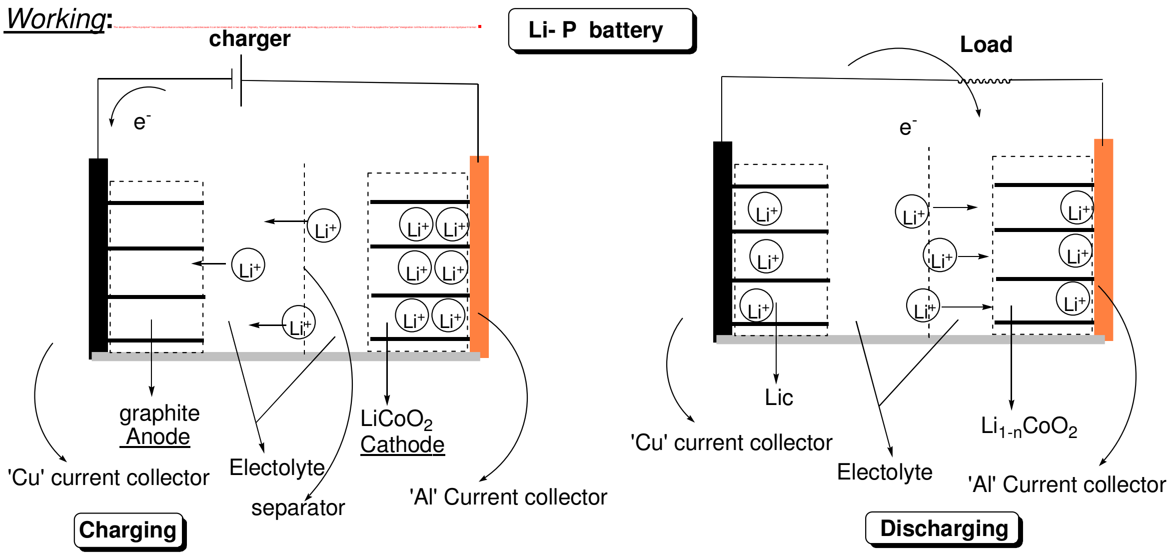
A typical Lip battery has four main components: Anode, cathode, electrolyte, and separator.

e) *Anode***:** finely divided Graphite adhere well to the copper foil
f) *Cathode***:**lithium-transition-metal-oxide ($LiCoO_2$ or $LiMn_2O_4$), a conductive additive, and a polymer binder of poly(vinylidene fluoride) adhere well to the aluminum foil

g) ***Electrolyte*:** lithium hexafluorophosphate ($LiPF_6$) salt, dissolved in solid polymer electrolyte.

h) *Separator* is a micro-porous film of polyethylene (PE) or polypropylene (PP). It prevent the electrodes from touching each other directly, and allows only the ions and not the electrode particles to migrate from one side to the other

***Working*:**



LiP cells work on the principle of intercalation and de-intercalation of lithium ions from cathode a positive electrode material and a negative electrode material, where the electrolyte providing a conductive medium.

When the lithium ion battery is constructed, it is in its uncharged state and no Li^+ ions between the graphite layers. When battery is charged, Lithium ions move from $LiCoO_2$ to the graphite (C_g) through the electrolyte materials and remains there. In this process, battery stores energy. When the battery is discharging, the lithium ions move back across the electrolyte to the $LiCoO_2$ electrode, producing the energy

$$LiCoO_2 \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_{1-n}CoO_2 + nLi^+ + ne^-$$ (The positive electrode (cathode) half-reaction)

$$C_g + nLi^+ + ne^- \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_nC$$ (The negative electrode (anode) half-reaction)

$$LiCoO_2 + C_g \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} Li_{1-n}CoO_2 + Li_nC$$ (Net cell reaction in LiP batteries)

Where n = 1 to 6

The fact is this battery operation does not actually involve true oxidation and reduction.In both cases, electrons flow through the external circuit to carry the charges. The electrons do not flow through the electrolyte, because as per electrons concernedit acts as an insulator. ButLi^+ions can move easily in between these electrodes through electrolyte material due to the layer structureof both Graphite and $LiCoO_2$.The movement of Li^+ions through the electrolyte and electrons through external circuit are interconnected processes.

On applying the moderate pressure on the stack of layers that compose the cell results in increased capacity retention, because the contact between the components is maximized,

Applications of LiPo:

1. A lithium-ion polymer battery used to power mobile phone, notebook computers, battery-powered electric vehicles etc.
2. Due to lower weight and increased capacity and power delivery, Used in radio controlled models such as aircraft, cars and model trains.
3. This type of battery are now in some ofhybrid vehicles
4. More recently in light aircraft and self-launching gliders are working with this Liop

Advantages:

i. They have low-self discharge rate, which is about 2% per three months

ii. They can easily produce batteries of almost any desired shape as per requirements of mobile phones and notebook computers.

iii. In Lip batteries 'electronic circuit' controls the charging and discharging process and protects the electrolyte and electrode materials from decomposition as appear in Li ion batteries.

iv. Unlike lithium-ion cylindrical and prismatic cells, which have a rigid metal case, LiPo cells have a flexible, foil-type (polymer laminate) case, so they are relatively unconstrained. By themselves the cells are over 20% lighter than equivalent cylindrical cells of the same capacity

Limitations:

a) Still this technology needs to improve a lot.Apple iPhone 3GS's Lithium-ion polymer battery, which has expanded due to a short circuit failure.

b) LiPo cells are affected by the same problems as other lithium-ion cells. Overcharging, over discharging, over-temperature, short circuit, crush and nail penetration may all result the pouch rupturing, electrolyte leaking.

c) Due to lack of a hard case to control their expansion, all LiPocells expand at over-charge. This may result in delamination, and thus bad contact of the internal layers of the cell which in turn brings diminished reliability and overall cycle life of the cell.

Lithium Ion Vs Lithium PolymerBatteries – What's the Difference?

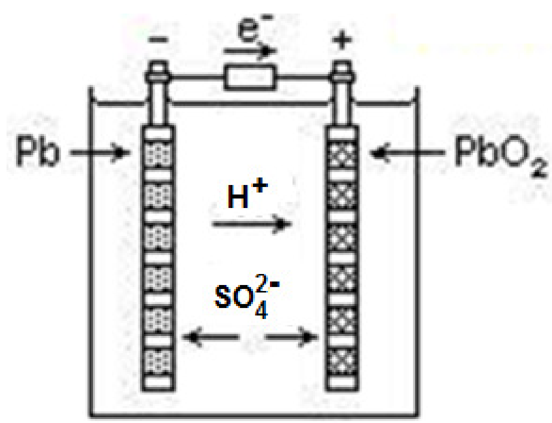
	Lithium-Ion Battery	Lithium-Ion Polymer Battery
electrolyte	$LiPF_6$ salt, dissolved in organic solvent mixture dimethylcarbonate, ethylene carbonate	$LiPF_6$ salt, dissolved in a solid polymer electrolyte
weight	Lighter than nickel-based secondary batteries with (Ni-Cd and NiMH)	Lighter and thinner than Li –ion battery, about 30% less weight to Li ion battery
Operating Temperature	-20ºC to 60ºC	Improved performance at low and high temperatures

Voltage	3.6 V	2.7 – 4.4 V
Capacity	Varies (generally up to twice the capacity of a Ni-Cd cellular battery)	Varies depending on the battery; and superior to standard lithium-ion
Discharge Rate	about 3.3 % per three month	about 2% per three months
Recharge Life	300 – 400 cycles for 100%	500 – 600 cycles for 100%
shapes	The chemical construction of this battery limits it to a rectangular shape.	Can be made in a variety of shapes
Manufacturing cost	40-50% higher than Ni-Cd battery	10-30 % higher than Li-ion battery
Uses	Widely in use	In use but still more or less in the experimental phase
Recommended for	Cellular telephones, laptops	Radio controlled models

Similarities between Lithium Ion and Lithium Polymer Batteries

"Lithium polymer" has technologically evolved from lithium-ion batteries and both are secondary type battery. Just like lithium-ion cells, LiP cells work on the principle of intercalation and de-intercalation of lithium ions betweencathode material and anode material, where the electrolyte providing a conductive medium

<u>Lead-acid battery</u>:



Lead-acid battery is the example for a storage cell. A storage cell is one that can operate both as a voltaic cell and as an electrical cell. When operating as a voltaic cell, it supplies electrical energy and as result it becomes run down. So it must be recharged from time to time and while charging it is considered as electrolytic cell.

Lead-acid battery consists to two types of electrodes, out of this one type are made of lead (-Ve) and other are with lead dioxide (PbO_2) (+Ve) or rather a paste of PbO_2 is pressed into a grid made of lead. These +Ve and -Ve electrodes are connected in parallel independently. The various plates are separated from the adjacent ones by insulators like strips of wood or rubber or glass fiber. The entire combination is then immersed in approximately 20-21 % dil H_2SO_4.The voltage of each cell is about 2.0 volts at these concentration at 25 ^{0}C.

During Discharging of Pb acid battery:

At –Ve (lead)terminal**:**The electrode loses electrons, which flow through the wire. In this reaction oxidation of lead takes place at the anode. The Pb^{+2} ions then combines with sulphate ions (SO_4^{2-}).

$$Pb \longrightarrow Pb^{+2} + 2e^-$$

$$Pb^{+2} + SO_4^{2-} \longrightarrow PbSO_4$$

At + Ve (PbO_2)terminal**:** The electrons released at lead plate flows to the PbO_2 electrode. As result it undergoes reduction (+4 to +2) and resulted Pb^{+2} ions then combines with sulphate ions.

$$PbO_2 + 4H^+ + 2e^- \longrightarrow Pb^{+2} + 2H_2O$$

$$Pb^{+2} + SO_4^{2-} \longrightarrow PbSO_4$$

So the net reaction during use or discharge is

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow PbSO_4 + 2H_2O + Energy$$

Finally, $PbSO_4$ is precipitated at the both the electrodes and cell ceases to function and further it is noted that during discharging operations, the concentrations of acid decreases.

During Charging of Pb acid battery:

Electrodes can be reactivated by passing an external EMF > 2 volts and following reactions takes place at electrodes.

At –Ve terminal**:**

$$PbSO_4 + 2e^- \longrightarrow Pb^{+2} + SO_4^{2-}$$

At +Ve terminal**:**

$$PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$$

The net reaction during charging is:

$$2PbSO_4 + 2H_2O + Energy \longrightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$$

During charging process the electrodes of cell are restored to their original conditions and the concentration of acids increases during charging operations.

Uses**:**

- In automobiles
- To supply current for electrical vehicles
- As gas engine ignition
- In telephone exchange, railway trains,
- Power stations
- In domestic inverters for un interruptible supply of power

Limitations:

Lowering of temperature causes the significant changes in voltage of Pb-acid batteries, it is just because of an increase in the viscosity of the fluids leads in the power output of the battery. Its ability can be recovered by keeping the battery at room temperature to deliver normal power.

Fuel cells

Definition: A fuel cell converts the chemical energy of the fuels directly into electricity.

$$\text{Fuel} + O_2 \xrightarrow{\text{Catalyst}} \text{Oxidation products + electricity}$$

Difference with batteries:

- A battery has all of its chemicals stored inside, and it converts those chemicals into electricity. *i.e.* battery eventually "goes dead" and as result it has to either throw away or recharge it.
- Fuel cell requires a fuel to flow in order to produce electricity. *i.e.* Chemicals constantly flow into the cell so it never goes dead. So the f*uel cell is also called as flow cell*
- **About fuel cell:** In fuel cells electricity is obtained without combustion from oxygen. Fuel cell accelerates the movement of the electrons directly. Most fuel cells today use hydrogen and oxygen as the chemicals.

Fuel cells are electrochemical cells in which reactants are supplied continuously and able to operate the cell without theoretical limit. *This helps for long term generation of electrical energy.*

Characteristics of Fuel cells

- They do not store chemical energy
- The efficiency of the fuel cell is about twice that of the conventional power plant for generating electricity.
- They are free of noise, vibration, heat transfer, thermal pollution etc.

H_2-O_2 fuel cell (alkaline fuel cell***)***

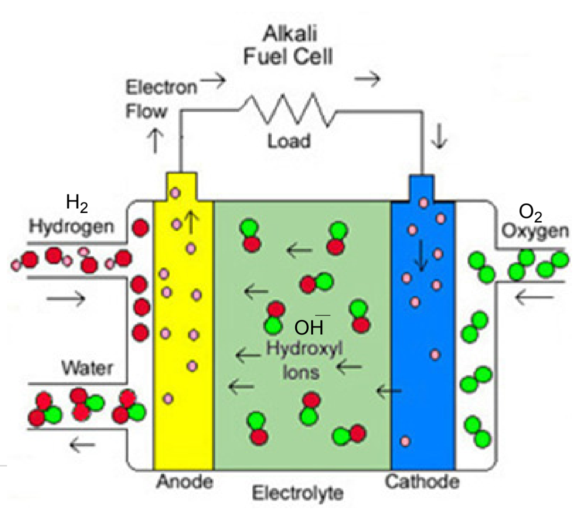
- This cell is also called the alkaline fuel cell **or** hydrogen fuel cell
- *H_2-O_2 fuel cell consists of two inert porous electrodes and electrolyte.*
- *Electrode: Made with graphite impregnated with finely divided platinum or alloy of palladium and silver or nickel in 3:1.*
- *Electrolyte: Aqueous KOH used as electrolyte.*
- *H_2 and O_2 gases are bobbled through the anode and cathode compartment respectively. Electrons generated at the anode move out through an external circuit creating electricity.*
- Electrical efficiency is about 75%
- Operating range is about 60 to 120 °C.
- *The cell output is 0.8 to 1.0 KW.*

H_2-O_2 fuel cell reaction:

$$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^- \quad \text{(Anode)}$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \quad \text{(Cathode)}$$

$$2H_2 + O_2 \longrightarrow 2H_2O \quad \text{(Overall cell reaction)}$$



The reaction at the anode is the combining of hydrogen gas (the fuel) with the electrolyte to form water and release electrons. At the cathode oxygen gas consumes electrons and so reacts with water in the electrolyte, this produces hydroxide ions. In this way the electrolyte is never used up, but is replenished at the same rate as it is consumed. This allows continuous operation of the hydrogen fuel cell.

Applications of H_2-O_2 fuel cell:

- *H_2-O_2 fuel cell is used as auxiliary energy source in space vehicles, submarines and military-vehicles.*
- *The byproduct is H_2O, which can be used by astronauts.*

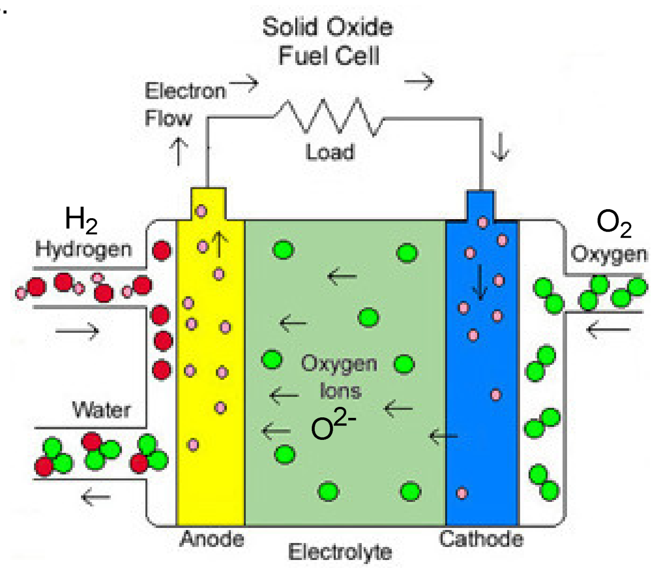
Advantages *of H_2-O_2 fuel cell:*

a) Hydrogen fuel cells are attractive alternative to gasoline powered engine, because they are pollution free.
b) The thermodynamic efficiency of fuel cells is high. They convert 75% of available energy to useful work. Whereas about 25 – 30 % for gasoline engines.
c) *For low temperature (-54^0C to -72^0C) operations potassium thiocyanate dissolved in liquid ammonia is employed as electrolyte.*

Disadvantages of *H_2-O_2 fuel cell:*

- Difficult to store and transport of highly flammable hydrogen
- Availability of alternative low price fuels.
- Productivity cost is very high
- Expensive catalysts (Platinum)

Solid Oxide fuel cells (SOFC):



- Solid oxide fuel cell consists of three components cathode, anode, and electrolyte.
- Solid oxide fuel cells use a hard, ceramic substances or calcium oxide or zirconium oxide as electrolyte. This electrolyte is sandwiched between the two electrodes.
- Solid oxide fuel cell electrodes are made with ceramic substances and no catalyst.
- A fuel gas containing hydrogen, flows through anode and oxygen from the air flows through the cathode.

- Operating temperature is about 1000°C. At this high operating temperature, oxygen ions (O^{2-}) are formed at the cathode and these ions migrate through the electrolyte membrane react with the hydrogen to form water.
- Electrons generated at the anode move out through an external circuit creating electricity.
- Efficiency is about 60%. Cells output is up to 5KW to 3MW.
- Water gas ($CO+H_2$) or other hydrocarbon (CH_4) fuels can be used as fuels.
- It is designed to capture and utilize the systems waste heat, overall fuel efficiencies could top 80-85%.

$$CO + H_2 + 2O^{2-} \longrightarrow CO_2 + H_2O + 4e^- \text{ (Anode)}$$

$$O_2 + 4e^- \longrightarrow 2O^{2-} \text{ (Cathode)}$$

$$CO + H_2 + O_2 \longrightarrow H_2O + CO_2 \text{ (Overall cell reaction)}$$

A ceramic is an **inorganic**, nonmetallic solid material comprising metal, nonmetal or metalloid atoms primarily held in ionic and covalent bonds.Ceramics are generally made by taking mixtures of clay, earthen elements, powders, and water and shaping them into desired forms.

Applications of SOFC**:**

- For commercial scale production
- Mobile power generation

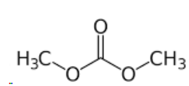
Advantage of SOFC**:**

- Since cell operates at high temperature, **catalyst is not required**
- Waste heat can be recycled to make additional electricity.
- High efficiency
- Solid electrolyte reduces the electrolyte management problems
- Low cost fuel ($CO+H_2$) can be used

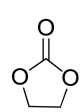
Disadvantage of SOFC**:**

- Solid electrolytes can crack, due to high operational temperature
- High temperature enhance the corrosion and breakdown of cell composition

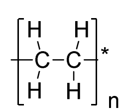
Structure of the compounds studied in this unit *(Just for information)*



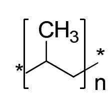
dimethylcarbonate



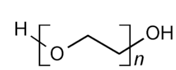
ethylene carbonate



polyethylene



polypropylene



poly(ethylene oxide)

Why cannot use fuel cells in regular life?

- Building inexpensive, efficient, reliable fuel cells is a far more complicated business.
- All fuel cells occupy a lot of space, much more than any other types of micro sources.

	H_2-O_2 fuel cell *(*alkaline fuel cell*)*	**Solid Oxide fuel cells (SOFC):**
Fuel	H_2	$CO + H_2$
Electrolyte	Aqueous solution of potasium hydroxide (KOH)	Solid oxide (calcium, zirconium)
Electrode	*graphite impregnated with finely divided platinum*	Ceramic substances without catalyst
Charge carried in electrolyte	OH^-	O^{2-}
Operational temperature	60 °C – 120 °C	1000 °C
Efficiency (%)	converts 75% of available energy	about 60%.
System output	10KW – 100KW	5KW –3MW
Applications	Military and space	For commercial scale production
Advantage	• Higher performance • Pollution free	• high efficiency • solid electrolytes cannot leak • no catalyst
Disadvantage	• Difficult to store and transport of highly flammable hydrogen. • Expensive Platinum catalysts	• Solid electrolytes can crack, due to high operational temperature
Cell reaction		

H_2-O_2 fuel cell reaction:

$$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^- \text{ (at Anode)}$$
$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \text{ (at Cathode)}$$
$$2H_2 + O_2 \longrightarrow 2H_2O \text{ (Overall cell reaction)}$$

SOFC *fuel cell reaction*:

$$CO + H_2 + 2O^{2-} \longrightarrow CO_2 + H_2O + 4e^- \text{ (at Anode)}$$
$$O_2 + 4e^- \longrightarrow 2O^{2-} \text{ (at Cathode)}$$
$$CO + H_2 + O_2 \longrightarrow H_2O + CO_2 \text{ (Overall cell reaction)}$$

Fuel Cell Applications or **Fuel cells today**

- Fuel cells have emerged as one of the most promising new power-generators because of their:
  - simplicity, high efficiency and eco-friendly nature

- non-interruption supply of electricity
- Advantage for silent operation
- Increased design flexibility

- Potential application of fuel cells ranges from systems of a few watts to megawatts.
- Fuel cell applications are classified as transportation, portable and stationary applications.
  - Mobile applications primarily include transportation systems.
  - Stationary applications primarily include combined heat and power systems for both residential and commercial needs. stationary fuel cells as units which provide electricity (and sometimes heat) but are not designed to be moved.

i) **Transportation-**mobile applications

Modern vehicle manufacturers, designed vehicle that works by using power produced by fuel cells.

- Light duty vehicles (LDVs), such as cars and vans
- Scooters and Motorcycles
- Loading Vehicles in airports i.e. baggage trucks
- Light Rail and trams
- Ferries and smaller boats
- Submarines
- Unmanned aerial vehicles (UAVs) and unmanned undersea vehicles (UUVs)

ii) Remote Power Source (for Portable Electronic Equipment**)**

Portable fuel cells are being developed in a wide range of sizes ranging from less than 5 W up to 500 kW. Portable fuel cells can be used as remote power generators in following fields.

- Telecommunication stations
- Weather stations
- Oceanic monitoring stations
- Rail-road crossing signals

iii) Military (Portable applications)

Fuel cells are especially suited for silent operations because of their low heat and no noise. Lower operating costs also apply

- Soldier portable power
- Field power
- Weapon systems
- Small vehicle propulsion
- Power source for border sensors

iv) Stationary-which provide electricity but are not designed to be moved

- Water pumping
- Schools and hospitals
- Lights and Communications

Compare primary Battery verses Secondary battery

PRIMARY BATTERIES	SECONDARY BATTERIES
These batteries are used once and discarded.	These batteries can be discharged and recharged multiple times
Ex:: galvanic cell, dry cell	Ex:: Ni-Cd storage battery, lithium ion batteries and lead-acid batteries
In this type, the cell reactions are irreversible. So when all the reactants are converted into product, no more electricity is produced and the batteries become dead	In this the material is present in one form during charging process and in during discharge process it turns into another form
In this battery operations involve true oxidation and reduction.	The fact is this battery operation does not actually involve true oxidation and reduction.
Energy densities are low. Can obtain max. of 1.5V	Energy densities are high. Can obtain min. 1.4V to max 4.4V, based on the name of the secondary battery
These are most commonly used in portable devices that have low current drain. Normally used in radios, hand lights etc.	They can be used widely; for example to power mobile phone, digital cameras, notebook computers, battery-powered electric vehicles etc.
can cause environmental pollution, because of their non-reusability	less environmentally damaging, because of their reusability
Low price, but need to replace time to time	Only initial expenditure, but maintenance free because of its 2-3 years of life time.

Compare Battery versus Fuel cell

Battery	Fuel cell
A fuel cell converts the stored chemical energy into electricity	A fuel cell converts the chemical energy of the fuels directly into electricity. $\text{Fuel} + O_2 \xrightarrow{\text{Catalyst}} \text{Oxidation products} + \text{electricity}$
a battery makes electricity from the energy it has stored inside the battery	fuel cell makes its electricity from fuel in an external fuel tank
a battery may run dead	a fuel cell will make electricity as long as fuel is supplied
Shows significant impact on the environment due to disposing or recycling batteries.	Replace the electricity source and often saves money over time and reduces the environmental impact of disposing or recycling batteries.
Used in portable toys, electronics for power supply	Used for commercial scale production and *by astronauts*
Ex: galvanic cell, dry cell (Primary battery)and Ni-Cd storage battery, lithium ion batteries and lead-acid batteries (Secondary battery).	*Ex:* *H_2-O_2 fuel cell* ***(or)*** *alkaline fuel cell* *Solid oxide fuel cells* *Methanol fuel cells*

Sensors **(Artificial sensors)**

Introduction:

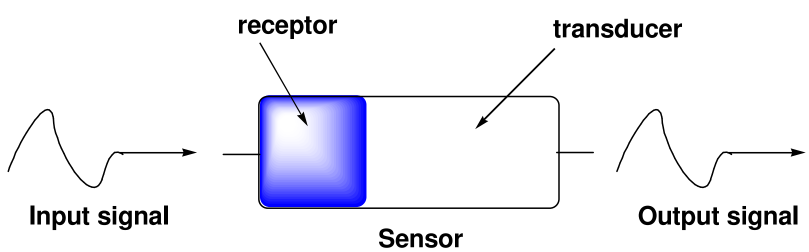
All living organisms contain biological sensors (Natural sensors) which functions similar to those of the mechanical devices.

For example: light – eyes, smell - nose, sound – ears, and so on. Interestingly, Mosquitoes have sensors in their antennas, which detect carbon dioxide and lactic acid up to 36 meters away. Therefore the mosquito's sensors can be considered as chemical sensor.

Sensors (Artificial sensors) are widely used now days. Simply, without the use of sensors, there would be no automation. For example: – Imagine the possibility to manually filling of water *bottles by* manufactures.

A **Sensor** converts the physical (temperature, blood pressure, humidity, speed, etc.) and chemical parameter into a measurable electrical signal. *i.e.* Sensors convert energy information. Ex: A thermocouple (temperature-measuring device) converts temperature to an output voltage. Mercury-in-glass thermometer is also considered as a sensor and in this temperature is measured based on the expansion and contraction of mercury which can be read on a calibrated glass tube.

Normally, Sensors consist of two important components namely 'receptor' and 'transducer'. Receptor generates non-electrical signals based on its interaction with analyte (chemical/physical environment) and Transducer converts these non-electrical signals into electrical signals suitable for human-readable display. So the transducer is said to be an active element of a sensor.



<u>A good sensor obeys the following rules</u>:

- Sensitive to the measured property
- Insensitive to any other property likely to be encountered in its application
- Does not influence the measured property
- Should be economical

<u>Def</u>**:** *A* **sensor** *is a sophisticated device that detects (input) events or changes in chemical/physical environment and provides corresponding information as electrical signals (output) suitable for quantification*.

Types of sensors:

The development of instrumentation, microelectronics and computers makes it possible to design various sensors utilizing most of the known chemical, physical and biological principles. Sensors are broadly classified into three types based on their working principles;**i) Chemical sensor ii) Physical sensor iii) Bio-sensor.** The Size of theses sensors are from micro to macro. All these sensors with a self-contained analytical device gives the readable information.

i) Chemical sensor- A chemical sensor is device that can provide information about the chemical environment in the form of a measurable signal. The provided chemical information, may originate from a chemical reaction of the analyte.

Few common chemical sensors: *a)* Electrochemical sensors (liquid electrolyte)b*)*Ion-selective sensors (electrodes)*c)*electrolytic conductivity sensors

Chemical sensors are widely used in different areas such as medicine, home safety, industrial hygiene, process controls, product quality controls, environmental pollution (emissions monitoring) and many others. In these applications, chemical sensors have resulted in both economic and social benefits.

ii) Physical sensors- A physical sensor is a device that provides information about a physical property of the system. A Physical sensor works based on the absorbance, refractive index, conductivity, and temperature changes. *i.e.* It works based on the principle where no chemical reaction takes place.

There are two categories of physical sensors; active and passive.

Active physical sensors - The sensor emits some form of energy into the environment and then measures the impact.

Ex: ultrasonic, laser, and IR sensors

Passive physical sensors - The sensor receives energy already in the environment. These sensors consume less energy, but often have signal and noise problems

Ex: camera: it uses the energy in the environment to capture a snapshot.

Radio: it uses the radio frequency in the environment *piezoelectricity:* (The word *piezoelectricity* means electricity resulting from pressure

It is important to note, in some cases it is not possible to decide whether a sensor operates on a chemical or on a physical principle. *For example*: when the signal is due to an adsorption process

iii) Biosensors-A biosensor is an analytical device which converts a biochemical response into measurable electrical signal.

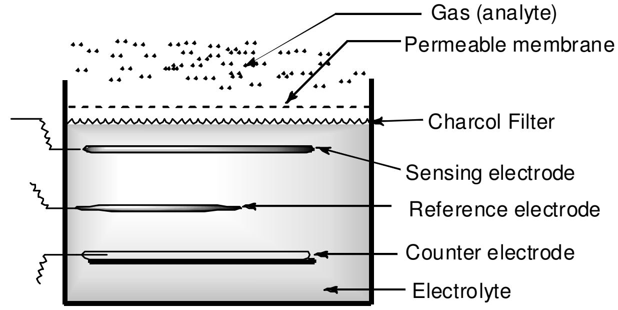
Ex: glucose sensor, alcohol sensor, sucrose sensor, uric acid sensor, immune sensorsdetectsHb,

Uses**:** a) to detectanalytes related to a biological component, such as cells, protein, nucleic acids, bio-polymers in biomedicine and biotechnology.

b) Used for food testing, medical care device, water testing, and biological warfare agent detection.

Electrochemical sensor:

Electrochemical sensors is one of the oldest (1950) and broadest types of sensors. They used to detect oxygen, toxic gases, ions such as Cu^{+2}, Pb^{+2}, Zn^{+2}, CN^{-}, Cl^{-}, Br^{-} at the sub-part-per billion levels, to calculate the pH of a solution and also to carry quantitative measurements.



Electrochemical sensor setup

Electrochemical sensors are many types and each electrochemical sensor is designed to be specific depends on its intended use. However, the basic construction and working principle of all types of electrochemical sensors are same.

Potentiometric sensor

A potentiometric sensor is a type of electro chemical sensor that may be used to determine the analytical concentration of some components of the analyte gas or solution. These sensors measure the electrical potential of an electrode when no voltage is present.

Major components inPotentiometric sensor / electrochemical sensor:

Potentiometric sensor comprised of two main sections namely

i) Electro chemical sensor cell ii) Supporting electronics.

An electrochemical sensor cell consists of the following major components *A)* Electrode *B)* Electrolyte *C)* Gas Permeable Membrane *D)* Filter

A) **Electrode:** Electrochemical sensor consists of three electrodes *(sensing electrode, counter electrode, reference electrode*) made from a noble metal (platinum or gold) catalyzed for an effective reaction with analyte (gas) molecules.

- At sensing electrode, either oxidation or reduction takes place based on the nature of the analyte.
- *Importance of reference electrode*:
    i) To improve the performance of the sensing electrode (sensor)
    ii) To maintain stable and constant potential at the sensing electrode
    iii) The micro type electrochemical sensors do not require reference electrode

B) **Electrolyte:** Generally, an electrolyte is an aqueous inorganic solution or gel. The electrolyte facilitates the cell reaction and carries the ionic charge across the electrodes efficiently.If the electrolyte evaporates quickly, the sensor's signal will deteriorate.

C) **Gas Permeable Membrane (also called hydrophobic membrane):** This is used to cover the sensing electrode, to control the amount of gas molecules / ions reaching the electrode surface. Such barriers are typically made of thin, low-porosity teflon membranes.

Functions of Gas Permeable membrane:

i) Gives protection to sensing electrode
ii) allow the proper amount of gas/ions to react at the sensing electrode
iii) filtering out unwanted particulates
iv) Prevents the leakage of electrolyte from sensor

D) **Filter:** Sometimes a scrubber filter is installed in front of the sensor to filter out unwanted gases. The most commonly used filter medium is activated charcoal. The activated charcoal filters out most chemicals except CO and H_2 gases.

Stable and constant potential should maintain at the sensing electrode. But the sensing electrode potential does not remain constant due to the continuous electrochemical reaction taking place on the surface of the electrode. It causes deterioration of the performance of the sensor over extended periods of time. A reference electrode is placed within the electrolyte in close proximity to the sensing electrode. No current flows to or from the reference electrode. A stable constant potential decided based on reference electrode is applied to the sensing electrode. However, the micro fuel cell-type electrochemical sensors do not require reference electrode.

Principle and working of potentiometric sensor /*electochemcial sensor*:

The signal is measured as the potential difference (voltage) between the working electrode and the reference electrode. The working electrode's potential must depend on the concentration of the analyte in the gas or solution phase. The reference electrode is needed to provide a defined reference potential.

Gas that comes in contact with the electrochemical sensor first diffuses through gas permeable membrane, and finally reaches the sensing electrode surface. The diffused gas at the surface of the sensing electrode undergoes either oxidation or reduction depending upon the gas, thereby the resulting potential difference between the sensing electrode and counter electrode causes a current to flow and this current is proportional to the gas concentration at electrode. This electrical output converted into a readable data by amplification with the help of supporting electronics, which works with external current.

***Example-1*:** oxidation reaction (CO, H_2S, NO, H_2 etc.) at sensing electrode

Sensing electrode: $2CO + 2H_2O \longrightarrow 2CO_2 + 4H^+ + 4e^-$

Counter electrode: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

Cell reaction: $2CO + O_2 \longrightarrow 2CO_2$

***Example-2*:** *R*eduction reaction (NO_2, Cl_2, O_3 etc.) at sensing electrodeWater formed at the cathode simultaneously undergoes oxidation. This type of sensors does not require the presence of O_2.

Sensing electrode: $2NO_2 + 4H^+ + 4e^- \longrightarrow 2NO + 2H_2O$

Counter electrode: $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Cell reaction: $2NO_2 \longrightarrow 2NO + O_2$

Advantages of electrochemical sensors:

i) Where a fiber optic sensor fails, electrochemical sensor may have advantage.
ii) A sensor is designed to detect a particular gas or vapor in the parts per million range

iii) Low power required for its working
iv) good resolution i.e. sensor can detect the smallest change in the quantity often in digital display
v) Once calibrated to a known concentration, the sensor will provide an accurate reading with an excellent repeatability.
vi) Economical, compare to other gas detection technologies

Disadvantages of electrochemical sensors:

- They are sensitive to temperature, so their application is limited.
- An electrochemical sensor usually has a short or limited shelf life, depending on the gas to be detected and the environment in which it is used.

Applications of electrochemical sensors:

Electrochemical *analysis* is a powerful analytical technique which offers high sensitivity, accuracy, and quality with relatively low-cost instrumentation. Some of its applications are:

i) To detect oxygen and toxic gases like CO, H_2S, SO_2, NO, NO_2 etc.
ii) To monitor the water steam discharge
iii) To monitor composition of plating baths and rinse system
iv) To monitor the pollutants in an environment.
v) To monitor continuously levels of key ingredients in oils and lubricants
vi) To monitor corrosion process
vii) To monitor blood samples and other body fluids for their ionic chemical contents concentrations
viii) To study chemical concentrations of gastric, tissue secretions, inner eye lid etc.
ix) For checking the ionic concentration of pesticide, insecticide and fertilizers etc.
x) for pharmaceutical, chemical and drug analysis
xi) To carry quantitative measurements, especially to determine the ions such as Cu^{+2}, Pb^{+2}, Zn^{+2}, CN^-, Cl^-, Br^- at the sub-part-per billion levels
xii) To calculate the pH of a solution

✓ **This material gives you a basic information**
✓ **Refer text book for more details**
