MODULE-2

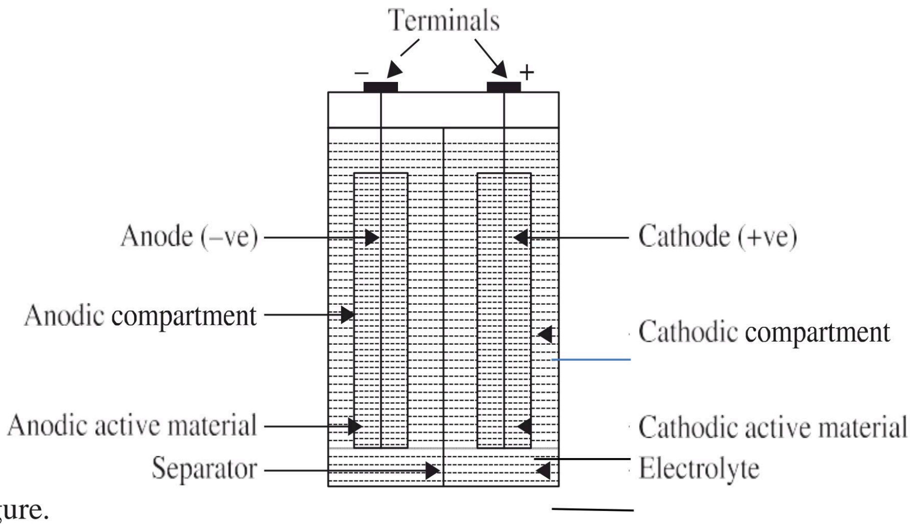
ENERGY STORAGE SYSTEMS

Definition: Battery is a device that consists of two or more galvanic cells connected in series or parallel or both, which converts chemical energy into electrical energy through redox reactions.

Example: Zn – Air battery, Lead-acid battery, Lithium batteries, etc.

Basic components of a battery:

A battery consists of four major components. They are anode, cathode, electrolyte and separator as



shown in the figure.

1. **Anode:** An electrode at the surface of which oxidation takes place. It releases electrons into the external circuit by undergoing oxidation. It is a negative electrode.

   $$M^{n+} + ne^{-} \leftrightarrow M$$

   It contains active materials which spontaneously take part in the oxidation reaction. To become
   effective anode, anodic material should possess the following properties.

2. **Cathode:** An electrode at the surface of which reduction takes place. It accepts electrons from anode through an external circuit. Reduction of active species occurs at cathode. It is a positive electrode.

   $$M^{n+} + ne^{-} \leftrightarrow M$$

   It contains active materials which spontaneously take part in the reduction reaction.

3. **Electrolyte:** It provides medium for migration of ions inside the battery between anode and cathode leading to the generation of electricity. It is the active mass in the anodic and cathodic compartments in the form of a solution or a slurry of an acid, alkali.

4. **Separator:** It is used to isolate anode and cathode in a battery to prevent internal short circuiting. It is permeable to ions but does not conduct electrons. It transports ions from

anode to cathode and vice versa. Fibrous forms of regenerated cellulose, vinyl polymers, polyolefins, Nafion are commonly used as separators.

CLASSIFICATION OF BATTERIES

Batteries are broadly classified into three categories:

1. **Primary Batteries:** In primary batteries, the chemical energy is converted into electrical energy as long as the chemical components are active. In these batteries, the reaction occurs only once and after that they have to be discarded. These batteries cannot be recharged as the chemical reactions which occur within the primary batteries are irreversible. *Examples:* Zn – air battery, Dry cell, Li – MnO_2 battery, etc.

2. **Secondary Batteries/Storage Batteries:** Secondary batteries are those which after discharging can be recharged. In these batteries chemical reactions taking place are reversible. The redox reaction which converts chemical energy into electrical energy can be reversed by passage of current.
   Examples: Lead storage battery, Ni-Cd battery, Ni-MH battery, Lithium ion battery, etc.

3. **Reserve Batteries:** In these batteries one of the components is isolated and incorporated into the battery when required. Usually, electrolyte is the component that is isolated, but some water activated batteries contain the electrolyte solute and only water is added for activation.
   Examples: Mg batteries activated by water (Mg – AgCl and Mg – CuCl), Zn – Ag_2O batteries, etc.)

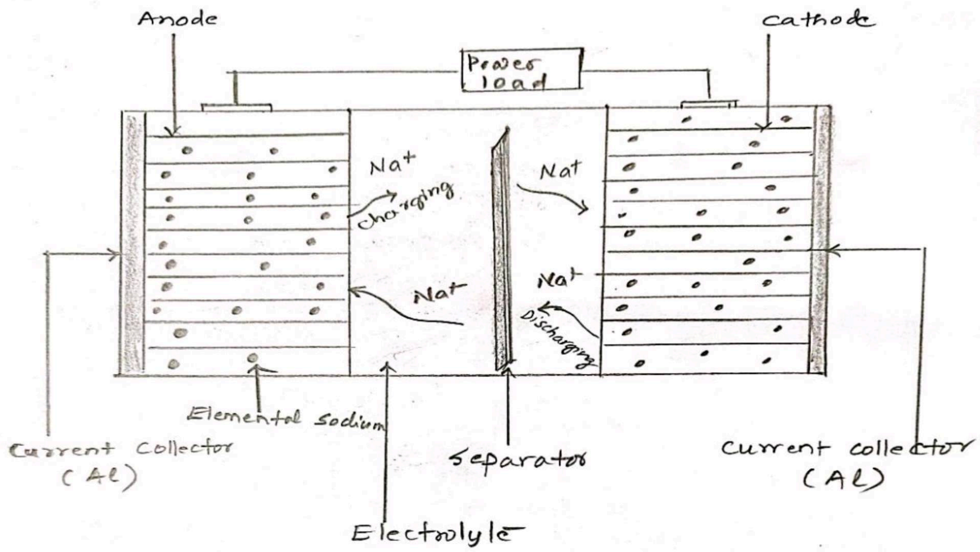
Sodium-ion battery (SIB):

Sodium-ion batteries (SIBs) are energy conversion and storage devices that use sodium-ions to shuttle positive charge between the anode & cathode in order to convert electrical energy to chemical energy and vice versa.

SIB is a type of rechargeable battery that uses sodium ions (Na^+) as its charge carriers. Its working principle and cell construction are almost identical with those of LIB types, but replace lithium with sodium.

SIBs are a potential alternative to lithium-based battery technologies, largely due to sodium's lower cost and greater availability. Since SIBs use abundant and cheap materials, they are expected to be less expensive than LIBs. The environmental impacts of SIBs are also lower. Although SIBs are heavier and larger than LIBs, they are feasible for stationary energy storage systems where the weight and volume are less crucial.

Construction:



Cell-representation: Na-C/Na^+, C/NaF_6 in ethylene carbonate/$NaMnO_2$

1. **Anode**: Hard carbon is used as the "standard" anode material in SIB, that stores sodium-ions coated on Al current collector.
2. **Cathode:** Cathode material is sodium incorporated metal layered such as $NaMnO_2$ coated on Al current collector.
3. **Electrolyte:** Electrolytes can be solids or liquids. The current most widely used electrolyte is sodium hexafluorophophate (NaF_6P) as the salt dissolved in a mixture of the solvents such as mixtures of ethylene carbonate and methylene carbonate solvents
4. **Separator:** Usually polypropylene microporous separators are used.

Working: SIBs generally contain two electrodes, one anode and one cathode, both consisting of the respective active materials coated on an aluminum foil current collector. A thin liquid-permeable sheet called the separator is placed between the two electrodes to keep them electrically insulated from each other, while allowing sodium ions to move freely between the electrodes. The anode is where the sodium is stored when the cell is in the charged state, while the cathode hosts the sodium-ions in the discharged state. The transport of positively charged sodium ions between the electrodes is enabled by a solvent salt solution called the electrolyte, while electrons move between the current collectors through an external circuit.

Reactions are reversed during charging of the battery.

Cell reactions:

At the anode: $Na\text{-}C \rightleftharpoons Na^+ + C + e^-$

At the cathode: $Na^+ + e^- + Na_{1-x}MnO_2 \rightleftharpoons NaMnO_2$

Overall reaction: $Na\text{-}C + Na_{1-x}MnO_2 \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} NaMnO_2 + C$

Advantages:

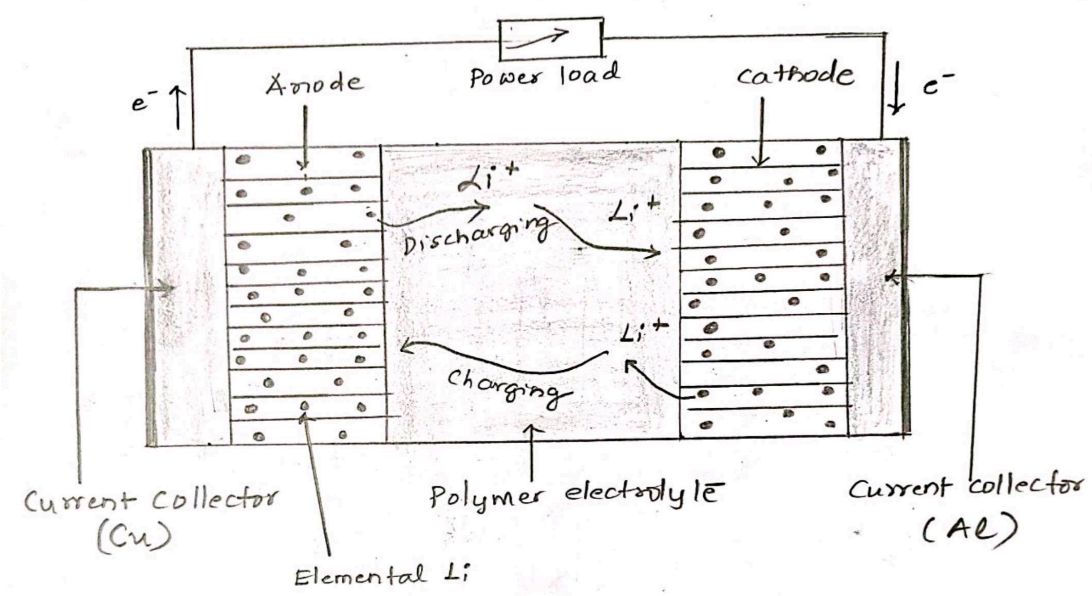
- Low-cost and environmental-friendly
- High stability and high efficiency
- Better safety characteristics
- These are high-rate batteries and operate at lower temperature.
- Fast charging

Applications:

1) Used in cellular phones and laptops.
2) In electric vehicles and power tools.

Lithium-polymer solid electrolyte battery:

Construction:



Cell representation: **Li_xC_6/Li^+, C/$LiPF_6$ in PEO/$LiCoO_2$**

1. **Anode:** Graphite electrode with Cu current collector.
2. **Cathode:** Lithium metal oxide [LiMO (Li_xCoO_2 | Li_xNiO_2 | Li_x MnO_2)] layer having aluminium foil as current collector.
3. **Electrolyte and separator:** Solid polymer electrolyte such as polyethylene oxide (PEO), Polymethyl meth acrylate (PMMA), Polyacrylo nitrile (PAN), Polyvinylidine fluoride (PVdF) gelled with lithium hexafluoro phosphate (LiF_6P) acts as both separator and electrolyte.

Working: Just as with other Li-ion batteries, these batteries work on the intercalation (movement) of lithium ions from a negative electrode material and a positive electrode material. Li^+ are generated at anode which diffuse to cathode trough electrolyte and Li atoms are inserted into the layers of metal oxide. During charging, Li^+ formed at cathode, diffuse to anode, converted into Li atoms and inserted into the layers of graphite(anode).

Reactions are reversed during charging of the battery.

Cell reactions:

At the anode: $Li_x–C_6 \rightleftharpoons xLi^+ + 6C + xe^-$

At the cathode: $xLi^+ + xe^- + Li_{1-x}CoO_2 \rightleftharpoons LiCoO_2$

Overall reaction: $Li_xC_6 + Li_{1-x}CoO_2 \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} LiCoO_2 + 6C$

Advantages:

- High energy density
- Low internal resistance
- Customizable shapes
- High voltage
- Light weight: Hence used in light weight devices such as smartphones and thin laptops as well as smart wearable
- Safety performance is good: safe from explosion unlike Li-ion batteries
- It does not lose its charging capacity as fast as a Li-ion battery. Its charging time is short.

Disadvantages:

- It supports less rechargeable life.
- It is expensive.

Applications:

Li polymer batteries are used in mobile devices, power banks, very thin laptop computers, portable media players, wireless controllers for video game consoles, wireless PC peripherals, and other applications.

FLOW BATTERY

In a battery, the electrolyte is the medium through which electrons can travel between the cathode and anode. In a flow battery, the anode and cathode themselves are electrolyte solutions.

A flow battery, or redox flow battery (after reduction–oxidation), is a type of electrochemical cell where chemical energy is provided by two chemical components dissolved in liquids that are pumped through the system on separate sides of a membrane.

OR

A redox flow battery is a type of electrochemical cell in which the chemical energy of a reversible redox couple reaction is converted into electrical energy.

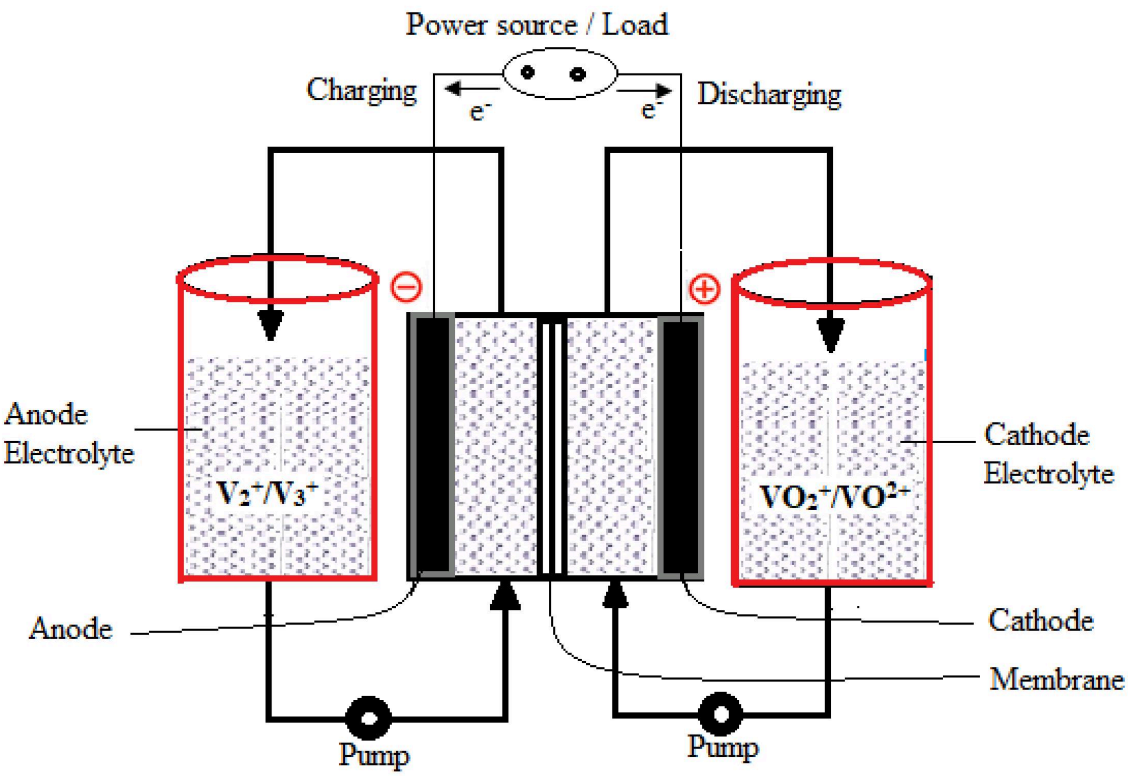
Vanadium redox flow battery

Construction:

Electrodes: Both the electrodes are carbon based. The most common types are carbon felt, carbon paper, carbon cloth, and graphite felt. Recently, carbon nanotube-based electrodes have attracted interest from the scientific community.

Electrolyte: Both electrolytes are vanadium-based. The electrolyte in the negative half-cells consists of V^{3+} and V^{2+} ions, While the electrolyte in the positive half-cells contains VO_2^+ (VO^{5+}) and VO^{2+}(VO^{4+}) ions. The electrolytes can be prepared by several processes, including electrolytically dissolving vanadium pentoxide (V_2O_5) in sulfuric acid. The solution remains strongly acidic in use.

Membrane: The most common membrane material is perfluorinated sulfonic acid (PFSA) (Nafion).



Cell

potential: 1.4-1.6 V

Working:

VRB is one of the most advanced flow battery systems with only redox couples [(V^{2+}/V^{3+} and VO_{2+}(V^{4+})/VO_2^+(V^{5+})] in anolyte (anode electrolyte) and catholyte (cathode electrolyte) electrolyte tanks. These are stored in mild sulfuric acid solutions. Having a single active element significantly diminishes cross contamination of the anolyte and catholyte. During the charge/discharge cycles, H^+ ions are exchanged between the two electrolyte tanks through the hydrogen-ion-permeable polymer membrane.

Cell reactions:

At the anode: $V^{2+} \rightleftharpoons V^{3+} + e^-$

At the cathode: $VO^{2+} + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$

$$V^{2+} + VO_2^+ + 2H^+ \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} VO^{2+} + V^{2+} + H_2O$$

Advantages:

Long charge-discharge cycle

Safe, non-flammable aqueous electrolyte

Wide operating temperature range

Good shelf life

Low maintenance

Can remain discharged indefinitely without damage

Disadvantages:

Relatively poor energy-to-volume ratio compared to standard storage batteries

High weight of aqueous electrolyte

Relatively high toxicity of oxides of vanadium

Applications: Battery can be used in utility-scale energy storage projects, micro grids, grid smoothing, backup power and in remote and off-grid power applications.

FUEL CELLS

Batteries and fuel cells appear to be similar but their working principle and aim are different. The electrochemical conversion of the free energy change of redox reactions into electrical energy is the working principle of any type of cell. The electrode reactions of primary batteries are irreversible and the cell produces EMF as long as the active materials are present in the cell, whereas the net cell reactions of secondary batteries are reversible. A fuel cell is an electrochemical cell which can convert the chemical energy contained in a fuel-oxidant system into electrical energy by an electrochemical process. Fuel cell consists of a fuel, an oxidant, an electrolyte and two electrodes.

The reactions that produce electricity take place at the electrodes. The fuel and the oxidant are supplied continuously.

Definition: **A fuel is defined as a galvanic cell in which the electrical energy is directly derived by the combustion of chemical fuels supplied continuously.**

It is a device that oxidises a fuel (hydrogen, natural gas, methanol, gasoline, etc) and an oxidant (oxygen) into electricity.

A fuel cell may be represented as follows:

Fuel | Electrode | Electrolyte| Electrode | Oxidant

In a fuel cell,

At anode: The fuel undergoes oxidation

$$\textbf{Fuel} \longrightarrow \textbf{Oxidized product} + \textbf{ne}^-$$

At cathode: The oxidant gets reduced

$$\textbf{Oxidant} + \textbf{ne}^- \longrightarrow \textbf{Reduced product}$$

Advantages:

- They offer high energy conversions.
- They produce energy as long as fuel and oxidant are supplied.
- Silent operation.
- They are eco-friendly as the products of the overall reactions are non-toxic.
- No need of charging.

Limitations/Disadvantages:

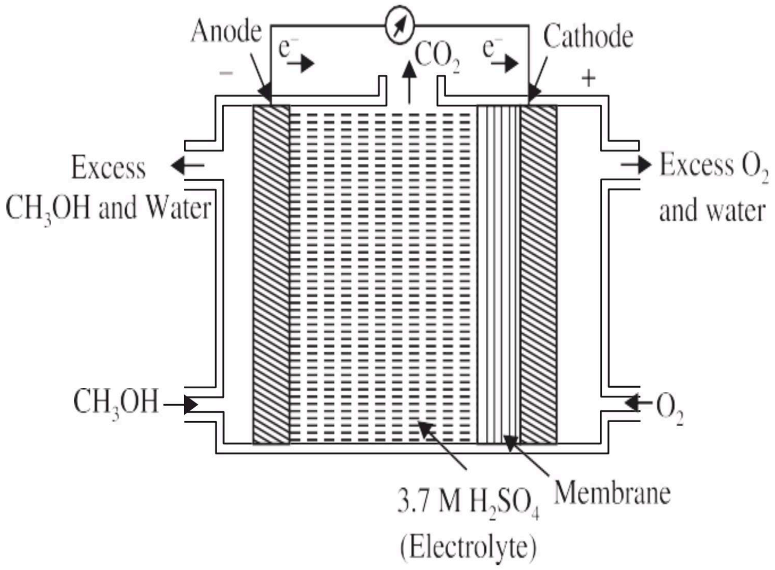
- The electrodes used are Pt, Ag or the alloys of noble metals which are costly. Hence cost of the power is high.
- Fuels and oxidant need to be stored in tanks under high pressure.
- Power output by a single unit is moderate.
- These are only energy conversion devices and not energy storage devices.

How fuels cells are different from batteries?

	Conventional Batteries	Fuel Cells
1.	Batteries are energy storage devices.	Fuel cells are energy conversion devices.
2.	Secondary batteries need charging.	Fuel cells do not need charging. They are not chargeable in conventional manner.
3.	The reactants and products form an integral part of batteries.	Reactants are continuously supplied and the products are constantly removed.
4.	Waste products in a battery may be harmful (Less eco-friendly).	Waste products in a fuel cell are harmless (More eco-friendly).

METHANOL-OXYGEN FUEL CELL

Electrodes: Pt
Fuel: CH_3OH
Oxidant: Oxygen
Electrolyte: H_2SO_4



The cell provides a potential of 1.20 V at 25°C.

It consists of two porous carbon electrodes. Anode is coated with platinum catalyst and cathode i s with silver catalyst. The electrolyte is an aqueous solution of H2SO4. Methanol is continuously supplied at the anode and oxygen is supplied at the cathode. Methanol adsorbed on anode electrode surface and undergoes oxidation giving CO2 and H+ ions. Electrons release at anode, move externally to cathode. H+ ions diffuse through the electrolyte and reacts with oxygen at cathode to produce water. A membrane is placed adjacent to cathode to prevent the diffusion of methanol to cathode or else methanol diffuses to cathode and undergoes oxidation itself.

The cell reactions are

At anode: $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

At cathode: $1/2\ O_2 + 6H^+ + 6e^- \longrightarrow$ 3H2O

Overall reaction: $CH_3OH + 1/2\ O_2 \longrightarrow CO_2 + 2H_2O$

Advantages of Methanol-Oxygen Fuel Cell

- Stable at all atmospheric conditions.
- CO_2, a product of the reaction can be easily removed.
- Easy handling.
- Methanol has low carbon content.
- The –OH group is readily oxidizable.

Applications

The cell finds applications in military and large scale power production.

Polymer electrolyte fuel cell:

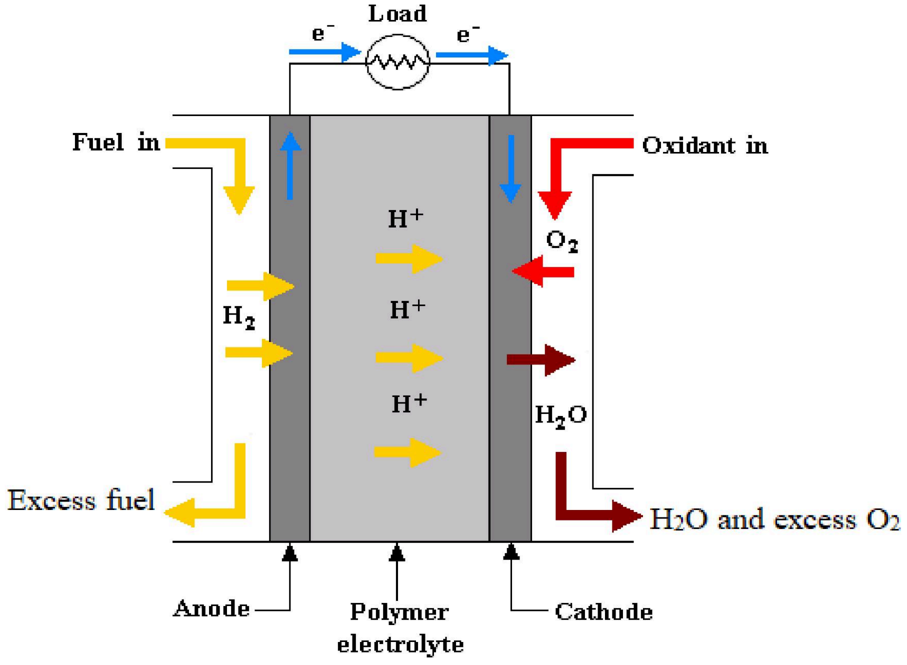
Polymer electrolyte fuel cells are electrochemical devices, converting the chemical energy of fuel directly into electrical energy. Their working principle is based on the anode-oxidation of hydrogen (fuel) to protons, and the reduction of oxygen to water at the cathode. These use a proton-conducting polymer membrane as the electrolyte. Hydrogen is typically used as the fuel. These cells operate at relatively low temperatures and can quickly vary their output to meet shifting power demands.

Fuel: Pure hydrogen, Methanol, Ethanol, etc.

Oxidant: Pure air or O_2

Electrodes: Both the electrodes are carbon based coated with platinum catalyst

Electrolyte: Proton exchange membrane such as Perfluorinated sulfonic acid (Nafion)



At anode, hydrogen is oxidized to liberate electrons which move through the external circuit ot the cathode. Protons diffuse through the PEM to the cathode. Oxygen molecules adsorb at the cathode, are reduced and react with protons and electrons to produce water. The product water is absorbed into the PEM or flows out.

Cell reactions:

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

Cathode: $\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O$

Overall: $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$

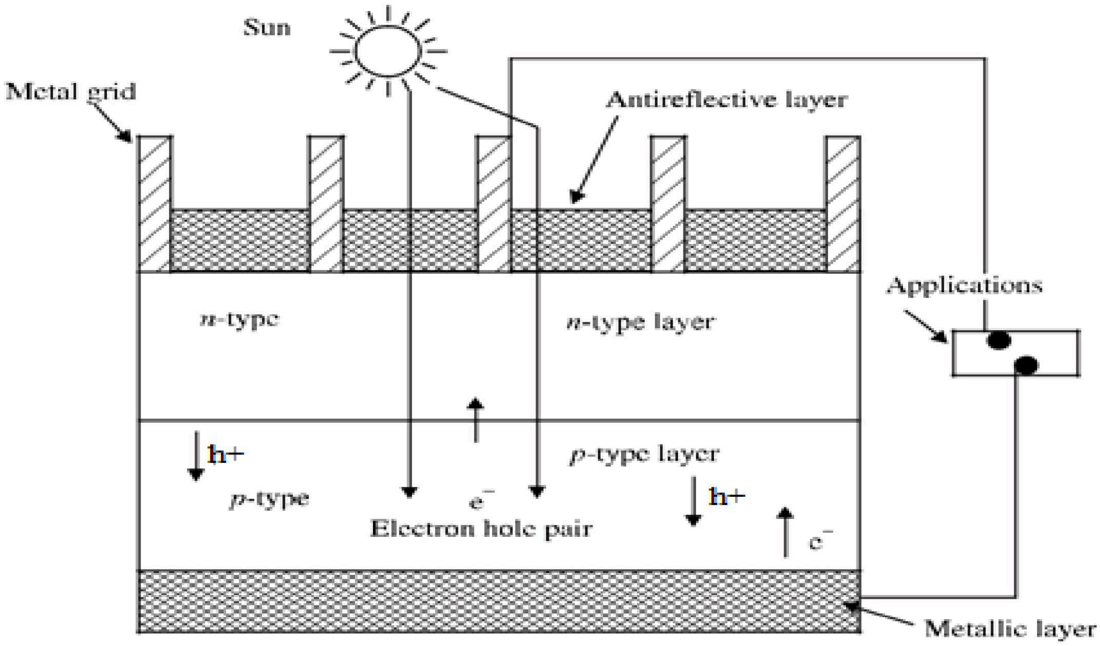
Applications: They can be used as power sources in electric vehicles, portable and stationary applications in hospitals, hotels.

SOLAR ENERGY

Photovoltaic cells or solar cells are semiconductor devices that convert sunlight into direct current. As long as light is shining on the solar cell, it generates electrical power. When the light stops, electricity stops.

Construction And Working Of Photovoltaic Cell

Construction:



A typical silicon photovoltaic cell is composed of a thin wafer consisting of an ultra-thin layer of phosphorous doped (n-type) silicon on the top and boron doped (p-type) silicon at the bottom. Hence a p-n junction is formed between the two. A metallic grid above the diode forms one of the electrical contacts and allows the light to fall on the semiconductor. The anti-reflective layer (Silicon nitride or TiO_2) present in between the metallic grid increases the transformation of sunlight to a semiconductor. The other metallic layer at the back of the semiconductor forms another electrical contact.

Working:

Electromagnetic radiation consists of photons. The photons carry a certain amount of energy. It is given by the Planck quantum equation [$E = (hc/\lambda)$], where h is Planck's constant, c is the velocity of light and l is the wavelength of the radiation.

When the electromagnetic radiations fall on the p-n junction diode, electron pair holes are generated. Electrons move and collect at the n-type end and the holes move towards the p-type end.

On connecting these two ends through conductor, current flows between them to an external circuit.

Applications:

- For producing electricity by using solar power plants.
- To provide electricity to satellites.
- In remote sensing techniques from space using satellites with objectives.
- To provide reliable weather monitoring and forecasting, thereby monitoring the climatic factors.

Advantages:

- Solar power is pollution free.
- It is a well-established technology.
- Low maintenance.
- It is a local resource.
- The source is inexhaustible.

Disadvantages:

- Not available at night.
- It is practical only in certain areas with favourable climate and latitude. It reduces in cloudy atmosphere.
- It produces DC power which must be converted to AC when used in distribution grids.