UNIT – III

ELECTROCHEMICAL ENERGY SYSTEMS

"*Man's brain may be compared to an electric battery...a group of electric batteries will provide more energy than a single battery.* " *__Napoleon Hill* .

3.1 INTRODUCTION

Batteries are the storehouses of electrical energy. They provide well contained energy conversion devices which greatly contributed to the needs of mankind. Zero emission vehicles of the future will be battery powered only. Many non-polluting energy conversion devices such as photovoltaic systems require the concomitant use of rechargeable batteries for energy storage.

In 1799, Alessandro Volta developed the first electrical battery. This battery, known as the Voltaic Cell, consisted of two plates of different metals immersed in a chemical solution. Faraday was the first to use the word "electrode" as a general term for a pole of a battery, 'anode' = negative electrode and 'cathode' = positive electrode of a battery.

Basic Components of a Battery

Anode

Anode is the electrode where oxidation takes place. Here electrons are released to the external circuit. It is marked negative as it is relatively more negative when compared to the other electrode. During recharging, this acts as cathode. Anode material should undergo oxidation easily. Lithium, zinc, cadmium, lead, etc. are widely used as anode.

Cathode

Cathode accepts the electrons produced at anode and the active pieces get reduced. It is the positive terminal of the cell. During recharging, this acts as the anode. Cathode material should be stable and must facilitate reduction reaction. Graphite, lead, nickel etc. are widely used as cathode materials.

Electrolyte

Electrolyte is an ionic conductor that provides connectivity between anode and cathode of the battery. The electrolytes used are acids, bases or salts having high ionic conductivity. Sometimes, solids are also used as electrolytes. It allows electronic movement between the electrodes during charging and discharging.

Separator

Direct contact of anode and cathode produces internal short circuit. These are insulating membrane that prevents or isolates anode and cathode electrically to prevent short circuit. Rubber, cellulose, vinyl polymers etc are widely used as separators.

A battery is an electrochemical cell or many electrochemical cells connected in series, to be used as a source of direct electric current at a constant voltage". A battery is a device which converts chemical energy into electrical energy through various chemical reactions.

A cell consists of an anode, cathode and an electrolyte. A battery consists of number of anodes, cathodes and electrolytes or a combination of two or more cells.

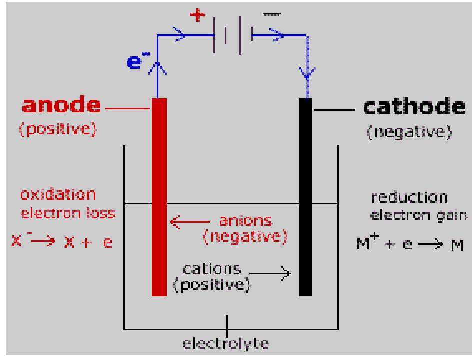


Fig.3.1 **Electrochemical cell**

3.1.1 Requirements of a battery

- It should have more storage capacity.
- It should be light and compact.
- It should provide power for a longer time period.
- It should be capable of recharging.
- It should give constant voltage
- It should be resistant to self-discharge.
- It should be cheaper.

3.1.2 Characteristics of a Battery

1. Voltage
2. Current
3. Capacity
4. Energy Efficiency
5. Power Density
6. Discharge or Discharge Rate
6. Cycle Life
7. Self Life

1. Voltage (Cell Potential)

Voltage of a battery is an electromotive force or difference of potential between any two electrodes and it is denoted by (V_C -V_A).

The theoretical standard cell voltage can be determined using E^0 values:

E^0cell = E^0 cathode – E^0 anode

The theoretical cell voltage is modified by the Nernst equation,

$E_{cell} = E^0_{cell} + (2.303RT)/nF \log[P/R]$

(where, P=product, R=reactant)

If the difference in the standard electrode potential is more, higher is the emf of the cell.

2. Current

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

Current(I) = q/t, with units of $A=Cs^{-1}$

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

3. Capacity

The energy stored in a battery is called the battery capacity. It is a measure of the charge stored by a battery, determined by the amount of electrical energy the battery can deliver over a certain period and is measured in Ampere-hour (Ah), capable of being provided by a battery during discharge.

Its value depends upon the size of the battery and is given by Faraday's relation,

$$C = \frac{wnF}{M}$$

Where, W = mass of active material and M = molar mass of the active material

It is the number of moles of the electro active material associated with the complete discharge of the cell.

4. Energy Efficiency

It is defined as the ratio of useful energy output to the total energy input.

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

Energy efficiency is using less energy to provide the same service. There are other definitions is a good operational one.

5. Power Density or Specific Power

Storage densityof electricity: It is the amount of electricity in Ampere per unit mass, which the storer can hold. In other words, it is the capacity per unit mass of the battery.

Energy density: It is the amount of energy stored in a given system or region of space per unit volume.

Power density (W/Kg or W/lit) is the power of the battery per unit weight that represents the speed at which the energy can be delivered to the load.

Power density = Energy density / Time

In energy transformers including batteries, fuel cells, motors etc., and also power supply units or similar, power density refers to a volume. It is then also called volume power density, which is expressed as W/m^3.

6. Discharge

Dischargeis the conversion of chemical energy stored within a cell to electrical energy and subsequent withdrawal of this electrical energy into a load.

Discharge rate: An expression of the speed which a battery is being discharged, at a specific point in time.

7. Capacity Retention / Stability / Cycle Life

Capacity retention is derived from the number of cycles that the cell undergoes charge-discharge processes. Although factors like electrolyte stability, temperature, etc, influence the capacity of degradation, phase stability of the electrode is the prime component in determining the cycle life of a cell/ battery.

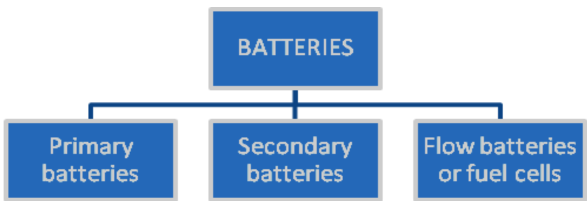
The actual operating life of the battery is affected by the rate and depth of cycles and by other conditions such as temperature and humidity. The higher the (Depth of Discharge) DOD, the lower the cycle life.

8. Self-Life (Expiration Date)

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

3.2 TYPES OF BATTERIES

Batteries are classified into three categories depending upon the recharging capacities:



1. Primary battery or Primary cells

These are cells in which the electrode reactions cannot be reversed by passing an external current. The reactions are possible only once and the battery will be dead after use. Hence it is non -rechargeable battery.

Example: Daniel cell, Leclanche cell, Mercury cell.

2. Secondary battery or Secondary cells

These are cells in which the electrode reactions can be reversed by passing an external current. Thus a secondary battery may be used through a large number of cycles of charging and discharging. Hence it is a rechargeable battery.

Example: Lead acid battery, Ni-Cd battery.

3. Fuel cell or flow battery

It is a device which converts chemical energy of the fuel directly into electrical energy. The chemicals used are usually very simple ones such as H_2 and O_2.

Example: H_2-O_2 fuel cell, Methanol fuel cell etc.

Table 3.1 Differences between Primary and Secondary batteries

Primary Batteries	**Secondary batteries**
Primary batteries are used only once	Secondary batteries can be used for several cycles.
Irreversible battery	Reversible battery
They are cheap.	They are expensive.
Initial cost is low.	Initial cost is very high.

Disposable.	Periodic recharging and regular maintenance is required.

3.3 SECONDARY STORAGE BATTERIES

3.3.1. LEAD-ACID BATTERY

- A lead-acid battery is a storage battery which can operate both as a voltaic cell and as an electrolytic cell. When it act as a voltaic cell it supplies electrical energy, on recharging, it acts as an electrolytic cell.
- It consists of lead (Pb) as the anode , lead dioxide (PbO_2) as the cathode andsulphuric acid of density 1.30gm/ml acts as electrolyte.
- Six lead-acid electrochemical cells connected in series are placed in polypropylene containers.
- The cell may be represented as: $Pb/PbSO_4 // H_2SO_4$ (aq) / PbO_2 / Pb

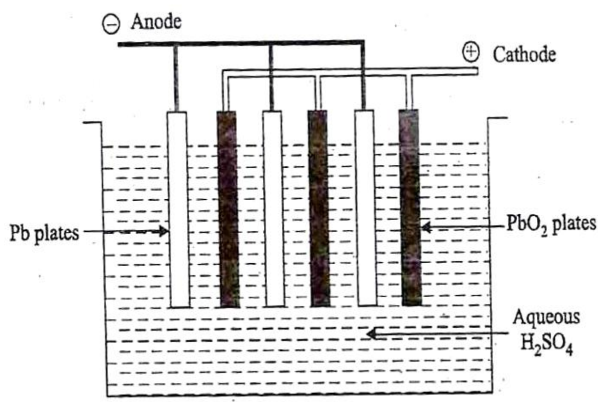


Fig 3.2 **Lead acid battery**

Working

Discharging

When the lead-acid storage battery operates, the following reaction occurs.

At anode*:* Lead is oxidised to Pb^{2+} ions, which further combines with SO_4^{2-} forming insoluble $PbSO_4$.

$$Pb_{(s)} \longrightarrow Pb^{2+}(aq) + 2e^-$$
$$Pb^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)}$$
$$\overline{Pb_{(s)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)} + 2e^-}$$

At cathode*:*PbO_2 is reduced to Pb^{2+} ions, which further combines with SO_4^{2-} forming insoluble $PbSO_4$.

$$PbO_{2(s)} + 4H^+ + 2e^- \longrightarrow Pb^{2+}{}_{(aq)} + 2H_2O$$
$$Pb^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)}$$
$$\overline{\mathbf{PbO_{(s)} + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O}}$$

Overall cell reaction

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} 2PbSO_{4(s)} + 2H_2O + \text{Energy}$$

From the above cell reactions, it is clear that $PbSO_4$ is precipitated at both the electrodes and H_2SO_4 is used up. As a result, the concentration of H_2SO_4 decreases and hence the density of H_2SO_4 falls below 1.2 gm/mol. Therefore, the battery needs recharging.

Charging

The cell can be charged by applying electric current across the electrodes that is slightly higher than the cell current in the opposite direction. The electrode reaction gets reversed. As a result, Pb is deposited on anode and PbO_2 on the cathode. The density of H_2SO_4 also increases.

The net reaction during charging is:

$$2PbSO_{4(s)} + 2H_2O + \text{Energy} \underset{\text{discharging}}{\overset{\text{charging}}{\rightleftharpoons}} Pb_{(s)} + PbO_{2(s)} + 2H_2SO_4$$

Advantages

- It produces very high current.
- It is made easily
- Six cells can make a car battery.
- The self-discharging rate is low when compared to other rechargeable batteries.
- Internal resistance is low.
- It is expected to function effectively for 300-350 cycles.

Disadvantages of lead-acid batteries

- Very large in size and heavy weight.
- Possibility of leakage as electrolyte is liquid.
- The performance of the battery at low temperatures is poor as sulphuric acid becomes viscous; therefore flow of current gets reduced.
- Recycling of the battery causes environmental hazards.
- Mechanical strain and normal bumping reduces battery capacity.
- The lead acid battery has the lowest energy density, making it unsuitable for handheld devices that demand compact size.

Uses

- Lead storage cells are mainly used in automobiles like cars, buses and trucks.
- It is used in gas engine ignition, telephone exchanges, hospitals and power stations.
- It is also used in Uninterrupted Power Supply (UPS), as a power system which provides current constantly without a break.

3.3.2 NICKEL-CADMIUM (NICAD) BATTERY

- A Nickel-Cadmium battery is a type of alkaline storage battery. It is a portable rechargeable cell and its cell voltage is fairly constant about 1.4 volts.
- In a Ni-Cd cell, the anode is cadmium and the cathode is nickel oxide (NiO_2). The electrolyte is a solution of KOH. The electrode and electrolytes are enclosed in a sealed container.

  It is represented as: $Cd / Cd(OH)_2 // KOH / NiO_2 / Ni$

Working

Discharging

The NICAD battery operates when cadmium is oxidised to Cd^{2+} ions and insoluble Cd $(OH)_2$ is formed. Ni^{2+} ions then combine with OH^- ions to form Ni $(OH)_2$.

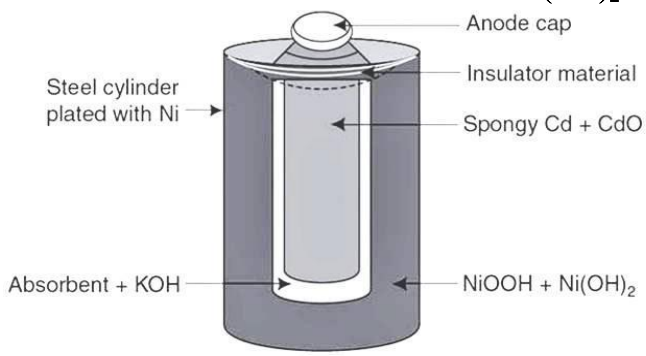


Fig.3.3 **NICAD Battery**

At anode : Cd is oxidised to Cd^{2+} and combines with OH^- to form $Cd(OH)_2$

$$Cd_{(s)} + 2OH^- \rightleftharpoons Cd(OH)_{2(s)} + 2e^-$$

At cathode: NiO_2 gains electrons (Ni undergoes reduction from +4 to +2) Ni^{2+} then combines with OH^- to form $Ni(OH)_2$.

$$NiO_{2(s)} + 2H_2O_{(l)} + 2e^- \rightleftharpoons Ni(OH)_{2(s)} + 2OH^-$$

Overall Reaction:

$$Cd(s) + NiO_2 + 2H_2O \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} Cd(OH)_{2(s)} + Ni(OH)_{2(s)} + \text{Energy}$$

Charging

The cell can be recharged by passing an excess current in the opposite direction to that of the cell current, the electrode reactions get reversed. During charging Cd gets deposited on the anode and NiO_2 on the cathode.

The net reaction during discharging and recharging is:

charging

$$Cd(OH)_{2(s)} + Ni(OH)_{2(s)} \rightleftharpoons Cd_{(s)} + NiO_2 + 2H_2O$$

From the above reactions, it is clear that

- No gaseous products are formed
- $Cd(OH)_2$ and $Ni(OH)_2$ formed adhere well to the surfaces, which can be removed by recharging the cell.

Advantages

- It has a longer life than a lead storage cell.
- Available in a wide range of sizes, high number of charge/discharge cycles.
- Possess good load performance and allows recharging even at low temperatures.
- It is compact and lighter and used in high current applications.
- It is smaller and lighter.
- Like a dry cell, it can be packed and sealed.
- It is the lowest cost battery in terms of cost per cycle.

Disadvantages

- It is very expensive.
- Cadmium is highly toxic.
- Relatively low energy density, low capacity when compared to other rechargeable systems.
- Has relatively high self-discharge and needs to be recharged after storage.

Uses

- It is used in emergency power applications and communication equipment.
- It is used in electronic calculators, electronic flash units, transistors and other battery powered small tools.
- Due to low temperature performance it is widely used in aircraft and space satellites.

3.3.3 NICKEL METAL HYDRIDE CELL

- A relatively new technology is adopted in the case of the chargeable sealed nickel-metal hydride battery with characteristics similar to those of the sealed Ni-Cd batteries. The Ni-H battery uses hydrogen absorbed in a metal alloy for the active negative material.
- A higher energy density can be achieved in the case of a metal hydride electrode than the cadmium electrode. Thus a smaller amount of the negative electrode is used in the nickel-metal hydride. This allows for a larger volume for the positive electrode, which results in a higher capacity or longer service life for the metal hydride battery.
- Moreover, as the metal hydride battery is free of Cd it is considered more environmentally friendly than the nickel-cadmium battery and may reduce the problem associated with the disposal of rechargeable nickel batteries.

- Nickel-metal hydride batteries consist of a positive plate of a highly porous sintered or a felt nickel substrate impregnated with nickel hydroxide as its principal active material, a negative plate of a highly porous structure using a perforated $LaNi_5$ alloy grid (a hydrogen – absorbing alloy). A synthetic nonwoven material separates the two electrodes, which serves as a medium for absorbing the electrolyte and a sealing plate provided with a self-resealing safety vent.
- When a NiMH cell is charged, the positive electrode releases hydrogen into the electrolyte. The hydrogen in turn is absorbed and stored in the negative electrode. The reaction begins when the nickel hydroxide ($Ni(OH)_2$) in the positive electrode and hydroxide (OH^-) from the electrolyte combine. This produces nickel oxyhydroxide (NiOOH) within the positive electrode, water (H_2O) in the electrolyte and one free electron (e^-). At the negative electrode the metal alloy (M) in the negative electrode, water (H_2O) from the electrolyte, and an electron (e^-) react to produce metal hydride (MH) in the negative electrode and hydroxide (OH^-) in the electrolyte.
- Because heat is generated as a part of the overall chemical reaction during the charge of a NiMH cell, the charging reaction described above is exothermic.
- The charging electrode reactions in Ni-H battery are as follows:

$$\text{Positive Electrode:} Ni(OH)_2 + OH^- \underset{\text{discharging}}{\overset{\text{charging}}{\rightleftharpoons}} NiOOH + H_2O + e^-$$

E°= 0.83 V

$$\text{Negative Electrode:} M + H_2O + e^- \underset{\text{discharging}}{\overset{\text{charging}}{\rightleftharpoons}} MH + OH^-$$

E°= 0.52 V

$$\text{Overall Reaction:} Ni(OH)_2 + M \underset{\text{discharging}}{\overset{\text{charging}}{\rightleftharpoons}} NiOOH + MH$$

E° = 1.35 V

  - In the charged state of the Ni-H battery, nickel oxyhydroxide is the active material of the positive electrode.

- Hydrogen is stored in a hydrogen absorbing alloy as metal hydride $LANi_5$ (negative active material). This metal alloy is capable of undergoing reversible hydrogen absorbing-desorbing reaction as the battery is charged and discharged.
- An aqueous solution of KOH is the major component of the electrolyte. The reactionin a nickel-hydride battery is that hydrogen moves from the positive electrode to the negative electrode during charge and reverse during discharge, with the electrolyte taking no part in the reaction; which means that there is no accompanying increase or decrease in the electrolyte.
- The discharge electrode reactions of the nickel-hydride battery are as follows:

  At anode:

  $MH + OH^- \leftrightarrow M + H_2O + e$ E° = 0.83V

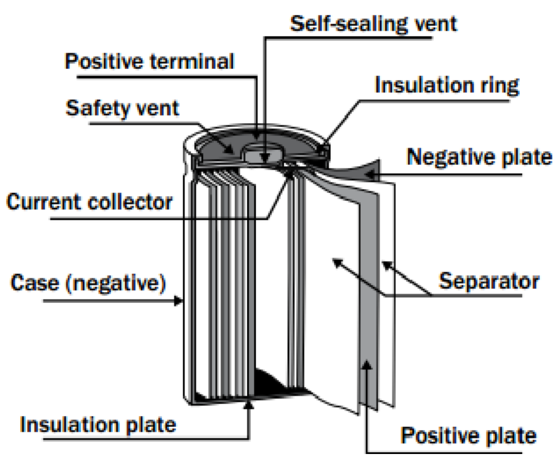
  At cathode:

  The nickel oxyhydroxide is reduced to nickel hydroxide

  $NiOOH + H_2O + e \leftrightarrow Ni(OH)_2 + OH^-$ E° = 0.52V

- The overall reaction on discharge is

  $MH + NiOOH \leftrightarrow M + Ni(OH)_2$ E° = 1.35 V



- Advantages:
- High capacity.
- No maintenance is required.
- Mini mum environmental problem.
- Rapid recharging capability.

- Long cycle life.
- Long shelf life in state of charge

Applications:

- The Ni-MH batteries are used in computers, cellular phone portable and consumer electronic applications where high specific energy is required.

3.3.4 LITHIUM BATTERY

Lithium is the lightest among all metals and it can float on H_2O. The electrochemical properties of lithium are excellent and it is a highly reactive material. These properties give lithium the potential to achieve very high energy and power densities in high density battery applications such as automotive and standby power.

Lithium battery is a solid state battery because instead of liquid or a paste electrolyte, solid electrolyte is used.

Construction

- The Lithium battery consists of a lithium anode and a TiS_2 cathode.
- A solid electrolyte allows the passage of ions but not electrons.

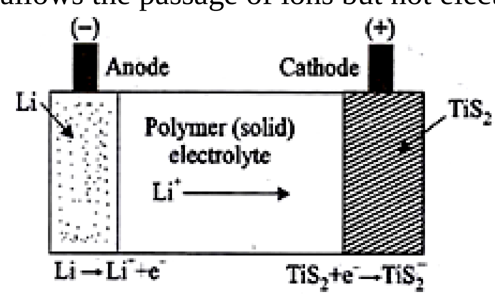


Fig.3.5 **Solid state lithium battery**

Working

Discharging

When the anode is connected to the cathode, Li^+ ions move from anode to cathode.The cathode receives Li^+ ions and electrons.

At Anode: $Li(s) \longrightarrow Li^+ + e^-$

At Cathode: $TiS_{2(s)} + e^- \longrightarrow TiS_2^-$

Overall cell reaction: $Li_{(s)} + TiS_2^-{}_{(s)} \longrightarrow Li^+ + TiS_2^- \longrightarrow LiTiS_2$

Charging

The Lithium battery is recharged by supplying an external current which drives the Li^+ ions back to the anode. The net reaction is:

Hence the cell is rechargeable. It gives high voltage 3.0 volts

Advantages of Li battery

- It generates a high voltage up to 3.0volt.

- Since Li is a light-weight metal, only 7g of lithium produces 1 mole of electrons.
- Since Li has the most negative E^0 value, it generates a higher voltage than the other types of cells.
- It can be made in different shapes and sizes.
- There is no risk of leakage from the battery, since all its constituents are solid.
- It possesses high energy density.

Disadvantage

Li battery is more expensive than other batteries.

Uses

- Button sized Li batteries are used in calculators, electronic flash units, transistors,
- Head phones and cordless appliances.

Lithium ion Battery (or) LIB

A Lithium ion battery is a type of rechargeable battery in which lithium ions move from the negative electrode (anode) to the positive electrode (cathode) during discharge and back when charging.

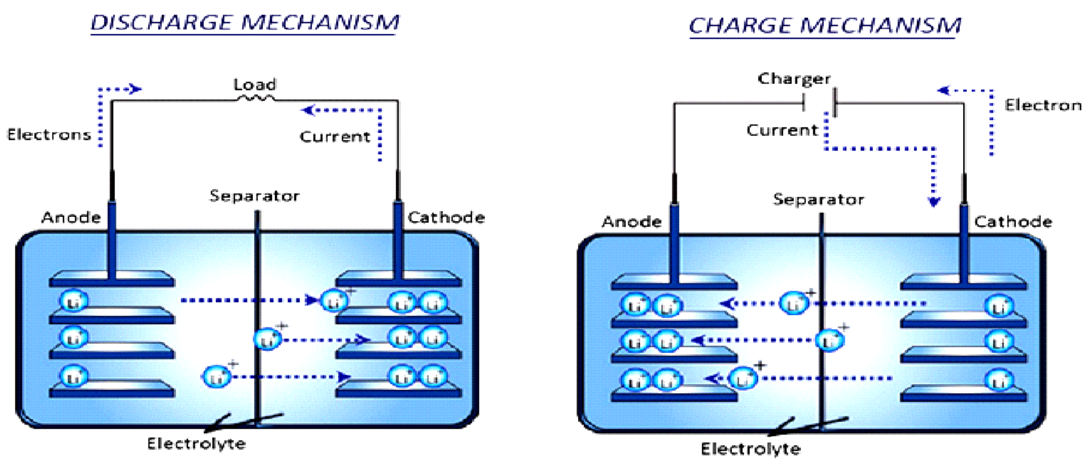


Fig3.6 **Lithium Ion Battery**

Construction:

- A positive electrode is made with lithium cobalt oxide $LiCoO_2$ or Lithium manganese oxide $LiMn_2O_4$ has a current collector made of thin aluminium foil.
- A negative electrode made with special carbon, usually graphite (C_6) has a current collector of thin copper foil.
- A separator is a fine porous polymer film.
- An electrolyte is made with lithium salt in an organic solvent.
- Eg. $LiPF_6$, $LiBF_4$ or $LiClO_4$ in ether.

Working

- The traditional batteries are based on galvanic action but Lithium ion secondary batteriesdepend on an intercalation mechanism.

- Intercalation is the reversible inclusion or insertion of a molecule into materials with layered structure.
- During discharge Li ions are dissociated from the anode and migrate across the electrolyte and are inserted into the crystal structure of the host compound of cathode.
- Electrons also flow from the negative electrode to the positive electrode through the external circuit.

Discharging

$$\text{At Anode: } Li_xC_6 \longrightarrow xLi^+ + xe^- + 6C$$
$$\text{At Cathode: } xLi^+ + xe^- + LiCoO_2 \longrightarrow Li_{1+x}CoO_2$$

Advantages

- A typical Li ion battery can store 150 watt-hours electricity in 1 kilogram of battery as compared to lead acid batteries which can store only 25 watt-hours of electricity in one kilogram.
- All rechargeable batteries suffer from self-discharge when stored or not in use.
- In LIB, there will be a three to five percent of self discharge for 30 days of storage.
- They have higher energy density than other rechargeable batteries.
- They are less heavy.
- They produce a high voltage of about 4 volts.
- They have improved safety i.e., more resistance to overcharge.
- Fast charge but slow discharge rate.

Disadvantages

- They are expensive.
- They are not available in standard cell types.

Applications

- LIB is used in cameras, calculators.
- They are used in cardiac pacemakers and other implantable device.
- They are used in telecommunications, equipment, instruments, portable radios, TVs and pages.
- They are used to operate laptop computers, mobile phones and aerospace applications.

"Like a battery, the human mind and body must be fully discharged to stretch their capacity." **— *Haresh Sippy*.**

3.4 SUPERCAPACITORS

In response to the changing global landscape, energy has become a primary focus of the major world powers and scientific community. As the concern grows over fossil fuel usage, in terms of global warming and resource depletion, there will be a progressive swing to renewable energy. This will necessitate the development of improved methods for storing electricity when it is available and retrieving it when it is needed. There has been great interest in developing and refining more efficient energy storage devices. One of such devices is the supercapacitor.

Definition

Super capacitors can be defined as a energy storage device that stores energy electro statically by polarising an electrolytic solution. Unlike batteries no chemical reaction takes place when energy is being stored or discharged and so super capacitors or ultra capacitors can go through hundreds of thousands of charging cycles with no degradation. Ultra capacitors are also known as double-layer capacitors or super capacitors.

These super capacitors have the following characteristics:

- Greater density of stored energy
- High power discharge; rapid charge and discharge
- Long useful life
- Start quickly, accelerate quickly, climbing powerfully
- The capacitance is 30 times as the lead acid batteries, it is the most important characteristic of the electrical automobile.

Types of super capacitor

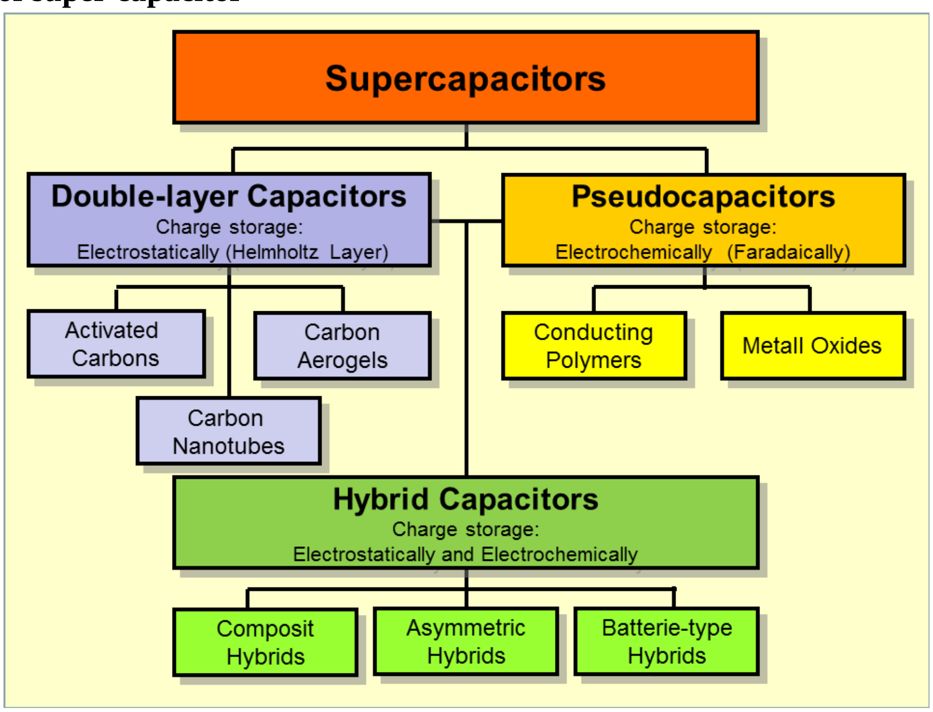


***Fig3.7 Types of* Battery**

3.4.1 ELECTROCHEMICAL DOUBLE LAYER CAPACITOR

Principle, construction and working

Principle Energy is stored in a supercapacitor by polarising the electrolytic solution. The charges are separated via electrode –electrolyte interface.

Construction

Super capacitor consists of a porous electrode, electrolyte and a current collector (metal plates). There is a membrane, which separates, positive and negative plated, is called a separator. The following diagram shows the ultracapacitor module by arranging the individual cell.

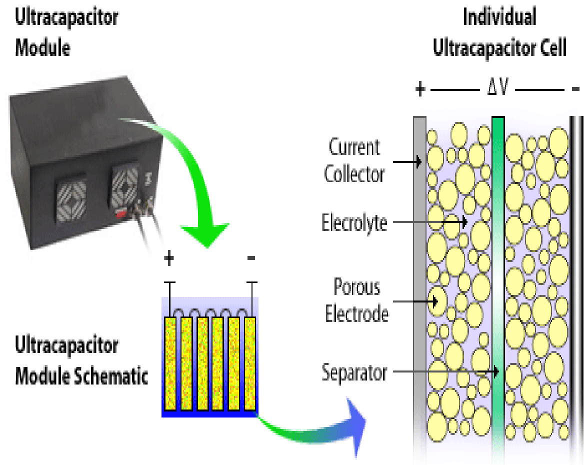


Fig3.8 Super capacitor

Working

There are two carbon sheet separated by a separator. The geometrical size of carbon sheets is taken in such a way that they have a very high surface area. The highly porous carbon can store more energy than any other electrolytic capacitor. When the voltage is applied to positive plate, it attracts negative ions from electrolyte. When the voltage is applied to negative plate, it attracts positive ions from electrolyte.

Therefore, there is a formation of a layer of ions on the both side of plate. This is called 'Double layer' formation. For this reason, the ultra-capacitor can also be called Double layer capacitor. The ions are then stored near the surface of carbon. The distance between the plates is in the order of angstroms. According to the formula for the capacitance,

$$\text{Capacitance} = \frac{dielectric\ \ constant\ \ of\ the\ medium\ \ \times area\ \ of\ the\ plate}{distance\ \ between\ \ the\ plates}$$

Ultra capacitor stores energy via electrostatic charges on opposite surfaces of the electric double layer. They utilize the high surface area of carbon as the energy storage medium, resulting in an energy density much higher than conventional capacitors. The purpose of having separator is to prevent the charges moving across the electrodes. The amount of energy stored is very large as compared to a standard capacitor because of the enormous surface area created by the typically porous carbon electrodes and the small charge separation (10 angstroms) created by the dielectric separator

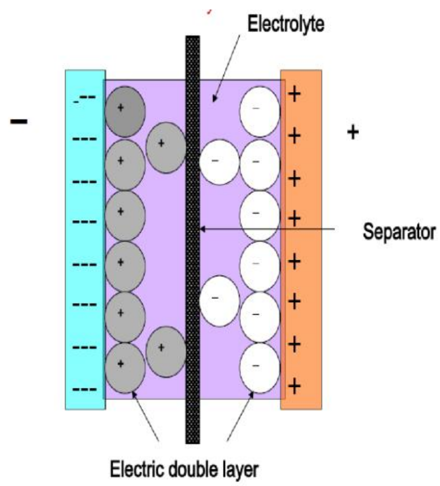


Fig3.9 Electrical Double layer

Advantages

- Long life: It works for large number of cycle without wear and aging.
- Rapid charging: it takes a second to charge completely
- Low cost: it is less expensive as compared to electrochemical battery.
- High power storage: It stores huge amount of energy in a small volume.
- Faster release: Release the energy much faster than battery.

Disadvantages

- They have low energy density the individual cell shows low voltage.
- Not all the energy can be utilized during discharge.
- They have high self-discharge as compared to battery.
- Voltage balancing is required when more than three capacitors are connected in series.

Applications

- They are used in electronic applications such as cellular electronics, power conditioning, uninterruptible power supplies (UPS),
- They used in industrial lasers, medical equipment.
- They are used in electric vehicle and for load levelling to extend the life of batteries.
- They are used in wireless communication system for uninterrupted service.
- There are used in VCRs, CD players, electronic toys, security systems, computers, scanners, smoke detectors, microwaves and coffee makers.

Activated carbons

- Activated carbon is the most commonly used electrode material in EDLCs. The activated carbon possesses a higher surface area than other carbon-based materials and is less expensive. It can be observed that the activated carbon can be obtained in different complex porous structures of micro pores (<20A wide) to macro pores (>500A) to achieve their high surface areas.

- There is an empirical relationship between the distribution of pore sizes, the energy density and power density of the device. Larger pore sizes correlate with higher power densities and smaller pore sizes correlate with higher energy densities. As a result, the pore size distribution of activated carbon electrodes is a major area of research in EDLC design.

Carbon aerogels

Carbon aerogels are also being used as electrode materials for EDLCs. Carbon aerogels are formed from a continuous network of conductive carbon nanoparticles with interspersed mesopores (mesopore (20-500A). Due to this continuous structure and their ability to bond chemically to the current collector, carbon aerogels do not require the application of an additional adhesive binding agent. As a binder less electrode, carbon aerogels have been shown to have a lower ESR (equivalent series resistance) than activated carbons. This reduced ESR, which yields higher power, is the primary area of interest in supercapacitor research involving carbon aerogels.

3.5 FUEL CELL

A voltaic cell involves oxidation-reduction reaction. All ordinary combustion reactions are redox reactions. However, when a fuel is burned, the electron exchange takes place only when the atoms of the oxidizing agent (oxygen or air) come in direct contact with the atoms of the substance being oxidized (the fuel). The energy is released principally as heat.

In a fuel cell, electric energy is obtained without combustion from oxygen and a gas that can be oxidized. Hence, a fuel cell converts the chemical energy of the fuels directly to electricity. The essential process in a fuel cell is:

Fuel + Oxygen ⟶ Oxidation products + Electricity

Characteristics of fuel cell

- They do not store chemical energy.
- Reactants are to be supplied constantly while products are removed constantly. In this respect, a fuel cell resembles an engine more than does a battery.
- The efficiency of a fuel cell is about twice that of a conventional power plant.
- Fuel cell generators are free of noise, vibration, heat transfer, thermal pollution.
- They do not run down like batteries as the reactions take place under nearly reversible conditions and the efficiency is higher in producing more useful work.

TYPES OF FUEL CELL

Fuel cells are distinguished on the basis of the type of electrolyte.

1. Hydrogen-Oxygen or Alkaline Fuel Cells (AFC)
2. Molten Carbonate Fuel Cells (MCFC)
3. Phosphoric Acid Fuel Cells (PAFC)
4. Solid Oxide Fuel Cells (SOFC)
5. Proton Exchange Membrane Fuel Cells (PEMFC)

6. Bio Fuel Cells (BFC)
7. Methanol Oxygen Fuel Cells (MOFC)

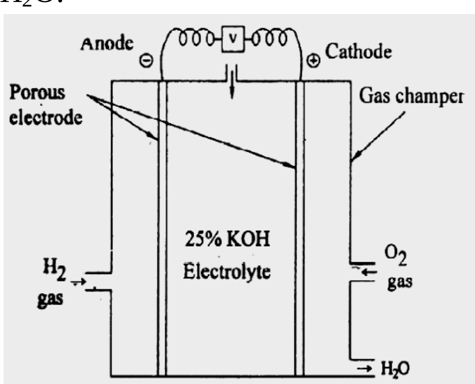
3.5.1 HYDROGEN OXYGEN FUEL CELL (OR) ALKALINE FUEL CELL

Construction

- One of the simplest and most successful fuel cell is hydrogen-oxygen fuel cell.
- The alkaline fuel cell or hydrogen-oxygen fuel cell was designed and first demonstrated publicly by Francis Thomas Bacon in 1959.
- It consists of porous carbon electrodes impregnated with suitable catalyst like finely divided platinum, or a 75/25 alloy of palladium and silver or nickel.
- Concentrated KOH or NaOH solution is placed between the electrodes to act as electrolyte. For low-temperature operating fuel battery (-54 ^{0}C to 72 ^{0}C), potassium thiocyanate dissolved in liquid ammonia is employed.
- The electrodes used here must be: (i) good conductors, (ii) good electron – sources or sinks and (iii) not be consumed or deteriorated by the electrolyte heat or electrode reactions.

Working

- Hydrogen and oxygen gases are bubbled through the anode and cathode compartment respectively.
- H_2 get oxidised in presence of Pt (electro catalyst) to form H^+. The electrons from anode are absorbed by O_2 at cathode which reacts with water from electrolyte to form OH^- ions. The two ions (H^+ and OH^-) combine in the electrolyte medium to form H_2O.



Anode : $2H_{2\,(g)} + 4OH^-_{(aq)} \longrightarrow 4H_2O_{(l)} + 4e^-$

Cathode : $O_{2\,(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$

Overall reaction $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$

***Fig.3.10.* Hydrogen-Oxygen fuel cell**

- The standard emf of the cell, $E^0 = E^0_{ox} + E^0_{red} = 0.83\ V + 0.40\ V = 1.23\ V$. In actual practice, the emf of cell is 0.8 to 1.0V.
- It may be noted that the only product discharged by the cell is water.
- A large number of these cells are stacked together in series to make a battery, called fuel cell battery or fuel battery.

Advantages

- It has high efficiency.
- It is portable and easy to maintain.
- It does not produce any harmful exhaust.
- It is fuel-efficient.
- Water produced from hydrogen-oxygen fuel cells can be used for drinking purpose.
- It can be used as a source in space flights.
- No noise and thermal pollution.

Disadvantages

- The corrosiveness of the electrolytes used.
- It needs to be stored in high tanks.
- It is difficult to predict the life time of fuel cells accurately.
- High cost of pure hydrogen and the catalyst needed for the electrode reactions. (Ex. Pt, Pd, Ag etc.,)
- Problem of handling gaseous fuels at low temperature or high pressure.

Applications

- Fuel cells are ideal for power generation.
- They are used for powering buses, boats and trains.
- Hospitals use fuel cells to provide electricity.
- All major auto makers are working to commercialise a fuel cell car.
- Fuel cells are used in smart phones, laptops and tablets.
- Hydrogen-oxygen fuel cells are uses as auxiliary energy source in space vehicles, submarines or other military-vehicles.
- The product water proved to be a valuable source of fresh water by the astronauts.

3.5.2 PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC)

A polymer electrolyte membrane fuel cell is one of the best candidates as a portable power source for commercial applications primarily because of its light weight, high energy high power, non emission and low temperature operation. It offers an order of magnitude higher power density than any other fuel cell system, which can operate on reformed hydrocarbon fuels with pre treatment and air.

Construction

- Proton exchange membrane fuel cells (PEMFC) also known as Polymer electrolyte membrane (PEM) fuel cells are consisted of a proton conducting electrolyte in solid polymer form.

- Electrodes (anode & cathode) are made of porous carbon containing a platinum or ruthenium catalyst
- The electrolyte is a polymer membrane, which is an electronic insulator, but an excellent conductor of hydrogen ions.
- The most commonly used membranes are based on per fluorosulfonic acid (PFSA) and Nafion (Tetrafluorethylene copolymer containing sulphonic acid group) the proton of which are free to migrate through the membrane.
- The electrolyte membrane is sandwiched between the anode and cathode to produce a single "membrane electrode assembly" (MEA), which is less than millimetre thickness.

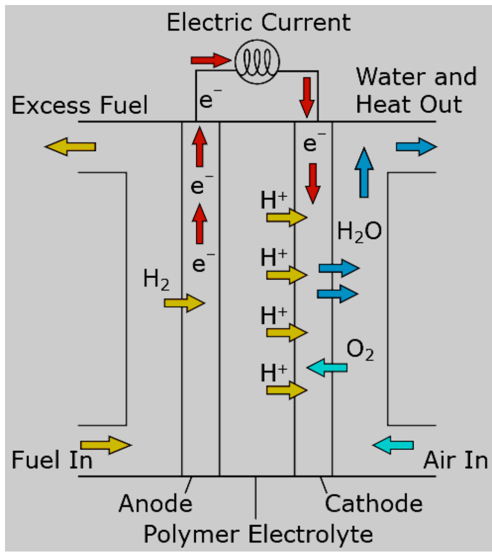


Fig.3.11 **Proton Exchange Membrane Fuel Cell**

The essential requirements of polymer electrolyte membranes include

- High proton conductivity.
- Low electronic conductivity.
- Impermeability to fuel gas or liquid.
- Good mechanical toughness in both the dry and hydrated states.
- High oxidative and hydrolytic stability.
- Chemical and thermal stability.
- Low water drag and low methanol crossover.

Working

- Pressurized hydrogen gas (H_2) enters cell on anode side, which is forced through catalyst. When H_2 molecule contacts platinum catalyst, it splits into H^+ ions and electrons.
- Electrons from anode are conducted through the external circuit and return to the cathode side of the fuel cell.

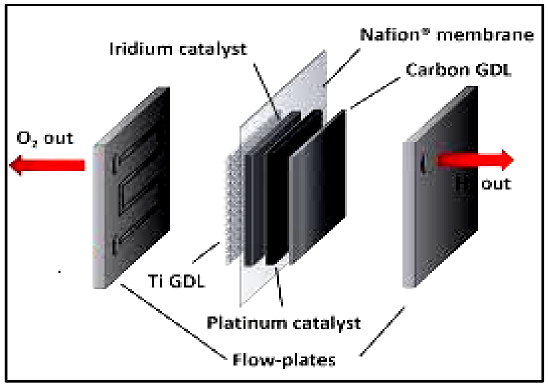


Fig.3.12 **Membrane Electrode Assembly**

- On the cathode side, oxygen gas (O_2) is forced through the catalyst forms oxide ion.
- The oxide ion attracts the H^+ ions through the membrane to form a water molecule (H_2O).

Anode	$H_2 \longrightarrow 2H^+ + 2e^-$
Cathode	$1/2\ O_2 + 2H^+ + 2e^- \longrightarrow H_2O$
Overall	$H_2 + 1/2\ O_2 \longrightarrow H_2O$

Advantages

- Use of solid polymer electrolytes eliminates the corrosion and safety concerns associated with liquid electrolyte fuel cells.
- Its low operating temperature 175^{o}C provides instant start up and requires no thermal shielding to protect personnel.
- Has high power density.
- It offers an order of magnitude higher power density than any other fuel cell system, which can operate on reformed hydrocarbon fuels with pre treatment and air.
- Offers the advantage of low weight and volume.

Disadvantages

- High cost.
- High methanol permeability.
- Environmental incompatibility with other materials.
- Expected life of PEMFC is very short and not suitable for DG (distributed generation).
- The most commonly used catalyst (Pt) is very expensive.
- Sensitive to fuel impurities (CO poisoning diminishes the efficiency of the cell).
- Hydrogen generation and storage is a significant problem.

3.5.3 METHANOL-OXYGEN FUEL CELL (DMFC)

The Direct Methanol Fuel Cell is relatively new technology. Like, PEM fuel cell the DMFC uses polymer electrolyte. But DMFC used liquid methanol or alcohol as fuel instead of reformed hydrogen fuel.

Construction

- The fuel cell consists of two electrodes.
- The anode consists of porous nickel electrode impregnated with a Pt/Pd catalyst.
- The cathode is nickel electrode coated with silver catalyst (oxygen electrode).
- The electrolyte KOH is placed in between the two electrodes.

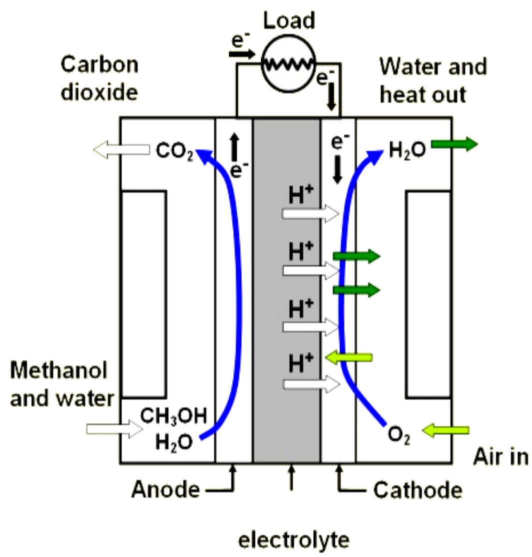


Fig3.13 **Methanol Oxygen Fuel Cell**

Working

- Air is allowed to bubble on the catalyst surface.
- 35 ml methanol of water is added at the anode.
- During chemical reactions the negative electrode draws hydrogen by dissolving liquid methanol (CH_3OH) in water in order to eliminate the need of external reformer.
- At the positive electrode the recombination of the positive ions and negative ions takes place to produce water as a by product.

Anode $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

Cathode $3/2\ O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$

Overall $CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 2H_2O$

- The protons produced migrate through the polymer electrolyte to the cathode where they react with oxygen to produce water.

- During the cell operation CO_2 and water vapour are liberated around the electrodes.
- Normally a single DMFC can supply only 0.3-0.5V under loaded conditions.

Advantages

- Easy transportation and handling.
- Readily available, relatively lesser cost.
- Stable at all atmospheric conditions.
- Negative electrode catalyst draws the hydrogen from the methanol and reduces overall cost due to the absence of reformer.

Disadvantages

- Methanol is very toxic and highly flammable.
- Methanol is made from non-renewable fossil fuels.
- It's of low efficiency because methanol can pass through the available membrane materials.

Applications

- All kinds of portable, automotive and mobile applications like powering laptop, computers, cellular phones, digital cameras.
- Fuel cell vehicles.
- Space craft applications.

3.5.4 SOLID OXIDE FUEL CELL (SOFC)

Solid oxide fuel cells (SOFCs) are best suited for large-scale stationary power generators that are able to provide electricity for factories and towns. SOFC use a hard non porous ceramic compound as electrolyte (calcium oxide or zirconium oxide), which operates extremely at high temperature 1000^oC.

SOFC differ in many respects from other fuel cell technologies.

- The anode, cathode and electrolyte are all made of ceramic substance
- Because of the ceramic make up the cells can operate at temperature as high as 1000^0C.
- The cells can be configured either as rolled tubes or as flat plates and manufactured using many of the technique now employed by the electronics industry.

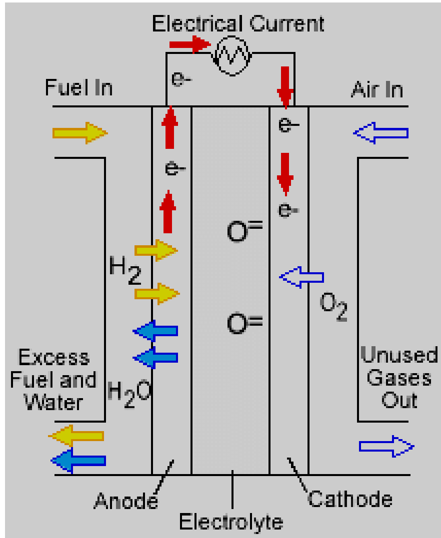


Fig3.14 **Solid Oxide Fuel Cell**

Construction

- It consist of two porous electrodes separated by a dense oxygen ion conducting electrolyte (solid ceramic oxides)
- The anode used is highly porous, electronically conducting Ni/Yittria-stabilised zirconia cermet (Ni/YSZ)
- The cathode is based on a mixed conducting perovskite lanthanum manganite ($LnMnO_3$)
- Yittria-stabilised zirconia is used as the oxygen conducting electrolyte. To improve the conductivity of electrolyte, Scandium-doped zirconium oxide can be used instead of YSZ but high cost of scandium limits the use of latter.
- SOFC use a hard non porous ceramic compound as electrolyte (calcium oxide or zirconium oxide), which operates extremely at high temperature 1000^oC
- The fuels used may be gas (natural gas, biogas, hydrogen) or liquid (methanol, diesel and gasoline).

Requirements of electrolyte

- Ions conductive-oxygen ion transport.
- Chemically stable (at high temperatures as well as in reducing and oxidizing environments).
- Gas tight/free of porosity.
- Uniformly thin layer.

Working

- It consists of two porous electrodes separated by a dense, oxide ion conducting electrolyte.
- Oxygen supplied at the cathode (air electrode) reacts with incoming electrons from the external circuit to form oxide ions.

- These ions migrate to the anode (fuel electrode) through the oxide ion conducting electrolyte.
- At the anode, oxide ions combine with hydrogen (and/or carbon monoxide) in the fuel to form water (and/or carbon dioxide), liberating electrons.
- Electrons (electricity) flow from the anode through the external circuit to the cathode, where oxygen in gas phase reduced to oxide ion.

When hydrogen is the fuel the reactions are:

$$\text{Anode} \quad H_2 + O^{2-} \longrightarrow H_2O + 2e^-$$

$$\text{Cathode} \quad 1/2\, O_2 + 2e^- \longrightarrow O^{2-}$$

$$H_2 - 1/2\, O_2 \longrightarrow H_2O + \text{Electrical energy} + \text{heat}$$

When carbon monoxide is the fuel the reactions are:

$$\text{Anode} \quad CO + O^{2-} \longrightarrow CO_2 + 2e^-$$

$$\text{Cathode} \quad 1/2\, O_2 + 2e^- \longrightarrow O^{2-}$$

$$\text{Overall} \quad CO + 1/2\, O_2 \longrightarrow CO_2$$

Advantages

- They can run on a wide Variety of fuels (gas or liquid).
- Precious metal (Pt) catalyst is not required.
- Long-term stability.
- They operate at high temperature (1000^oC)
- They are not sensitive to CO poisoning.
- They have a relatively low cost.
- They have a relatively high efficiency about 50-60%
- Waste heat can be recycled to make additional electricity, which improves efficiency (upto 85%).
- They have a fast start up.
- The electrolyte has a relatively high resistance.
- The compact size and cleanliness of SOFCs make them especially attractive for urban area.

Disadvantages

- High operating temperature which results in mechanical and chemical compatibility issues.

Uses

- Solid oxide fuel cells (SOFCs) are best suited for large-scale stationary power generators that are able to provide electricity for factories and towns.

3.5.5 BIO FUEL CELL

Biofuel cell is a device that converts chemical energy into electrical energy by the catalytic reaction of microorganisms or enzymes.

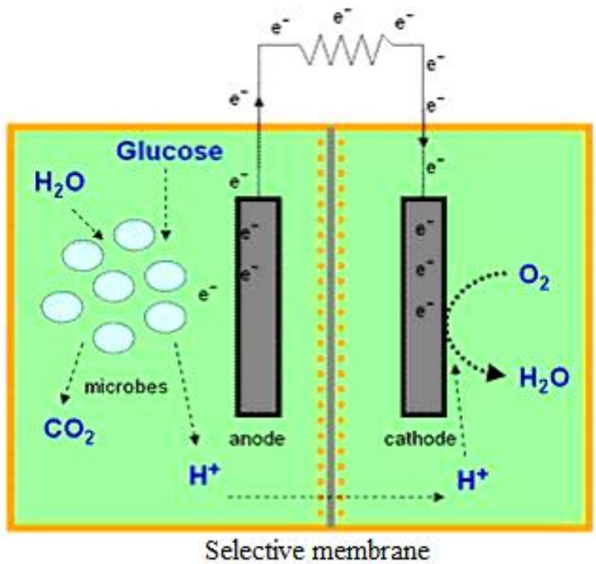


Fig3.15 **Bio Fuel Cell**

Construction

- Microorganisms are able to convert enormous amounts of energy from an incomparable range of chemical substrates.
- Bio-fuel cells are a subset of fuel cells that employ biocatalysts such as a microbe, enzyme or even organelle interacting with an electrode surface. The main types of biofuel cells are defined by the type of biocatalyst used.
- Microbial fuel cells employ living cells to catalyze the oxidation of the fuel, whereas enzymatic fuel cells use enzymes for this purpose.
- Like other cells, Biofuel cells require porous anode and cathode structures and a polymer electrolyte membrane or a salt bridge to separate the electrodes.
- It consists of organic substrate (Glucose or Urea) which acts as a fuel which is oxidized by living organisms
- Bio anode: It contains fuel oxidizing enzymes like glucose oxidase, alcohol hydrogenase and glucose dehydrogenase.
- Bio cathode: It contains oxygen reducing enzymes like laccase, bilirubin oxidase, and ascorbate oxidase.
- Fuel: Organic substrate like Glucose or Urea.

Working

- At the anode, microorganisms or enzymes oxidize organic matter and produce CO_2, proton (H^+) and electron.

$$C_6H_{12}O_6 + 6H_2O \longrightarrow 6CO_2 + 24H^+ + 24e^-$$

- At the cathode, either living organisms (microbes) or enzymes act as catalysts for oxidant reduction and accept electrons, the same principle as the conventional fuel cells.

$$24H^+ + 24e^- + 6O_2 \longrightarrow 12H_2O$$

- Overall Reaction

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

- Some microorganisms cannot transfer the electron to the anode, and therefore mediators such as thionine, methyl viologen, etc. have to be used to facilitate the electron transfer.
- However, recent development has shown that there exist electrochemically active bacteria such as *Shewanellaputrefaciens*, *Aeromonashydrophila*) which can transfer electron directly to the electrode without mediators.

Advantages

- More efficient than turbine (~25%) or solar (~15%) electricity generation.
- Does not require substrate to be combustible.
- Does not require the use of toxic and expensive heavy metals or metalloids.
- Is not limited by the reactivity of the electron donor.
- Do not produce toxic end products.

Disadvantages

- Its current output was generally very low 10^{-5} to 10^{-6} A
- Raw materials like vegetable and fruit extracts, petroleum extracts and human waste should be available in plenty.

Potential Applications

- Powering monitoring devices in remote locations.
- Decentralized domestic power source.
- Conversion of waste organic matter to electricity instead of methane.
- Conversion of renewable biomass to electricity instead of ethanol.
- Bioremediation of environmental contaminants.

"It is my conclusion that the human mind and body is essentially a single cell rechargeable battery that is charged from the atmospheric DC voltage and the Earth."

— Steven Magee, Health Forensics.