Chapter 2

Solar Cell

2.1 Solar Cell

Solar cell (photovoltaic cell or photoelectric cell) is a solid state device that converts the energy of sunlight into electricity by photovoltaic or photoelectric effect. In photo voltaic effect, generated electrons are transferred between different bands (i.e. from the valence band to conduction bands) within the material resulting in the buildup of a voltage between two electrodes. In photoelectric effect electrons are ejected from a material's surface upon exposure to radiation.

The photovoltaic effect was first observed by French physicist A. E. Becquerel in 1839. The first solar cell was made in 1883 by Charles Fritts, who coated the semiconductor Selenium with an extremely thin layer of gold to form the junction. In 1946, Russell Ohl patented the modern semiconductor junction solar cell. The first commercial solar cell was first developed by Daryl Chapin, Calvin Souther Fuller and Gerald Pearson in 1954 using a diffused silicon p-n junction.

2.2 Generations of Solar Cell

Solar cells are classified into three generations. The generation indicates the order in which each became important. At present there is a concurrent research into all three generations. The first generation technologies are still the most highly represented in commercial production accounting for over 85% of all cells produced.

2.2.1 First Generation Solar Cell

First generation solar cells are the silicon based photovoltaic cell. Generally silicon based solar cells are more efficient and long lasting than non-silicon based solar cells. They are prevalent due to their high efficiency. Single junction silicon devices are approaching the theoretical limiting efficiency of 33%.

First generation solar cells are the most expensive to produce because of the amount of money it takes to extract silicon from sand and then purify it before growing the crystals. First generation cells consist of large area, high quality and single junction devices. The technology involves high energy and labor inputs. There are four types of silicon based cells used in the production of solar panels for commercial use i.e. monocrystalline silicon cell, polycrystalline silicon cell, amorphous silicon cell and hybrid silicon cell.

Construction of solar cells

Silicon based solar cells are made using single crystal wafers, polycrystalline wafers or thin films. Single crystal wafers are made from a large crystal ingot which has been grown at 1400°C. It is very expensive process. The silicon must be of very high purity and have a near perfect crystal structure. Casting method is used to produce polycrystalline wafers. In this method molten silicon is poured into a mould and allowed to set, and then it is cut into wafers. Polycrystalline silicon is significantly cheaper to produce. Amorphous silicon based solar cells are based on thin film technologies. Thin films are made by depositing silicon onto a glass substrate from a reactive gas such as silane.

For solar cell production, silicon is doped by atoms to create n-type or p-type region thereby producing a p-n junction. The doping can be done by temperature diffusion process. The wafers are placed in a furnace with the dopant introduced a vapor. In thin film devices the introduction of dopant can occur during the deposition of the films or layers. Electrical contacts are made to the front and the back of the cell by evaporating or screen printing metal on to the wafer.

Working of Solar cell

Solar cells are made of two layers of silicon. One layer is p-type silicon and another is n-type silicon. When the p layer is kept next to n layer a diode is created. When a photon hits the silicon the energy of the photon can be absorbed by a silicon atom freeing an electron from the atom and leaving behind a hole. The electron then moves towards the n-type layer while the hole moves towards the p type layer. Hence, current flows through the solar cell. The working of solar cell is shown in figure 2.

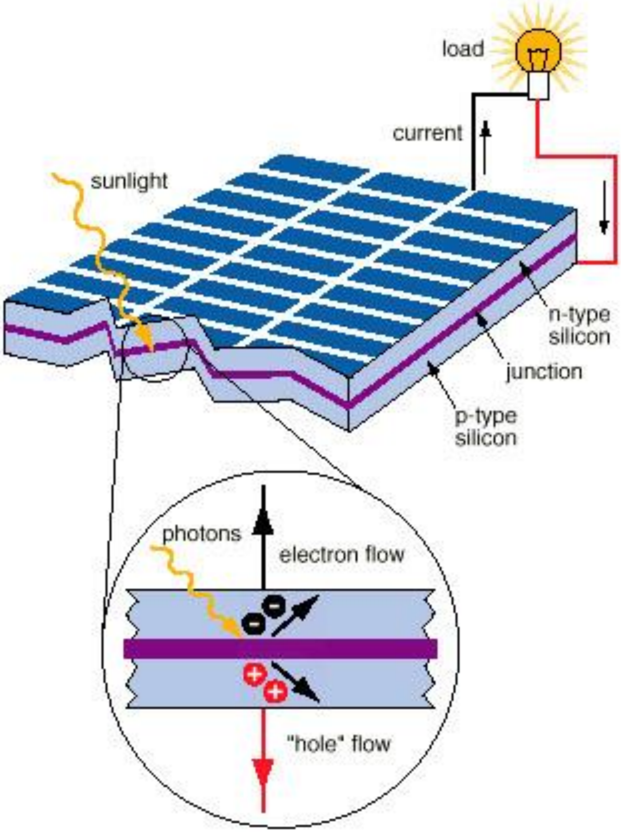


Figure 2: The working of a solar cell [1]

2.2.2 Second Generation Solar Cell

The second generation solar cells also called thin film solar cells is significantly cheaper to produce than first generation cells but have lower efficiencies. Second generation technologies have been gaining market share since 2008. They are mounted on a glass substrate. The great advantage of second generation thin film solar cell, along with low cost is their flexibility. The efficiencies are lower compared to first generation cells. Thin film technologies reduce the amount of material required in creating a solar cell.

The most successful second generation materials include amorphous silicon, microcrystalline silicon, Cadmium Telluride (CdTe) and Copper Indium Gallium Selenide (CIGS). The big appeal of these types of solar cells is that they are less expensive (below $1.00/watt to produce).

Cadmium Telluride Solar Cell (CdTe)

A Cadmium Telluride Solar Cell uses a thin layer of semiconducting Cadmium Telluride (CdTe) to absorb and convert sunlight into electricity. The Cadmium present in the cells would be toxic if released. P- type CdTe is sandwiched with n-type Cadmium Sulfide to form p-n junction. As of 2013, CdTe cell efficiency approached 19.6% in the laboratory **[2]**.

Copper Indium Gallium Selenide Solar Cell (CIGS)

Copper Indium Gallium Selenide (CIGS) is a direct bandgap material. Co-evaporation and sputtering methods are used to fabricate CIGS thin film solar cell. The heterojunction is formed between the semiconductors CIGS and ZnO, separated by a thin layer of CdS. As the absorption coefficient of CIGS is very high, it strongly absorbs sunlight. The efficiency of CIGS solar cell is 20% which is the record to date for any thin film solar cell **[3, 4]**.

Gallium Arsenide multijunction Solar Cell

For special applications such as satellites and space exploration, high efficiency multijunction cells were developed. The multijunction solar cells are also called Tandem solar cells. They consist of multiple thin films. For example a triple junction cell may consist of the semiconductors Gallium Arsenide (GaAs), Germanium (Ge) and Gallium Indium diphosphate ($GaInP_2$). The semiconductors are chosen to absorb nearly the entire solar spectrum, thus generating electricity from as much of the solar energy as possible. GaAs based multijunction solar cells have proved to be the most efficient solar cells on the laboratory scale. The efficiency of triple junction cell has reached 42.3% **[5, 6]**. However this efficiency is gained at the cost of increased complexity and manufacturing price. The high price and price to performance ratio of multijunction solar cells have limited their use.

2.2.3 Third Generation Solar Cells

Third generation Solar Cells are the cutting edge of solar technology. Still in the research phase, third generation solar cells have moved well beyond silicon based cells. The third generation solar cells do not need the p-n junction necessary in traditional silicon and other semiconductor based solar cells. Third generation technologies aim to enhance electrical performance of second generation technology while maintaining very low production costs. The third generation solar cells include non-semiconductor technologies, polymer based cells, dye sensitized solar cells, quantum dot technologies and up conversion technologies.

Organic/Polymer Solar Cell

Organic solar cells are a relatively novel technology. Organic solar cells and Polymer solar cells are built form thin film (~100 nm) of organic semiconductors including polymers such as polyphenlylene vinylene, copper phthalocyanin, carbon fullerenes and fullerene derivatives. Organic solar cells are potentially cost effective for photovoltaic applications. As the optical absorption coefficient of organic molecules is quite high, a large amount of light can be absorbed with a small amount of material. Compared to silicon based devices organic/polymer solar cells are light weight, inexpensive and flexible. The disadvantages of organic solar cells are low efficiency, low stability and low strength compared to inorganic photovoltaic cells.

Organic solar cells are composed of electron donor and electron acceptor materials rather than semiconductor p-n junctions. The two layers of electron donor and electron acceptor materials are sandwiched between two metallic conductors. Generally a layer of Indium Tin Oxide (ITO) with high work function and a layer of low work function metal such as Aluminium, Magnesium or Calcium are brought together. The basic structure of organic solar cell is shown in figure 2. The organic solar cells differ from inorganic semiconductor solar cells in that they do not rely on the large built in electric field of a p-n junction to separate the electrons and holes created when photons are absorbed. The active region of organic solar cell includes two materials, one which act as an electron donor and the other as an electron acceptor. When a photon is absorbed by material, electron-hole pair is generated. The charges tend to remain bound in the form of an exciton and are separated when the exciton diffuses to the donor-acceptor interface. The exciton diffusion length of most of the polymers is short which limit the efficiency of such a device. The organic solar cells had reached efficiencies of above 8% by 2014 **[7]**.

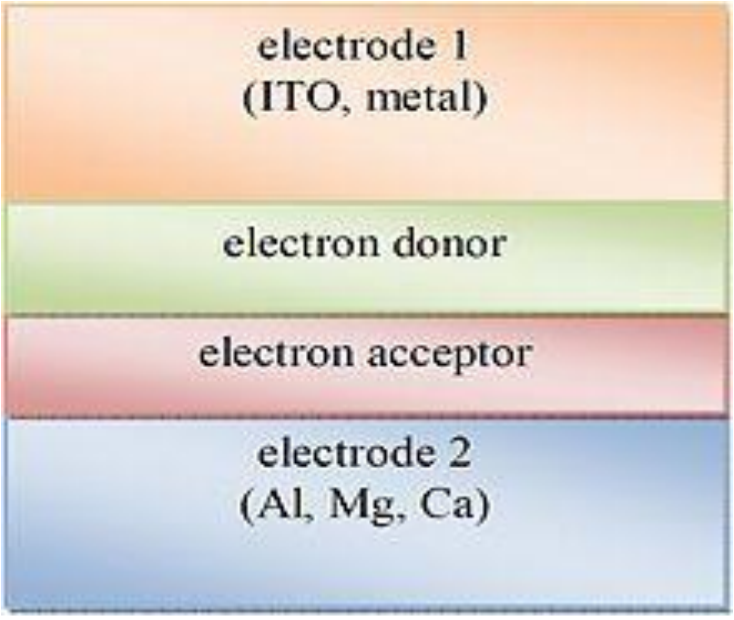


Figure 2: Basic structure or Organic Solar Cell

Dye Sensitized Solar Cell

The dye sensitized solar cell is a low cost solar cell. This cell, also known as the Gratzel cell, was invented by Michael Gratzel and Brian O'Regan in 1991. The first attempt was made by using chlorophyll as sensitizer in 1970 when scientist coated TiO_2 crystals with chlorophyll. However the devices only achieved 0.01% efficiencies because there was very little charge carrier separation. In 1988, Gratzel asked one of his graduate students to use nanoparticles of TiO_2. He managed to get current of microamperes. With refinement current in milliamps was achieved. Gratzel published his revolutionary work in nature reporting 7% efficiency. The efficiency of DSSC has reached 10.4%.

Structure and Materials

The schematic structure of DSSC is shown in figure 3. The diffenret components of DSSC are described in this section.

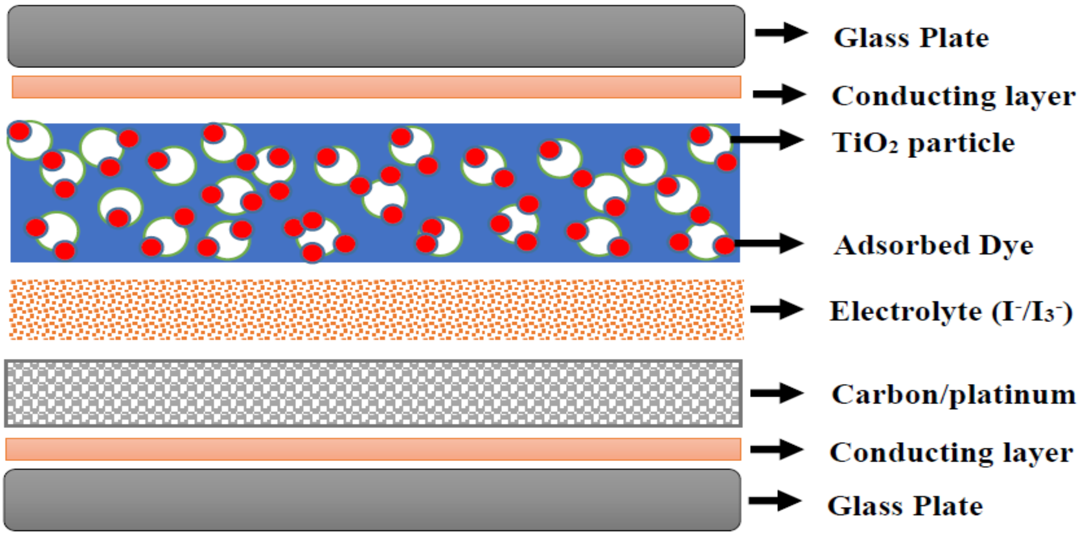


Figure 3: Schematic structure of DSSC

The dye sensitized solar cell encloses three primary parts, one is anode , another is cathode and third one is electrolyte solution. Anode is made of glass plate on which thin conducting layer of indium or flouride doped tin oxide is coated. On this conducting plate a thin uniform layer of TiO_2, preferably with high porosity and high surface area is formed. Being a wide band gap material ,TiO_2 absorbs only a fraction of solar spectrum. The plate is then immersed in a photosensitive dye. Generally ruthenium polypyridine dye is used which gives the highest efficiency. Instead of synthetic dye, natural dyes can be also used for sensitization. This plate is also termed as working electrode. The counter electrode or cathode is also prepared on conducting plate. On this plate a thin layer of platinum, carbon or graphite is coated. A thin layer of electrolyte containg iodide/triodie ions is formed on platinum or carbon coated plate. The two plates are then joined and sealed.

Conducting Glass plate

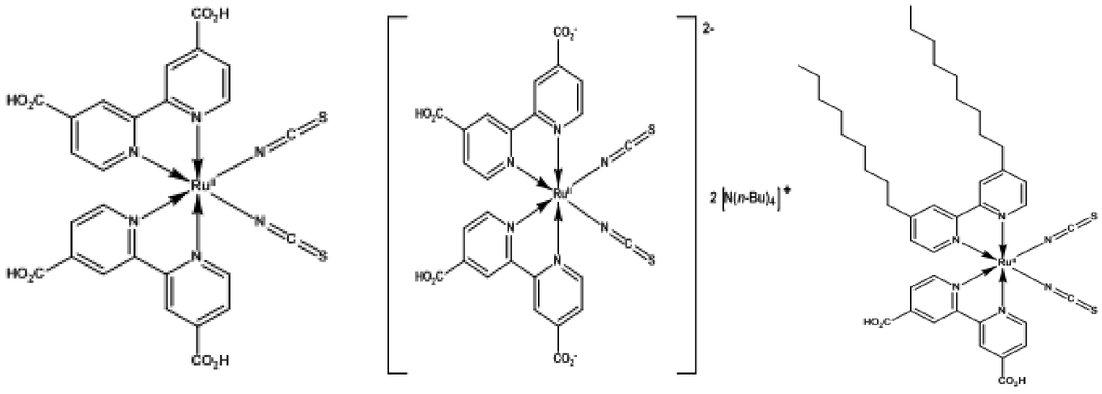
The transparent conduicting glass plate is used as a substrate for DSSC. The substrate must have low sheet resistancs and high transparency for high solar cell performance. A thin layer of transparent conducting oxide (TCO) is coated on glass plate. Indium doped tin oxide (ITO) and flourine doped tin oxide (FTO) are famous TCO materilas. The sheet resistanc should be independent of temperature upto 500 ^{0}C as sintering of the TiO_2 electrode is carried out at 450 ^{0}C. ITO coated conducting plate shows low sheet resistance at room temperature but this resistance increases significantly with temperature. Generally, FTO is used as a TCO substrate for DSSC.

Photoelectrode

Photoelectrodes are also known as anode or working eletrode. The metal oxide semiconductors used for making photoelectrode of DSSC are essenstially wide bandgap material. Different seminocducting materials used in DSSC are TiO_2, ZnO, SnO_2 and Nb_2O_5 **[8]**. TiO_2 is widely used semiconducting material for photoelectrode as it is cheap, chemically inert and easy to synthesize. The performance of DSSC is greatly influenced by properties like particle size, porosity and thickness of TiO_2 film. It has been reported that mixture of submicron sized particles with nano crystalline TiO_2 can improve phtocurrent density as it increases scattering effect. The one dimensional nanostructures like nanotubes and nanorods have also been used in DSSC to prepare photoelectrode **[9, 10]**. Electrons can easily migrate through these structures compared to nanoparticles and thus travel time of electron is redued. The special geometry with high surface area of nanotubes and nanorods leads to increase in dye loading **[11]**. These structures can be sytnhesized by hydrothermal method, sol gel method, alumina template and electrochemical etching method **[12].** It has been reported that increase in thickness of TiO_2 film leads to increase in short circuit current density (J_{sc}) as dye loading increases. There is a decrease in open circuit voltage (V_{oc}) of the cells beyond certain thickness because of more recombination taking place in thicker film **[13]**. Reduction in particle size also results in increase in short circuit current density as more dye can be adsorbed in the film, but reduction in particle size increases the number of grain boundries, which causes recombination and reduces V_{oc}. For efficient DSSC the particle size of TiO_2 nanoparticles should be 20-25 nm and the thickness of the film should be 10-12 µm.

Dye (photosensitizer):

Dye molecules must fulfill certain criteria in order to be used as a photosensitizer in DSSC. A dye molecule should absorb photons in whole of the visible region and near IR region of solar spectrum. The extinction co-efficient must be high. The perifery of the dye molecules should be hydrophobic to prevent water induced desoprtion of dye from TiO_2 surface and enhance the long term stability **[14]**. To avoid non radiative decay of excited state to ground state the dye should not aggregate on the surafce of TiO_2 which generally occurs in thicker film **[15]**. Different kind of dyes have been used in DSSC. Ruthenium (Ru) metal complexes are the most common and efficient dyes because the excited states of the complexes have long life time and oxidized Ru has long term chemical stability. The three very common Ru cmplex dyes are N-3, N-719 and Z-907. The structures of these dyes are shown in figure 4. The chemcial formula and IUPAC name of Ru complex dyes are given in Table 1.



N-3 **N-719** **Z-907**

Figure 4: Structure of Ruthenium based Dyes

Table 1: Chemical formula and IUPAC name of Ruthenium based dyes

Dye	Formula	Name
N-3	$C_{26}H_{16}N_6O_8RuS_2$	cis-bis (isothiocyanato) bis(2, 2´-bipyridyl -4,4´-dicarboxylato)ruthenium(II)
N-719	$C_{58}H_{86}N_8O_8RuS_2$	Di-tetrabutylammonium cis-bis (isothiocyanato) bis(2, 2´-bipyridyl -4,4´-dicarboxylato)ruthenium(II)
Z-907	$C_{42}H_{52}N_6O_4RuS_2$	cis-bis (isothiocyanato) bis(2, 2´-bipyridyl -4,4´-dicarboxylato) (4,4´-di-nonyl-2´´-bipyridyl)ruthenium(II)

Various metal free Pyrrole and Fluorene based organic dyes have been synthesized with the aim of replacing the expensive Ruthenium complexes.

Because of rarity, high cost and the complicated synthesis of Ruthenium complexes research has focused on the alternative, easily available, low cost and environment friendly dyes extracted from natural sources like fruts, flowers and leaves. Several natural dyes extracted from capsicum, balck rice, rosa xanthina, red cabbage, rossela flower, blue pea flower, curcumin, red perilla etc. have been used for sensitization in DSSC **[16, 17, 18, 19]**. The colours of these dyes are due to the pigments present in them. The list of pigments and their compounds are given in Table 2.

Table 2: Natural Dyes

Pigment	Compound	Color
Porphyrin	chlorophyll	Green
Ceratoid	Carotene & lycopene	Yellow, orange, red
	xanthophyll	yellow
Flavonoid	Flavone	yellow
	Flavonol	yellow
	Anthocyanin	Red, blue, purple, magenta

Electrolyte:

The electrolyte contains redox couple which regenerates the oxidized dye. The electrolyte should have following properties to be used in DSSC **[20, 21]**.

1. The dye should be regenerated efficiently by electrolyte after the process of dye excitation and electron injection to conduction band of oxide semiconductor.
2. The conductivity of electrolyte should be high ($\sim 10^{-3}$S.cm^{-1}).
3. The electrolyte should infiltrate thorugh the pores of the photoanode and establish contact with both the electrodes.
4. The electrolyte should not desorp the dye from photoanode.

5. The electrolyte should not react with the sealant.
6. The electrolyte should not udergo any chemical changes.
7. The electrolyte should be stable upto ~80^0C.

The cell performance depends on ion conductivity of electrolyte. The ion conductivity of electrolyte is strongly affected by viscosity of solvents. For better performance of DSSC, low viscosity solvents are desired. Iodide/triodide redox couple is most widely used electrolyte in DSSC due to their better performance. Generally electrolyte is a mixture of different iodides, iodine and solvents. NaI, LiI, KI, tetraalkylammonium iodide (R_4NI) and imidazolium-derivative iodides are the other iodides used for electrolyte preparation. Acetonitrile, propionitrile, methoxyacetonitrile, proylene carbonate and ethelyne carbonate are the commonly used solvents.

Counter Electrode:

Counter electrode is another important component of DSSC like photoanode and electrolyte. The counter electrode is used to complete the electric circuit of DSSC. To reduce the tri-iodide, the surface of the counter electrode is activated using a suitable catalyst. Low charge transfer resistance and good chemical stability are most important characteristics that the catalyst must have. Platinum is most efficient and commonly used catalyst but problem associated with platinum is its excessive cost.

Platinum can be deposited on FTO substrate by various techniques like sputtering, dip coating, electrophoretic deposition, etc. It has been reported that the thickness of 2 nm is sufficient for DSSC operation **[22]**. Other low cost materials such as carbon, conducting polymers, CoS, TiN and poly(3,4-ethylene-dioxythiophene) have also been used as counter electrode in DSSC. Apart from platinum, carbon and its allotropes such as carbon black, carbon nanotubes and graphene are the most studied materials for counter electrode **[23, 24, 25]**. Although the electrocatalytic activity of carbon and its allotropes is poor yet it remains as an attractive material due to its chemical stability.

Mechanism:

The dye sensitized solarcell is working on the principle of photosynthesis. The different steps of process are listed below. The mechanism of dyesensitized solar cell is shown in figure 5.

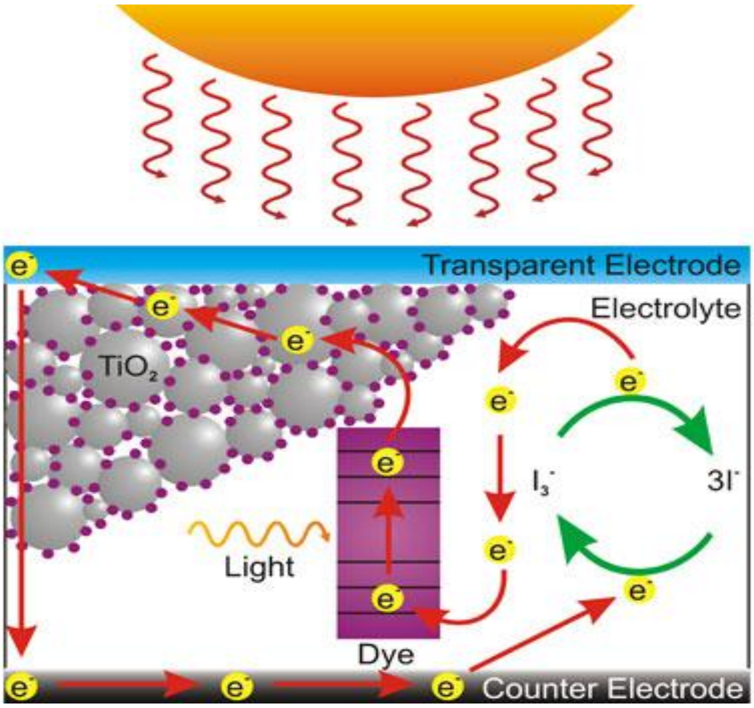


Figure 5: Mechanism of dye sensitized solar cell

1) The incident light is absorbed by the photosensitive dye. By photon absorption, the electrons of photosensitizer are excited from ground level (D) to excited state

(D^*). The excited electrons are transferred to conduction band of TiO_2 by oxidizing the photosensitizer (D^+).

$$D + h\nu = D^*$$

$$D^* \rightarrow D^+ + e^-$$

The electrons in conduction band of TiO_2 are transported between TiO_2 particles and finally reach the counter electrode through the circuit.

2) The oxidized photosensitizer regains electron from electrolyte solution and oxidizes I^- to I_3^-.

$$D^+ + e^- = D$$

3) The oxidized I_3^- ion gets electron from carbon or platinum coated electrode and reduces to I^- ion.

$$I_3^- + 2\ e^- = 3I^-$$

Advantages:

Dye sensitized solarcell is most efficient third generation solarcell. They are fabricated with the low cost materials and technolgies. It is an attractive option to replace silicon based solarcell. The price to perfoemance ratio of DSSC is quite higher than other solarcells.

Dye sensitized solarcell can work efficiently under low light intensity or cloudy weather. DSSC shows higher efficiency than traditional silicon solarcell at higher temperature. It also works properly at lower temperatures.

DSSCs are made of light weight materials. They require no special protection from rains and hence are easy to maintain. DSSC can be printed on any flexible surface.

Disadvantages:

Dye degradation

The dyes in dye sensitized solar cell degrade when exposed to ultraviolet radiation. However, techniques have been developed to overcome this problem. The barrier layer may include UV stabilizer or UV absorbing luminescent chromophores (which emit at longer wavelengths) and antioxidants to protect and improve the efficiency of the cell.

Rarity of Dye materials

Most of the components of dye sensitized solar cells are common and inexpensive. Dye sensitized solar cell uses complexes of the relatively rare metal ruthenium as a dye, which is not practical for large scale applications. A great deal of research is being carried out on alternative dyes including metal free organic and natural dyes. Metal free and natural dyes generally have lower efficiencies than dyes that incorporate metals.

Low Efficiency

Dye sensitized solar cells have efficiencies of about 5-11%, which is significantly lower than most other solar cell technologies. A metal free organic dye is reported to have an overall efficiency at 5.1%. Because of lower efficiency a dye sensitized solar cell array must be significantly larger than other photovoltaic arrays in order to produce the same amount of power.

Freezing of electrolyte

The major disadvantage to dye sensitized solar cell design is the use of liquid electrolyte. The liquid electrolyte has temperature stability problem. At lower temperature this electrolyte can freeze and stop the flow of current. Higher temperatures cause the liquid to expand and it may leak form the cell which reduce the efficiency of cell. Replacing the liquid electrolyte with a solid has been a major ongoing field of interest.

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