Battery technology

If chemical reaction takes place at two separate electrodes, electrical power can be generated in an external conducting circuit connecting the two electrodes. Galvanic cells are therefore a means of directly converting chemical energy into electrical energy.

The basic electrochemical unit in battery is galvanic cell. It is an arrangement of two or more galvanic cells in series or parallel to provide necessary current. The battery is the first source of electrical energy developed by man. They are used in broad areas like

1. In the supply of electrical power to mobile systems like cars aero planes, space satellites, portable appliances etc
2. In the supply of electrical power to stationary appliances beyond reach of electrical lines, such as remote transmitters, automatic whether stations etc
3. In back up power sources to equipments that must be kept operational even in event of power failure such as lighting and equipments in hospitals, operating theatres, flight control equipments etc.

The principal components of a battery are

1. Container OR battery housing
2. Separator
3. Current collector
4. Electrolyte
5. Active material

The battery components selected should fulfill some important requirements.

1. The electrode reaction must be rapid to avoid severe loss of cell voltage as current is drawn. For secondary batteries charging must be fast
2. The two electrodes must have sufficiently different equilibrium half potentials, so that useful cell voltage can be obtained.
3. The active components of the cell should only react when the external circuit is closed. There should be no self-discharge.
4. The battery should have as large power and energy density as possible

5. The cell components should be cheap and easily available. They should not be poisonous and should be disposable without any environmental pollution

Battery characteristics

A battery is designed to perform a particular function, which depends on its characteristics. The important characteristics of battery are as below

Voltage

The voltage battery depends on the free energy in the overall chemical reaction. There fore it depends on choice of electrode reactions. By Nernsts equation

$$E_{cell} = E^0_{cell} - \frac{2.303RT}{nF}\log Q$$ where Q is reaction quotient

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

So to derive maximum voltage the difference between electrode potentials of two half cells must be high. The cell voltage also depends on other factors

$$E_{cell} = E_c - E_a - |\eta_A| - |\eta_C| - iR_{cell}$$

Where η_A and η_C are over potentials of anode and cathode respectively. R_{cell} is resistance of the cell.

Therefore both electrode reactions must be very rapid to reduce overpotential. The resistance of the cell must be low and conductivity of the electrolyte must be high to minimize the voltage drop.

CURRENT

It is the rate at which battery is discharging. To construct a efficient battery, large quantity of active materials must be maintained for rapid electron transfer without any excessive voltage penalty.

CAPACITY

It is the charge in ampere hours (Ah) that can be obtained from the battery.

Faraday's relation for capacity, C = WnF/M

Where W = mass of active material

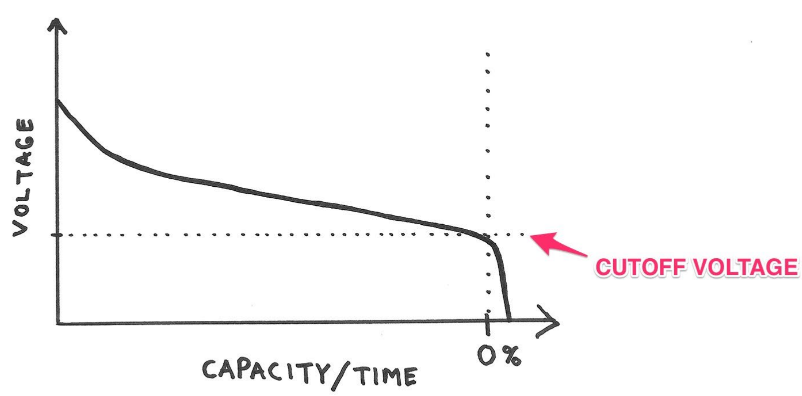
M = molecular mass of active material

n = number of electrons

Therefore, amount of active material actually consumed during discharge determines the practical capacity of battery.

The capacity also depends on the discharge conditions. It is measured by monitoring voltage vs time for fixed discharge of current I amperes.

The capacity C = it. Where t is the time required by the battery during discharge of fixed current of i amperes to reach a value E_{min}^{cell} where the battery is no longer useful. If we plot V against t at a fixed current discharge of i amperes, the flatness of curve represents battery voltage during discharge. The length of flat curve is measure of capacity. Flatter and longer the curve better is the capacity.



ELECTRICITY STORAGE CAPACITY

It is the amount of charge per unit weight stored in the battery.. The weight includes that of complete battery, i.e. electrolyte, current collectors, terminals, battery housing, and other subsidiary elements. A high storage density depends on good batter design minimizing the weight of all subsidiary elements and also appropriate selection of electrode reactions.

For example use of lithium lightest metal as anode would give 1F of charge for just 7g of lithium.

ENERGY DENSITY

It is the ratio of energy available from the cell or battery to its weight.

It can be represented as , ENERGY DENSITY = $itE_{ave}{}^{cell}/W$

It is measured by determining the capacity and noting average potential during discharge and total weight of battery. It depends on the cell voltage and the factors, which determine the storage density. The unit of energy density is $Whkg^{-1}$

POWER DENSITY

It is the power per unit weight of the battery AND IS GIVEN BY iEcell per unit weight of battery. During discharge power density decreases. The requirement of battery may be continuous power density above certain value or high value for short period. It is expressed as WKg-1

CYCLE LIFE

Primary batteries are for single discharge, but secondary battery is rechargeable. The cycle life is number of charge/ discharge cycles that are possible before failure occurs. The cycle life of storage battery must be high. The charging should reform the active materials in suitable state for further discharge.

Reasons for failure to achieve high cycle life is

1. corrosion at contact points
2. shedding of active material from the plate
3. shorting between electrodes due to irregular crystal growth and changes in morphology

SHELF LIFE

Batteries need to be stored for longer time without self-discharge. Self discharge occurs when there is reaction n between the anode and cathode active material or corrosion of current collectors.

TOLERNCE TO SERVICE CONDITIONS

The battery has to be tolerant to different service conditions such as variation in temperature, vibration and shock

ENERGY EFFICIENCY

When secondary batteries are used for energy storage on large scale, the energy efficiency becomes important.

$$\% \text{ Energy efficiency} = \frac{\text{Energy released on discharge}}{\text{Energy required for charge}} \times 100$$

This depends on overpotentials involved in both discharge and charge reactions, battery resistance and charge discharge rates.

Types of batteries

Primary battery:

These are batteries which cannot be recharged and reused. If one or both the electrode reactions are irreversible the battery is termed as primary battery. They are also called as irreversible batteries.

$$\text{Chemical energy stored in primary battery} \xrightarrow[\text{conversion}]{\text{direct}} \text{Electrical energy}$$

This battery delivers electrical energy at the expense of chemical energy as long as the active materials are present in the active state. Once these have been consumed the cell must be discarded. Zn-MnO_2 battery, Li-MnO_2 battery

Secondary battery

These are batteries, which can be recharged and reused. These are called storage or reversible batteries. If the electrochemical reactions can be reversed and the battery can be recharged by the application of external electrical current in the opposite direction, then the battery is said to be secondary battery.

$$\text{Chemical energy stored in secondary battery} \underset{\text{Conversion}}{\overset{\text{direct}}{\rightleftarrows}} \text{Electrical energy}$$

Ex: lead storage battery, Ni-Cd battery

Reserve battery

In this type of battery, the key component is separated from the rest of the battery and the battery is stored in an active state, and made active prior to the application. The key component is usually electrolyte. Batteries which use highly reactive components are designed in this form to eliminate self discharge and deterioration. The reverse design is also used for batteries required to meet extremely long environmentally severe storage requirements. They are used to deliver high power for relatively short period of time after activation. Ex: Mg-water activated battery, Zn-Ag_2O, thermal reserve battery

Modern batteries:

RESERVE BATTERIES

Batteries, which use highly active component materials to obtain the required high energy, high power, and/or low-temperature performance, are often designed in a reserve construction to withstand deterioration in storage and to eliminate self-discharge prior to use. These batteries are used primarily to deliver high power for relatively short periods of time after activation in such applications as radiosondes, fuzes, missiles, torpedoes, and other weapon systems. The reserve design also is used for batteries required to meet extremely long or environmentally severe storage requirements. In the reserve structure, one of the key components of the cell is separated from the remainder of the cell until activation. In this inert condition, chemical reaction between the cell components (self-discharge) is prevented, and the battery is capable of long-term storage.

The electrolyte is the component that is usually isolated, although in some water-activated batteries the electrolyte solute is contained in the cell and only water is added. The reserve batteries can be classified by the type of activating medium or mechanism that is involved in the activation:

Water-activated batteries*:* Activation by fresh- or seawater.

Electrolyte-activated batteries*:* Activation by the complete electrolyte or with the electrolyte solvent. The electrolyte solute is contained in or formed in the cell.

Gas-activated batteries*:* Activation by introducing a gas into the cell. The gas can be either the active cathode material or part of the electrolyte.

***Heat-activated batteries**:* A solid salt electrolyte is heated to the molten condition and becomes ionically conductive, thus activating the cell. These are known as thermal batteries.

Activation of the reserve battery is accomplished by adding the missing component just prior to use. In the simplest designs, this is done by manually pouring or adding the electrolyte into the cell or placing the battery in the electrolyte (as in the case of sea water activated batteries). In more sophisticated applications the electrolyte storage and the activation mechanism are contained within the overall battery structure, and the electrolyte is brought automatically to the active electrochemical components by remotely activating the activation mechanism.

MAGNESIUM WATER-ACTIVATED BATTERIES:

The water-activated battery was first developed in the 1940s to meet a need for a high energy- density, long-shelf-life battery, with good low-temperature performance, for military applications. The battery is constructed dry, stored in the dry condition, and activated at the time of use by the addition of water or an aqueous electrolyte. Most of the water-activated batteries
use magnesium as the anode material. Several cathode materials have been used successfully
in different types of designs and applications. The magnesium/ silver chloride seawater-activated battery was developed by Bell Telephone Laboratories as the power source for electric torpedoes. This work resulted in the development of small high-energy-density batteries readily adaptable for use as power sources for sonobuoys, electric torpedoes, weather balloons, air-sea rescue equipment, pyrotechnic devices, marine markers, and emergency lights.

Construction:

Water-activated cells consist of an anode, a cathode and a separator.

***Anode* (*Negative Plate*):** The anode is made from sheet magnesium.

***Cathode* (*Positive Plate*):**

Silver chloride is a special case. Silver chloride can be melted, cast into ingots, and rolled into sheet stock in thicknesses from about 0.08 mm up. Since this material is malleable and ductile, it can be used in almost any configuration. Silver chloride is nonconductive and is made conductive by superficially reducing the surface to silver by immersion in a photographic
developing solution. No base grid need be used with silver chloride.

Separators: Separators are nonconductive spacers placed between the electrodes. Woven or nonwoven fabric, absorbent, nonconductive material is utilised for the dual purpose of separating the electrodes and absorbing the electrolyte.

Working: The electrochemical reactions are as follows,

Anode: $Mg \rightarrow Mg^{2+} + 2e^-$

Cathode: $2AgCl + 2e^- \rightarrow 2Ag^+ + Cl^-$

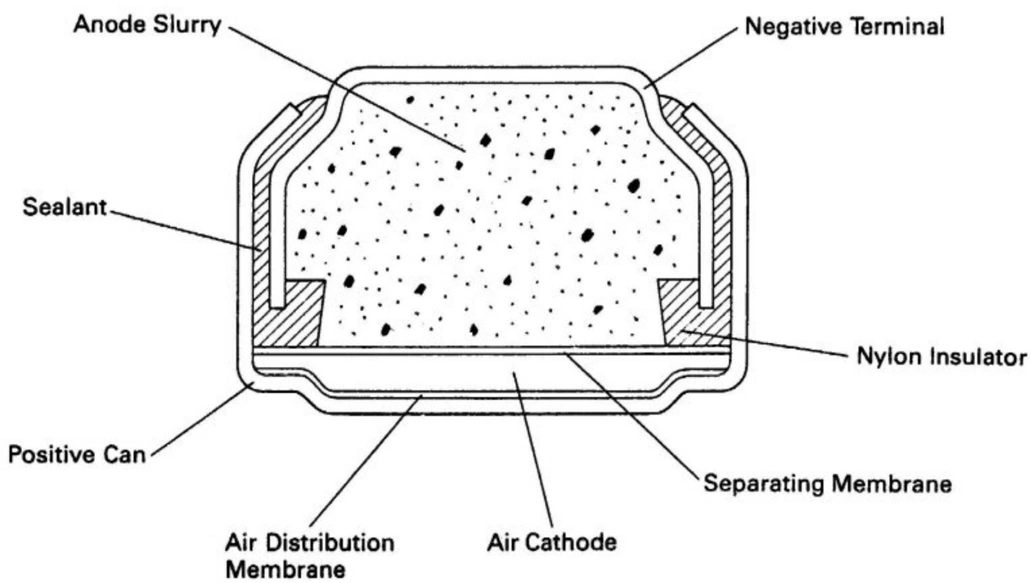
Overall: $Mg + 2AgCl \rightarrow MgCl_2 + 2Ag$

Applications:

Sonobuoys, electric torpedoes, weather balloons, air-sea rescue equipment, pyrotechnic devices, marine markers, and emergency lights.

Zinc air batteries:

This battery uses oxygen directly from the atmosphere to produce electrochemical energy and hence active materials does not contribute to the mass of the battery and offers high energy density of about $100 whkg^{-1}$. Oxygen diffuses in to the cell and is used as cathode reactant. The air cathode cataytically promotes the reaction of oxygen with an alkaline electrolyte. The cell consists of an anode made up of granulated powder of zinc mixed with an aqueous alkaline electrolyte 30% KOH and gelling agent to immobilize the composite and to ensure adequate contact with zinc granules. Cathode is carbon/ catalyst mixture with nickel coated steel mesh support with wet proofing agent and with an outer layer of air permeable Teflon layer. The anode and cathode housing act as terminals. The containers are provided with plastic gasket as insulation between the two. The electrodes are separated by electrolyte absorbent material. The catalyst contains graphite blended with MnO_2. Graphite provides conducting medium. Air access holes on cathode can provide path for O_2 to enter the cell and diffuse to cathode catalyst site.



Electrode reactions are

Anode: $2Zn + 4OH^- \underset{\text{Charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 2ZnO + 2H_2O + 4e^-$

Cathode: $O_2 + 2H_2O + 4e^- \underset{\text{Charge}}{\overset{\text{discharge}}{\rightleftharpoons}} 4OH^-$

Overall reaction: $2Zn + O_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2ZnO$

During cell reaction electrolyte remains invariant and air cathode acts only as a reaction site and it is not consumed. A very thin cathode of the cell permits the use of large zinc anode.

Applications:

1. Railway and military radio receivers
2. Hearing aids and watches
3. Emergency lighting in buildings and electric fences for cattle control which require long-term provision of low current.

Lithium batteries:

Lithium is light weight metal with good electrical conductivity. It has very high negative standard electrode potential of –3.05 V. It can be coupled with other electrodes with high standard electrode potential to get good battery system.

For all these features lithium metal is used as an efficient anode material, to develop high performance primary and secondary batteries. Lithium batteries refer to large family of batteries with common feature having lithium as anode. The electrolytes used in lithium batteries cannot be aqueous solutions because of high reactivity of lithium with water. Therefore, nonaqueous solution is used in Li batteries. Ex: THF, ether, acetonitrile etc. It gives very high-energy density. 1F is released by the dissolution of 7g of lithium metal.

Classification: Lithium batteries are classified into primary and secondary batteries. Primary battery is not chargeable and the secondary battery is chargeable.

Based on the type of cathode material used, lithium primary cells are classified as follows:

(a) Soluble-cathode cells: In this type of cells liquid or gaseous cathode materials, such as sulphur dioxide or thionyl chloride, are used. These substances dissolve in the electrolyte or are the electrolyte solvent.

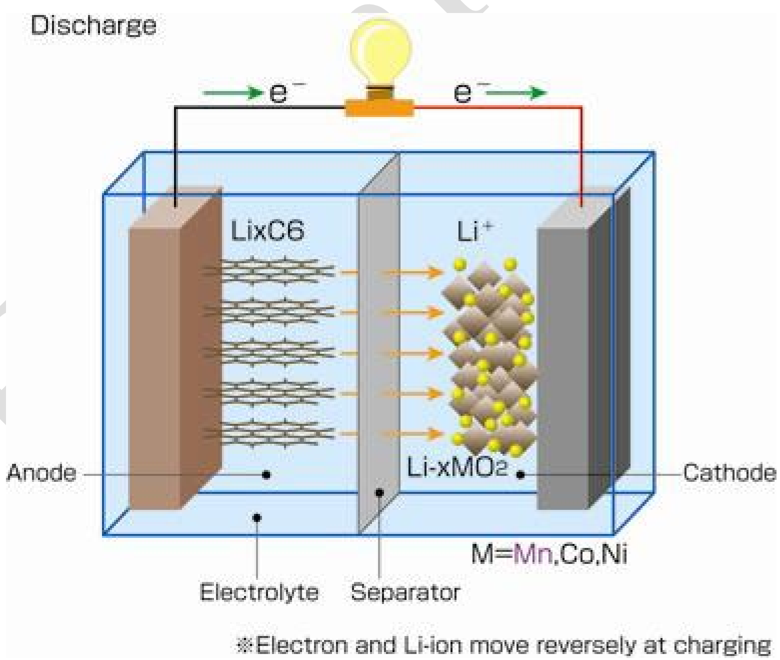
(b) Solid-cathode cells: These types of cells use solid material for the cathode substances, such as V_2O_5 , MnO_2 , CuS, Fe_2S_3 , CuO, etc.

(c) Solid electrolyte cell: these types of cells use electrolytes in the solid form itself as the cathode. PbI_2, PbS, etc., are used as solid electrolyte cathodes. The electrolytes used in lithium batteries cannot be aqueous solutions, because of the high reactivity of lithium with water. Therefore, non aqueous electrolytes are to be used in lithium batteries.

The different types of electrolytes used are of the following types:

1. Lithium salt solutions in organic solvents such as propylene carbonate, dioxolane, THF, ethers, acetonitrile, etc.
2. Solvents like thionyl chloride, sulfuryl chloride, which are also the electro active species at the cathode, mixed with lithium salts to provide ionic conductivity.
3. A lithium ion conducting solid electrolyte such as LiI or LiI + Al_2O_3
4. An organic polymer, which can conduct lithium ions. e.g., Polyethylene oxide.
5. A molten salt. e.g., Molten LiCl + KCl Lithium batteries based on the combinations of the above types of solvent-electrolyte system and positive electrodes have been produced and tested.

Lithium ion battery



The three primary functional components of a lithium-ion battery are,

Anode active material: (negative electrode): Carbon (GRAPHITE)

Cathode active material: (positive electrode): Lithiated transition metal oxide (layered oxide) ex: lithium cobalt oxide.

The electrolyte: The electrolyte is typically a mixture of organic carbonate solvents such as ethylene carbonate or diethyl carbonate containing complexes of lithium ions.

The separator: is a very thin sheet of microperforated plastic. As the name implies, it separates the positive and negative electrodes while allowing ions to pass through. These non-aqueous electrolytes generally use non-coordinating anion salts such as lithium hexafluorophosphate ($LiPF_6$), lithium hexafluoroarsenate monohydrate ($LiAsF_6$), lithium perchlorate ($LiClO_4$), lithium tetrafluoroborate ($LiBF_4$) etc.

Working:

Both electrodes allow lithium ions to move in and out of their interiors. During *insertion* (or *intercalation*) ions move into the electrode. During the reverse process, *extraction* (or *deintercalation*), ions move back out. When a lithium-ion based cell is discharging, the positive Lithium ion moves from the negative electrode (usually graphite) and enters the positive electrode (lithium cobalt oxide). When the cell is charging, the reverse occurs.

At anode:

$$xLiC_6 \rightleftharpoons xLi^+ + xC_6 + xe^-$$

At cathode:

$$Li_{1-x}CoO_2 + xLi^+ + xe^- \rightleftharpoons LiCoO_2$$

Overall reaction:

$$xLiC_6 + Li_{1-x}CoO_2 \rightleftharpoons xC_6 + LiCoO_2$$

In a lithium-ion battery the lithium ions are transported to and from the positive or negative electrodes by oxidizing the transition metal, cobalt (Co), in $Li_{1-x}CoO_2$ from Co^{3+} to Co^{4+} during charge, and reduced from Co^{4+} to Co^{3+} during discharge. The popularity of the Li-ion battery is due to the advantages offered over other secondary (or rechargeable) batteries:

1. Lighter than other rechargeable batteries for a given capacity
2. Li-ion chemistry delivers a high open-circuit voltage **3.7 v**
3. Low self-discharge rate (about 1.5% per month)
4. Do not suffer from battery memory effect
5. Environmental benefits: rechargeable and reduced toxic landfill
6. However Li-ion batteries have also struggled with issues such as:
7. Poor cycle life, particularly in high current applications
8. Rising internal resistance with cycling and age
9. Safety concerns if overheated or overcharged
10. Applications demanding more from Li-ion battery capacity

Uses

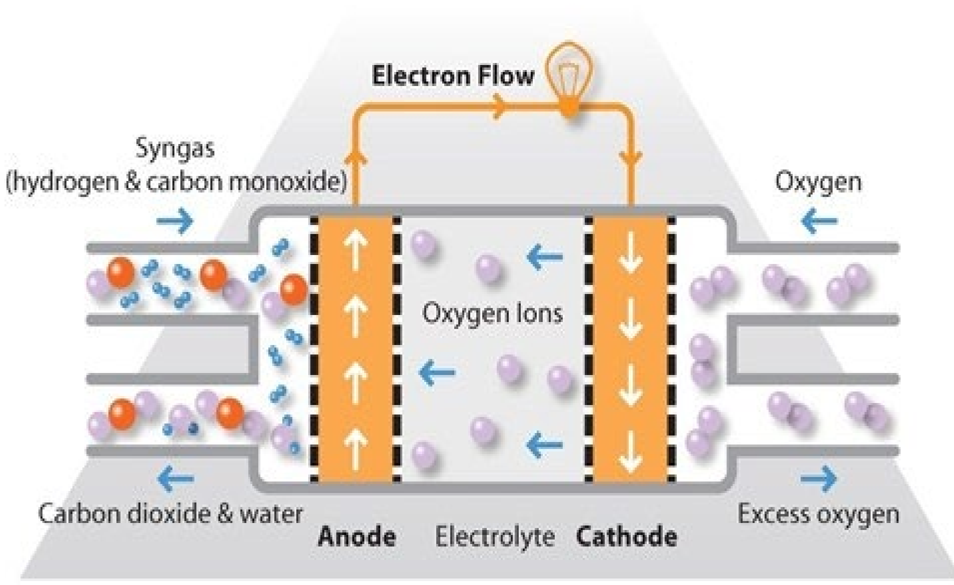
Li-ion batteries provide lightweight, high energy density power sources for a variety of devices. To power larger devices, such as electric cars, connecting many small batteries in a parallel circuit is more effective and more efficient than connecting a single large battery. Such devices include:

- *Portable devices*: these include mobile phones and smartphones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights).

- *Power tools*: Li-ion batteries are used in tools such as cordless drills, sanders, saws and a variety of garden equipment including whipper-snippers and hedge trimmers.

- *Electric vehicles*: Because of their light weight Li-ion batteries are used for energy storage for many electric vehicles, electric cars, hybrid vehicles, advanced electric wheelchairs, model aircraft.

Fuel Cells



Fuel cells are galvanic cells in which the chemical energy contained in a fuel is converted directly into electrical energy by means of electrochemical process in which fuel is oxidized at the anode. These possibilities of generating electrical energy at will by continuously feeding electrochemical active material to a suitable cell has interested the scientific work in this area. There is strong requirement of system in space programmes which provides energy density of the order of $kWkg^{-1}$. Therefore, development of fuel cells has led to the strong interest in fuel cell technology.

The fuel cells differ from a conventional battery in the following aspects.

a. In fuel cell reactants is fed from outside the cell and do not form integral part as in a battery.

b. The fuel cells do not store chemical energy as in a battery

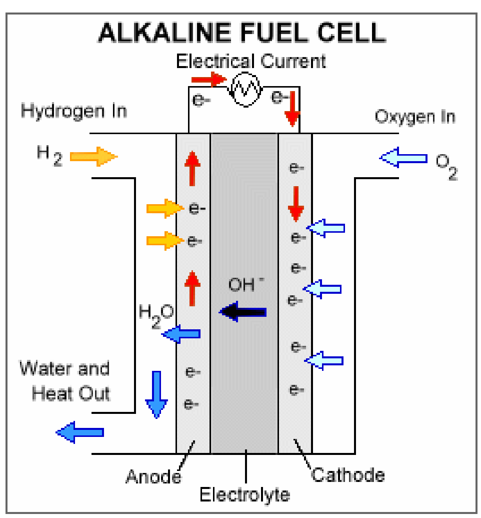
c. Reactants are constantly supplied and products are constantly removed from fuel cell

Advantages of fuel cells:

1. Theoretical efficiency is 100%, but actually 50-80% of efficiency can be observed owing to over voltage and cell resistance.
2. They are eco-friendly since the products of the overall reactions are not toxic and hence do not cause pollution problems.
3. They can produce direct current for long periods at low cost.
4. No need of charging.

Types of fuel cells

1. Alkaline fuel cells:



These cells work with 30% aqueous KOH as electrolyte and working temperature of up to 90^0C. These make use of inexpensive materials like O_2,H_2 and alkali. The cell when started at room temperature has lower efficiency but gets warmed up during the operation and the efficiency rises to the optimum value. Electrodes are non noble metals like porous sintered nickel, silver net etc

$H_2 + 2OH^- \longrightarrow 2H_2O + 2e-$

At cathode: $O_2 + H_2O + 2e- \longrightarrow 2OH-$

The overall cell reaction is $H_2 + O_2 \longrightarrow H_2O$

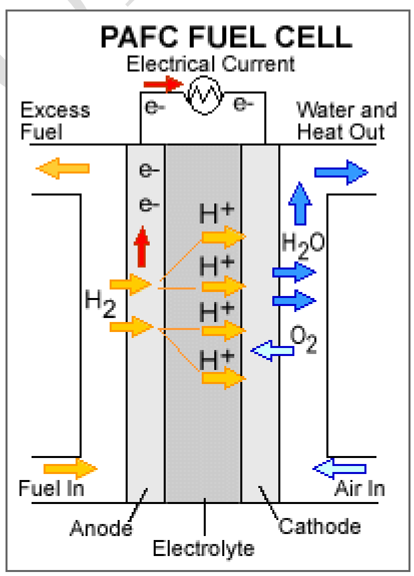
In this type of cell reactants must be free from CO_2, because the alkali reacts with CO_2 to form carbonates as precipitate which would block the pores of electrodes.

Ex: H2- O2 fuel cell

Applications:

1. Space programmes
2. Military applications
3. Portable and emergency power generation equipments

2. Polymer electrolyte membrane fuel cells:



This uses a polymer membrane as its electrolyte. This membrane is an electronic insulator but an excellent conductor of H+ ions. The polymer used consists of fluorocarbon backbone (–CF_2-CF_2-) similar to teflon to which sulphonic acid groups are attached. The protons on sulphonic acid group are free to migrate through the membrane. The electrodes used are typical gas diffusion electrodes made up of porous carbon impregnated with platinum catalyst. Hydrogen gas is passed through anode and the reaction is

Anode: $2H_2 \longrightarrow 4H^+ + 4e^-$ Oxidation

H+ ions pass through the polymer electrolyte to the cathode where they are combined catalytically with O2 to form water.

Cathode $4H^+ + O_2 + 2e^- \longrightarrow 2H_2O$ Reduction

The electrolyte also acts as separator between anode and cathode to separate two reactant gases. Proper water management is important for efficient operation. Dehydration of membrane reduces proton conductivity and excess of water leads to flooding of electrodes. The reactant gases must be free from CO to prevent poisoning of catalyst. The cell is operated lower than 100^0C

Applications: They are used in automobiles, military, and terrestrial orbital missions

Super capacitor

1. **Introduction**

The supercapacitor, also known as ultracapacitor or double-layer capacitor, differs from a regular capacitor in that it has very high capacitance. A capacitor stores energy by means of a static charge as opposed to an electrochemical reaction. Applying a voltage differential on the positive and negative plates charges the capacitor. This is similar to the buildup of electrical charge when walking on a carpet. Touching an object releases the energy through the finger.

A capacitor is a passive electronic component comprising a pair of conducting plates separated by a dielectric. Capacitors store electrical energy as electrostatic charge with equal quantities of positive and negative charges on opposite faces of the conducting plates resulting in a voltage difference between the faces. When the two faces are

connected by an external load, current flows until complete charge balance is attained and the stored energy is released. The capacitor can then be retrieved to its charged state by applying voltage. Since the charge is stored physically without any chemical or phase changes, the process is highly reversible and the charge–discharge cycle can be repeated over and over again, virtually without limit. The quantity of charge (Q) stored in a capacitor is equal to the device voltage (V) times proportionality constant (C) called capacitance, i.e. Q = CV ---------(1).

In Eq. (1), capacitance C is in Farad, charge Q is in Coulomb and the voltage V is in Volt. In vacuum, the capacitance of such a capacitor is proportional to the area (A) of the conductors divided by the thickness (d) of the dielectric separating them as shown in Fig. 1,

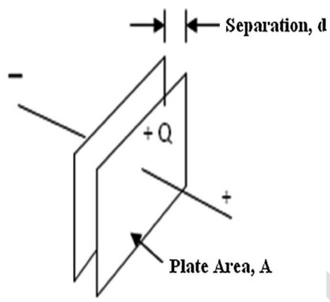


Fig. 1. Schematic sketch of a parallel-plate capacitor.

C= --------------(2)

In Eq. (2), proportionality constant $\varepsilon_0 = 8.9 \times 10^{-12}$ F m $^{-1}$ is the permittivity of the free space or vacuum. With the dielectric material of relative permittivity (ε_r), which increases the energy stored in the device, the capacitance (C) is then expressed as:

C = ------------(3)

On substituting Eq. (3) in Eq. (1), we get, Q = V ---------------(4)

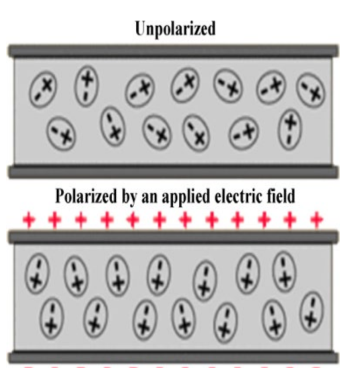


Fig. 2. A dielectric medium showing the orientation of charged particles creating polarization effects. **Electrical double-layer capacitor:**

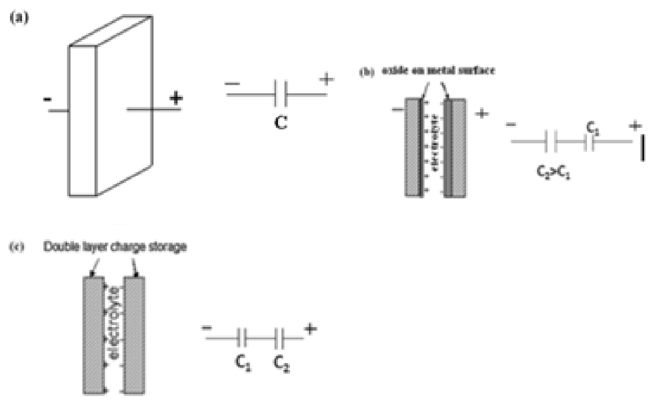


Fig. 3. Schematic sketches for (a) electrostatic, (b) electrolytic and (c) electrochemical capacitors

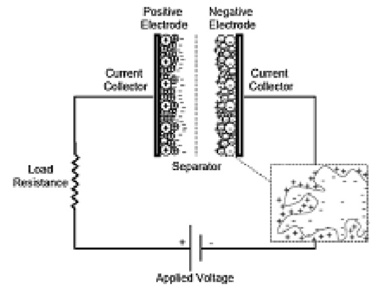


Fig. 4. Schematic sketch of an electrical double-layer capacitor

Electrical double-layer capacitor: It has long been accepted that an electrical double-layer exists at the electrode/electrolyte interface that governs adsorption phenomena and influences charge transfer reaction rates. As shown in (Fig.3c), the electrical double-layer stretches to about a few A^0 and stores electrostatic energy like a capacitor. It is noteworthy that the existence of the electrical double-layer has always been inferred from indirect observations of related properties and quantities, but never directly probed. It was realized only recently that the energy stored per unit surface area is significant and becomes technologically attractive with the introduction of materials with high active-surface-areas, such as activated carbons. In the electrical double-layer, solvated ions are attracted to the solid surface by an equal but opposite charge in the solid as shown in Fig. 4. These two parallel regions of charge form the source of the term electrical double-layer where the charge separation as measured in molecular dimensions is less than 10^{-9} m. As the surface area of activated carbon is nearly1000 $m^2\ g^{-1}$ of material, this creates a capacitor cell with very high specific capacitance of nearly 10^5 F kg^{-1} and the possibility of realising devices rated at many thousands of Farad. Owing to their appreciably high capacitance, these capacitors are also referred to **as supercapacitors or ultracapacitors.**

Electrical-doublelayer capacitors (EDLCs):

These capacitors rely on carbon-based structures utilizing nonfaradaic electrostatic charging of the electrical double-layer formed at the electrode–electrolyte interface and are hence termed as electrical-double-layer capacitors.

EDLCs store electrical energy at the electrolyte/carbon interface through reversible ion adsorption onto the carbon surface, thus charging the electrical double-layer through a non-faradaic contribution between an electronic conductor, namely the carbon, and a liquid ionic-conductor, namely the electrolyte. The few nano-meter thick electrical double-layers at the phase boundary between the electrode and electrolyte can be referred to as a nano-dielectric similar to a parallel-plate capacitor wherein the current collector of each electrode contacts high-surface-area-conductive carbon impregnated with an electrolyte. At the negative electrode, the negative charges received during charge by an external source are balanced by the positive charges of the electrolyte cations that accumulate on the surface and within the pores of the carbon particles. The counter electrode charges itself positively against the surrounding solution.

Because of the formation of the electrical double-layer at each electrode/electrolyte interface, a complete cell is formed by two capacitors in series and the overall capacitance (CT) is expressed

as: --------------------------(7)

In Eq. (7), C+ is the capacitance of cathode/electrolyte interface and C− is the capacitance of anode/electrolyte interface. In an ideal electrical-double-layer capacitor, only charge separation takes place at the electrode and there are no oxidation or reduction reactions. Accordingly, charge (Q) stored in such a capacitor is related to its capacitance (C) and voltage (V) as: Q = CV. Consequently, the capacitance is voltage independent but does depend on electrode surface area, the double-layer thickness and dielectric constant of the electrolyte. Traditionally, activated carbons have been used in EDLCs. But conducting carbons with graphitic structure also include template and carbide-derived carbons, nanotubes, nanohorns, onions (multishell fullerenes), polyhedral particles, carbon blacks and graphene.

Electrochemical capacitors have limited energy density but are known to exhibit high power densities. Accordingly, electrochemical capacitors cannot replace batteries but can complement them in many applications. Applications that can benefit from electrochemical capacitors include medical, such as X-ray and MRI (magnetic-resonance imaging), spot and contact welding, audio-line stiffening, actuators, large electric motor starting and power quality such as initial pulse power for UPS systems.

Merits and demerits of supercapacitors

The vivid merits of supercapacitors are fast charging, long cyclelife, high power, little maintenance, wide temperature-range and limited heat-dissipation. The demerits of the supercapacitors are high equivalent series resistance, low energy, high rate of self discharge, high leakage-current and high cost.

Table 1
Comparison table among selected electrochemical energy storage technologies.

Characteristics	Capacitor	Supercapacitor	Battery
Specific energy (W h kg^{-1})	< 0.1	1–10	10–100
Specific power (W kg^{-1})	$\gg 10{,}000$	500–10,000	< 1000
Discharge time	10^{-6} to 10^{-3}	s to min	0.3–3 h
Charge time	10^{-6} to 10^{-3}	s to min	1–5 h
Coulombic efficiency (%)	About 100	85–98	70–85
Cycle-life	Almost infinite	$> 500{,}000$	about 1000

* Data taken from [2].

Table 2
Comparison between batteries and supercapacitors [1].

Comparison parameter	Battery	Supercapacitor
Storage mechanism	Chemical	Physical
Power limitation	Reaction kinetics, mass transport	Electrolyte conductivity
Energy storage	High (bulk)	Limited (surface area)
Charge rate	Kinetically limited	High, same as discharge
Cycle life limitations	Mechanical stability, chemical reversibility	Side reactions

Applications of electrochemical capacitors

The major applications of electrochemical capacitors appear to be in high-pulse power and short-term power hold. Some applications of electrochemical capacitors are discussed below.

1. Memory back-up

Many appliances now incorporate digital components with memory where even a very brief interruption in the power supply could cause the loss of stored information. In such applications, the

capacitor can act as a back-up supply for short periods. Batteries are the alternative to the capacitors for these applications but batteries have a limited lifetime, and therefore need to be replaced regularly. Electrochemical capacitors are a preferred choice as back-up power supply due to their long lifetime.

2. Electric and hybrid electric vehicles

Battery-powered electric vehicles have the limitations of low power-density, limited charge/discharge cycles, high-temperature dependence, and long charging-time. Electrochemical capacitors are bereft of these limitations albeit they are faced with other limitations such as low energy-density and high costs. Peak-load requirements that result from accelerating or climbing up-hills could be met by the high-power device, namely the electrochemical capacitors bank. An electrochemical capacitor is presently the power supply in hybrid cars for start/stop application. When a hybrid vehicle stops,its internal combustion engine (ICE) shuts down which is restarted by the electrical system powered by an electrochemical capacitor that is recharged when the ICE resumes powering the vehicle. This helps reducing fuel consumption. Electrochemical capacitors are ideally suited for city-transit buses with stop-and-go driving, in trash trucks that can experience as many as a thousand start/stop cycles during a day, and in delivery vans that operate on similar drive cycles. The primary challenges for any energy storage unit used in heavy duty hybrid vehicles are the long cycle-life and the need to dissipate the heat generated due to charge/discharge losses. Electrochemical capacitors are highly efficient and have limited heat dissipation owing to their low-energy content.

3. Power quality:

Static-synchronous-compensator system injects or absorbs power from a distribution line to compensate for any voltage fluctuations. Such a system requires a DC energy storage device of some sort from which energy could be drawn or stored. Since the majority of voltage perturbations on the distribution bus are short-lived, usually not lasting more than 10 cycles, electrochemical capacitors are an attractive option for energy storage and delivery to improve the power quality.

4. Battery improvement

Batteries are being used widely in the portable power appliances, such as UPS, laptops, and mobile phones. Many such devices draw high-power pulsed currents which result in the reduction of battery performance. Batteries in parallel with electrochemical capacitors could be an effective alternative for these applications.

5. Portable power supplies

Most devices presently using battery power supplies have long recharge time and need to be charged overnight. These need to be replaced with the electrochemical capacitors that can be quickly charged and discharged. Indeed, for any portable electronic equipment with moderate energy demands, electrochemical capacitors are ideally suited as rechargeable stand-alone power sources.

6. Renewable energy applications

In solar photovoltaic applications, batteries need to be replaced every 1–3 years because of continuous cycling that has a detrimental effect on batteries. But electrochemical capacitors can be charged and discharged quickly for large number of cycles, and need to be replaced every 20 years only, which is similar to the life-span of the photovoltaic panels. Life-cycle costs are therefore reduced by eliminating frequent maintenance requirements. Energy efficiency is always of primary concern in renewable power generation. In this regard electrochemical capacitors are attractive as they exhibit much higher charging efficiency than batteries.

7. Micro-scale energy scavenging systems

Products and systems can be designed around supercapacitor technology for efficient energy storage and its retrieval later. The concept is to generate electrical energy at anytime from see-saw,

swing, health-club equipment, exercising equipment, etc., with little effort and its retrieval on demand.

Technology challenges

For many applications, relatively higher cost of electrochemical capacitors is currently the primary reason for not being the energy storage technology of choice. Despite their high-level of performance, electrochemical capacitors are simply too expensive to compete against the other available approaches. For some applications, potential users find electrochemical capacitors to be attractive but find their energy density to be too low. Hence increasing energy density and lowering cost are the primary challenges facing electrochemical capacitor developers.

RAGONE PLOT

A **Ragone plot** is a plot used for performance comparison of various energy-storing devices. On such a plot the values of energy density (in W·h/kg) are plotted versus power density (in W/kg). Both axes are logarithmic, which allows comparing performance of very different devices (for example, extremely high and extremely low power).Conceptually, the vertical axis describes how much energy is available, while the horizontal axis shows how quickly that energy can be delivered, otherwise known as power, per unit mass. Fuel cells have high energy density as they can be supplied with fuel and oxidant continuously while their power density is low as the reactions are slow. On the other hand supercapacitors discharge fast ,so their power density is high but only small amount of energy can be stored, so energy density is low.

Fig. Ragone plot

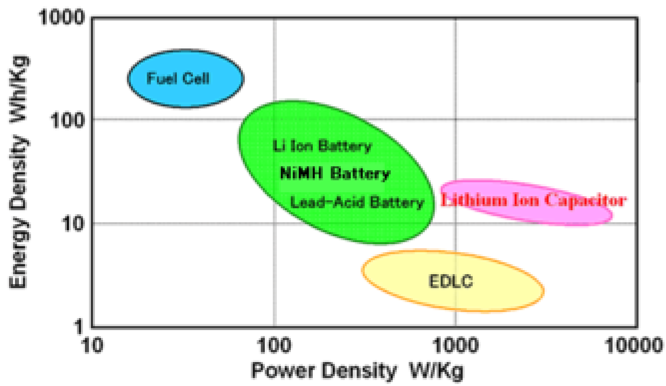
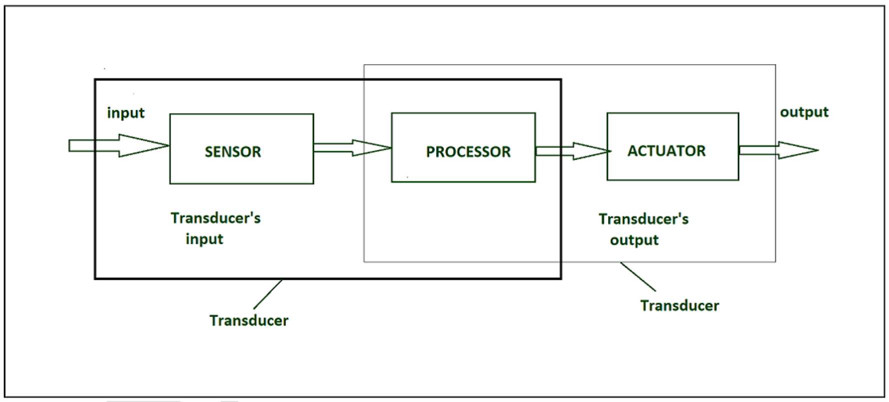


Fig- Wikipedia

A Sensor is a characteristic of any device or material to detect the presence of a particular physical quantity. The output of the sensor is a signal, which is converted to human readable form. It performs some function of input by sensing or feeling the physical changes in the characteristics of a system in response to stimuli.

What are Sensors?

Sensors are the devices that can detect and response to changes in the environment. These changes can be in form of light, temperature, motion, moisture or any other physical property. The sensor converts these physical changes into signal that can be measured. Sensors play an important role in IoT which will make an ecosystem for collecting, analysing, and processing data about a specific environment so that it can be monitored, managed, and controlled more easily and efficiently. Sensors bridge the gap between the physical world and the logical world.



Transducer: It converts the signal from one physical form to another physical form. it is also called energy converter. For example, microphone converts sound to electrical signal. It is based on the principle of conservation of energy.

Classification of Sensors

The Sensor can be classified as

Based on Power Requirement

- **Active Sensors:** These Sensors require an external excitation signal or power source to work.
- **Passive Sensors**: These Sensors do not require any external power source and it can directly generate the output response.

Based on Means of Detection

The Sensors can be according to detection method they use such as electrical, biological, chemical, or radioactive detection.

Based on the Conversion Phenomenon

This classification is based on the input and output conversion

1. **Photoelectric**: It Changes light to electrical signals.
2. **Thermoelectric:** It Changes temperature difference to electrical voltage.
3. **Electrochemical**: It Changes chemical reactions to electrical signals.
4. **Electromagnetic**: It Changes magnetic fields to electrical signals.
5. **Thermoptic**: It Changes temperature changes to electrical signals.
6. **Based on Output Type**
7. **Analog Sensors:** It produce an output signal which is usually in the form of voltage, current, or resistance, proportional to the measured quantity.

- **Digital Sensors**: It provides discrete or digital data as output.
- **Types of Sensors**

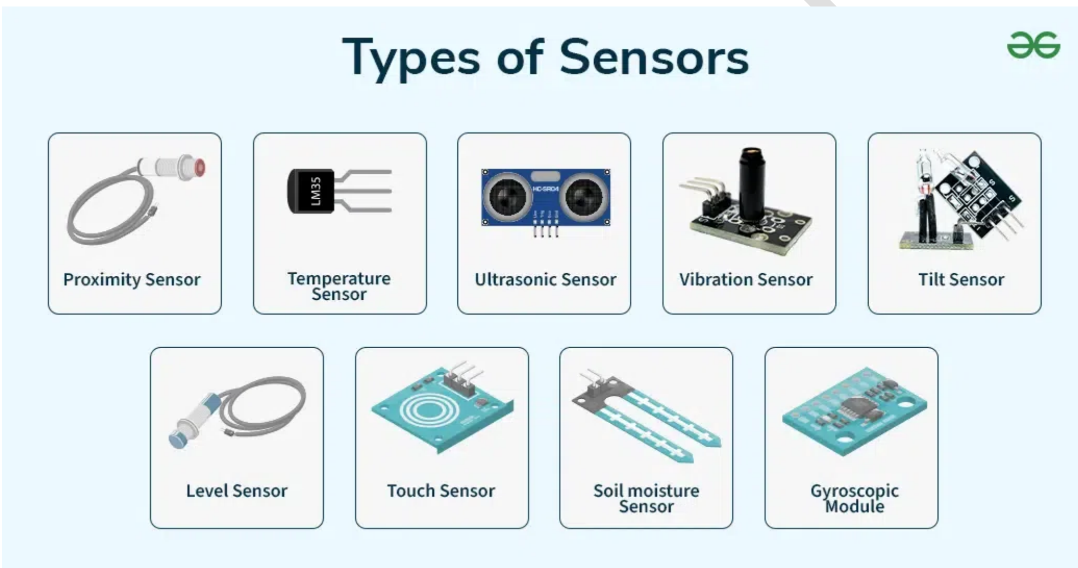
We live in the world of sensors, there are different types of sensors in our homes, offices, cars etc. by working to make our lives easier by turning on the lights by detecting our presence, adjusting the room temperature, detect smoke or fire, make us delicious coffee, and automatic door closing and so on. here we will discuss types of sensors one by one in detail:

- **Temperature sensors:** Monitoring temperature of used devices in industrial applications. it is used to measure temperature. this can be air temperature, liquid temperature or the temperature of solid. It can be analog or digital. In an **Analog Temperature Sensor**, the change in the Temperature correspond to change in its physical property like resistance or voltage. LM35 is a classic Analog Temperature Sensor. In **Digital Temperature Sensor**, the output is a discrete digital value, DS1621 is digital sensor which generates 9 bits temperature data.

- **Accelerometer sensors:** It measures the rate of change of velocity and this sensor generate magnitude and acceleration of the acceleration. Accelerometer sensor sensor ADXL335 provides 3 axes (X, Y, and Z) values in analog voltage. it is used in car electronics, ships, and agricultural machines.
- **Alcohol sensors:** as the name suggests it detects alcohol. Usually, alcohol sensors are used in breathalyser devices, which determine whether the person is drunk or not. Law enforcement personnel use breathalysers to catch drunk-and-drive culprits.
- **Radiation sensors:** Radiation Sensors/Detectors are electronic devices that sense the presence of alpha, beta, or gamma particles and provide signals to counters and display devices. Radiation detectors are used for surveys and sample counting.
- **Position sensors:** Position Sensors are electronic devices used to sense the positions of valves, doors, throttles, etc. and supply signals to the inputs of control or display devices. Key specifications include sensor type, sensor function, measurement range, and features that are specific to the sensor type. Position sensors are used wherever positional information is needed in a myriad of control applications. A common position transducer is a so-called string-pot, or string potentiometer.
- **Gas sensors:** It measures and detects concentration of different gases which is present in the atmosphere or any other environment.
- **Torque sensors:** This sensor is used for measuring the rotating torque and it is used to measure the speed of the rotation.
- **Optical sensors:** it is also called photosensors which can detect light waves at different points in the light spectrum including ultraviolet light, visible light, and infrared light. it is extensively used in smartphone, robotics and Blu-ray players.
- **Proximity sensors:** This sensor is used to detect the distance between two objects or detect the presence of an object. it is used in elevators, parking lots, automobiles, robotics, and numerous other environments.

- **Touch sensors:** Touch sensing devices detect physical contact on a monitored surface. Touch sensors are used extensively in electronic devices to support trackpad and touchscreen technologies. They're also used in many other systems, such as elevators, robotics and soap dispensers.
- **Image sensor:** it is used for distance measurement, pattern matching, color checking, structured lighting, and motion capture and it is also used in different applications such as 3D imaging, video/broadcast, space, security, automotive, biometrics, medical, and machine vision.

Given below the types of sensors:



Application of Types of Sensors

Given below are the Application of Types of Sensors

- **Automotive Industry:** They are used in the Automotive industry for monitoring engine temperature, speed and other parameters.
- **Smart Homes**: They are used in the Smart Homes for detecting movements, Control HVAC and other measurements.
- **Robotics:** They are used in the Robotics for object recognition, Tracking the position and measuring force.

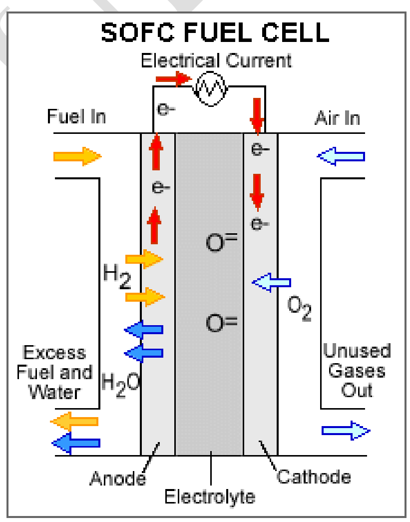
- **Transportation**: Sensors such as GPS , Load, and Speed sensors are used in transportation infrastructure.

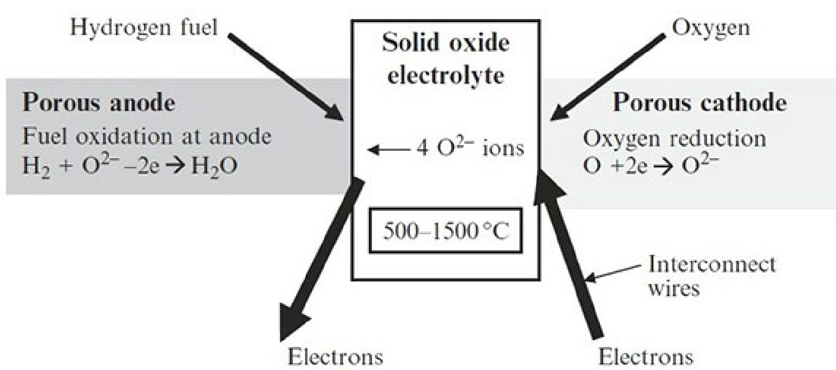
Conclusion

Sensors play an important role in modern technology. It provides accurate and reliable data for various applications. From detecting environmental changes to ensuring the safety and efficiency of electronic systems. In this article we have gone through the definition of the sensors, seen it classification with its different, also we have gone through its major Applications.

SOLID OXIDE FUEL CELLS:

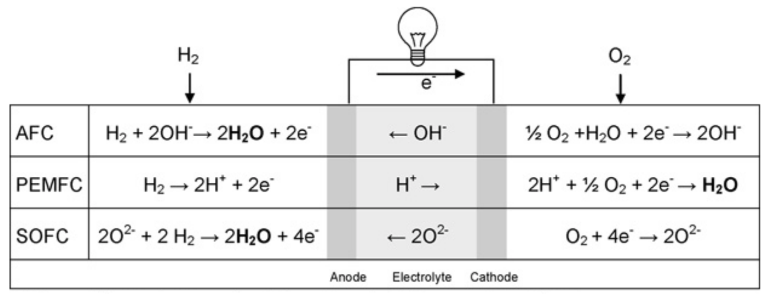
The electrolyte is solid nonporous matal oxide usually ZrO_2 doped with Y_2O_3. Operating temperature is 1000^0C.The cathode is porous Sr doped with $LaMnO_3$. The anode is Ni on ZrO_2.





Application:

During operation large quantity of heat is produced, which can be used for space heating ,stationary power source.



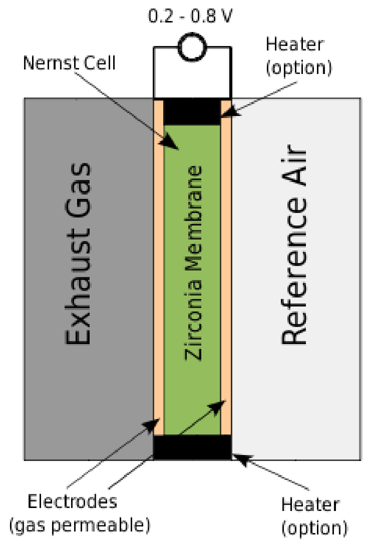
O_2 sensors

An Oxygen sensor or lambda sensor is an electronic device that measures the proportion of O_2 in the gas or liquid being analyzed.

A gasoline engine burns gasoline in the presence of oxygen. It turns out that there is a particular ratio of air and gasoline that is "perfect," and that ratio is 14.7:1 (different fuels have different perfect ratios -- the ratio depends on the amount of hydrogen and carbon found in a given amount of fuel). If there is less air than this perfect ratio, then there will be fuel left over after combustion. This is called a **rich** mixture. Rich mixtures are bad because the unburned fuel creates pollution. If there is more air than this perfect ratio, then there is excess oxygen. This is called a **lean** mixture. A lean mixture tends to produce more nitrogen-oxide pollutants, and, in some cases, it can cause poor performance and even engine damage.

The oxygen sensor is positioned in the exhaust pipe and can detect rich and lean mixtures. The Oxygen Sensor detects the amount of oxygen in the exhaust gas and sends a signal to the engine control unit which adjusts the air fuel mixture to the optimal level. Too much oxygen in the exhaust gas indicates a lean mixture, which can cause performance problems, including misfires. Too little oxygen indicates a rich mixture, which wastes fuel and results in excess exhaust emissions.

Construction and operation:



1. An O_2 sensor is actually a galvanic cell. The zirconium dioxide, or zirconia, lambda sensor is based on a solid-state electrochemical fuel cell. The sensor contains two platinum electrodes with an electrolyte between them. ZrO_2 doped with some Y_2O_3 is the electrolyte used. Due to doping some oxygen vacancies are created in the crystal lattice. The mobility of O_2^- ions is greatly enhanced and the conductivity is due to oxygen ions.

2. Cell voltage is given by $= \frac{2.303RT}{4F}\log\frac{p1}{p2}$ where p_1 and p_2 are the partial pressure of O_2 in reference air and exhaust gas respectively.

3. Its two electrodes provide an output voltage corresponding to the quantity of oxygen in the exhaust relative to that in the atmosphere.

4.An output voltage of 0.2 V represents a "lean mixture" of fuel and oxygen, where the amount of oxygen entering the cylinder is sufficient to fully oxidize the carbon monoxide (CO), produced in burning the air and fuel, into carbon dioxide (CO_2).

5. An output voltage of 0.8 V represents a "rich mixture", one which is high in unburned fuel and low in remaining oxygen. The ideal setpoint is approximately 0.45 V. This is where the quantities of air and fuel are in the optimum ratio, such that the exhaust output contains minimal carbon monoxide.

6. O_2 sensors operate at a minimum temperature of 360ºC.

7. The O_2 sensor allows fuel management system to maintain the ideal air/fuel ratio across various engine operation conditions.

8. Automobiles using a 3-way catalyst are equipped with O2 sensors.

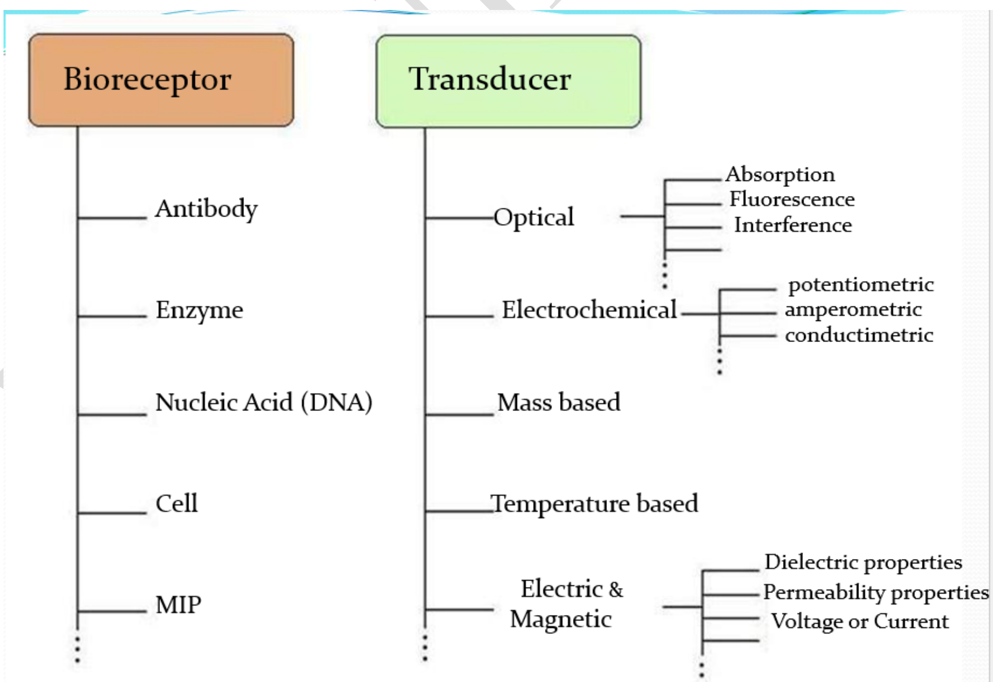
9. Leaded gasoline contaminates the O2 sensors and catalytic convertors and results in failure of the sensor. Other reason for failure could be presence of impurities in gasoline.

Applications: Most common applications of O_2 sensors are:

1. Measure exhaust gas concentrations of O_2 in IC engines
2. Divers use to measure partial pressure of O_2 in their breathing gas
3. Scientists use as probes to measure respiration or production of O_2
4. In O_2 analysers used in medical applications such as anesthesia monitors, respirators etc.

Introduction to Biosensors

A biosensor is an analytical device which is used to determine the presence and concentration of a specific substance in a biological analyte.

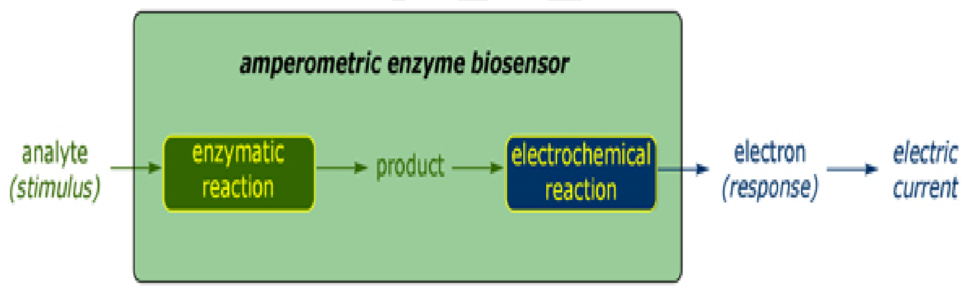


Applications of biosensors

- Glucose monitoring in diabetes patients ←**historical market driver**
- Environmental applications e.g. the detection of pesticides and river water contaminants such as heavy metal ions
- Remote sensing of airborne bacteria e.g. in counter-bioterrorist activities
- Detection of pathogens
- Determining levels of toxic substances before and after bioremediation
- Detection and determining of organophosphate
- Routine analytical measurement of folic acid, biotin, vitamin B12 and pantothenic acid as an alternative to microbiological assay
- Determination of drug residues in food, such as antibiotics and growth promoters, particularly meat and honey.
- Drug discovery and evaluation of biological activity of new compounds.
- Protein engineering in biosensors
- Detection of toxic metabolites such as mycotoxins

Amperometric biosensor

Amperometric biosensors are self-contained integrated devices based on the measurement of the current resulting from the oxidation or reduction of an electroactive biological element providing specific quantitative analytical information.



Blood Glucose Monitoring

What is it?

- Blood Glucose Monitoring is a way of checking the concentration of glucose in the blood using a glucometer.

What is the purpose?

- Provides quick response to tell if the sugar is high or low indicating a change in diet, exercise or insulin.
- Over time, it reveals individual of blood glucose changes.

Why monitor blood glucose?

- Reduces risk of developing complications with diabetes.
- Allows diabetics to see if the insulin and other medications they are taking are working.
- Gives diabetics an idea as to how exercise and food affect their blood sugar.
- May prevent hypoglycemia or hyperglycemia

Amperometric Glucose Biosensor

- Developed by Updike and Hicks
- Enzyme Glucose oxidase catalyze the oxidation of glucose by molecular oxygen producing glucolactone and hydrogen peroxide.
- In order to work as a catalyst, GOx requires a redox cofactor –flavin adenine dinucleotide (FAD), works as an initial electron acceptor and is reduced to $FADH_2$.

$$\text{Glucose} + \text{GOx} - \text{FAD}^{+} \longrightarrow \text{Glucolactone} + \text{GOx} - \text{FADH}_2$$

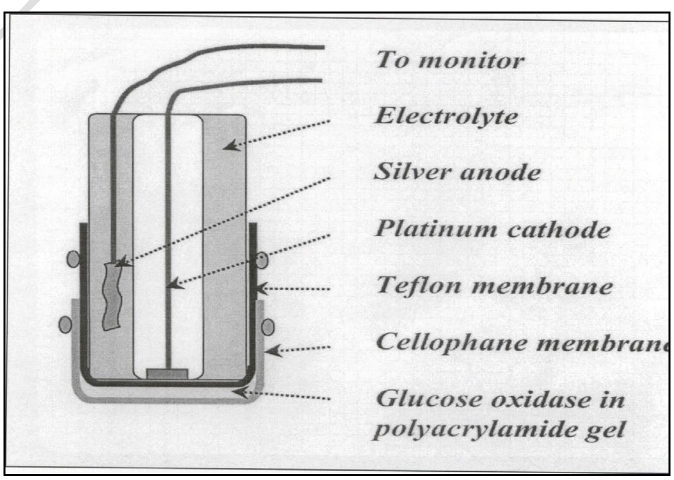
- The cofactor is regenerated by reacting with oxygen, leading to the formation of hydrogen peroxide

$$\text{GOx} - \text{FADH}_2 + O_2 \longrightarrow \text{GOx} - \text{FAD} + H_2O_2$$

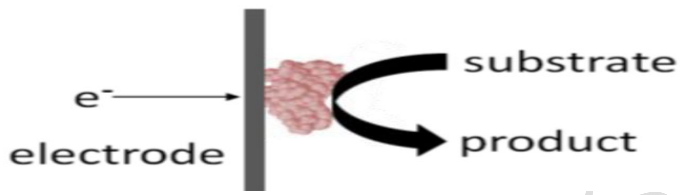
- Hydrogen peroxide is oxidized at a platinum electrode. The number of electron transfers, at electrode surface is directly proportional to the number of glucose molecules present in the blood.

$$H_2O_2 \longrightarrow 2H^{+} + O_2 + 2\,e^{-}$$

- Three strategies used for the electrochemical sensing of glucose are
  - By measuring oxygen consumption
  - By measuring the amount of hydrogen peroxide produced by the enzyme reaction
  - By using a diffusible or immobilized mediator to transfer the electrons from Gox to the electrode.



- The third-generation glucose biosensors are based on the direct electron transfer between the active center of enzyme and the electrode.
- The intrinsic barrier to electron flow is the globular structure of glucose oxidase with the active site, containing FAD/$FADH_2$ redox cofactor, buried deep inside a cavity of ~ 13 A° is a major hinderance for direct electron transfer.
- Carbon nanotubes immobilized electrode surface provide suitable orientation for enzyme immobilization and establish connection between electrode surface and deeply buried



HYDROGEN PRODUCTION AND STORAGE:

Hydrogen is the simplest element. An atom of hydrogen consists of only one proton and one electron. It is also the most plentiful element in the universe. Despite its simplicity and abundance, hydrogen does not occur naturally as a gas on the Earth – it is always combined with other elements. Water, for example, is a combination of hydrogen and oxygen (H2O).

Hydrogen holds the potential to provide clean, reliable and affordable energy supply that can enhance economy, environment and security. It is flexible and can be used by all sectors of economy. It is non-toxic and recyclable. Due to these qualities, it is considered to be an ideal energy carrier in the foreseeable future. An energy carrier moves and delivers energy in a usable form to consumers.

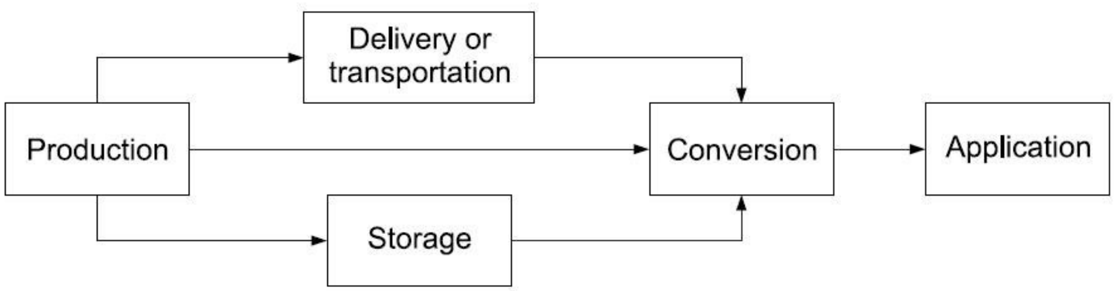
Hydrogen can be produced by using a variety of energy sources, such as solar, nuclear and fossil fuels and can be converted to useful energy forms efficiently and without detrimental environmental effects. When burned as fuel or converted to electricity it joins with oxygen to produce energy with water as the only emission. When air is used for combustion instead of oxygen, some NO x is also produced, which can be reduced by lowering the combustion temperature.

Despite all these benefits, realization of hydrogen economy faces multiple challenges. Unlike gasoline and natural gas, hydrogen has no existing, large scale

supporting infrastructure. Building of such an infrastructure will require major investment. Although

hydrogen production, storage and delivery techniques are currently in commercial use by the chemical and refining industries, existing hydrogen storage and conversion technologies are too costly for widespread use in energy applications. The individual segments of hydrogen energy system; production, delivery, storage conversion and end use applications are closely interrelated and interdependent as shown in figure below. Design and application of a hydrogen economy must carefully consider each of these segments as well as the whole system.

Hydrogen can be produced in centralized facilities and distributed to an energy conversion site via pipeline or stored and shipped via rail or road. It can also be produced at decentralized locations onsite where it will be stored and/or fed directly into conversion device for stationary, mobile or portable applications.



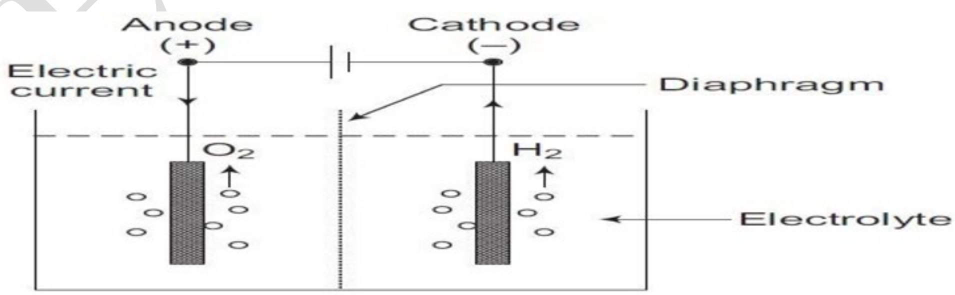
PRODUCTION:

Hydrogen is the third most abundant element on the earth, it does not exist in Free State, except for small quantities in the upper atmosphere. It is, therefore, not a primary energy source. However, large amounts of combined hydrogen are present in compounds such as water, fossil fuels and biomass. It can therefore, be produced through two routes: (a) Fossil fuels, such as natural gas, coal, methanol, gasoline etc., and biomass are decomposed by thermo-chemical (steam reforming or partial oxidation) methods to obtain hydrogen. The CO produced in the process is eliminated by water gas shift reaction. This route of hydrogen production causes CO emission. The energy content of the produced hydrogen is less than the energy content of the original fuel, some of it being lost as excessive heat during production. (b) Hydrogen can also be produced by splitting water into hydrogen and oxygen by using energy from nuclear or renewable sources such as solar, wind, geothermal, etc., through electrical or thermal means (i.e. electrolysis and thermolysis respectively). Water splitting is also possible through biophotolysis process using solar radiation. Splitting of water is thus possible at the expense of renewable energy to produce secondary fuel H_2. On use, H_2 and O_2 recombine to produce water again and energy is released. This route is therefore a clean and sustainable route of energy supply.

1. **Thermo-chemical Methods**

Steam reforming of methane is the most energy efficient, commercialized technology currently available and most cost effective when applied to large, constant loads. The method accounts for 95 per cent of the hydrogen production in USA.

2. **Electrolysis** of Water Electrolysis is the simplest method of hydrogen production. Currently, this method is not as efficient or cost effective as thermo-chemical method using fossil fuels or biomass. But it would allow for more distributed hydrogen generation and open the possibilities for use of electricity generated from renewable and nuclear resources for hydrogen production. An electrolysis cell essentially consists of two electrodes, commonly flat metal or carbon plates, immersed in an aqueous conducting solution called electrolyte, as shown in figure below. A direct current decomposes water into H_2 and O_2, which are released at cathode (–ve electrode) and anode (+ve electrode) respectively. As water itself is poor conductor of electricity, an electrolyte, commonly aqueous KOH is used.



Ideally, a decomposition voltage of 1.23 V per cell should be sufficient at normal temperature and pressure; however, due to various reasons a voltage of about 2 V per cell is applied in practice. The energy required is 3.9–4.6 kWh per m 3 of hydrogen produced. About 60–70 per cent of this energy is actually utilized in electrolysis.

Therefore, the efficiency of electrolysis process is about 60–70 per cent, which can be improved up to 80 per cent by using catalyst such as porous platinum or nickel. A diaphragm (usually woven asbestos) prevents electronic contact between the electrodes.

and passage of gas or gas bubbles. Electrolysis method is most suitable when primary energy is available as electrical energy, e.g. solar photovoltaic energy. It is also suitable where cheap electricity is available from other sources such as wind, geothermal, etc.

3. Thermolysis of Water

When primary energy is available in the form of heat (e.g. solar thermal), it is more logical to produce hydrogen by splitting water directly from heat energy using thermolysis. This would be more efficient than conversion of heat, first to electricity (using heat engine – generator) and then producing hydrogen through electrolysis.

The efficiency of thermal plant is usually in range 32–38 per cent and that of electrolysis is 80 per cent. The overall efficiency through thermal-electrical-hydrogen route would thus be only 25–30 per cent.

4. Biophotolysis

In this method the ability of the plants (especially algae) to split water during photosynthesis process is utilized. An artificial system is devised, which could produce hydrogen and oxygen from water in sunlight using isolated photosynthetic membrane and other catalysts. Since this process is essentially a decomposition of water using photons in the presence of biological catalysts, the reaction is called photolysis of water. There are three distinct functional components coupled together in the system as shown in figure below:

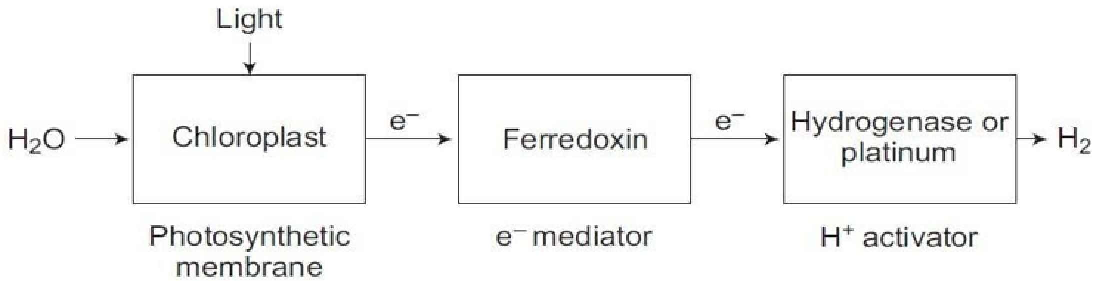
(i) Photosynthetic membrane, which absorbs light, split water to generate oxygen, electrons and protons

(ii) an electron mediator, which is reducible by photo-synthetically generated electrons

(iii) a proton activator that will accept electrons from the reduced mediator and catalyze the reaction:

$2H^{+} + 2\ e^{-} \longrightarrow H_2$

A system with chloroplast (small bodies containing the chlorophyll in green plants) as a photosynthetic membrane to split hydrogen and oxygen, ferredoxin as e^{-} mediator and hydrogenase (an enzyme) or finely dispersed platinum as proton activator, has been successfully tested.



STORAGE:

- Hydrogen can be stored as a discrete gas or liquid or in a chemical compound. For a given amount of energy, hydrogen weighs about one third of the fossil fuels, but it is bulkier. In gaseous form it occupies 3.6 times the volume occupied by natural gas and in liquid form it occupies 3.8 times the volume occupied by gasoline.
- However, in practice the volume penalty is 20 to 50 per cent less, since hydrogen can be converted to other forms of energy at the user end more efficiently than fossil fuels.
- Large amounts of hydrogen for subsequent distribution would probably be stored in the underground facilities similar to those used for natural gas, e.g. depleted oil and gas reserves and aquifers. On low or moderate scale, hydrogen is frequently stored in strong steel tank or cylinder.
- The storage of compressed hydrogen gas in tanks is the most mature technology though the very density of hydrogen translates to inefficient use of space. The inefficiency can be mitigated with high compression such as 350–700 atm. However, further improvement in cost, weight and volume efficient storage is required in order to make it more acceptable by the end user.

- Hydrogen can also be stored as compact storage in liquid form at low temperature. It takes up low storage volume but requires cryogenic containers, as boiling point of hydrogen is 20 K. Furthermore, the liquefaction of hydrogen is energy intensive process and results in large evaporative losses. About one third of the energy content of hydrogen is lost in the process.
- Hydrogen can be stored at high densities in reversible metal hydrides. When required, it can be released by heating the hydride and original metal (or alloy) is recovered for further recycling. The chemical equations are:

Charging H_2 + Metal hydride + heat (hydrogen is stored and heat is released)
Discharging

The pressure of gas released by heating depends mainly on temperature. At fixed temperature, the pressure remains essentially constant until the hydrogen content is almost exhausted. Metal hydrides offer the advantage of lower pressure storage, comfortable shape and reasonable volumetric store efficiency but have weight penalties and thermal management issues.

It is also very safe. In case of accidental breakdown of storage, the gas remains in hydride and does not escape. To be suitable as a storage medium, metal hydride should have following desirable properties:

(i) The metal (or alloy) should be inexpensive.

(ii) The hydride should contain a large amount of hydrogen per unit volume and per unit mass.

(iii) Formation of hydride from metal by reaction with hydrogen should be easy and the hydride should be stable at room temperature.

(iv) The gas should be released from hydride at significant pressure and moderately high temperature (preferably below 100 °C). The reactions with three more promising hydrides of alloys are given below:

(i) Lanthanum-Nickel: $La\,Ni_5 + 3\,H_2 \underset{\text{Dischareg}}{\overset{\text{Charge}}{\rightleftarrows}} (La\,Ni_5)\,H_6 + \text{heat}$

(ii) Iron-Titanium: $Fe\,Ti + H_2 \underset{\text{Dischareg}}{\overset{\text{Charge}}{\rightleftarrows}} (Fe\,Ti)\,H_2 + \text{heat}$

(iii) Magnesium-Nickel: $Mg_2\,Ni + 2\,H_2 \underset{\text{Dischareg}}{\overset{\text{Charge}}{\rightleftarrows}} (Mg_2\,Ni)\,H_4 + \text{heat}$

These hydrides contain somewhat more hydrogen than an equal volume. In theory $(La\,Ni_5)\,H_6$ Contains 1.35 per cent of hydrogen by weight, $(Fe\,Ti)\,H_2$ contains 1.9 percent and $(Mg_2\,Ni)\,H_4$ contains 3.6 per cent. Due to heavy weight, hydride storage is not suitable for mobile storage such as vehicles.

Some complex-based reversible hydrides such as aluminates have recently demonstrated improved weight performances over metal hydrides along with modest temperatures for hydrogen recovery.

1. Hydrogen Production

Hydrogen is not a primary fuel; it must be produced from hydrogen-containing compounds such as water, hydrocarbons, or biomass. Production methods are broadly classified into **thermochemical**, **electrochemical**, **biological**, and **photonic/solar** processes.

A. Thermochemical Methods

1. Steam Methane Reforming (SMR)

Reaction:

$CH_4 + H_2O \rightarrow CO + 3H_2$

$CO + H_2O \rightarrow CO_2 + H_2$ (Water–Gas Shift)

- **Features**
  - Most widely used (≈ 70% of world H_2).
  - High efficiency ~65–75%.
  - Produces CO_2 → not green unless combined with **CCS** (Blue Hydrogen).

2. Partial Oxidation (POX)

- **Reaction:** $CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$
- **Features:** Fast, exothermic, lower H_2 yield than SMR.

- **3. Autothermal Reforming (ATR)**
- Combines SMR + POX → controlled heat balance.
- Good for large-scale plants.

B. Electrochemical Methods

1. Water Electrolysis

Splits water using electricity.

a. Alkaline Water Electrolysis (AWE)

- Electrolyte: KOH/NaOH solution.
- Cheaper, mature, moderate efficiency (60–70%).
- Slower response.

b. Proton Exchange Membrane (PEM) Electrolysis

- Uses polymer membrane (Nafion).
- High purity H_2, high current density, fast response.
- Higher cost (Pt/Ir catalysts).

c. Solid Oxide Electrolyzer Cell (SOEC)

- High temperature (700–900°C).
- Highest efficiency (80–90%).
- Still developing.

C. Thermolysis / Pyrolysis

1. Methane Pyrolysis

- $CH_4 \rightarrow C\ (solid) + 2H_2$
- No CO_2 emission.
- Produces solid carbon as by-product.

D. Photochemical & Photoelectrochemical (PEC) Methods

1. Photocatalytic Water Splitting

- Semiconductor absorbs sunlight → electrons & holes split water.
- TiO_2, CdS, perovskites used.

- Still research-level; low efficiency.

2. PEC Cells

- Integrated solar + electrolyzer.
- Direct H_2 from sunlight.

2. Hydrogen Storage

Hydrogen has **high gravimetric energy density** but **very low volumetric density**, so storage is a major challenge.

Storage methods are:

A. Physical Storage

1. Compressed Hydrogen Gas

- Stored at **350 bar or 700 bar** cylinders.
- Materials: carbon-fiber composite tanks.
- Pros: mature technology.
- Cons: large volume, safety issues.

2. Liquid Hydrogen (Cryogenic)

- Stored at **−253°C**.
- High volumetric density.
- Challenges:
  - Energy-intensive liquefaction (30–40% of energy).
  - Boil-off losses.

B. Material-Based Storage

1. Metal Hydrides

- Metals/Alloys absorb $H_2 \rightarrow MH_x$
- Examples: $LaNi_5$, MgH_2, TiFe.

Pros:

1. High volumetric density.
2. Safer than compressed gas.

Cons:

- Slow kinetics (MgH_2).
- High temperature for desorption.

2. Complex Hydrides

- Examples: $NaBH_4$, $LiBH_4$, AlH_3.
- Very high H_2 density.
- Need catalysts/heat.

3. Carbon-Based Materials

- Activated carbon, CNTs, graphene.
- Store H_2 by physisorption.
- More effective at low temperatures (cryogenic).

4. Metal–Organic Frameworks (MOFs)

- Porous crystalline materials.
- High surface area (> 6000 m^2/g).
- Good for cryo-adsorption.

C. Chemical Storage

1. Ammonia (NH_3)

- Carries 17.6 wt% hydrogen.
- Easy to liquefy (−33°C).
- Cracked for H_2 at point of use:

  $2NH_3 \rightarrow 3H_2 + N_2$

2. Liquid Organic Hydrogen Carriers (LOHCs)

- Organic liquids that undergo hydrogenation/dehydrogenation.
- Example: Methylcyclohexane ↔ Toluene + H_2.
- Use existing fuel infrastructure.

3. Comparison of Storage Methods

Method	Advantages	Drawbacks
Compressed Gas	Simple, mature	Low energy density, heavy tanks
Liquid H_2	High density	Expensive, boil-off
Metal Hydrides	Safe, compact	Heavy, slow kinetics
MOFs/Carbon	High surface area	Usually, low storage at room temp
Ammonia	Easy transport	Toxic; requires cracking
LOHCs	Uses existing fuel systems	Slow reaction, catalyst cost

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4. Applications of Hydrogen

- Fuel cells (PEMFC, SOFC)
- Steel production (green steel)
- Ammonia synthesis
- Mobility (cars, buses, trucks)
- Long-duration energy storage
- Refineries (hydrocracking, desulfurization)

5. Challenges

- High production cost for green hydrogen.
- Storage and transport difficulties.
- Need for better catalysts (non-Pt).
- Infrastructure development.
- Safety concerns (leakage, embrittlement).

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