Physics

Cluster – Energy Storage Devices

B. Sc. VI – Semester

Study Material

(As per the syllabus of Adikavi Nannaya University, Rajamahendravaram)

Prepared by

P.S. Brahmachary M.Sc., M.Phil.

Lecturer in Physics

D.R.G. Government Degree College

Tadepalligudem

West Godavari

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P.S. Brahmachary M.Sc., M.Phil. P.No. 9492512250

Chapter - I
Energy storage

Introduction:

- Energy storage is defined as "storing energy in really recoverable form When the supply exceeds the demand for use at other times".
- Carrying energy to Where it is wanted is called "distribution" and keeping it available until when it wanted is called" storage".
- Storage of primary fuels(e.g. coal, oil and gas) is also a form of energy storage, but the term 'energy storage' generally applies to secondary energy rather than primary energy.

Need of energy storage

1. The effective utilization of intermittent and variable energy source such as solar, wind etc., often requires energy storage.
2. In some circumstances, electrical energy may be generated either on land or at sea i.e. at a location that is too distance from the consumption centre. Then energy storage or transporting it to the load centre is needed.
3. Electrically Propelled Vehicles, which are expected to come into increasing use, require some form of energy storage. Since the vehicle must carry its energy supply, the storage system must be readily transport.
4. Energy storage is also required for 'load leveling' in an electric utility to reduce over all cost of generating electric power.
5. More efficient plants may be operated continuously at rated power level. The excess Power during off peak period is stored for the use when the demand exceeds the base load.
6. In addition to this, energy storage also contributes to consistency, efficiency, power quality, transmission optimization and black start functions.

Different modes of Energy Storage (or) Energy Storage Methods (or) systems:

Energy can be stored in various forms and the storage methods are classified on the basis of the form in which it is stored. Some of the important energy storage methods are

1. Mechanical energy storage
   a. Pumped storage
   b. Compressed air storage
   c. Fly wheel
2. Electrochemical Energy storage (Secondary battery storage)
3. Electrolytic hydrogen storage
4. Reversible chemical reaction energy storage
5. Electromagnetic energy storage
6. Electrostatic energy storage

7. Thermal (heat) energy storage
    a. Sensible heat storage
    b. Latent heat storage
8. Biological storage

Fly wheel

- Flywheels have been used extensively to smooth out power pulses from reciprocating (Interchangeable) engines.
- Same principle may be extended to store surplus electric energy, a specially designed flywheel known as super flywheel is used for energy storage.
- The flywheel driven by an electric motor during off peak hours stores mechanical energy (kinetic energy) as its speed is increased.
- The stored energy may be retrieved when required, to produce electrical energy by coupling a generator to it.
- The same machine serves both as a motor when the electric energy is supplied to it and as a generator when flywheel serves as a prime mover and electrical energy is regenerated.
- The energy recovery efficiency is estimated to be in more than 90% depending on frictional losses.

The rotational kinetic energy of the object

$$E = \frac{1}{2} I\omega^2$$

Where I = Moment of inertia of the object about the axis

ω = Angular velocity

But moment of inertia $I = \frac{1}{2} ma^2$

Here m = mass a = radius

The energy density is $W_m = \frac{E}{m} = \frac{1}{4} a^2\omega^2$

when energy is added to the flywheel its speed rises to a higher value. Similarly when energy is retrieved its speed falls. For a flywheel to serve as useful store of energy it must rotate as fast as possible. However its angular velocity is limited by the strength of the material, which has to resist the centrifugal forces tending to fling it apart. For a uniform wheel of density ρ the maximum tensile stress is

$$\sigma_{max} = \rho\, a^2\omega^2$$

In general for a particular shape

$$W_m = \frac{1}{4} K\, a^2\omega^2$$

And $W_{m,max} = \frac{K\,\sigma_{max}}{4\rho}$ Where K is constant = 1

- ✓ Conventional materials such as steel give low energy densities. Much higher energy density can be obtained by using lightweight fibre composite materials, such as fiberglass which have higher tensile strength and lower density.

- ✓ To make the best use of these materials, flywheels should be made in unconventional shapes with the strong fibres aligned in the direction of maximum stress. Such systems can have energy densities of higher values.

Hydrogen storage

- ❖ Energy can be both stored and transported as hydrogen, which serves as a secondary fuel. The input energy, usually electrical, helps decompose water by electrochemical (electrolysis) reaction into its constituent elements, hydrogen and oxygen.
- ❖ The Oxygen has no inherent energy value, but the hydrogen can contain up to 90% of applied electric energy, depending on the technology. This hydrogen can be stored and latter combusted to provide heat or to power fuel cell.
- ❖ In case of thermal energy input, it is possible to decompose water by heat, as a result of a series of chemical reactions.
- ❖ The chemical energy in hydrogen can be converted into, thermal, mechanical or electrical energy.
- ❖ One possibility is to burn hydrogen in air, in a manner simulator to natural gas, to produce thermal energy for use in home or industry.
- ❖ Hydrogen can also serve as fuel in place of gasoline in automobiles to obtain mechanical energy. Hydrogen fired steam turbine may also be used to obtain mechanical energy.
- ❖ Electrical energy can be generated from mechanical energy thus obtained by using a generator. Electrical energy may also be obtained more efficiently from hydrogen by means of fuel cell.

Hydrogen can be stored in three ways

a) Gas form:- Storage of hydrogen gas even incompressible state is bulky. It occupies more volume than natural gas. Compression to a storage pressure of 350 bar, the value usually assumed for Automotive Technologies, consumes up to 12% of hydrogen HHV (High heating value) if performed adiabatically.

b) Liquid form :- Hydrogen can also be stored in liquid form. But since its boiling point is 20 K these stores are difficult to maintain due to refrigeration requirements and safety issues

c) Metal hydride form:- Hydrogen can be stored as reversible metal hydrides in large volumes. When required, hydrogen is released by heating of the hydrade.
One such example is given below.

$$Mg_2 Ni + 2 H_2 \underset{\text{Discharging}}{\overset{\text{Charging}}{\rightleftharpoons}} (Mg_2 Ni) H_4 + Heat$$

This reaction is reversible and the hydride store can be replenished with hydrogen

Thermochemical energy storage system

Thermal energy storage TES is an advanced technology for storing thermal energy that can mitigate environmental impacts and facilitate more efficient and Clean Energy systems.

Thermochemical TES is an emerging method with the potential for high energy density storage.

Where space is limited, therefore thermochemical TES has the highest potential to achieve the required compact TES.

The main types of TES are sensible and latent.

- Sensible TES systems store energy by changing the temperature of the storage medium, which can be water, braine Rock soil etc.
- Latent TES systems store energy through phase change, ex: cold storage water / Ice and heat storage by melting paraffin waxes.
- Latent TES units are generally smaller than sensible storage units. More compact TES can be achieved based on storage that utilise chemical reactions.
- Such thermochemical storage systems have, recently in the subject of increased attention and could be especially beneficial where space is limited.
- Thermochemical TES systems are not yet commercial and more scientific. Research and development is required to better understand and design these Technologies.
- To resolve other practical aspects before commercial implementation, in particular a better understanding of their efficiency is required.

Chemical energy storage

The chemical TES category includes soroption and thermochemical reactions.

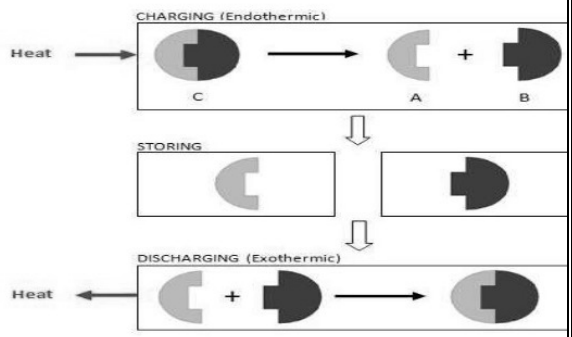
- In thermochemical energy storage, energy is stored after a dissociation reaction and then recovered in a chemically reverse reaction.
- Thermochemical energy storage has a higher storage density than the other types of TES, allowing large quantities of energy to be stored using small amounts of storage substances.
- Energy storage based on chemical reaction is particularly appropriate for long term storage applications. ex: seasonal storage of solar heat because the process involves almost no energy losses during the storing period. Storage is usually done at ambient temperature.
- **Sorption**

- Sorption systems (adsorption and absorption) are based on a chemical processes and thus are also considered chemical heat storage.
- Adsorption occurs when an adsorptive accumulates on the surface of adsorbent and shapes a molecular or atomic layer.
- The adsorptive can be a liquid or gas while the adsorbent can be a solid or liquid. Adsorption is a process that occurs when a substance is distributed into a liquid or solid and forms a solution

Principles of thermochemical energy storage

The main principle of thermochemical TES is based on a reaction that can be reversed

$$C + heat \rightleftarrows A + B$$



In this reaction, a thermochemical material C absorbs energy and is converted chemically into two components A and B which can be stored separately.

The reverse reaction occurs when A and B are combined together and C is formed. Energy is released during this reaction and constitutes the recovered thermal energy from the TES. The storage capacity of this system is the heat of reaction when C is formed

C is the thermochemical material (TCM) for the reaction, while A and B are reactants. Substance A can be a Hydroxide, hydrate, carbonate, ammoniate etc. and B can be water, carbon monoxide, Ammonia hydrogen etc. there is no restriction on phases, but usually C is a solid or a liquid and can be any phase.

In general a TES cycle includes the three main processes 1) charging 2) storing 3) discharging

Charging

* Charging process is endothermic. Thermal energy is absorbed from an energy resource which could be a renewable energy source and/or conventional energy sources, like fossil fuels.
* This energy is used for dissociation of thermochemical material and is equivalent to the heat of reaction or enthalpy of formation.
* After this process, two materials A and B with different properties are formed that can be stored.
* The reaction during charging can be written as $C + heat \rightleftarrows A + B$

Storing

* After the charging process, components A and B are separately store with a little or no energy losses. The materials are usually stored at ambient temperatures, leading to low thermal losses. Any other energy losses are due to degradation of the materials.

Discharging

During this process A and B are combined in an exothermic reaction. The energy released from this reaction permits the stored energy to be recovered. After discharging, component C is regenerated and can be used again in the cycle.

The discharging reaction can be written as $A + B \rightleftarrows C + heat$

Chapter - II

Electrochemical energy storage systems

Battery definition:

Two or more electrochemical cells, electrically interconnected, each contains two electrodes and an electrolyte is called battery. The redox (oxidation-reduction) reactions that occur at these electrodes convert electrochemical energy into electrical energy.

In everyday usage, 'battery' is also used to refer to a single cell. In 1800, Alessandro Volta invented the first modern battery.

Types of batteries

Basically batteries can be classifieds into two types 1) primary batteries and 2) secondary batteries.

Primary batteries

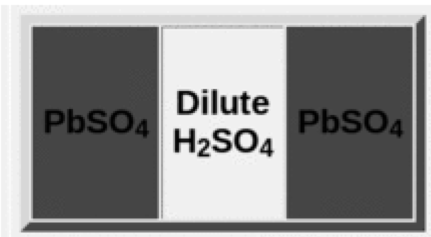
In primary batteries, the electrochemical reaction is not reversible.
During discharging the chemical compounds are permanently changed and electrical energy is released until the original compounds are completely exhausted.
Thus the cells can be used only once.

Secondary batteries

In secondary batteries, the electrochemical reaction is reversible and the original chemical compounds can be reconstituted by the application of an electrical potential between the electrodes injecting energy into the cell.
Such cells can be discharged and recharged many times.

Lead acid battery

The **lead–acid battery** was invented in 1859 by French physicist Gaston Planté and is the oldest type of rechargeable battery. It was the 1st storage battery. Even though it is having a very low energy-to-weight ratio and a low energy-to-volume ratio, due to its ability to supply high surge currents, it is widely used . This feature, along with their low cost, make them attractive for use in motor vehicles to provide the high current required by automobile starter motors.



As they are inexpensive compared to newer technologies, lead–acid batteries are widely used.

Electrochemistry

Discharge

Fully discharged: two identical lead sulfate plates ⟶

In the discharged state both the positive and negative plates become lead(II) sulfate (PbSO4), and the electrolyte loses much of its dissolved sulfuric acid and becomes primarily water. The discharge process is driven by the conduction of electrons from the negative plate back into the cell at the positive plate in the external circuit.

Negative plate reaction

$Pb(s) + HSO_4^-(aq) \rightarrow PbSO4(s) + H^+(aq) + 2e^-$

Release of two conducting electrons gives lead electrode a net negative charge.

As electrons accumulate they create an electric field which attracts hydrogen ions and repels sulfate ions. The hydrogen ions screen the charged electrode from the solution which limits further reactions unless charge is allowed to flow out of electrode.

Positive plate reaction

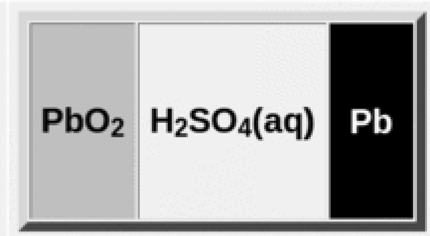
$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

The total reaction can be written as

$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightleftarrows 2PbSO_4(s) + 2H_2O$ ⟶ Discharging, ⟵ Charging

Charging

Fully recharged: Lead anode, Lead oxide cathode and sulfuric acid electrolyte ⟶



In the fully charged state, the negative plate consists of lead, and the positive plate lead dioxide, with the electrolyte of concentrated sulfuric acid. Then the specific charge is 1.28 and emf is 2.1V

Ion motion

During discharge, H+ produced at the negative plates moves into the electrolyte solution and then is consumed into the positive plates, while HSO_4^- is consumed at both plates.

The reverse occurs during charging. Liquid-medium cell rapidly discharge and rapidly charge more efficiently than other gel cells.

Measuring the charge level

Because the electrolyte takes part in the charge-discharge reaction, this battery has one major advantage. It is relatively simple to determine the state of charge by measuring the specific gravity of the electrolyte; the specific gravity falls as the battery discharges. Some battery designs include a simple hydrometer using colored floating balls.

Nickel-Cadmium Batteries

- The **nickel–cadmium battery** (**NiCd battery** or **NiCad battery**) is a type of rechargeable battery using nickel oxide hydroxide and metallic cadmium as electrodes.
- Wet-cell nickel-cadmium batteries were invented in 1899.
- A NiCd battery has a terminal voltage during discharge of around 1.2 volts which decreases little until nearly the end of discharge. This is lower than the 1.5 V of alkaline and zinc–carbon primary cells. NiCd batteries are made in a wide range of sizes.
- The materials are more costly than that of the lead–acid battery,
- Sealed NiCd cells were at widely used in portable power tools, photography equipment, flashlights, emergency lighting.
- Due to the environmental impact of the disposal of the toxic (Poisonous) metal cadmium, the usage of this cell is decreased.

Electrochemistry

A fully charged NiCd cell contains:

- a nickel(III) oxide-hydroxide as positive electrode plate
- a cadmium as negative electrode plate
- a separator, and
- an alkaline electrolyte (potassium hydroxide).

- NiCd batteries usually have a metal case with a sealing plate equipped with a self-sealing safety valve.
- The positive and negative electrode plates, isolated from each other by the separator and are rolled in a spiral shape inside the case. This is known as the jelly-roll design.
- This design allows a Ni–Cd cell to deliver a much higher maximum current than an equivalent size alkaline cell.
  - ✓ The chemical reactions at the cadmium electrode during discharge are:

$$Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^-$$

  - ✓ The reactions at the nickel oxide –hydroxide electrode are:

$$2\,NiO\,OH + 2H_2O + 2e^- \longrightarrow 2\,Ni(OH)_2 + 2OH^-$$

The net reaction during discharge is

$$2\,NiO\,OH + Cd + 2H_2O \longrightarrow 2\,Ni(OH)_2 + Cd(OH)_2$$

Note : During recharge, the reactions go from right to left.

The alkaline electrolyte (commonly KOH) is not consumed in this reaction and therefore its specific gravity does not change, unlike in lead–acid batteries. So, it is not a guide to measure state of charge.

Applications :-

1. Ni–Cd batteries are used in wireless telephones, emergency lighting, and other applications. With a relatively low internal resistance, they can supply high surge currents.
2. This makes them a favourable choice for remote-controlled electric model airplanes, boats, and cars, as well as cordless power tools and camera flash units.
3. Ni–Cd batteries had an majority of the market share for rechargeable batteries in home electronics.
4. Ni–Cd cells are available in the same sizes as alkaline batteries, AAA,D, as well as several multi-cell sizes, including the equivalent of a 9 volt battery.
5. In addition to single cells, batteries exist that contain up to 300 cells (nominally 360 volts, actual voltage under no load between 380 and 420 volts). This many cells are mostly used in automotive and heavy-duty industrial applications

Comparison with other batteries

1. The batteries are more difficult to damage than other batteries.
2. The battery performs very well under rough conditions, perfect for use in the portable tools.
3. Ni–Cd batteries normally last longer, in terms of number of charge/discharge cycles.
4. Compared to lead–acid batteries, Ni–Cd batteries have a much higher energy density.
5. The terminal voltage of a Ni–Cd battery declines more slowly as it is discharged.
6. Nickel–metal hydride (NiMH) batteries are the newest, and most similar, competitor to Ni–Cd batteries.
7. The primary trade-off with Ni–Cd batteries is their higher cost and the use of cadmium. They are also more costly than lead–acid batteries because nickel and cadmium cost more.
8. Ni–Cd batteries contain between 6% - 18% cadmium, which is a toxic heavy metal and therefore requires special care during battery disposal.

Lithium battery

- Lithium is the lightest metal and it can float on water.
- The electrochemical properties of lithium are excellent and it is also a highly reactive material.
- Lithium batteries are primary batteries in which lithium metal (or) lithium compound acts as a Anode. A lithium cell can produce voltage from 1.5 V to 3 V basing on the types of materials used.

There are two types of lithium-based batteries available.

1. Lithium batteries
2. Lithium-ion batteries

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

- These batteries are re-chargeable batteries. Therefore, Lithium ion batteries are considered as best than pure Lithium batteries.

Lithium-ion battery (Li-ion Battery)

Principle

- ✓ Li-ion batteries are secondary batteries, in which lithium ions move between atomic layers within the lithium electrolyte, from the negative electrode to the positive electrode during discharge and back when charging .
- ✓ Because of this reason, the lithium - ion batteries are called ‘ Rocking chair, ‘Swing’ cells.
- ✓ Since neither the anode nor the cathode materials change, the operation is safer than that of a Lithium metal battery.

Construction & Working

Li-ion cell has a four-layer structure.

- ❖ A positive electrode made with Lithium Cobalt Oxide - **cathode**
- ❖ A negative electrode made with specialty carbon (Graphite) - **anode**
- ❖ A **separator** is a fine porous polymer film.
- ❖ An **electrolyte** made with lithium salt in an organic solvent. It is a conductive medium for lithium ions.
- ❖ The electrolytes are selected in such a way that there should be an effective transport of Li-ion to the cathode during discharge.

Electrical energy flows out from the battery when electrons flow through an external circuit during discharge and in to the battery during charge, respectively.

Electrochemistry

The positive (cathode) electrode half-reaction in the lithium-doped cobalt oxide substrate is

$$CoO_2 + Li^+ + e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} LiCoO_2$$

The negative (anode) electrode half-reaction for the graphite is

$$LiC_6 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} C_6 + Li^+ + e^-$$

The full reaction (left: charged, right: discharged) being:

$$LiC_6 + CoO_2 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} C_6 + LiCoO_2$$

Depending on materials, the voltage, energy density, life and safety of a lithium-ion battery can change .

The lithium ion is inserted and exerted into the lattice structure of anode and cathode during charging and discharging

During discharge current flows through external circuit and light glows

During charging, no the electrons flows in the opposite direction.

- During charging, lithium in positive electrode material is ionized and moves from layer to layer and inserted into the negative electrode.
- During discharge Li ions are dissociated from the anode and migrate across the electrolyte and are inserted into the crystal structure of the cathode.
- At the same time the compensating electrons travel in the external circuit and are accepted by the host to balance the reaction.
- The process is completely reversible.

Advantages

- They have high energy density than other rechargeable batteries.
- They are less weight.
- They produce high voltage out about 4 V as compared with other batteries.
- They have improved safety, i.e. more resistance to overcharge.
- No liquid electrolyte means they are immune from leaking.
- Fast charge and discharge rate.

Disadvantage

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

Applications

- The Li-ion batteries are used in cameras, calculators.
- They are used in cardiac pacemakers and other implantable device
- They are used in telecommunication equipment, portable radios and TVs, pagers.
- They are used to operate laptop computers and mobile phones and aerospace application.

Batteries applications

1. Miniature (Small) batteries : These batteries are used in electric watches, calculators medical devices. Mostly these are primary batteries.
2. Batteries for portable equipment : Flash lights. toys, portable radio, T.V., mobile phones in all these devices secondary cells such as NiCad, Li-ion batteries are used. Alkaline primary cells are also used.
3. SLI (Starting Lighting and Ignition) Batteries : Mostly these are Lead acid batteries. These are used in cars, buses, trucks, lawn movers and wheel chairs.
4. Vehicle traction batteries : In general, these batteries are NiMH and Lithium batteries. These are used in lift trucks and locomotives.
5. Stationary batteries : These are mostly Lead acid batteries, Lithium batteries. These are used in emergency power, communication base stations, remote relay stations etc.
6. Military and aerospace : Fuel cells, Nickel Hydrogen, water activated batteries are used in satellites, robots, weapons.
7. Special purpose : Lead acid batteries are used in submerines.

Solid-state batteries

We know that most of the batteries use a liquid electrolyte for the flow of ions from one electrode to another electrode.

But batteries with liquid electrolytes have the following disadvantages.

- Safety issues
- Expensive sealing system
- Failure modes

In order to overcome these difficulties, a solid electrolyte can be used in place of the liquid electrolyte. Such batteries are known as solid state batteries. Hence solid state batteries are more advantageous.

- ✓ **Solid-state battery** is a battery technology that uses both solid electrodes and solid electrolytes, instead of the liquid or polymer electrolytes found in Lithium-ion batteries.
- ✓ The technology is seen as an alternative to Li-ion battery technology.
- ✓ The primary difference lies in the mechanism is ions travel from one electrode to another through a solid electrolyte membrane.
- ✓ Solid state batteries use redox reactions to store and deliver energy.
- ✓ Oxidation occurs at the anode, reduction occurs at the cathode and the battery is able to use this phenomenon to store energy during charge and release energy during discharge.
- ✓ Solid state electrolytes are fast ion conductors. Solids that allow ions to move freely throughout the solids crystalline medium are taken as electrolyte.
- ✓ If the ionic conductivity is higher then power density is higher and the internal resistance of the battery is less.
- ✓ The solid electrolyte is bad conductor of electrons, so the self-discharge rate is less.
- ✓ Solid electrolytes often come in the form of gels, glasses and crystals with new internal structures.
- ✓ Choice of solid electrolyte depends on the chemistry of the battery and the ions available for conduction.
- ✓ In the case of lithium ion solid state batteries, a solid electrolyte like Li-Ion is an excellent Li+ conductor.

Advantages of Solid State Batteries

- ✪ The most important advantage of solid state batteries is the avoidance of electrolyte leakage.
- ✪ The liquid electrolyte in lithium ion cells is highly flammable and leakage due to rupture can lead to disastrous consequences.
- ✪ Replacing the flammable liquid with a solid electrolyte can prevent thermal runaway.

- ✪ Thermal runaway reaction is a series exothermic reactions when a cell rapidly discharges its stored energy and an increase in temperature that occurs.
- ✪ The more cycles (Charging + discharging) a cell experiences, the more deposits will form within the cell leading to a short life. A solid electrolyte avoids this problem and allow the cells to survive hundreds of thousands of cycles. So the life time increases.

Molten solvent Batteries

Molten-salt batteries (including **liquid-metal batteries**) are a class of battery that uses molten salts as an electrolyte and offers both a high energy density and a high power density.

Rechargeable liquid-metal batteries are used for electric vehicles and also for grid energy storage, to balance out irregular renewable power sources such as solar panels and wind turbines.

Molten salt has different technologies; electro-chemistry, heat transfer, chemical oxidation/reduction baths, and nuclear reactors.

The general characteristics of molten salts are

1. Can function as solvents
2. Have good heat transfer characteristics
3. Function like a fluid (like water)
4. Can attain very high temperatures (> 700° C)
5. Can conduct electricity
6. Some molten salts have chemical catalytic properties

One of the interesting features of molten salts is their ability to conduct electricity.

Ex:- Solid sodium chloride (NaCl, or table salt) does not conduct electricity; it is an insulator. If NaCl is placed into water, the mutual attraction both sodium (Na) and chlorine (Cl) have for water molecules cause their bonds to break (dissolving) and form ions (charged atoms or molecules) within the water. These electrically charged ions can conduct electricity if there is a voltage .

Attractive alternative

- Due to the high demand for lithium and limited reserves, sodium as electrolyte (also called **sodium-ion battery** or sodium ion) is an attractive alternative because of the large supply and low cost.

- The cathode and anode are separated by a membrane which allows sodium ions to pass. As a result an alloy is generated in the anode.

- Sodium-sulfur batteries have a high efficiency (typically above 89%), but they must also be heated to more than 300 degrees C.

During World War II a scientist named Georg Otto Erb developed the molten salt battery for use in military applications.

The war ended before Erb's batteries found for real use, but British Intelligence wrote a report about the technology and the United States adopted the technology for military use.

Molten salt batteries have two main advantages. First, you can store them for a long time (50 years or more) with no problems. Once the salt melts (usually from a pyrotechnic charge), the battery can produce a lot of energy for a relatively short period of time due to the high ionic conductivity of the electrolyte (about three times that of sulfuric acid).

The electrolyte was a mixture of potassium chloride and lithium chloride and melts at about 350 to 400 degrees Celsius. He used nickel and magnesium for electrodes. Potassium chloride is used as a salt substitute, so it isn't dangerous to handle . The lithium compound, however, is slightly toxic

Advantages:

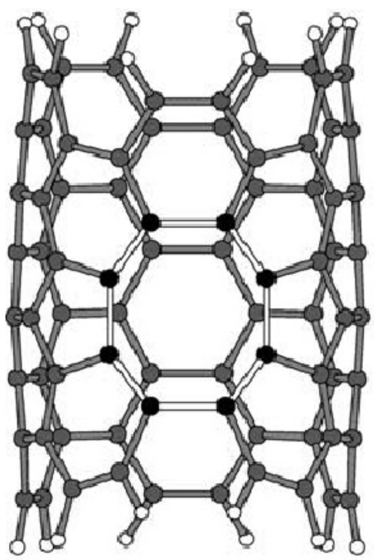
- cheap materials
- simple production
- has an infinite life
- a high degree of safety

Disadvantages :

- a high operating temperature
- low energy density
- high self-discharge in some types

Role of carbon nano tubes in electrodes

The increasing demands for higher energy density and higher power capacity of Li-ion secondary batteries lead to search for electrode materials with high capacities and performance better than those available today.



- ✓ Carbon nanotubes (CNTs), have been considered as ideal additive materials to improve the electrochemical characteristics of both the anode and cathode of Li-ion batteries.
- ✓ These electrodes have enhanced energy conversion and storage capacities.
- ✓ Because they have unique 1D tubular structure, high electrical and thermal conductivities and extremely large surface area.
- ✓ Recent development of electrode materials for LIBs

(Lithium Ion Batteries) has been run mainly by hybrid nanostructures consisting of Li storage compounds and CNTs.

- ☆ The electrical and thermal conductivities of CNTs are as high.
- ☆ The superior mechanical properties of CNTs are its Young's modulus and strength. CNTs are the strongest and stiffest materials.
- ☆ The extraordinary properties and unique structure of CNTs make them best materials for a variety of applications.
- ☆ CNTs are one-dimensional and are taken as one of the most best material for the anode materials of LIBs.

CNTs of Different structures as Anode for LIBS

- ✪ It is known that the structure of CNTs is of great importance for the electrochemical performance of LIBs when CNTs are used as anode materials.
- ✪ This means that the defects, lengths, and diameters of CNTs can influence the performance of CNT-based anode materials.
- ✪ The structural changes, including the lateral defects on the surface of CNTs and the shortening of the length of CNTs, can increase the Li insertion capacity.
- ✪ The diameter of the CNTs can be controlled by adjusting the conditions such as temperature, catalyst, pressure, and so on.
- ✪ The presence of holes on the surfaces of CNTs gives better diffusion of lithium ions into the tubes, thereby increasing their capacity.

- ☞ The diameter is another parameter of the structure of CNTs that can affect the lithium adsorption and diffusion, both inside and outside the CNTs.
- ☞ With an increase in tube diameter, the external Li adsorption energy decreases, but the internal Li adsorption energy increases.

- ☞ Another important influential morphological factor is the length of CNTs, which has also been reported to be able to influence the lithium diffusion of CNTs.
- ☞ Lithium ions inserted into CNTs undergo a one-dimensional random walk inside the carbon nanotube, and effective diffusion will decrease if the tube is too long.

Chapter - III

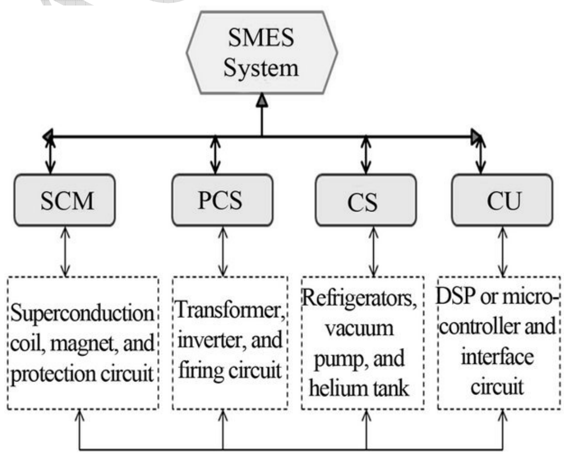
Superconducting Magnetic Energy Storage (SMES)

Introduction

- ❖ There are devices which can store large amounts of energy, but do not react so fast. In the other end there are fast acting devices which store smaller amounts of energy. Superconducting Magnetic Energy Storage (SMES) is placed in this group.
- ❖ Superconducting Magnetic Energy Storage (SMES) is an energy storage system that stores energy in the form of dc electricity by passing current through the superconductor and stores the energy in the form of a dc magnetic field.
- ❖ The conductor for carrying the current operates at cryogenic temperature where it becomes superconductor and thus has virtually no resistive losses as it produces the magnetic field.
- ❖ The magnetic field is created by flow of direct current through the coil.
- ❖ SMES systems are highly efficient; the efficiency is greater than 98%.

Components of SMES system

- ❖ Superconducting coil with the magnet
- ❖ The power conditioning system (PCS)
- ❖ The cryogenic system
- ❖ The control unit



Superconducting Coil

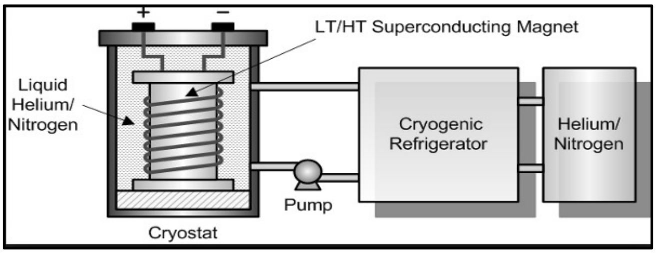
- ❑ This is the main part of a SMES system
- ❑ Most superconducting coils are wound using conductors which consists of many fine filaments of a niobium-titanium (NbTi) alloy fixed in a copper medium.
- ❑ The Size of the coil depends upon the energy storage requirement .

Power Conditioning System

- ➢ The power conditioning system has an inverter and a rectifier to transform alternating current (AC) to direct current or convert DC back to AC.
- ➢ An ac/dc PCS is used for two purposes:

1. One is to convert electric energy from dc to ac.
2. The other is to charge and discharge the coil.

Cryogenic Unit



- The SMES coil must be maintained at a very low temperature to maintain a superconducting state. For commercial SMES temperature is about 4.5 K.
- It uses helium or liquid nitrogen as coolant.
- The refrigerator consist of one or more compressors -cold box.
- It affect the overall efficiency and cost of SMES system.

Control system

- This establishes a link between power demands from the grid and power flow from the SMES coil.
- It maintains system safety and sends system status information to the operator.
- Modern systems are tied to the internet to provide remote observation and control.

Operation Of SMES

- There are three different modes of operations of the SMES coil :-

1. Charging mode
2. Stand-by mode
3. Discharging mode

Applications Of SMES

- Paper industry
- Motor vehicle assembly
- Petrochemical Refineries
- Chemical & pharmaceutical Companies

Advantages of SMES

- SMES systems have the ability of fast response.
- They can switch from charge to discharge state (vice versa) within seconds.
- The absence of moving parts and high efficiency are additional advantages.
- It can be used in places where other technologies such as battery system or compressed air are not feasible.

Disadvantages

- Main drawback of the SMES technology is the need of large amount power to keep the coil at low temperature. This increases the cost of the unit.
- To achieve commercially useful levels of storage, around 1 GW.h a SMES installation would need a loop of around 160 km.
- Another problem is the infrastructure required for an installation.

Capacitor

- Capacitor is a device that is used to store an electric charge or electrical energy directly due to the creation of an electrostatic field created between two metal "plates".
- It is basically an arrangement of two conductors. A capacitor consists of two conductors which are separated by a dielectric medium. Any non-conducting substance can be used as a dielectric material. Ex : porcelain, teflon, mica, cellulose are generally preferred.
- It stores electrical charge and is capable of discharging it whenever required.
- It blocks Direct Current (DC) and allows Alternating Current (AC) to pass through it. Therefore, they are widely used to extract AC components from DC + AC components.
- One of the common applications of a capacitor can be found in a flash camera. A capacitor in a flash camera charges up and stores the electric charge. It releases the charge to a light bulb and thus flash is created whenever the picture is taken.

Capacity of the condenser

$C = \frac{q}{V}$ q= Charge on plate V = Potential difference

$C = \frac{\epsilon A}{d}$ A = Area of the plate d= Distance between the two plates $\epsilon = Permitivity\ of\ the\ dielectric\ medium$

Energy stored in the capacitor

$U = \frac{1}{2}.\frac{q^2}{C} = \frac{1}{2}.C\,V^2 = \frac{1}{2}.q.V$ ∵ q = CV

Types

Three major types of capacitors are ceramic, electrolytic, and tantalum :

- Electrolytic capacitors - They look like small cylinders and range in value from 1 μF to several Farads.
- Ceramic capacitors - They are quite smaller in size and value, ranging from a few Pico Farads to 1 μF.
- Tantalum capacitors – They are quite similar in size to ceramic. They can hold more charge, up to several hundred μF. They tend to be accurate and stable.

Uses (or) applications

- High Voltage Electrolytic used in power supplies.
- Axial Electrolytic - lower voltage smaller size for general purpose where large capacitance values are needed.
- High Voltage disk ceramic - small size and capacitance value, excellent tolerance characteristics.
- Metalised Polypropylene; small size for values up to around 2μF.
- Sub–miniature Multi layer ceramic chip (surface mount) capacitor has relatively high capacitance for size achieved by multiple layers. Having several capacitors in parallel.

Battery

- ✓ Battery is a device that consists of electrochemical cells that convert stored chemical energy into electrical energy.
- ✓ Originally, it was called the Voltaic battery. The first battery was created by using copper and zinc rings. The set up was placed in an acid solution which is known as the electrolyte.
- ✓ A battery consists of two electrodes, namely cathode and anode. In a battery, the positive electrode is called cathode. The negative electrode is called anode.
- ✓ The two terminals are connected in order to form a circuit. Electrons move through the wire and electricity is produced. The basic mechanism remains the same till now.
- ✓ A modern battery has zinc carbon package. Zinc serves as a container as well as an anode. A carbon rod is used as a positive terminal. A paste of zinc chloride and ammonium chloride dissolved in water is used as electrolyte. The electrons that move from anode are collected by the carbon and then are returned to cathode portion of the battery.
- ✓ A battery is a combination of 2 or more cells connected in series or parallel to generate a voltage which is equivalent to the sum of the voltages of the cells.

Energy supplied by the battery to the circuit $U = Eit$

E = emf of the cell i = Current t = time

Types

- Alkaline battery
- Lead-acid battery
- Lithium battery
- Lithium-ion battery
- Nickel-cadmium or NiCad battery
- Zinc-carbon battery or standard carbon battery

Uses

- Wet-cell – Lead acid batteries are used to power vehicles; also used in industry.
- Dry-cell non-rechargeable – these are the most common types of household battery.
- Dry-cell rechargeable batteries – these are widely used in power tools, cordless appliances, mobile phones etc.

Comparison between the capacitor and battery

S.No.	Capacitor	Battery
1.	Capacitors store the charge in the form of electric field.	Battery stores the energy in the form of chemical reactions and then it convert into electrical energy.
2.	A capacitor voltage is variable and is proportional to the amount of electrical charge stored on the plates.	Battery voltage is constant before it is discharged.
3.	A capacitor is capable of handling high voltage applications and ideal for high frequency uses.	**A battery** can usually store a larger amount of electrical charge.
4.	The rate at which a capacitor is able to charge and discharge is usually faster.	The process gets delayed in case of a battery due to the chemical reaction involved while converting chemical energy into electrical energy.
5.	The polarity is reversed during discharge	The polarity does not change.
6.	Dielectric is placed between the two plates of the capacitor.	Electrolyte is placed between the two electrodes of the battery.
7.	Energy stored $U = \frac{1}{2}.C\,V^2$	Energy supplied U = Eit

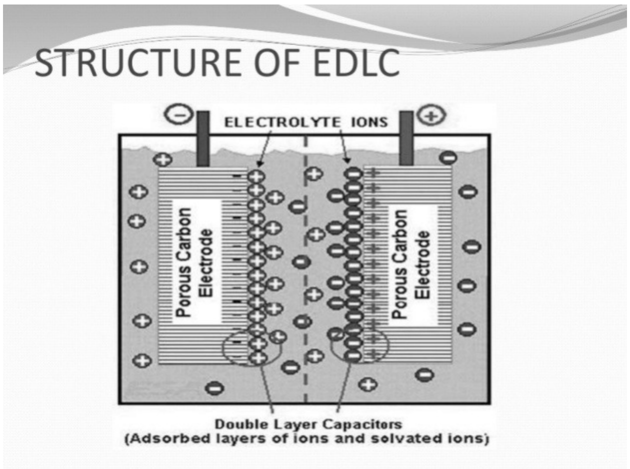
SUPERCAPACITOR

- In 1957 H. Becker developed a "Low voltage electrolytic capacitor with porous carbon electrodes".
- That capacitor came to known as Super capacitor as it stored very high amount of energy.
- A super capacitor is an electrochemical capacitor that has an very high energy density about 100 times greater as compared to general capacitors.
- Super capacitor is also known as Electric Double Layer Capacitor(EDLC) or Ultra capacitor.
- The capacitance range is from 100 Farad to 5KFarad.

Basic Design & principle

- ✓ Electrochemical capacitors (super capacitors) consist of two electrodes separated by an ion permeable membrane (separator) and an electrolyte electrically connecting both electrodes.
- ✓ When the voltage is applied, ions in the electrolyte form electric double layers of opposite polarity to the electrode's polarity.
- ✓ For example, positive electrodes will have a layer of negative ions and negative electrodes will have a layer of positive ions.
- ✓ So, these are called "electric double layer capacitors" (EDLC)

CONSTRUCTION



- ✪ Super capacitors are constructed with two metal foils, each coated with an electrode material such as activated carbon.
- ✪ The electrodes are kept apart by an ion- permeable membrane (separator) used as an insulator to protect the electrodes against short circuits and this arrangement is soaked in an electrolyte.
- ✪ The construction is subsequently rolled or folded into a cylindrical or rectangular shape and is packed in an aluminium can.

I. **Electrodes**:- 1) Carbon nano tubes, carbon aero gels are used for super capacitors plates or electrodes because Carbon nano tubes greatly improve capacitor performance, due to the high surface area and high conductivity. They are highly porous.

II. **Electrolytes**:- Sodium perchlorate ($NaClO_4$) or lithium perchlorate ($LiClO_4$) are used as electrolytes because of
1) Wide working temperature (-900^{o}c to 4000^{o}c).
2) Non flammable and low toxic.
3) Non-corrosive to electrode & packing components.

III. **Separator**:- Polyacrylonitrile $(C_3H_3N)_n$ is used as a separator (thickness 0.3-0.8 nm) because of
1) Unique tensile strength (103MegaPascals).
2) Electrical conductivity (1.5x104 S/m).
3)Not degraded easily.

IV. **Packing:-** Aluminium as a packing component.

WORKING

- ➢ In a super capacitor, there is no conventional dielectric.
- ➢ Both plates of capacitor are soaked in an electrolyte and separated by a very thin insulator.
- ➢ When the plates are charged, an opposite charge forms on either side of the separator, creating an electric double- layer.
- ➢ Due to this, super capacitors are often called as electric double-layer capacitors.

ADVANTAGES

a) Stores high amount of energy.
b) Have high capacitance.
c) Quick charging and discharging time.
d) Little degradation over thousands of cycles & Maximum life cycle.
e) Low toxicity& Safe.
f) High cycle efficiency (95%)
g) Wide working temperature (-400c to 600c).
h) Eco-friendly.
i) Extremely low internal resistance.

DISADVANTAGES

- Low energy density; usually holds 1/5 – 1/10 of a battery.
- Cannot use the full energy spectrum for some applications.
- The voltage varies with the energy stored.
- Have high self-discharge rate.
- Individual capacitors have low voltages. So, serial connections are needed to obtain higher voltages.
- Requires expert electronic control.
- Cannot be used in AC and high frequency circuits.
- It has limitations due to its high cost, self discharge, packaging problems etc.

APPLICATIONS

- In start up mechanism for Automobiles.
- Used in Diesel engine start up in submarines & tanks.
- China is experimenting with a new form of electric bus that runs without power lines but runs on power stored in large super capacitors, which are quickly recharged whenever the electric bus stops at any bus stop, and get fully charged in the terminus.
- In 2006two commercial bus routes began to use super capacitor buses, one of them is route 11 in Shanghai.
- Backup power system in missiles.
- Power source for laptops, flash in cameras.
- Voltage stabilizer.

Chapter - IV

Fuel cells

Fuel cell :- A **fuel cell** is an electrochemical cell that converts the chemical energy from a fuel into electricity through an electrochemical reaction of hydrogen fuel with oxygen or another oxidizing agent.

- ✓ Fuel cells are different from batteries and they require a continuous source of fuel and oxygen (usually from air) to sustain the chemical reaction.
- ✓ Fuel cells can produce electricity continuously, as long as fuel and oxygen are supplied.
- ✓ But in batteries the chemical energy comes from chemicals already present in the battery.

Differences between a fuel cell and a battery

S.No.	Battery	Fuel cell
1.	A battery makes electricity from the energy it has stored inside the battery.	A fuel cell makes its electricity from fuel in an external fuel tank.
2.	A battery may run dead, when the chemicals are over in the battery.	A fuel cell will make electricity as long as fuel is supplied. For hydrogen fuel cells, hydrogen is the fuel. When hydrogen in the tank runs low, replace it with a full tank.
3.	Recharging of a battery takes larger time (a couple hours).	It is much faster to refill a hydrogen tank (a couple minutes, depending on the tank).
4.	The life time of battery is some what less than fuel cell.	The lifetime of fuel cells is a couple years longer than batteries.
5.	Battery gives less and less energy back every time you recharge them. Disposing or recycling batteries gives environmental impact.	Here recharging does not arise and no environmental impact.
6.	The biggest difference between the two is that a battery stores energy.	While a fuel cell generates energy by converting available fuel. A fuel cell can have a battery as a system component.
7.	The electrical energy contained within a battery is either from the factory where it was made or from charging the battery via an outlet.	As long as you have access to your energy source, you have access to electricity

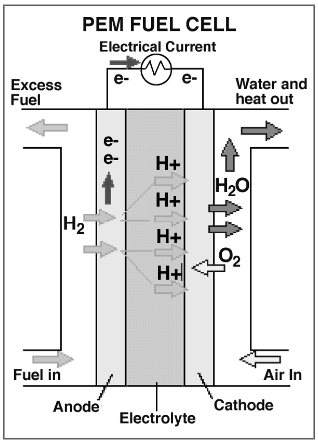
Components of fuel cell

1) Anode
   - ➢ Negative electrode of the fuel cell.
   - ➢ Conducts the electrons that are freed from the hydrogen molecules so that they can be used in an external circuit.
   - ➢ Etched channels disperse hydrogen gas over the surface of catalyst.

2) Cathode
   - Positive electrode of the fuel cell
   - Etched channels distribute oxygen to the surface of the catalyst.
   - Conducts electrons back from the external circuit to the catalyst
   - Recombine with the hydrogen ions and oxygen to form water.
3) Electrolyte
   - Proton exchange membrane (PEM).
   - Specially treated material, only conducts positively charged ions.
   - Membrane blocks electrons.
4) Catalyst
   - Special material that facilitates reaction of oxygen and hydrogen
   - Usually platinum powder very thinly coated onto carbon paper or cloth.
   - Rough & porous maximizes surface area exposed to hydrogen or oxygen
   - The platinum-coated side of the catalyst faces the PEM.

Principle &Working of fuel cell

- A fuel cell is a device that uses hydrogen (or hydrogen-rich fuel) and oxygen to create electricity by an electrochemical process.
- A single fuel cell consists of an electrolyte sandwiched between two thin electrodes (a porous anode and cathode).
- Hydrogen, or a hydrogen-rich fuel, is fed to the anode where a catalyst separates hydrogen's negatively charged electrons(e-) from positively charged ions H+ (or) (protons).



$$H_2 \xrightarrow{\text{Catalyst}} 2H^+ + 2e^-$$

The electrons from the anode side of the cell cannot pass through the membrane to the positively charged cathode. Electrons are conducted through the anode & make their way through the external circuit and do useful work such as turning a motor etc. and return to the cathode side of the fuel cell.

H^+ ions react with OH^- of electrolyte and form water.

$$2H^+ + 2OH^- \longrightarrow 2H_2O \quad \text{Hydraxyl ions in electrolyte}$$

On the cathode side, oxygen gas (O_2) is forced through the catalyst and forms two oxygen atoms.

$$O_2 \longleftrightarrow 2(O)$$

At the cathode, oxygen combines with electrons and with species such as protons or water, resulting in water or hydroxide ions, respectively

$$(O) + H_2O + 2e^- \longrightarrow 2OH^-$$

These OH^- ions migrate towards electrolyte and are absorbed there.

- ⊗ So, the electrolyte is invariant. This is the prime requirement of the cell i.e. the composition of the electrolyte does not change.
- ⊗ The amount of power produced by a fuel cell depends upon several factors, such as fuel cell type, cell size, the temperature at which it operates, and the pressure at which the gases are supplied to the cell.
- ⊗ A single fuel cell produces enough electricity for only the smallest applications. Therefore, individual fuel cells are typically combined in series into a fuel cell stack (pile). A typical fuel cell stack may consist of hundreds of fuel cells.

Advantages of fuel cells

Fuel cells have various advantages compared to conventional power sources, such as internal combustion engines or batteries.

1. Fuel cells have a higher efficiency than diesel or gas engines.
2. Most fuel cells operate silently. They can be suited within buildings such as hospitals.
3. Fuel cells do not need conventional fuels such as oil or gas and therefore, they are less expensive.
4. Since hydrogen can be produced anywhere where there is water and air, generation of fuel is available.
5. Low temperature fuel cells (PEMFC, DMFC) have low heat transmission and ideal for military applications.
6. The maintenance or life cycle costs of fuel cells is simple since there are few moving parts in the system.
7. A fuel cell is less complicated than a conventional gas or diesel engine.
8. High temperatures or corrosion or any of the structural weaknesses are not found in fuel cells like in other engines.
9. It will continue to operate indefinitely, without complication, as long as it has a fuel source.
10. They produce zero or very low emissions, especially Green House Gases (GHGs) depending on the fuel used.
11. In general its end pipe emission is water vapour.
12. The unit manufacturing is simple and flexible in size.

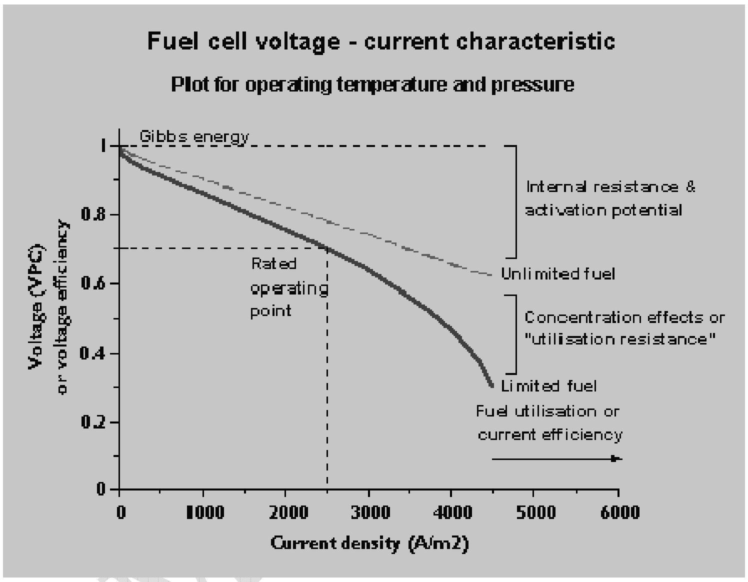
Disadvantages

1) Replacing the present oil-based infrastructure with hydrogen will cost billions or trillions of dollars.
2) Although abundant hydrogen is available in the universe, it is not so readily available it has to be extracted (for example through electrolysis etc.) and currently, the process is high priced and inefficient.
3) Its production at energy plants creates excessive carbon dioxide.
4) When it burns, a hydrogen flame is virtually invisible; and has the tendency of escaping, in small amounts from any tank. So, explosions are possible. On the positive side, hydrogen is so light & it dispersed in to air very quickly.
5) The storage is a major issue, a hydrogen tank is currently too large for a car.
6) As it is a very flammable gas, it leads to storage problems.
7) Hydrogen has some limitations that make it impractical for use in most applications.

8) So it would be much more convenient if fuel cells could use fuels that are more readily available.
9) This problem is solved by a device called a reformer.
10) A reformer turns hydrocarbon or alcohol fuels into hydrogen, which is then fed to the fuel cell.

Performance characteristics

Current-voltage characteristic



- ✪ The fuel cell characteristic is the graph drawn between the current drawn and voltage and is shown in the figure.
- ✪ At near zero currents the conditions approach the constant theoretical conditions.
- ✪ Pressure losses, concentration changes and temperature variations are very small as the fuel passages are large compared with the fuel flows and the reaction is very small.
- ✪ Hence the voltage efficiency remains high at low currents.
- ✪ But for a finite fuel flow rate the fuel utilization or current efficiency will be very low.
- ✪ As current increases, the voltage reduces due to the internal resistance, over-potentials, and concentration effects.

  Note :- over-potential is the difference between the experimental voltage and thermodynamically prescribed voltage, of the half reactions at each electrode

- ✪ When excess fuel is supplied, the voltage decreases approximately linearly with current.
- ✪ When the fuel flow rate is limited the fuel utilization or current efficiency increases with current but the linear relationship still applies up to approximately 80% utilization.
- ✪ If the fuel flow is regulated proportional to the current, current efficiency will be constant. Hence the voltage efficiency and overall efficiency is higher at low loads.

Performance at high currents and fuel utilizations

- ✪ Theoretically the fuel utilization cannot be greater than unity, and hence the maximum current that can be drawn from the fuel cell is limited.
- ✪ Assuming perfect distribution of fuel or uniform partial pressure over the cell area, the voltage loss is negligible until all the fuel is used.

Fuel cell efficiency

The fuel cell thermodynamic efficiency is given by the ratio of the Gibb's function change (dG) to the Enthalpy change (dH) in the overall cell reaction.

The Gibbs function change (dG) measures the electrical work and the enthalpy change (dH) is a measure of the heating value of the fuel.

But $dG = dH - TdS$

dH = Total energy of the system.

TdS = "Unavailable" energy i.e. energy that cannot be converted to useful work.

dG = "Free" energy or the energy available to do useful work.

$$Efficiency = \frac{dG}{dH}$$

For the hydrogen -oxygen reaction: dH = - 68,317 cal/g mole of H_2, and dG = - 56,690 cal/g mole of H_2 .

The efficiency of the Ideal Fuel Cell is therefore:

$$Efficiency = \frac{56,690}{68,317}\ x\ 100 = 83\%$$

Another measure of the fuel cell efficiency is known as the "Voltage Efficiency" and is the ratio of the actual voltage (V_A) under operating conditions to the theoretical cell voltage (1.23V).

$$Voltage\ efficiency = \frac{Actual\ Voltage}{Theoritical\ Voltage} = \frac{V_A}{1.23}$$

To increase the rate of reaction and performance

At the anode, hydrogen reacts, releasing energy. It does not mean that the reaction proceeds at an unlimited rate. The 'activation energy' must be supplied to get the energy.

The reaction will proceed slowly except at very high temperatures.

The three main ways to increase the slow reaction rates are

- ✪ Using catalysts,
- ✪ Raising the temperature,
- ✪ Increasing the electrode area.

- ✓ The first two can be applied to any chemical reaction. But the third is special to fuel cells and is very important.
- ✓ The rate at which the reaction happens will be proportional to the area of the electrode.

- ✓ The electrode area is plays a vital role in the performance of a fuel cell.
- ✓ The straightforward area (length × width) is not the only issue & the electrode is made highly porous. This has the effect of greatly increasing the effective surface area.
- ✓ Modern fuel cell electrodes have a microstructure that gives them surface areas that can be hundreds or even thousands of times their straightforward area (length × width). The microstructural design and manufacture of a fuel cell electrode is a very important issue for practical fuel cells.
- ✓ In addition to these surface area considerations, the electrodes may have to introduce a catalyst and should be maintained at high temperatures in a corrosive environment.

Losses in an Actual Fuel Cell

- ⊗ **Activation Losses**: These losses are caused by the slowness of the reaction taking place on the surface of the electrodes. A proportion of the voltage generated is lost in driving the chemical reaction that transfers the electrons.
- ⊗ **Ohmic Losses**: The voltage drop due to the resistance to the flow of electrons through the material of the electrodes. This loss varies linearly with current density.
- ⊗ **Concentration Losses**: Losses that result from the change in concentration of the reactants at the surface of the electrodes as the fuel is used.
- ⊗ **Fuel Crossover Losses**: Losses that result from the waste of fuel passing through the electrolyte and electron conduction through the electrolyte. This loss is typically small, but can be more important in low temperature cells.

Problems with Fuel Cells

Chapter - V

Classification of Fuel Cells

Fuel cells can be classified in different ways

Based on the type of Electrolyte

1. Alkaline Fuel cell (AFC)
2. Phosphoric Acid Fuel cell (PAFC)
3. Polymer Electrolytic Membrane Fuel Cell (PEMFC) Solid Polymer Fuel Cell (SPFC) and Proton Exchange Membrane Fuel cell (PEMFC)
4. Molten Carbonate Fuel Cell (MCFC)
5. Solid Oxide Fuel Cell (SOFC)

Based on Types of Fuel (or) oxidant

The fuels used are a) Hydrogen b) Fossil fuels c) Hydrocarbon fuels d) Alcohol fuels e) Hydrazine fuels

1. Hydrogen (pure)-Oxygen (pure) fuel cell
2. Hydrogen rich gas-air fuel cell
3. Ammonia –air fuel cell
4. Synthesis (mixture) gas- air fuel cell
5. Hydro carbon (gas)- air fuel cell

Based on operating temperature

1. Low temperature fuel cells - from 25^{o}C to 100 ^{o}C
2. Medium temperature fuel cells - from 100 ^{o}C to 500 ^{o}C
3. High temperature fuel cells - from 500 ^{o}C to 1000 ^{o}C
4. Very high temperature fuel cells - above 1000 ^{o}C

Based on regeneration

Primary fuel cell : It is the cell in which the reactants are passed only once through the cell and the products of the reaction are discarded. e.g. Hydrogen – Oxygen fuel cell

Secondary Cell : It is the cell in which the reactants are passed through the cell many times because they are regenerated by the products by thermal, electrical, Photochemical and radiochemical reactions

1. Thermal fuel cells
2. Electrical fuel cells
3. Photochemical fuel cells
4. Radiochemical fuel cells

Alkaline Fuel Cells (AFC)

- ❖ Alkaline fuel cells (AFCs) were one of the first fuel cell technologies developed and they were the first type widely used in the U.S. space program to produce electrical energy and water in spacecraft (rocket ship).
- ❖ It was originally used by NASA(National Aeronautics and Space Administration) on space missions.

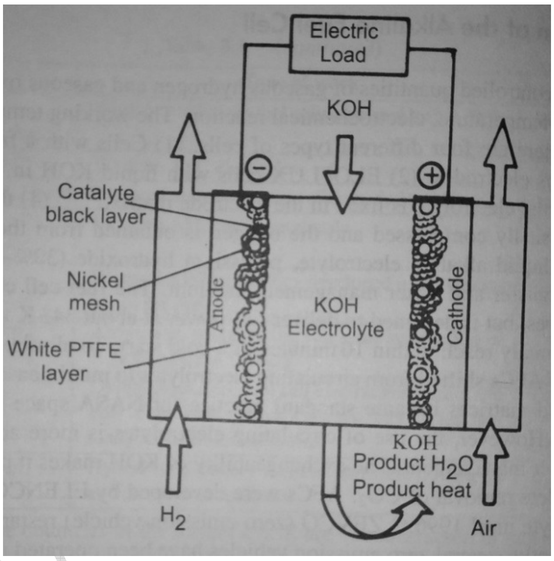
- These fuel cells use a solution of potassium hydroxide in water as the electrolyte and can use a variety of non- expensive metals as a catalyst at the anode and cathode. High-temperature AFCs operate at temperatures between 100ºC and 250ºC.
- More-recent AFC designs operate at lower temperatures also roughly 23ºC to 70ºC.
- AFCs are high-performance fuel cells due to the rate at which chemical reactions take place in the cell. They are also very efficient, reaching efficiencies of **60 percent** in space applications.

Description :

The alkaline fuel cell converts gaseous Hydrogen and gaseous Oxygen in to electricity directly and at low temperature by electrochemical reaction.

The alkaline fuel cell uses circulating liquid as alkaline electrolyte such as 40% aqueous potassium hydroxide. This is an heat transfer and water management medium.

The main problem is the contamination of electrolyte by atmospheric CO_2. This problem can be solved by changing the electrolyte at regular intervals. This is used in zero emission vehicle.



Working principle :

In this, Hydrogen fuel is supplied to the anode.

The negative ions OH^- travel through the electrolyte to the anode and they combine with hydrogen to generate water and electrons.

At the negative electrode (anode) Hydrogen is Oxidized with the help of catalyst.

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

Oxygen from air is supplied to the cathode. This Oxygen combines with the electrons from the external circuit and water and gives Hydroxyl ions OH^-

At the positive electrode (cathode) Oxygen is reduced with the help of catalyst.

$$\frac{1}{2}O_2 + 2e^- + H_2O \rightarrow 2OH^-$$

The voltage between the anode and cathode for single cell is 0.9 V to 0.5 V.

The over all reaction is $H_2 + \frac{1}{2}O_2 \rightarrow H_2O + Electrical\ Energy\ + Heat$

Electrodes

- Platinum – Cobalt alloy exhibits superior activity.
- The anode and cathode are multi layered gas diffusion electrodes.
- The electrodes consists of active Electrocatalystic layers and hydrophobic layers.
- The active layer is a mixture of organic powder and carbon-catalyst.
- Hydrophobic layer is low soluble compounds in water.

- These layers are pressed onto a conducting metal mesh. The active layer is in the mesh and hydrophobic layer is on the gas side of electrode.
- Nickel electrodes show a higher activity for Hydrogen oxidation.
- In the presence of CO_2 , carbonates are formed and precipitated on the electrodes and in electrolyte. This leads to potential blockage.

$$CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$$

Disadvantages :-

- ☆ Expensive and useful only for applications in space
- ☆ Require very pure and costly gases.
- ☆ Can not work using air because it is poisoned by carbon dioxide ƒ
- ☆ Even the small amount of CO_2 in the air can affect the cell's operation and it necessary to purify both the hydrogen and oxygen used in the cell.
- ☆ This purification process is costly.
- ☆ CO_2 can combine with KOH to form potassium carbonate which will increase the resistance.
- ☆ Poisoning also affects the cell's lifetime (the amount of time before it must be replaced), further adding to cost.

Advantages :-

- ⊗ AFCs work well at low temperature
- ⊗ Cost is less of a factor for remote locations such as space or under the sea.
- ⊗ Effectively compete in most mainstream commercial markets, these fuel cells will have to become more cost effective.
- ⊗ AFC stacks have been shown to maintain sufficiently stable operation for more than 8,000 operating hours.

Limitations

Preparation of electrodes : The electrodes consist of porous materials and are covered with layer of catalyst. It is difficult to distribute the catalyst on the electrode layer. The pores are used to transport the reactants.

Cost of electrode : The preparation of electrode with noble metal is very expensive.

Life time of the electrode : The electrolyte is corrosive and the metal used as catalyst are very sensitive to high polarization. If Ni, Ag are used as catalysts to reduce the cost, they degrade (corrupt) easily in the electrolyte.

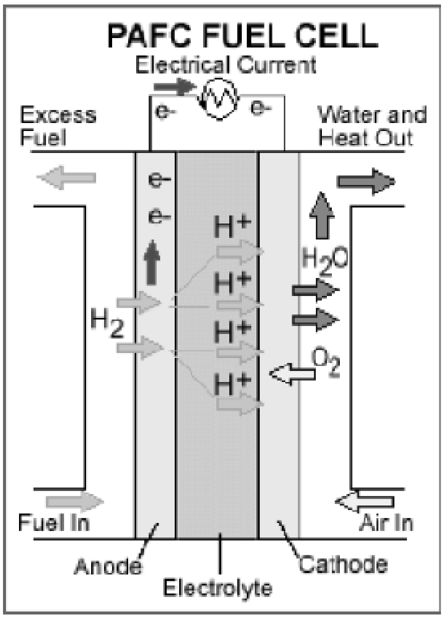
Contaminating electrolyte and electrodes : Carbonates are formed on electrodes and in the electrolyte due to the presence of CO_2. This reduces the reactions and also blocks the potential and the electrolyte should be changed periodically.

Performance : Slightly decrease of performance is due to reduced conductivity of the electrolyte.

Phosphoric Acid Fuel Cells (PAFC)

- The phosphoric acid fuel cell (PAFC) is considered the "first generation" of modern fuel cells. It is one of the most mature (developed) cell types and the first to be used commercially.
- This type of fuel cell is normally used for stationary power generation, but some PAFCs have been used to power large vehicles such as city buses.
- PAFCs are more tolerant of impurities like hydro carbons fuels.
- They are 85 percent efficient when used for the co-generation of electricity and heat but less efficient at generating electricity alone (37 to 42 percent).
- PAFCs are also less powerful than other fuel cells for a given weight and volume. As a result, these fuel cells are large and heavy in general..
- PAFCs are also expensive. Like PEM fuel cells, PAFCs require an expensive platinum catalyst, which raises the cost of the fuel cell.
- It has been under development for more than 20 years

PAFC Design and Operation



- Phosphoric acid fuel cells use liquid phosphoric acid as an electrolyte.
- The acid is contained in a Teflon-bonded silicon carbide medium and porous carbon electrodes containing a platinum catalyst.
- The small pore structure of this medium is the best to keep the acid in place through capillary action.
- Some acid entered in the fuel or oxidant streams and addition of acid may be required after many hours of operation.
- Fuel and oxidant gases are supplied to the backs of the porous electrodes by parallel grooves formed into carbon or carbon-composite plates.
- These plates are electrically conductive and conduct electrons from an anode to the cathode of the adjacent cell.
- In phosphoric acid fuel cells, protons move through the electrolyte to the cathode to combine with oxygen and electrons, producing water and heat.
- In most designs, the plates are "bi-polar" in that they have grooves on both sides - one side supplies fuel to the anode of one cell, while the other side supplies air or oxygen to the cathode of the adjacent cell.
- The byproduct water is removed as steam on the cathode (air or oxygen) side of each cell by flowing excess oxidant to the backs of the electrodes.
- This water removal procedure requires that the system be operated at temperatures around 190^oC.

- At lower temperatures, the product water will dissolve in the electrolyte and not be removed as steam. At approximately 210°C the phosphoric acid begins to decay.
- Excess heat is removed from the fuel cell stack by providing carbon plates containing cooling channels to every few cells.
- Either air or a liquid coolant, such as water, can be passed through these channels to remove excess heat.

Electrochemical reactions in PAFC

At the anode:

- ✓ Hydrogen is split into two hydrogen ions (H^+), which pass through the electrolyte to the cathode and two electrons which pass through the external circuit (electric load) to the cathode.

At the cathode:

- ✓ The hydrogen ions, electrons and oxygen combine to form water and heat.

$$\text{Anode: } H_2 \rightarrow 2H^+ + 2e^-$$

$$\text{Cathode: } 1/2\, O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

Advantages

1. It has the tolerance (acceptance) towards a large variety of fuel gases.
2. CO_2 is normally rejected from the electrolyte.
3. Material costs are low but not the electrode cost.

Disadvantages

1. Valuable and costly metal is required for the electrode.
2. It has slow start up due to slightly higher operating temperatures.
3. These cells give low specific power and power density.

PAFC Performance Characteristics

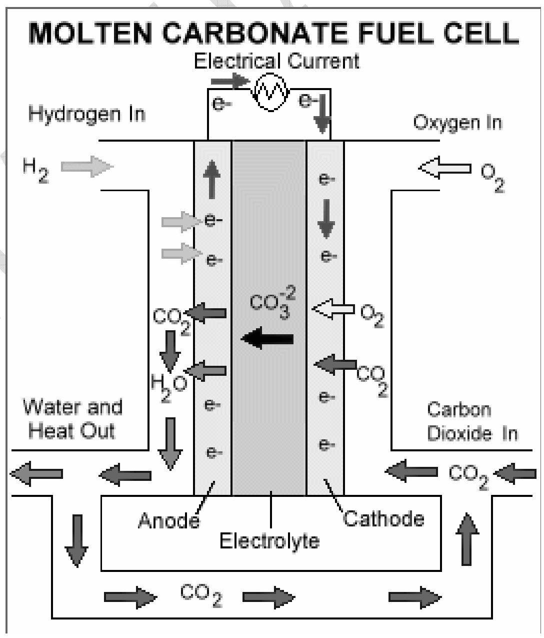
- PAFC power plant designs show electrical efficiencies in the range from 36% to 42% .
- The higher efficiency designs operate with pressurized reactants.
- The higher efficiency pressurized design requires more components and likely higher cost.
- PAFC power plants supply usable thermal energy at an efficiency of 37% to 41% .
- A portion of the thermal energy can be supplied at temperatures of ~ 250°F to ~ 300°F.
- The PAFC has a power density of 160-175 watts/ft^2 of active cell area

Molten Carbonate Fuel Cells (MCFC)

- The molten carbonate fuel cell was first constructed in 1921 and the real development of the cell was initiated in 1950.
- The operating temperature is in between 600^oC and 650^oC . So, these are high temperature fuel cells.
- It is the second generation fuel cell.
- These cells can operate on no. of fuels i.e. from hydrogen to carbon monoxide containing gases, gasified coal and reformed natural gas.
- The oxidant is constituted by a mixture of air and carbon dioxide.
- The electrons are transferred from anode to cathode through the external circuit.

Design & Operation :

- The molten carbonate fuel cell uses a **molten carbonate salt as the electrolyte.** It has the potential to be fuelled with coal- derived fuel gases, methane or natural gas.
- These fuel cells can work at up to 60% efficiency. In molten carbonate fuel cells, negative charges are conducted by carbonate anions (CO_3^{-2}) from the cathode to the anode through molten electrolyte where they combine with hydrogen to generate water and electrons.



- Molten carbonate fuel cells (MCFCs) are currently being developed for natural gas and coal-based power plants for electrical utility, industrial, and military applications.
- MCFCs are high-temperature fuel cells that use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic lithium aluminum oxide ($LiAlO_2$) matrix.
- Since they **operate at extremely high temperatures of 650ºC** and above, non-precious metals can be used as catalysts at the anode and cathode, reducing costs.

- Unlike alkaline, phosphoric acid and polymer electrolyte membrane fuel cells, MCFCs don't require an external reformer to convert more energy-dense fuels to hydrogen.
- Due to the high temperatures at which they operate, these fuels are converted to hydrogen within the fuel cell itself by a process called internal reforming, which also reduces cost.
- Although they are more resistant to impurities than other fuel cell types, scientists are looking for ways to make MCFCs resistant enough to impurities from coal, such as sulfur.

- ☆ The primary disadvantage of current MCFC technology is durability. The high temperatures at which these cells operate and the corrosive electrolyte used accelerate component breakdown and corrosion, decreasing cell life.
- ☆ Scientists are currently exploring corrosion-resistant materials for components as well as fuel cell designs that increase cell life without decreasing performance.

Electrochemical reactions :
The reactions at anode and cathode are as follows

Anode Reaction:

- The anode process involves a reaction between hydrogen and carbonate ions (CO_3^-) from the electrolyte.
- ⇨ The reaction produces water and carbon dioxide (CO_2) while releasing electrons to the anode.

$$CO3^{-2} + H_2 \rightarrow H_2O + CO_2 + 2e^-$$

Cathode Reaction:

- The cathode process combines oxygen and CO_2 from the oxidant stream with electrons from the cathode to produce carbonate ions which enter the electrolyte.
- The need for CO_2 in the oxidant stream requires a system for collecting CO_2 from the anode exhaust and mixing it with the cathode feed stream.

$$CO_2 + \frac{1}{2}O_2 + 2e^- \rightarrow CO3^{-2}$$

Overall Cell Reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

- 2 faradays of electricity is generated by the use of 1 mol of CO_2 at the cathode. So, it is desirable to recycle CO_2 to get invariant electrolyte.
- Increasing the operating temperature increases the rate of the electrochemical reaction and thus increases the current which can be obtained at a given voltage.
- The natural gas would be reformed to produce hydrogen within the fuel cell itself.

Cathode material : The material used for MCFC cathode must have high electrical conductivity and low solubility in the molten carbonates. Initially cathode is made of Silver or copper, now it is constituted of porous Nickel.

Anode material : MCFC anode pores are smaller than the gas filled large pores of cathode but larger than electrolyte filled cathode. Ceramic material must be incorporated into anode structure to stabilize it from sintering, pore growth and loss of surface area. The structure of this electrode is stabilized from all these effects by adding 2% - 10% chromium.

Electrolyte and matrix : In the conventional MCFC the electrolyte is formed by an alkali molten carbonate Li_2CO_3-K_2CO_3 in 62 – 38 mole ratio. This mixture was gradually replaced by Li_2CO_3-Na_2CO_3 in 52 – 48 mole ratio in the second generation. This has higher ionic conductivity and higher cell performance.

Matrix support material is the mixture of ceramic particles that forms the capillarity net work which contain electrolyte. This does not participate in the electrical and electrochemical processes.

Matrix cracking : The matrix should be gas –tight for the separation of fuel and the oxidant. If cracks occur in the matrix, then oxidant and fuel will react and local over heating of cell occurs. Also reduction of cathode or oxidation of anode causes performance loss.
Thermal cycling of the stack is considered as the major cause for matrix cracking.
Sintering (heating to melting point) as well as mechanical creep of components and dissolution of cathode causes thinning of porous components.

Contaminants :
Contaminants in the fuel such as sulphur or chlorine compounds interfere with electrode working. It is expected that appropriate gas clean-up is necessary to maintain the low level contaminants.
Life time limiting issues for MCFC

1. Dissolution of NiO2 cathode
2. Electrolyte losses
3. Corrosion of separator plate
4. Electrolyte maintenance capacity
5. Catalyst deactivation
6. Matrix cracking
7. High temperature creeping of porous components
8. Contaminants

Solid Oxide Fuel Cells (SOFC)

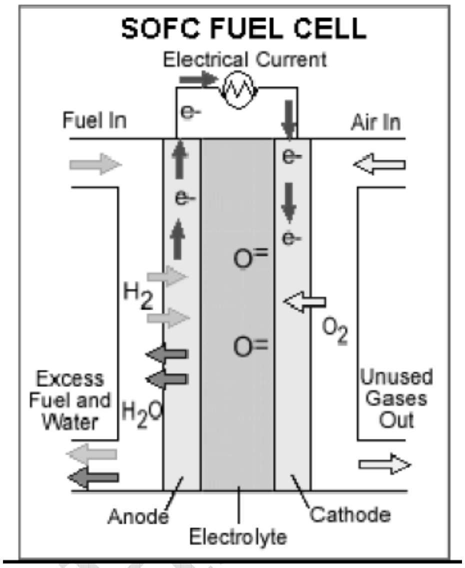
Design & Operation
SOFC cells differ from other fuel cell technologies.

1. They are composed entirely of solid state material.
2. The cells operate at very high temperature 1000^{o}C which is very hotter than any other cell.
3. There is no restriction on the cell configuration (Design).
4. Since the electrolyte is a solid, the cells do not have to be constructed in the plate-like configuration like other fuel cell types.
5. They are constructed in two designs a) tubular cells or rolled tubes b) flat plates cells

The principal components in SOFCs are electrolyte, anode, cathode and interconnect.

Electrolyte :The required properties of the electrolytes are fixed by the high operating temperature. These constraints restricted the choice to oxide based ceramics. They use a solid ceramic electrolyte, such as **zirconium oxide stabilized with yttrium oxide,** instead of a liquid and operate at 800 to 1,000°C.

The electrolyte materials must have good ionic transfer but the electronic conductivity in the electrolyte must be sufficiently low in order to minimize internal shortage and provide high energy conversion efficiency. The electrolyte must remain gas tight during the life of the cell.



The materials used as electrolytes in SOFC are Zirconia, ceria and a new family of perovskiets.
Ex:- Cerium oxide doped with yttrium, Cerium oxide doped with gadolinium etc.

Cathode materials : Noble metals are not needed for cathode because of their high cost. It should have high electronic conductivity and negligible anion conductivity. Heterometallic oxides are selected depending on electrolyte, operating temperature and the cell design.
Ex : $La_{0.6}\ Ca_{0.4}\ MnO_3$

Anode materials : Anode material require high stability in reducing atmosphere as fuel gas reduces. In general SOFC anodes are made by composite powder mixture of electrolyte mixture and Nickel Oxide.
Ex:Ru- YSZ (Yttria stabilized Zirconia), Ni-YSZ

Interconnects :
Interconnects are necessary to combine single cells to form stack by connecting the cathode to the anode of the adjacent cell. These are in contact with an oxidizing and a reducing medium at anode and cathode.

Efficiencies are around 60 per cent and are expected to be used for generating electricity and heat in industry and potentially for providing auxiliary (back-up) power in vehicles.
.

Electrochemical reactions
Anode Reaction:
In solid oxide fuel cells, negative ions travel through the electrolyte to the anode where they combine with hydrogen to generate water and electrons.

$2H_2 + 2O^{-2} \rightarrow 2H_2O + 4e^-$
Cathode Reaction:
$$O_2 + 4e^- \rightarrow 2O^{-2}$$
Overall Cell Reaction:
$$2H_2 + O_2 \rightarrow 2H_2O$$

- ⊗ High temperature operation removes the need for precious-metal catalyst, thereby reducing cost. They are not poisoned by carbon monoxide (CO), which can even be used as fuel.
- ⊗ This allows SOFCs to use gases made from coal.

- Scientists are currently exploring for developing lower-temperature SOFCs operating at or below 800ºC that have fewer durability problems and cost less.
- Since the Solid Oxide Fuel Cell (SOFC) uses a solid-phase electrolyte, it reduces corrosion and eliminates the electrolyte running problems associated with the liquid electrolyte fuel cells.
- To achieve adequate ionic conductivity in such a ceramic, however, the system must operate at about 1000°C .
- At that temperature, internal reforming of carbonaceous fuels should be possible and the waste heat from such a device would be easily utilized by conventional thermal electricity generating plants to yield excellent fuel efficiency.
- One of the major options of SOFCs in future is the use of fuel mixture of $CO\text{-}H_2\text{-}H_2O$ produced fro coal gasification plants or steam reforming of hydrocarbons particularly Methane.
- The fuel cell will compete with many other types of energy conversion devices, including
- ✓ The gas turbine in city's power plant,
- ✓ The gasoline engine in your car and
- ✓ The battery in your laptop.

Polymer electrolyte membrane (PEM) fuel cells (PEMFC)

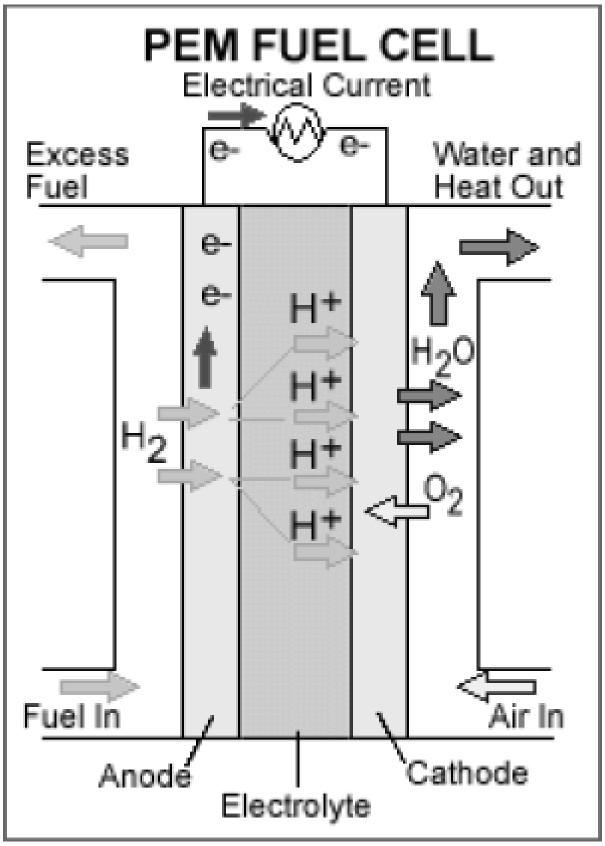
- **In polymer electrolyte membrane (PEM) fuel cells,** protons move through the electrolyte to the cathode to combine with oxygen and electrons, producing water and heat.
- Polymer electrolyte membrane (PEM) fuel cell uses a polymeric membrane as the electrolyte, with platinum electrodes. These cells operate at **relatively low temperatures.**
- These cells are the best for cars, for buildings and smaller applications.
- Polymer electrolyte membrane (PEM) fuel cells—also called proton exchange membrane fuel cells — deliver high power density and offer the advantages of low weight and volume, compared to other fuel cells.
- PEM fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst. They **only hydrogen, oxygen from the air**, and water to operate and do not require corrosive fluids like some fuel cells.

- They are normally fueled with pure hydrogen supplied from storage tanks or onboard reformers

- **Polymer electrolyte membrane** fuel cells operate at relatively low temperatures, around 80°C .
- **Low temperature operation** allows them to start quickly (less warm-up time) and results in less wear on system components, resulting in better durability.
- However, **it requires that a noble metal catalyst (normally platinum)** be used to separate the hydrogen's electrons and protons, adding to system cost.
- The **platinum catalyst is also extremely sensitive to CO poisoning**, making it necessary to employ an additional reactor to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel. This also adds cost.
- Developers are currently exploring platinum/ruthenium catalysts that are more resistant to CO.

Anode: $H_2 = 2H^+ + 2e^-$

Cathode: $1/2\, O_2 + 2H^+ + 2e^- = H_2O$



These are leading cells to replace the aging alkaline fuel-cell technology, which was used in the Space Shuttle.

The membrane must conduct hydrogen ions (protons) but not electrons as this would effect "short circuit" in the fuel cell.

The membrane must also not allow any gas to pass to the other side of the cell, a problem known as **gas crossover**.

Splitting of the hydrogen molecule is relatively easy by using a platinum catalyst. A cheaper alternative to platinum is catalyst Cerium(IV) oxide catalyst

Alternatively, methanol, and some other biofuels can be fed to a PEM fuel cell directly without being reformed, thus making a direct methanol fuel cell (DMFC). These devices operate with limited success.

Applications of fuel cells

1. **Power**
   Stationary fuel cells are used for commercial, industrial and residential primary and backup power generation. Fuel cells are very useful as power sources in remote locations, such as spacecraft, remote weather stations, large parks, communications centers, rural locations including research stations and in certain military applications. Fuel cells can be used with low-quality gas or waste-water treatment plants to generate power and lower methane emissions.

2. ***Automobiles***
   As of 2015, two fuel cell vehicles have been introduced for commercial lease and sale in limited quantities: the Toyota Mirai and the Hyundai ix35 FCEV.
   Toyota FCHV-BUS at the Expo 2005.
   As of August 2011, there were a total of approximately 100 fuel cell buses deployed around the world.

3. ***Forklifts***
   A fuel cell forklift (also called a fuel cell lift truck) is a fuel cell-powered industrial forklift truck used to lift and transport materials. In 2013 there were over 4,000 fuel cell forklifts used in material handling in the US

4. ***Motorcycles and bicycles***
   In 2005 a British manufacturer of hydrogen-powered fuel cells, Intelligent Energy (IE), produced the first working hydrogen run motorcycle called the ENV (Emission Neutral Vehicle).
5. Boats
   The world's first fuel-cell boat HYDRA used an AFC system with 6.5 kW net output.

6. ***Submarines***
   The Type 212 submarines of the German and Italian navies use fuel cells to remain submerged for weeks without the need to surface.

7. **Portable power systems**
   Portable power systems that use fuel cells can be used in the leisure sector .