

Unit-V

Advanced energy systems

Syllabus

Battery technology: Introduction to Electrochemistry, characteristics of battery, Lithium-Ion battery, metal air battery. Battery technology for e-mobility: Super capacitors: Storage principle, types (EDLC, pseudo and hybrid) with examples and applications. Photovoltaics: organic/inorganic solar cells, quantum dot sensitized (QDSSC's). Photo catalytic water splitting.

5.1. Battery technology

Introduction to electrochemistry

Electrochemistry deals with chemical reactions that produce electricity and the changes associated with the passage of electrical current through matter. The reactions involve electron transfer, and so they are oxidation-reduction (or redox) reactions. Many metals may be purified or electroplated using electrochemical methods. Devices such as automobiles, smartphones, electronic tablets, watches, pacemakers, and many others use batteries for power. Batteries use chemical reactions that produce electricity spontaneously and that can be converted into useful work. All electrochemical systems involve the transfer of electrons in a reacting system. In many systems, the reactions occur in a region known as the cell, where the transfer of electrons occurs at electrodes.

Electrochemical Devices

Electrochemical cell is a device in which chemical energy is converted into electrical energy or electrical energy into chemical energy by oxidation-reduction reaction. The electrode where oxidation occurs is called anode and the electrode where reduction occurs is called cathode.

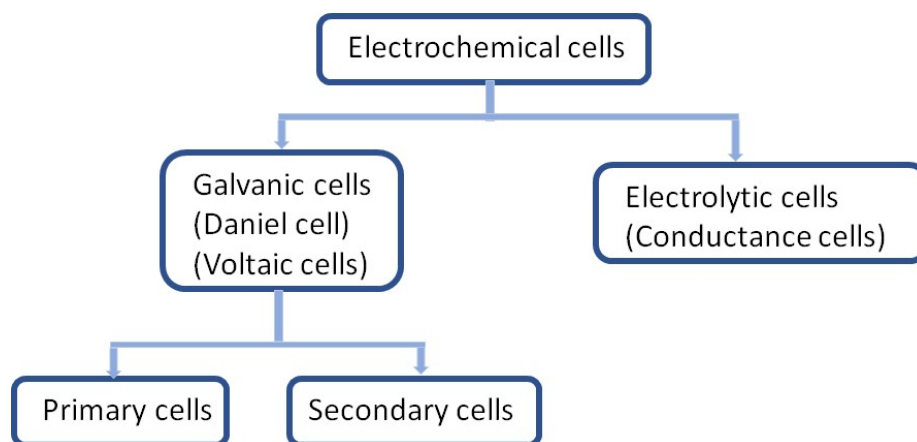


Figure 5.1: Classification of electrochemical cells

Types of electrodes:

- **Metal-metal ion electrode:** This type of electrode consists of a metal in contact with a solution of its own ions. Eg: 1. Zinc in a solution of zinc sulphate, copper in a solution of copper sulphate.
- **Metal-metal ion salt electrode:** This type of electrode consists of a metal in contact with one of its sparingly soluble salts and a solution of a soluble salt having a common anion with the sparingly soluble salt. Eg: 1. Calomel electrode $\text{Hg(l)} | \text{Hg}_2\text{Cl}_2\text{(s)} | \text{KCl}$ Or $\text{Pt, Hg(l), Hg}_2\text{Cl}_2\text{(s)} | \text{KCl (....M)}$, Silver-Silver chloride electrode $\text{Ag, AgCl (s)} | \text{KCl (....M)}$
- **Metal gas electrode:** A gas electrode consists of a particular gas flushed around an inert electrode (Pt), which is dipped in a solution containing ions to which the gas is reversible. The metal provides electrical contact and facilitates the establishment of equilibrium between the gas and its ions. Eg: SHE: $\text{Pt} | \text{H}_2 \text{ (1atm)} | \text{H}^+ \text{ (1M)}$, Chloride electrode $[\text{Pt}/\text{Cl}_2/\text{Cl}]$.
- **Redox electrode:** This type of electrode consists of an inert electrode (Pt or Au) immersed in a mixed solution containing both the oxidized and reduced forms of a molecule or ion. Eg: $\text{Pt} / \text{Fe}^{2+} : \text{Fe}^{3+}$, $\text{Pt} / \text{Sn}^{2+} : \text{Sn}^{4+}$
- **Ion selective electrode:** In ion selective electrode, a membrane is in contact with a solution, with which it can exchange ions. These are the electrodes in which certainly respond to specific ions and determine the potential. Example-Glass electrode.
- **Reference electrode:** Reference electrodes are those whose potentials are known.

Introduction to battery:

CELL: A cell designates a single unit. The conversion of chemical energy into electrical energy is a function of cells or batteries.

BATTERY: A Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at a constant voltage.

Uses: Batteries are used in calculators, watches and pacemakers for heart hearing aids, computers, car engines, standby power supplies, emergency lightning in hospitals, electroplating industrial tractions and military and space applications. Batteries have revolutionized the telecommunication system and are ushering a new era of transportation with the possible replacement of petrol driven automobiles by the electrically powered ones. In modern days portability of electronic equipment's in the form of handsets has been made possible by batteries.

Components of Battery: The cell consists of three major components.

- Anode: The anode selected with the following properties in mind; efficiency as a reducing agent, high columbic output (Ah/g) good conductivity, stability ease of fabrication and low cost.
- Cathode: The cathode must be an efficient oxidizing agent, be stable when in contact with the electrolyte, and have a useful working voltage.
- Electrolyte: The electrolyte must have good ionic conductivity but not be electrically conductive. This would cause internal short circuiting. Electrolyte should be non-reactive with the electrode materials.

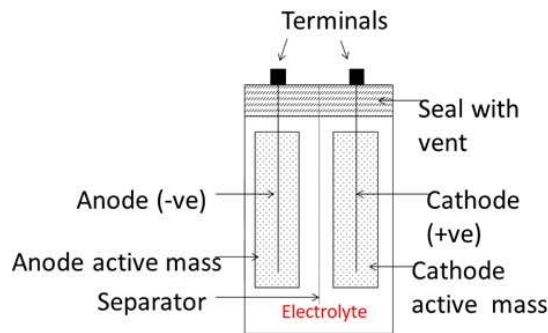


Figure 5.2: Structure of typical battery

Mechanism of working of battery: During discharging, the Battery acts as voltaic cell i.e. oxidation takes place at the negative electrode (anode) and reduction takes place at the positive electrode (cathode). During charging, The Battery acts as an electrolytic cell. The current flow is reversed and oxidation takes place at the positive electrode (anode) and reduction takes place at the negative electrode (cathode).

Criteria for commercial batteries

An efficient commercial cell should have following basic characteristics

- Portability: cells should be easily transportable without any environmental issues
- Compact: Battery should be more compact and light weight
- Economy: battery should have less price with continuous electric supply.
- Power and energy density: batteries should have high power and energy density
- Recharging; It should be able to charge as well as discharge battery in faster rate with recyclability
- Cycle and shelf life: Batteries should be having high cycle life and shelf life without self-discharge.

Characteristics of battery

The suitability of any battery for particular application is based on certain characteristic properties. Some of

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- **Voltage (V):** In general, high voltage is desired from any battery. The voltage of any battery depends on the emf of the cells which constitute the battery system. The emf of the cell depends on the free energy in the overall cell reactions as given by Nernst equation. $E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303 RT}{nF} \log Q$ Where $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$ and Q is the ratio of the molar concentrations of product and reactants. From the above equation, emf of the cell and the voltage available from the battery is dependent on the standard electrode potential difference between the cathode and anode, temperature and the extent of the cell reaction. To get required high voltage, the difference in the standard electrode potential should be more; temperature of the reaction and q value should be low. The conductivity of the electrolyte should be high.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{2.303 RT}{nF} \log \frac{\text{Product}}{\text{Reactant}}$$

- **Current (A):** Current is a measure of the rate at which the battery is discharging. Higher the rate of spontaneous reaction, higher is the current. Higher the surface area of the electrodes, higher is the rate of reaction. Current is measured in Ampere (A).

$$I = \frac{V}{R}$$

Where I is the current, V is voltage and R is resistance of the battery.

- **Capacity (Ah):** Capacity is a measure of the amount of electricity that may be obtained from the battery. It is expressed in Ah (ampere hours). It is proportional to the amount of charge in Coulombs that may be transported from anode to cathode through the external circuit. The charge (C) in Coulombs is given by the Faraday's relation:

$$C = \frac{w \times n \times F}{M}$$

Where, C is Capacity of battery (in Ah), W is Weight of the active material (Kg), n is number of electrons involved in discharge reaction, F is Faraday's constant, 96500 C/mol, M is Molar mass of electro active materials.

- **Energy density (Wh/Kg):** It is the amount of electricity stored in the battery per unit weight of the battery. i.e., it is the capacity per unit weight. It can be expressed in Coulombs/kg or in Ah/kg. The weight includes the weight of all components of the battery (i.e. total weight of active material, electrolyte, terminals etc.). A high storage density depends on a good battery design and also the appropriate selection of electrode reaction.

$$\text{Energy density} = \frac{I(\text{current}) \times t(\text{time}) \times V(\text{Voltage of a battery})}{\text{Weight of a battery}}$$

- **Power density (W / Kg):** The ratio of the power available from a battery to its weight or its volume (W / V) is called power density. The power density will decrease during discharge and while recharge it will increase.

$$\text{Power density} = \frac{I(\text{current}) \times V(\text{EMF of battery})}{\text{Mass of electroactive material}}$$

- **Energy efficiency:** it is the ratio of energy released during discharge to energy consumed during charging. The energy efficiency of a rechargeable battery is given by

$$\text{Energy Efficiency} = \frac{\text{Energy released during charging}}{\text{Energy supplied during charging}} \times 100$$

- **Cycle life:** The number of recharges per discharge cycles that are possible before the failure of a secondary battery is called cycle life. In secondary battery it is essential for the discharge per recharge cycles to perform the active material in a suitable state for further discharge reaction. The discharge per recharge cycles depends on the correct chemical composition, morphology and proper distribution of active material in the battery.
- **Shelf life:** The duration of storage under specific condition at the end of which battery still retaining the ability to give specific performance is called shelf life. Shelf life for most of the storage must be good. Good shelf life for a battery is possible when there is no self-discharge or corrosion in current collectors.

Classification of batteries:

Majorly batteries are classified in to three categories

- **Primary battery:** non-rechargeable (cell reactions are irreversible) - Self-discharges whether used or not, lechlanche cells (Zn/C) - Popular low-cost system, Applications: Torch light, portable radios, toys, novelties, etc. Mg/MnO₂ CELLS - High-capacity system: Applications: Military communication equipment, voting machines, etc.

- **Secondary battery:** Rechargeable (cell reactions are reversible), Lead-Acid Battery (Pb/H⁺), Nickel-Cadmium Battery (Ni-Cd), Nickel-Iron Battery (Ni-Fe), Nickel-Metal hydride Battery (Ni-MH), Lithium battery (Li-LiM_xO_y), lithium-Ion battery (C-LiM_xO_y), Lithium-Ion Polymer Battery (C-LiM_xO_y)
- **Reserve battery:** one of the key cell components, usually the electrolyte, is kept isolated from the rest and is added at the time of need Examples: Mg/Cu₂Cl₂, Mg/AgCl (sea water activated battery), Applications: Torpedoes, Sea beacons (Mainly in Meteorology and Defense fields), Li/FeS₂ (Thermally activated battery). Applications: In Missiles and rockets.

Lithium-ion batteries: A Lithium-ion battery is rechargeable battery which stores the energy by reversible reduction of lithium ions. This battery is widely used in the portable electronic gadgets, e vehicles and all medical equipments because of their energy density and compactness. This type of battery is more advanced when compared to other types of battery such as lead acid and nickel cadmium battery. Further these types of batteries are majorly classified as primary and secondary batteries.

Criteria of selection of anode materials for lithium-ion battery

Desired characteristics of anode materials

- Large capability of Lithium adsorption: porous anodes
 - High efficiency of charge/discharge
 - Excellent cyclability: high cycle life
 - Low reactivity against electrolyte: Chemical stability
 - Fast reaction rate
 - Low cost
 - Environmental -friendly, non-toxic
- Commercial anode materials used in lithium batteries: Hard Carbon, Graphite

Criteria of selection of Cathode materials for lithium-ion battery

Desired characteristics of Cathode materials

- High discharge voltage
- High energy capacity
- Long cycle life
- High power density
- Light weight
- Low self-discharge

- Absence of environmentally hazardous elements

Commercial cathode materials for lithium ion battery: LiCoO_2 , LiMn_2O_4 , LiNiO_2 , LiFePO_4

Electrolytes used in the lithium-ion battery

Electrolyte is one of the important components of battery ecosystem. In general ether-based electrolyte along with lithium salts are used as electrolytes.

The electrolyte should have following Characteristics in order to employ them in battery technology

- Inert: solvent stability
 - High ionic conductivity, low viscosity
 - low melting point & high dielectric constant (ϵ)
 - Appropriate concentration of Lithium salt
 - Chemical/thermal stability, High flash point (T_f), nontoxic,
 - Low cost
 - Environmental -friendly, non-toxic
- Commercial electrolytes: LiPF_6 in Carbonate solvent, propylene carbonate, 1,2 dimethoxy ethane

Role of electrolyte in battery technology

- Ion conductor between cathode and anode
- Generally, Lithium salt dissolved in organic solvent
- Solid electrolyte is also possible if the ion conductivity is high at operating temperature.

Separators: Separator is a membrane placed between a battery electrode. The main function of a separator is to keep the two electrodes apart to prevent electrical short circuits while also allowing the transport of ionic charge carriers that are needed to close the circuit during the passage of current in an electrochemical cell.

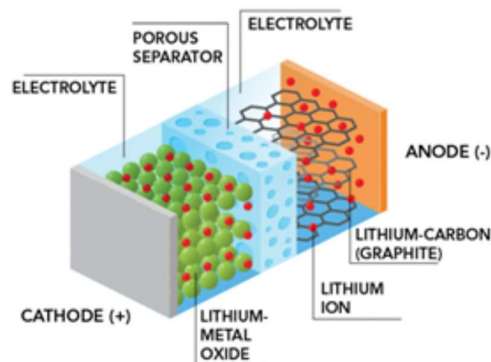


Figure 5.3: separator in battery technology

Primary lithium batteries: These are batteries in which redox reactions proceed only in the one direction. The reactants in these batteries are consumed after a certain period of time, rendering them dead. A primary battery cannot be used once the chemicals inside it are exhausted. An example of a primary battery is the dry cell – the household battery that commonly used to power TV remotes, clocks, and other devices. Best example for this battery is lithium-ion battery.

Lithium Primary battery (Li-MnO₂-Battery)

In primary lithium-ion battery, lithium metal used as anode and manganous dioxide used as cathode. During the discharge lithium gets converted into lithium ion and it reacts with MnO₂ to become an irreversible LiMnO₂ compound. Hence this type of a battery is primary battery.

Anode: Li

Cathode: MnO₂(heat treated)

Electrolyte-Lithium salt like LiCl, LiBr, LiAlCl₄ in mixed organic solvent like 1, 2-dimethoxy ethane and Propylene carbonate

Reactions:

Anode reaction: $\text{Li} \rightarrow \text{Li}^+ + \text{e}^-$

Cathode reaction: $\text{Li} + \text{MnO}_2 + \text{e}^- \rightarrow \text{LiMnO}_2$

Overall reaction..... $\text{Li} + \text{MnO}_2 \rightarrow \text{LiMnO}_2$

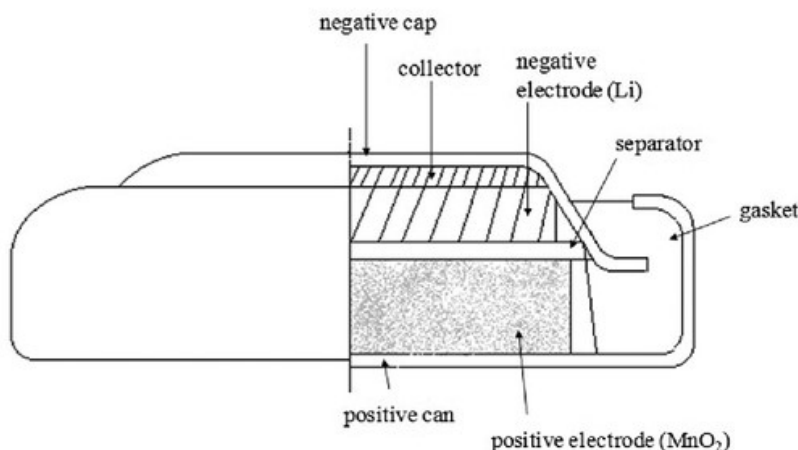


Figure 5.4: Structure of non-rechargeable lithium-ion battery (button cell)

Secondary lithium-ion batteries:

These are the rechargeable lithium-ion batteries. Here electroactive materials are converted into electro inactive materials during discharge and during charging again this electro inactive material can be converted into electroactive materials with the help of external

electricity. Examples: Lithium cobalt oxide battery, Lithium Nickel Cobalt Aluminium Oxide, Lithium iron phosphate etc...

Li-ion batteries can use a number of different materials as battery electrodes. The most common combination is that of lithium cobalt oxide (cathode) and graphite (anode), which is most commonly found in portable electronic devices such as cellphones and laptops. Other cathode materials include lithium manganese oxide and lithium iron phosphate. Li-ion batteries typically use dimethoxy ether as electrolyte with lithium salts.

Lithium cobalt oxide battery

Lithium Cobalt is a mature, proven, industry-standard battery technology that provides long cycle life and very high energy density. The polymer design makes the cells inherently safer than "canned" construction cells that can leak acidic electrolyte fluid under abusive conditions. The cell voltage is typically 3.7 Volts.

Construction of LiCoO₂ battery

- Positive electrode: Lithiated form of a transition metal oxide (lithium cobalt oxide-LiCoO₂ or lithium manganese oxide LiMn₂O₄)
- Negative electrode: Carbon (C) usually graphite (C₆)
- Electrolyte: solid lithium-salt electrolytes (LiPF₆, LiBF₄, or LiClO₄) and organic solvents

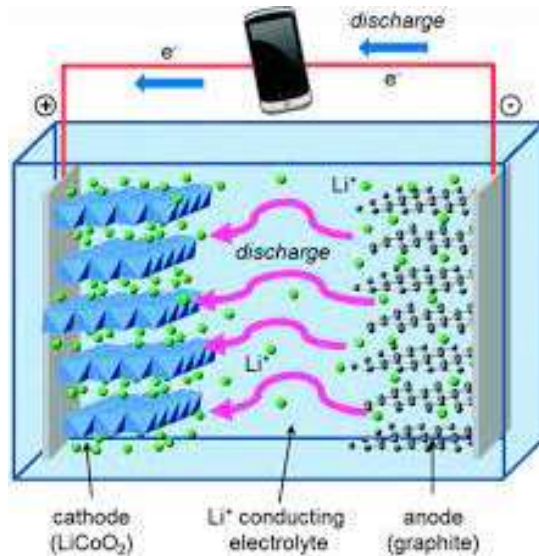


Figure 5.5a: Structure of lithium-ion battery

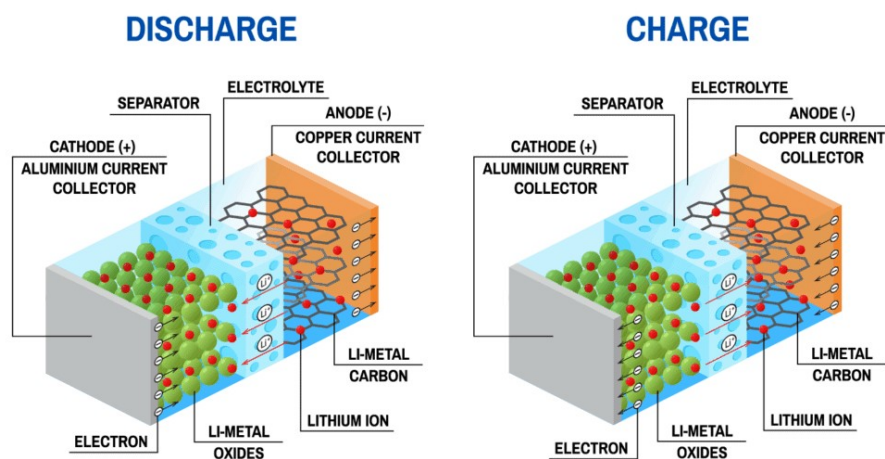


Figure 5.5b: Schematic representation of LiCoO_2 battery working mechanism

Solid electrolyte interphase (SEI) layer: A passivation layer called the solid electrolyte interphase (SEI) is formed on electrode surfaces from decomposition products of electrolytes. The SEI allows Li^+ transport and blocks electrons in order to prevent further electrolyte decomposition and ensure continued electrochemical reactions.

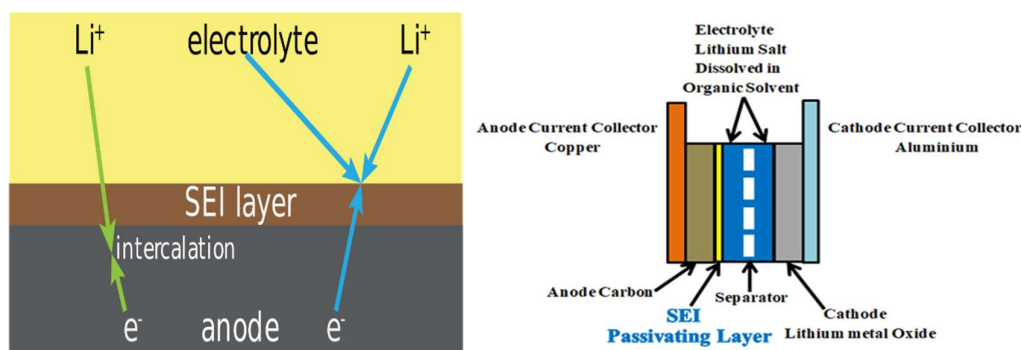


Figure 5.6: Role of solid electrolyte interphase

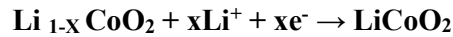
Mechanism of working: in lithium cobalt oxide battery, generally lithium salts are used as electrolytes along with 1, 2 dimethoxy ethane and propylene carbonate. The main reason behind the selection of this solvent is its density and high boiling inert nature. During the discharging reaction the lithium metal in the anode compartment converts in to lithium ion and it moves through SEI and separator towards cobalt cathode. In the cathode it reacts with Cobalt oxide and the electron to form LiCoO_2 . And this process is reversible during charging. During discharging movement of lithium ion takes place from anode to cathode and it moves from cathode to anode when connected to external power supply.

Charging and discharging reaction

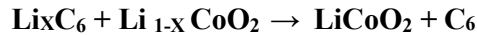
At anode (discharge)



At cathode (discharge)

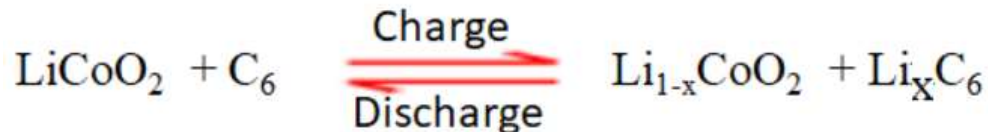


Overall reaction



In the above reaction x can be 1 or 0, With discharge the Co is oxidized from Co^{3+} to Co^{4+} .

The reverse process occurs when the battery is being charged. The chemical reaction that takes place inside the battery is as follows, during charge and discharge operation:



Advantages and limitations of lithium-ion batteries

When compared to other type of commercial batteries such as lead acid and nickel metal hydride batteries lithium batteries have several advantages. Few of them listed below

Advantages of lithium-ion batteries:

- Light weight compared to other batteries
- Higher theoretical energy density than other types of batteries
- Rate of loss of charge is very less
- Operates at higher voltages than other batteries
- High adaptability to several applications
- As there is no memory effect, no need to completely drain the battery
- Low self-discharge compared to lead acid battery
- Easy maintenance

Limitations of lithium-ion batteries:

- Sourcing of lithium is difficult
- As lithium is not abundant, extraction of it doesn't meet global need
- Expensive than the other commercially available battery
- This battery is temperature sensitive; at higher temperature it may degrade with explosion
- Extra protection is required if want to employ them in large scale application

- Disposal may a problem because of heavy metal cathodes

Metal air batteries

Metal air battery is one of the most advanced batteries in which metal incorporated in carbon matrix acts as anodes and air its self-acts as cathode. Amongst all the studied metal air battery lithium air battery is more attractive because of its high energy density along with light weight.

In general lithium ions move between the anode and the cathode across the electrolyte. Under discharge condition, electrons follow from the external circuit to do electric work and the lithium ions migrate to the cathode. During charging the lithium metal in the anode, freeing O_2 at the cathode. In case of non-aqueous lithium air battery Li_2O_2 or LiO_2 are the byproducts. Similarly in aqueous lithium air battery $LiOH$ is the byproduct. Further aqueous lithium air battery requires a protective layer to protect the lithium metal in the anode.

Components and working of lithium air battery

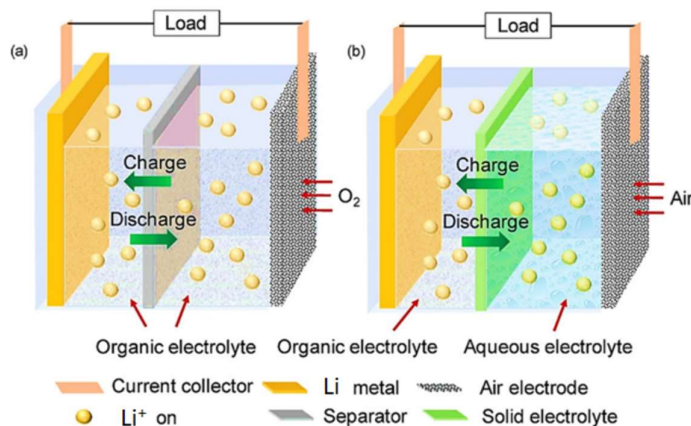


Figure 5.7: lithium air battery

Generally, lithium air batteries consist of lithium anode and porous cathode which will allow air from it. Then air its self-acts as cathode. Also, these lithium air batteries can have different electrolyte systems such as aqueous and non-aqueous. The chemical reaction in these types of batteries is given below.

Non aqueous lithium air battery

Anode: lithium metal

Cathode: Oxygen (air)

Anodic reactions: $Li \rightarrow Li^+ + e^-$

Cathodic reactions: $Li^+ + e^- + O_2 \rightarrow Li_2O^*$

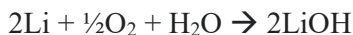
$Li^+ + e^- + Li_2O^* \rightarrow Li_2O_2^*$

Aqueous lithium air battery

Acidic electrolyte



Alkaline aqueous electrolyte



The electrical energy is provided by the chemical reaction between the lithium metal and O₂ from the air. The oxygen electrode has to be porous in order to allow the transport of gasses. The lithium electrode will be protected by a solid electrolyte interphase (SEI), which can be artificially prepared or spontaneously formed by the reaction of lithium with the electrolyte. Lithium–air batteries can also be built in the full solid state by using a solid electrolyte.

The main advantages of lithium air batteries are

- High theoretical specific energy of lithium
- Light weight of lithium
- Use of light weight oxygen
- High theoretical capacity of lithium metal

In the case of non-aqueous lithium air batteries, two main discharge products have been proposed: Li₂O₂ and Li₂O. In the case of aqueous lithium–oxygen batteries, the theoretical specific energies are lower, due to the presence of hydrating water molecules in some of the species involved in the reactions. The main byproduct in the aqueous lithium air battery is LiOH.

- Limitations of lithium air battery
- Poor reversibility
- Inferior long term cyclability
- Electrolyte evaporation

5.2. Super capacitor

Introduction to super capacitor

Supercapacitors, also known as electrochemical capacitors, utilize high surface area electrode materials and thin electrolytic dielectrics to achieve capacitances several orders of magnitude larger than conventional capacitors. In doing so, supercapacitors are able to attain greater energy densities while still maintaining the characteristic high-power density of conventional capacitors. A supercapacitor (SC), also called an ultracapacitor, is a high-capacity capacitor with a capacitance value much higher than other capacitors, but with lower

voltage limits, that bridges the gap between electrolytic capacitors and rechargeable batteries. It typically stores 10 to 100 times more energy per unit volume or mass than electrolytic capacitors, can accept and deliver charge much faster than batteries, and tolerates many more charge and discharge cycles than rechargeable batteries.

Definition: A supercapacitor are double-layer electrolytic capacitor that can store large amounts of energy nearly 10 to 100 times more energy when compared to the electrolytic capacitors. It is widely preferred than batteries because of its faster charging capacity and faster delivery of energy. It has more charging and discharging cycles than rechargeable batteries. The capacitance of this capacitor is also measured in Farad's (F). The main advantage of this capacitor is its efficiency and high-energy storage capacity.

Construction of Super capacitor

Electrochemical capacitors (supercapacitors) consist of two electrodes separated by an ion-permeable membrane (separator), and an electrolyte ionically connecting both electrodes. When the electrodes are polarized by an applied voltage, ions in the electrolyte form electric double layers of opposite polarity to the electrode's polarity. For example, positively polarized electrodes will have a layer of negative ions at the electrode/electrolyte interface along with a charge-balancing layer of positive ions adsorbing onto the negative layer. The opposite is true for the negatively polarized electrode. Additionally, depending on electrode material and surface shape, some ions may permeate the double layer becoming specifically adsorbed ions and contribute with pseudo capacitance to the total capacitance of the supercapacitor.

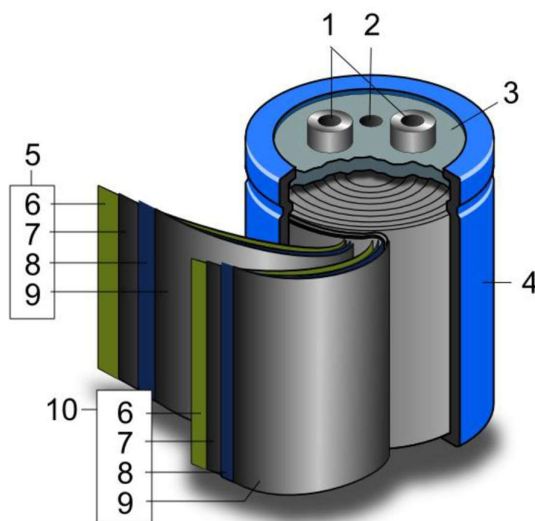


Figure 5.8: Schematic representation of super capacitor (1. terminals, 2. safety vent, 3. sealing disc, 4. aluminum can, 5. positive pole, 6. separator, 7. carbon electrode, 8. collector, 9. carbon electrode, 10. negative pole)

Principles of Energy storage

The supercapacitor has the self-discharging capacity and unlimited charging-discharging cycles. These types of capacitors can work with low voltages (2-3 volts) and can be connected in series to produce high voltage, which is used in powerful equipment. It can store more energy and releases instantly and more quickly when compared to batteries. When this capacitor is connected to the circuit or DC voltage source, the plates are charged and opposite charges are formed on both sides of the separator, which forms a double-layer electrolytic capacitor. To charge a supercapacitor, connect the positive side of the voltage source to the positive terminal of the supercapacitor and the negative side of the voltage source is connected to the negative terminal of the supercapacitor. If the supercapacitor is connected to 15 volts voltage source, then it charges up to 15 volts. As the voltage is increased beyond the applied voltage source, the supercapacitor may get damaged. So, the resistor is connected in series with the voltage source and capacitor to decrease the amount of current flowing through the capacitor and it doesn't get damaged. The constant current supply and limited voltage supply is suitable for the supercapacitor. When the voltage is increased gradually, the amount of current flowing through the capacitor changes. In the fully charged mode, the current drops by default.

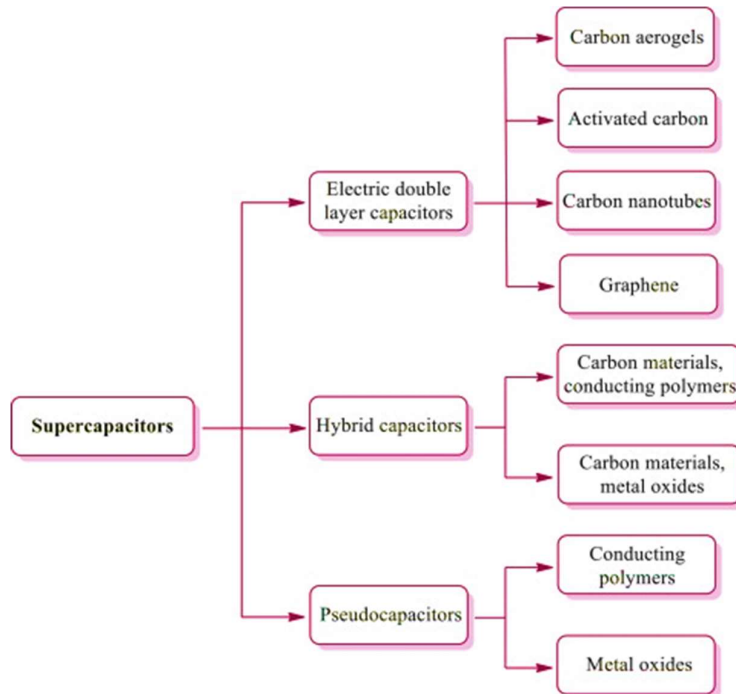


Figure 5.9: super capacitors classification

- **Electrostatic double-layer capacitors (EDLCs)** : EDLCs use carbon based materials as electrodes with higher electrostatic double-layer capacitance, achieving separation of charge in a Helmholtz double layer at the interface between the surface of a conductive electrode and an electrolyte.
- **Electrochemical pseudo-capacitors:** Use metal oxide or conducting polymer electrodes with a high amount of electrochemical pseudo capacitance additional to the double-layer capacitance. Pseudo capacitance is achieved by Faradaic electron charge-transfer with redox reactions, intercalation or electro sorption.
- **Hybrid capacitors:** Hybrid capacitors are lithium-ion capacitor, use electrodes with differing characteristics.

Electrostatic double-layer capacitors (EDLCs)

Electrochemical double-layer capacitors (EDLCs) are constructed from two similar carbon-based electrodes, an electrolyte, and a separator. These type of super capacitors store the energy very similar to conventional capacitors. These EDLCs store charge electrostatically, or non-Faradaically, and there is no transfer of charge between electrode and electrolyte. These EDLCs store the charge using an electrochemical double-layer. As voltage is applied, charge accumulates on the surface of both the electrodes. This is followed by the natural attraction of unlike charges, ions in the electrolyte solution diffuse across the separator into the pores of the electrode of opposite charge. In this architecture electrode are designed to avoid recombination of ions. Due to this a double-layer of charge is produced at each electrode. These double-layers, coupled with an increase in surface area and a decrease in the distance between electrodes, allow EDLCs to achieve higher energy densities than conventional capacitors. Due to the non-transferring of charges between electrolyte and electrode, there are no chemical or composition changes associated with non-Faradaic processes. For this reason, charge storage in EDLCs is highly reversible, which allows them to achieve very high cycling stabilities. The performance characteristics of an EDLC can be adjusted by changing the nature of its electrolyte.

An EDLC can utilize either an aqueous or organic electrolyte. Aqueous electrolytes, such as H_2SO_4 and KOH , generally have lower minimum pore size requirements compared to organic electrolytes, such as acetonitrile. In these EDLCs generally carbon-based materials are used because of their higher surface area, lower cost, and more established fabrication techniques than other materials, such as conducting polymers and metal oxides. Different forms

of carbon materials that can be used to store charge in EDLC electrodes are activated carbons, carbon aerogels, and carbon nanotubes.

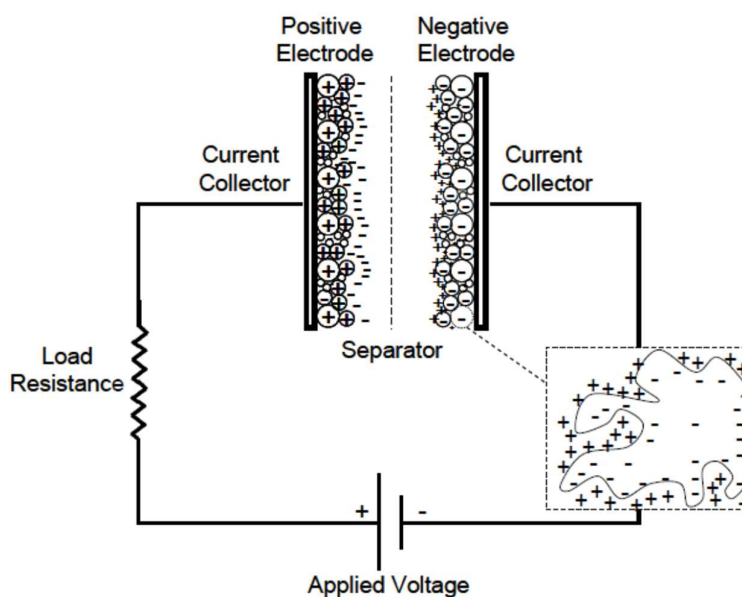


Figure 5.10: Electrolytic double layer capacitor

Electrochemical Pseudo capacitance:

Applying a voltage at the electrochemical capacitor terminals moves electrolyte ions to the opposite polarized electrode and forms a double-layer in which a single layer of solvent molecules acts as separator. Pseudo capacitance can originate when specifically adsorbed ions out of the electrolyte pervade the double-layer. This pseudo capacitance stores electrical energy by means of reversible redox reactions on the surface of suitable electrodes in an electrochemical capacitor with an electric double-layer. Pseudo capacitance is accompanied with an electron charge-transfer between electrolyte and electrode coming from a de-solvated and adsorbed ion whereby only one electron per charge unit is participating. This faradaic charge transfer originates by a very fast sequence of reversible redox, intercalation or electrosorption processes. The adsorbed ion has no chemical reaction with the atoms of the electrode since only a charge-transfer take place. The electrons involved in the faradaic processes are transferred to or from valence electron states (orbitals) of the redox electrode reagent. They enter the negative electrode and flow through the external circuit to the positive electrode where a second double-layer with an equal number of anions has formed. The electrons reaching the positive electrode are not transferred to the anions forming the double-layer, instead they remain in the strongly ionized and "electron hungry" transition-metal ions

of the electrode's surface. As such, the storage capacity of faradaic pseudo capacitance is limited by the finite quantity of reagent in the available surface.

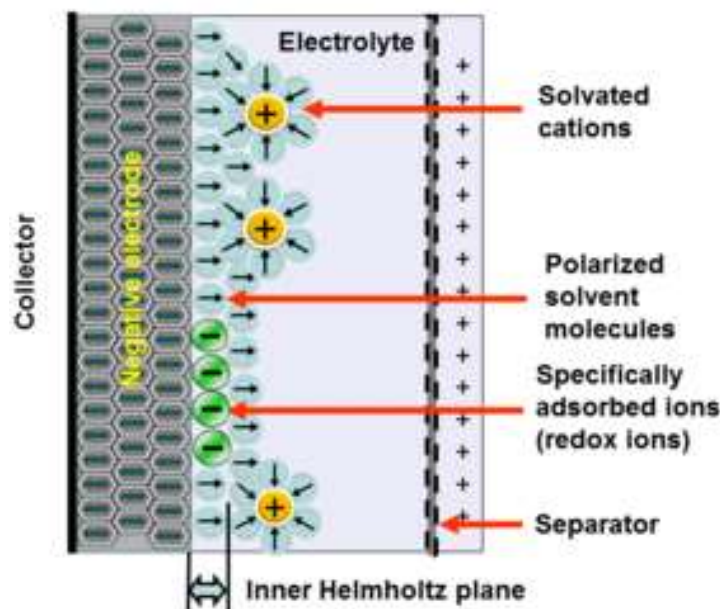


Figure 5.11: Electrochemical pseudo capacitance

The pseudo-capacitors store electrical energy by electron charge transfer between electrode and electrolyte. This can be done by Redox (reduction-oxidation reaction). Reduction-oxidation: Reduction-oxidation occurs when one atom gains (or losses) an electron and another atom lose (or gains) an electron. In pseudo capacitors oxidation-reduction reaction occurs in between electrode and electrolyte solution. In pseudo-capacitors, the charge storage (capacitance) results from the charge transfer between electrolyte and electrode. When voltage is applied to the pseudo-capacitor, the charged atoms or ions in the electrolyte move towards the oppositely charged electrode. In between the surface of the electrode and adjacent electrolyte, two electric layers or electric double layers are formed. These two electric layers are separated by electrolyte molecules. The charged atoms in the electrolyte within the double layer act as electron donors and transfers electrons to the atoms of electrode. As a result, the atoms in electrode become charged. Thus, charge is stored at electric double layers. The pseudo-capacitors use conductive polymers or metal oxide as electrodes. The amount of electric charge stored in a pseudo-capacitor is directly proportional to the applied voltage.

Hybrid Capacitors

Hybrid supercapacitors have higher operating voltage (3.8 V maximum) and much higher capacitance and energy density (up to 10 times) than symmetric supercapacitors. They also have much lower self-discharge and standby current. They can be discharged to zero volts for

safety; hybrid supercapacitors cannot be discharged fully. From a construction standpoint, they are very similar, but a hybrid supercapacitor uses an anode made from graphite laced with lithium and a different electrolyte. Utilizing both Faradaic and non-Faradaic processes to store charge, hybrid capacitors have achieved energy and power densities greater than EDLCs without the sacrifices in cycling stability and affordability that have limited the success of pseudo capacitors. The schematic representations of hybrid capacitors are given below.

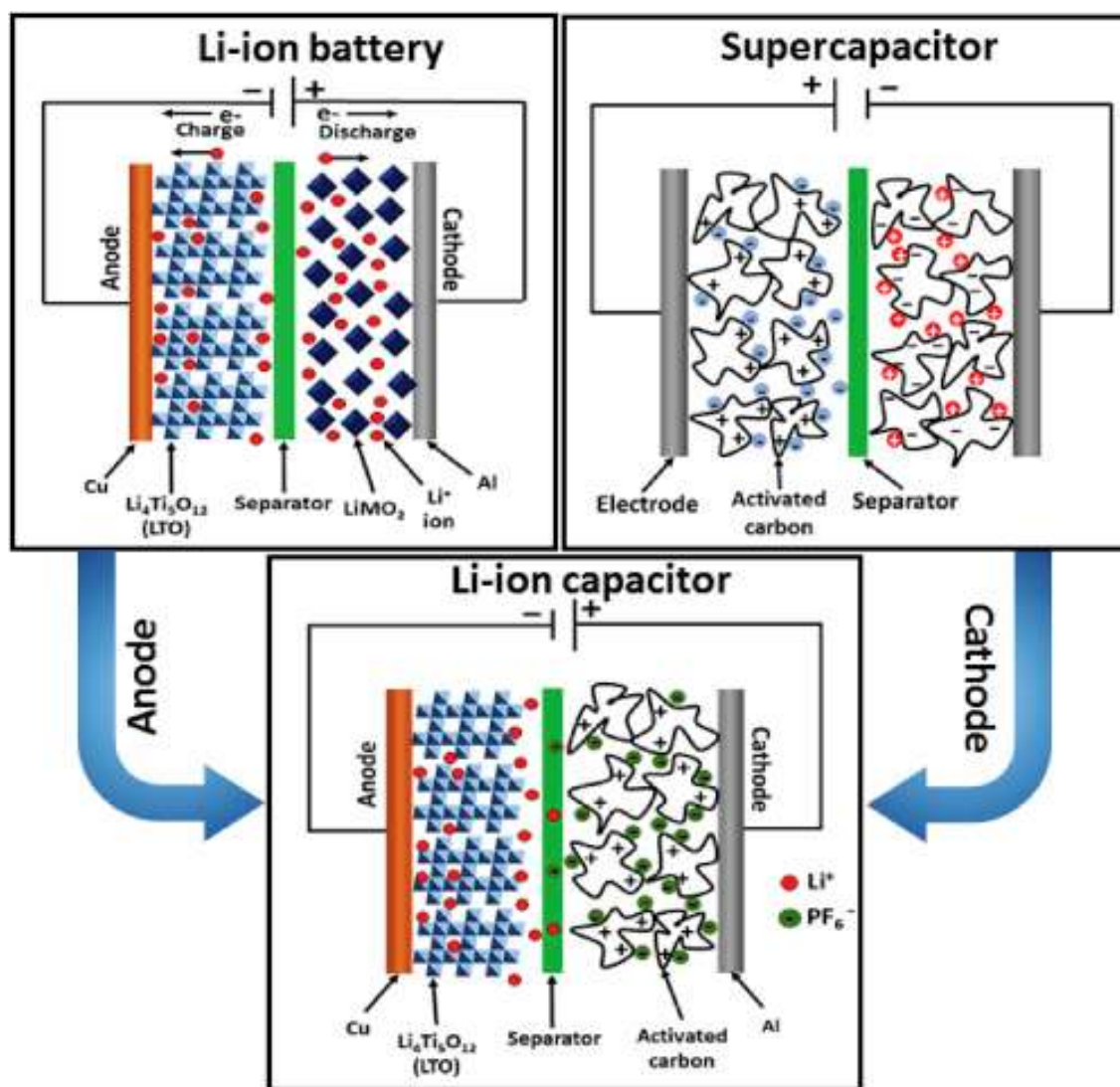


Figure 5.12: Schematics representation of hybrid capacitor

Importance of Electrolytes in super capacitors

Characteristics of electrolyte used in super capacitors

- Wide potential window
- High ionic conductivity

- High chemical and electrochemical stability
- High chemical and electrochemical inertness to ES components
- Wide operating temperature range
- Well-matched with the electrolyte materials
- Low volatility and flammability
- Environmentally friendly
- Low cost

Advantages and limitations of super capacitor

These super capacitors are having advantages as well as limitation some of them highlighted below.

Advantages of super capacitor

- High energy storage.
- Wide operating temperature (-40 °C to 60 °C).
- Eco-friendly.
- Quick charging time.
- Maximum life cycle.
- High cycle efficiency (95%).
- High specific power up to 17 kW/kg.
- Extremely low internal resistance.
- Safe

Limitations of super capacitors

- 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 cells have low voltages, and so serial connections are needed to obtain higher voltages.
- Requires expert electronic control.
- Cannot be used in AC and high frequency circuits.
- High cost.

Applications of super capacitor

- In startup mechanism for Automobiles.
- Used in Diesel engine start up in submarines & tanks.
- In quickly recharged electric bus

- Backup power system in missiles.
- Power source for laptops, flash in cameras.
- Voltage stabilizer.
- To deliver high power and bridge power gaps
- Industrial and electronic applications
- Used in wind turbines, electric and hybrid vehicles
- Regenerative braking to release the power in acceleration
- To start power in start-stop systems
- Regulate voltage in the energy grid
- To capture and assist the power in lower loads and lifted loads
- Back-ups the power in a quick discharging state.

5.3. Photovoltaics

Introduction:

Solar energy is a renewable energy and it inexhaustible. The earth is receiving approximately 1.8×10^{11} MW of energy which is thousands of times larger than the requirement of energy for present consumption. Thus, solar energy is the only energy that fulfils all our present and future energy needs if we utilize properly. Solar energy can be directly converted in to heat energy or electricity. A solar cell, or photovoltaic cell, is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect.

Background: After Edmund Bequerel discovered the photovoltaic effect, William Adams and Richard Day observed the photovoltaic effect in a sample of selenium placed between two metal electrodes. This was the first solid photovoltaic device. The photovoltaic effect in this device originates from the association of selenium and metal. Twenty years later, Charles Fritts developed the first large-area photovoltaic device. Each of these early cells was comprised of a metal electrode/ semiconductor/ semitransparent thin metal electrode with a bottle neck to transmit incident light. Due to this limitation, the resulting power conversion efficiency was limited to less than 1%. In the 1950s, PV cells achieved significant improvement over PCE and found a first practical application. In 1954, Bell Labs revealed the first high-power silicon PV cell, which used a p-n junction and reported a PCE of 6%. Excited by this outstanding achievement, the New York Times forecasted that solar cells would eventually harness the “limitless energy of the sun.” In 1958, PV array-powered radios appeared on the US Vanguard I space satellite, and this was the first time PV technology was practically utilized. In this

period, there also appeared PV cells made of cadmium sulphide, gallium arsenide, cadmium telluride, and indium phosphide. However, each technology had its own disadvantage. For example, cadmium, which is used in CdS and CdTe PV cells, is a toxic element, GaAs-based PV cells are very expensive to produce, and the indium used in InP PV cells is limited. Therefore, silicon-based PV cells were regarded as the most promising PV technology.

Advantages of Solar Cells

- Solar cell is renewable energy which can be continuously drawn from the sun.
- It is economic friendly energy because once it installed there will be minimum maintenance charges for small usage.
- Solar energy is environment friendly and green energy because it doesn't produce any greenhouse gasses and no pollutants.
- It doesn't involve any combustion reaction or radioactive residue hence no pollution
- Disadvantages of Solar Cells
- Space utilization: Solar cells required large area for installation
- It requires high investment cost for a big power plant
- During the rainy season power production is less hence grid maintenance will be difficult.
- Solar energy is produced only in the day time hence storage will be a big challenge

Classification of solar cells

The solar cells are broadly classified as i) Inorganic solar cells and ii) Organic/polymer solar cells. Amongst them inorganic solar cells are currently in global market. The amorphous silicon solar cells are classified under inorganic solar cells. There are three types of PV cell technologies that dominate the world market: monocrystalline silicon, polycrystalline silicon, and thin film. Higher efficiency PV technologies, including gallium arsenide and multi-junction cells, are less common due to their high cost, but are ideal for use in concentrated photovoltaic systems and space applications.[3] There is also an assortment of emerging PV cell technologies which include Perovskite cells, organic solar cells, dye-sensitized solar cells and quantum dots solar cells.

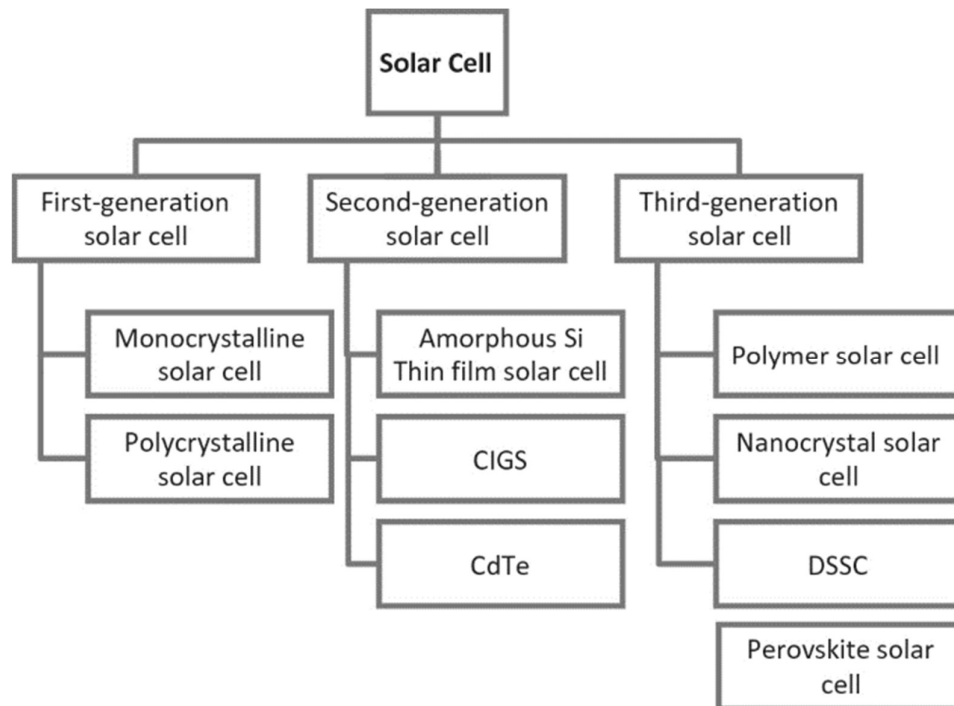


Figure 5.13: Classification of solar cells

Amorphous silicon solar cells

Construction: A typical silicon solar cell consists of n-type material (Phosphorus doped silicon) and a p-type (Boron doped silicon) material made of silicon. In the fabrication of device these n-type and p-type materials are joined to form a p-n junction. On top of n type connecting front electrodes are placed. The metal back contact is attached to p-type layer. An antireflective coating is filled in between the front electrodes to avoid the reflection of sunlight. Finally p-type and n-type layers are joined externally to the circuit. The complete solar cells are sealed to avoid the environmental contact.

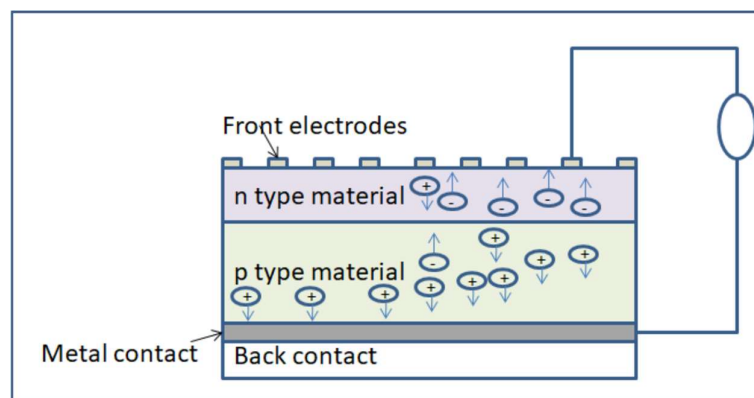


Figure 5.14: Representation of amorphous silicon solar cells

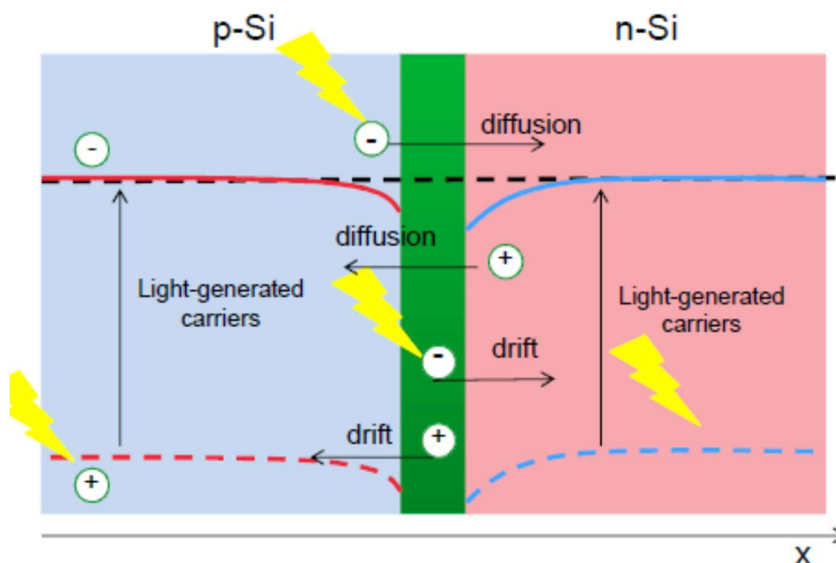


Figure 5.15: Working mechanism of Silicon solar cells

Working: When sunlight is incident on solar cells photon strikes on p-n junction. Then electron hole pair will be created at the junction by the absorption of photon. This electron hole pair diffuses towards respective layer based on affinity. The electrons diffuse towards n-type later and holes are diffused towards p-type layer. These layers are connected externally through a circuit, hence current will be generated.

Organic photovoltaics

Brief history: The first two-component OPV was proposed by Tang in 1986, but efficiencies remained very low for several years due to the reliance on bilayer cells. Excitons can only dissociate at the interface between donor and acceptor, and can generally only diffuse approximately 10nm before decaying back to the ground state. In contrast, a total active layer thickness of above 100nm is usually required to absorb light efficiently – meaning bilayer cells are either too thin to properly absorb, or too thick for efficient exciton dissociation.

The solution to this was proposed in 1995, and is known as the bulk heterojunction (BHJ) cell.^{9,10} Here instead of a strict two-layer system, the donor and acceptor materials are intimately mixed at the nanoscale level – allowing interfaces at an appropriate diffusion distance to be dispersed across the active layer whilst maintaining the necessary thickness for absorption.

Introduction: An OPV cell is a type of solar cell where the absorbing layer is based on organic semiconductors (OSC) – typically either polymers or small molecules. For organic materials

to become conducting or semiconducting, a high level of conjugation (alternating single and double bonds) is required. Conjugation of the organic molecule results in the electrons associated with the double bonds becoming delocalized across the entire length of conjugation. These electrons have higher energies than other electrons in the molecule, and are equivalent to valence electrons in inorganic semiconductor materials. Laboratory OPV cells manufactured on glass. However, in organic materials, these electrons do not occupy a valence band but are part of what is called the 'highest occupied molecular orbital' (HOMO). Just like in inorganic semiconductors, there are unoccupied energy levels at higher energies. In organic materials, the first one is called the lowest unoccupied molecular orbital (LUMO). Between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the OSC is an energy gap - often referred to as the band gap of the material. With increased conjugation, the band gap will become small enough for visible light to excite an electron from HOMO to LUMO.

The bandgap in organic semiconductors is called HOMO-LUMO gap and it is determined by the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), it is usually in the range of 1-4 eV, similar as the bandgap of inorganic semiconductors.

Exciton: An exciton is a bound state of an excited electron and a hole which are attracted to each other and bounded by Coulomb forces.

Organic solar cells: As with other PV technologies, the purpose of an OPV is to generate electricity from sunlight. This is achieved when the energy of light is equal to or greater than the band gap, leading to absorption and excitation of an electron – from the HOMO to the LUMO. The excited electron will leave behind a positively-charged space known as a 'hole'. Due to the opposite charges of the hole and electron, they become attracted and form an electron-hole pair, also known as an 'exciton'. To remove the charged particles from the solar cell, the electron-hole pair must be separated, and this process is known as 'exciton dissociation'. Typically in an inorganic semiconductor, the attraction between the electron and hole is small enough to be overcome by thermal energy at room temperature. This is due to a high dielectric constant – meaning there is significant screening between the electron and hole, reducing the attraction between them. The ease in separating the electron and hole allows easy exciton dissociation.

Working mechanism of organic solar cells:

When sunlight falling on the cell some photons of the light are absorbed by solar cell. Some of the absorbed photons will have energy greater than the energy gap between valence band and conduction band in the semiconductor crystal. Hence, one valence electron gets energy from one photon and becomes excited and jumps out from the bond and creates one electron-hole pair. These electrons and holes of e-h pairs are called light-generated electrons and holes. The light-generated electrons near the p-n junction are migrated to n-type side of the junction due to electrostatic force of the field across the junction. Similarly, the light-generated holes created near the junction are migrated to p-type side of the junction due to same electrostatic force. In this way a potential difference is established between two sides of the cell and if these two sides are connected by an external circuit current will start flowing from positive to negative terminal of the solar cell.

The photoactive layer in modern organic solar cells usually consists of two materials, electron-donor and electron-acceptor, in order to successfully dissociate the tightly bound exciton that occurs in organic semiconductors. The exciton is dissociated by the electric field that arises at the donor-acceptor interface, which occurs because of the potential difference between the materials. The electron-donor is usually a polymer and the electron-acceptor a fullerene, small molecules or another polymer. The photovoltaic mechanisms in an organic solar cell can be described by four fundamental steps: Exciton generation, Exciton diffusion, Exciton dissociation and Charge carrier transport, which are illustrated in following figure.

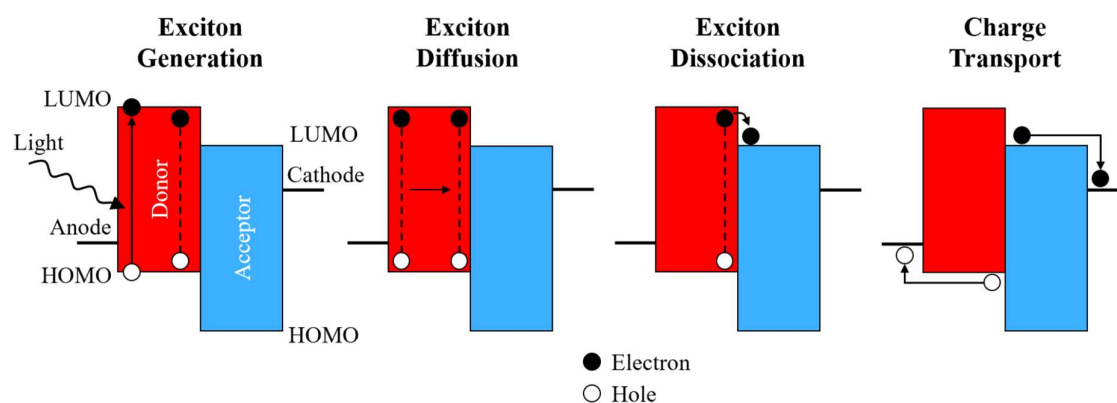


Figure 5.16: Steps involved in the current generation

Step 1. Exciton generation: Upon illumination of the active material, an electron is excited to the LUMO by absorption of a photon with energy larger than the HOMO-LUMO gap (band gap). The light absorption will generate electron-hole pairs, so-called excitons, where the electron and the hole are attracted to each other and bounded by Coulomb forces.

Step 2. Exciton diffusion: The generated exciton can diffuse through the material to the donor-acceptor interface. Due to the short lifetime of the exciton in organic materials, the exciton diffusion length is in order of 10 nm.

Step 3. Exciton dissociation: If the exciton reaches the donor-acceptor interface within its lifetime, it dissociates into a free electron and hole due to the local electric fields caused by an energy level offset between the two materials.

Step 4. Charge carrier transport: Free charge carriers are transported to the electrodes through the donor and acceptor material by an internal electric field caused by electrodes with different work functions. The electrons are collected at the cathode and the holes at the anode.

Device architecture

The device geometry of typical organic solar cells is illustrated in Figure. When designing the solar cells, it is preferable to choose materials for substrates, electrodes and electron transporting layer/hole transporting layer (ETL/HTL) with as large bandgap as possible, so all absorption happens in the active layer. Depending on if the solar cell is illuminated through the anode or the cathode the performance of the device can be different. That may depend on parasitic absorption from one of the materials before the active layer. Parasitic absorption refers to an optical absorption process that does not generate an electron/hole pair.

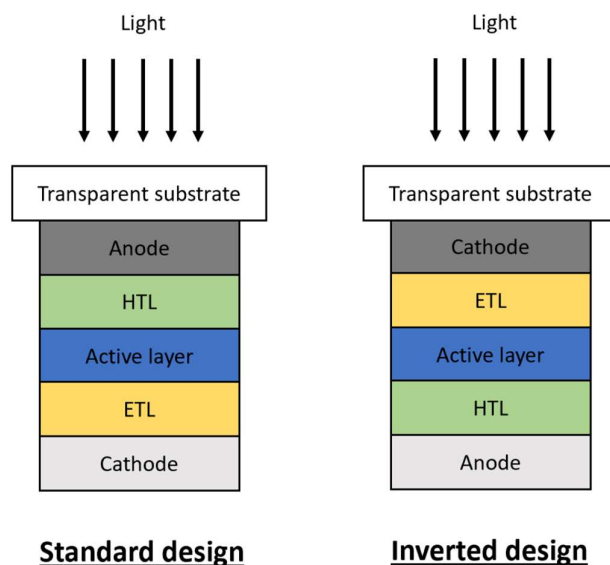


Figure 5.17: Device architecture of organic solar cells

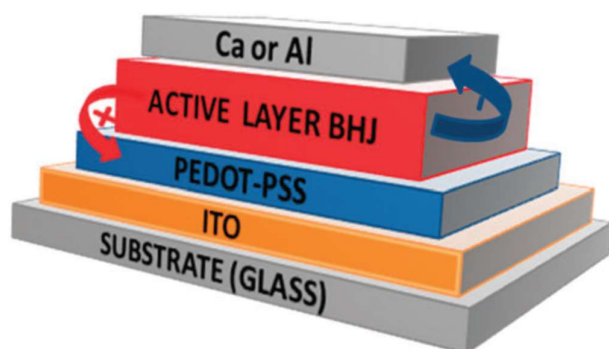


Figure 5.18: Bulk heterojunction layer configuration

Bulk hetero junction solar cells: Bulk heterojunctions are made by creating interpenetrating networks of the donor and the acceptor components. With the two components interpenetrating one another, an exciton will never be far from the interface. The interfacial area will be large and the diffusion length of the excitons can be short. This puts many constraints on how to manage the morphology of the interpenetrating network. This is due to the fact that once the disassociation has taken place, the electron and the hole need to have a clear path to get to the cathode and the anode respectively. If the morphology is such that the path closes somewhere along the way, the electron and the hole will be lost. Bulk heterojunctions, are described as systems of interpenetrating “fingers” of the donor component and the acceptor component sandwiched between the anode and cathode. This system has a large interfacial area, the interface is not far from where the exciton is generated, and once the exciton disassociates, the electron and the hole will have a clear path to their respective electrodes. Creating perfecting aligned interdigitating fingers.

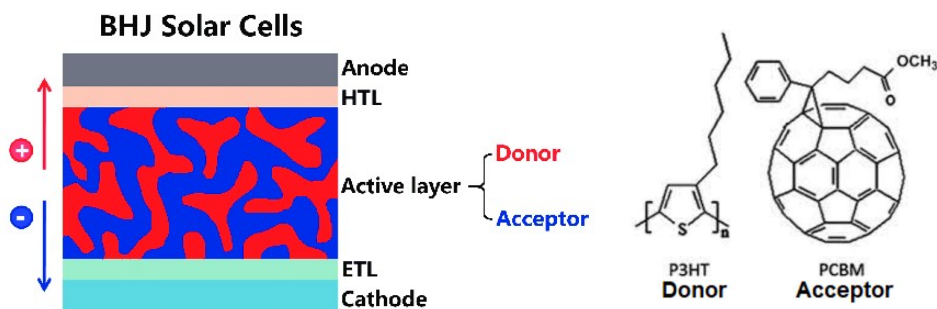


Figure 5.19: Representation of bulk heterojunction

Recombination

At several stages, the electron and hole can recombine – at which point the absorbed energy used for initial excitation is wasted. This can happen in two ways i) The initially-produced electron-hole pair recombine before exciton dissociation. ii) Free electrons and holes can recombine, regardless of their source. These two steps lead to energy loss.

Materials used in organic photovoltaics

Active materials: in general, thiophene based conjugated molecules/polymeric structures are employed as active layers in organic photovoltaics. Because these materials have excellent thermal and electrical stability with adoptability. One of such material is poly 3 hexyl thioophene. This material having very broad absorption spectra which is matching to solar spectrum hence it has been employed as active layer. The structure of poly(3hexylthiophene) is represented in below figure.

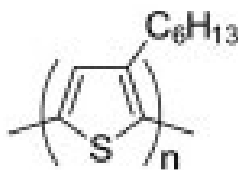


Figure 5.20: Synthesis of poly(3hexylthiophene)

In the above synthesis 2,5 dibromo 3 hexyl thiophene is treated with Grignard reagent to obtain the mono substituted product. Then this monosubstituted Grignard product is converted to polymer by the use of catalyst Dichloro(1,2-bis(diphenylphosphino)ethane) nickel. Then the obtained polymer is purified by reprecipitation using methanol.

Hole transport layer: The HTL material is chosen based on many criteria. In order to create the driving force for holes to move towards the anode of the device, the HTL should have a high enough work function to match the HOMO of the donor. To prevent the drift of electrons towards the anode, the HTL should have its conduction band (CB) above the LUMO of the material. Another important criterion is, it should be transparent to light to pass through in to active layer. Further it should be cost effective. In general Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) is employed as HTL in organic photovoltaics because of its transparency and tunable work function. The structure of PEDOT: PSS is given below.

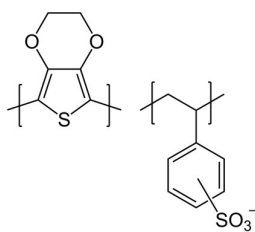
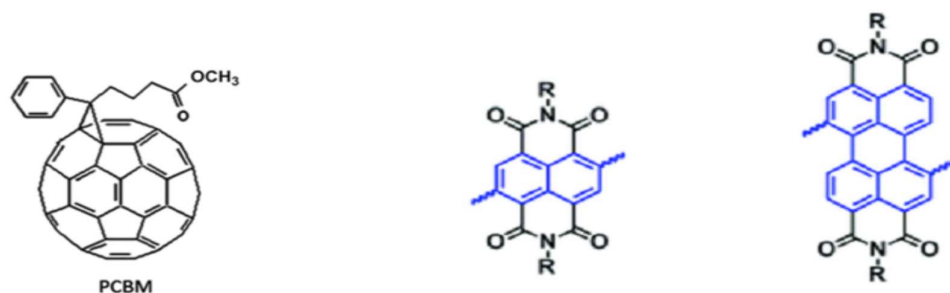


Figure 5.21: Structure of PEDOT: PSS

Electron transport layer: The main role of an electron transport layer (ETL) between the active layer and the cathode is to reduce the recombination of the free charge carriers (electrons and holes or exciton) with their counterparts. The LUMO level of the ETL material must be aligned to the LUMO level of the cathode material so as not to render the electron transport towards the cathode. Examples of ETL material are PCBM-61, Naphthalene and perylene dimides are represented below.



Phenyl-C61-butyric acid methyl ester Naphthalene diimide, Perylene diimide

Figure 5.22: Structures of electron transport materials

Dye Sensitized Solar Cells

Photovoltaic effect is a process in which conversion of sunlight directly in to electrical energy. The process of light dependent voltage between two electrodes in an electrode system was first discovered by Henry Becquerel in the year of 1839. In 1954 first silicon solar cell was discovered the initial efficiency was found to be 6%. The discovery of DSSC was started in 60s by German scientists Gerischer and Tributsch. Later Michel Grätzel a Swiss scientist introduced porous electrode consists of Nano TiO_2 for construction of DSSC, which helped to increase the efficiency of solar cells up to 7%. This discovery of DSSC is a pioneer in the field of photovoltaics, thereafter vast research is going on in the field.

Quantum dots (QDs)

Quantum dots are tiny particles or nanocrystals of a semiconducting material with diameters in the range of 2-10 nanometers. When they are illuminated by UV light, an electron in the quantum dot can be excited to a state of higher energy. In the case of a semiconducting quantum dot, this process corresponds to the transition of an electron from the valence band to the conductance band. The excited electron can drop back into the valence band releasing its energy as light. The color of that light depends on the energy difference between the conductance band and the valence band. Potential applications of these quantum dots include

solar cells, LEDs, lasers, quantum computing, cell biology research and medical imaging. Examples for QD sensitizers such as CdS, CdSe, PbS, PbSe, CdTe etc.

Quantum dot sensitized solar cells

It consists of two electrodes cathode and anode generally cathode is made of graphite or platinum. Anode is made of transparent conducting oxide such as Indium tin oxide. Anode is coated with a layer of nano porous materials (TiO_2 or ZnO). Further these nano porous materials are coated with CdSe quantum dots as light absorbing materials. Here the nano porous materials act as semiconductor also it provides road way for electrons. The quantum dots with suitable energy levels helps in electron transfer process. A triiodide electrolyte system is employed in between the electrodes, which helps in electron transfer process.

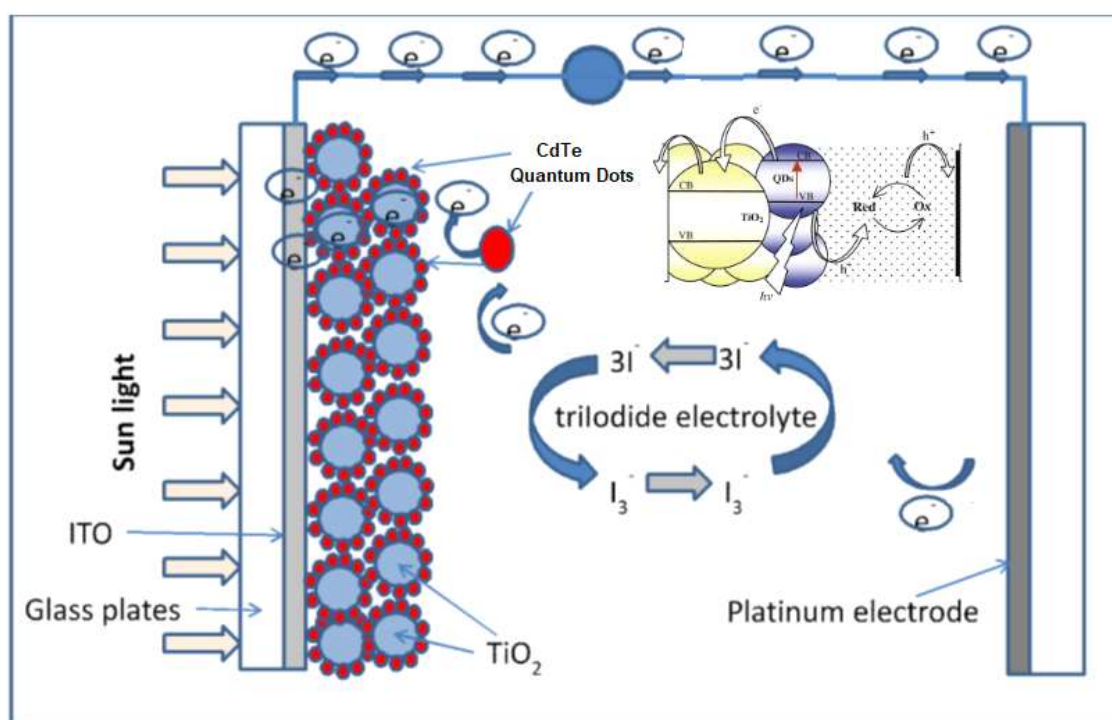


Figure 5.23. Construction and working of quantum dye sensitized solar cells.

Mechanism of Working

When light photon strikes the solar cell, it passes through ITO layer and it reaches the quantum dots. Once the photon hits the quantum dots, it undergoes excitation with the liberation of electron, which travels through the network TiO_2 nanoparticles (because of matching in energy levels) and finally it reaches to cathode. The cell is completely filled with Triiodide electrolyte. The electron from the cathode directly reduces the triiodide molecule to three iodide molecules. Further this iodide molecule oxidizes to form triiodide again with the

liberation of electrons, which can be easily absorbed by quantum dots. And similar cycle continues whenever sunlight falls on the solar cells.

5.4. Green Fuel

Demand for green fuel technologies is rising given their potential to accelerate the transition to more sustainable forms of energy while still supporting current energy models with all their regional variations. Amongst all green fuels hydrogen is considered to be the best alternative. Hydrogen is a zero-emissions source of fuel for trains, buses and cars. It can be used as a feedstock gas for industries such as chemical, refining and steel. In addition, it is a source of heat and power for buildings, and can buffer energy generated from renewable sources.

Hydrogen Production

Over the last decades, an increasing interest has been devoted to the generation of hydrogen from solar-powered water splitting devices as a direct approach to generate a clean and sustainable energy vector. Among the different alternatives, a direct photocatalytic process is the most straightforward, where a light absorber is able to produce hydrogen and oxygen under light irradiation without an external bias.

Photocatalytic water splitting:

The photocatalytic generation of solar fuels by suitable photocatalytic materials suspended in water is certainly one of the most attractive and challenging pathways for decarbonizing current energy systems. From the outside, it seems as a simple approach combining water, solar light, and a semiconductor. However, each of these components plays a key role in the overall efficiency of the reaction, and mostly, many factors including thermodynamic, kinetic, and other requirements hold back this technology from its maximum potential. Photocatalyst must be semiconductor. The minimum requirement is to generate electrons-hole pairs due to irradiation, normally by a UV-vis source. But it must also have a suitable crystalline phase, which ensures the formation of the electron-hole pairs and does not favor its recombination.

Material requirement of photo catalysts

- Band gap: band gap of the materials used in catalysis should be more than 1.23 eV and sufficiently small to make efficient use of solar spectrum (<3eV). Ans it should be having band levels suitable for water splitting.
- High crystallinity: Defects can act as recombination sites
- Long term stability: Charge transfer used for water splitting and not for corrosion

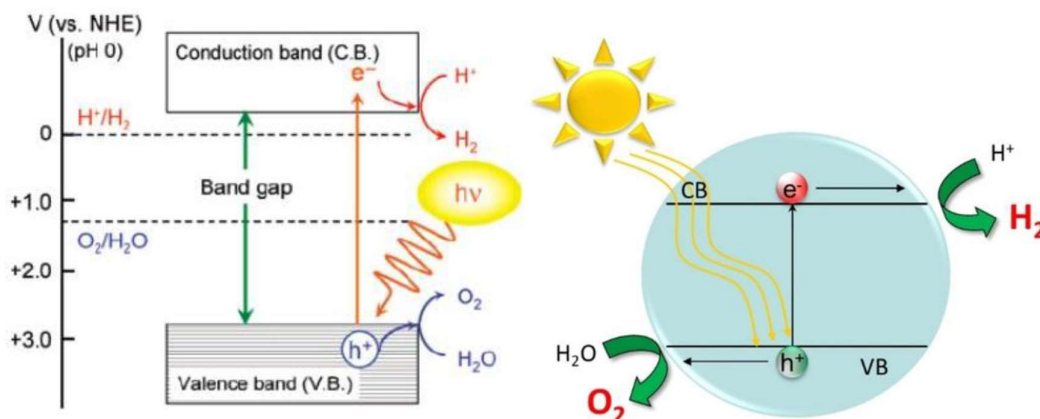


Figure 5.24: Band diagram of catalyst

Water splitting electrode should be

- Efficient light absorber
- Charge separator
- Charge conductor

Photocatalytic water splitting is an artificial photosynthesis process with photocatalysis in a photoelectrochemical cell used for the dissociation of water into its constituent parts, hydrogen and oxygen, using light.

Water splitting electrodes work much like the leaves of the plants during photosynthesis. They absorb energy from the sunlight and use it to generate charge carriers. Negatively charged electrons and positively charged holes. These charges are delivered to water and water molecules swipe electron away to form hydrogen gas and whereas holes strip the molecules of electron to form oxygen gas.

Hydrogen Storage:

Hydrogen energy storage is an area of growing interest due to the greater storage capacity offered by hydrogen over batteries, as well as the benefits offered by the renewable generation afforded by hydrogen as a fuel. Hydrogen can be stored either as a gas or as a liquid. Hydrogen gas storage typically requires the use of high-pressure tanks (350-700 bar or 5000-10,000 psi), while liquid hydrogen storage requires cryogenic temperatures to prevent it boiling back into a gas (which occurs at -252.8°C). Hydrogen can also be stored on the surface of (adsorption) or within solid materials (absorption).

General method of hydrogen storage

In modern practice hydrogen can be stored in three different ways

1. As a gas under high pressures (in pressure cylinder)

2. In liquid form under cryogenic temperatures (at low temperature storage)
3. On the surface of or within solid and liquid materials (Metal hydrides as well as carbon nano tubes and metal organic frame works)