

# Chapter 1

## DYE SENSITIZED SOLAR CELLS (DSSC)

### 1.1 Introduction

The phenomenon of sensitization is well known to mankind. The semiconducting materials are often functioning by the sensitization of their charge carriers namely the electrons and holes. In the case of wide band gap semiconductors, the separation of the charge carriers requires considerable expansion of energy. The life on earth has always been sustained by solar power either directly or indirectly. It appears that mankind has resorted to the direct use of solar power for their energy needs and hence a variety of options are being examined including direct conversion of photons into electricity which is termed as photo-voltaics. Since the photons are used for the separation of electron hole pair, one has to resort to materials where the occupying state of the electron (valence band) should be different from the state (conduction band)  $k$  from which the electron is displaced in terms of energy and symmetry. Since the energy levels of both occupied and unoccupied states are continuous in conductors. The excited state of the electron will tend to recombine easily with the hole generated. Hence it is necessary that the states from which electrons are removed must be energetically different from the states at which the electrons are placed on excitation. This situation is obtainable in semiconductors or insulators where valence band (the state from which electron is excited) and conduction band (the state to which the electron is excited) are separated both in terms of energy and the symmetry of the wave functions is also mostly different. However, the anxiety to utilize solar energy for excitation places a restriction on the use of semiconductors and that too only small band gap semiconductors since most of the radiation ( in terms of energy) from the solar spectrum can be harnessed. However, not all small band semiconductors are stable under strong illumination conditions or amenable to be used as photo-anodes in the photo-voltaic devices. Among the available and exploited semiconductors (nearly 400 in number [1]), only a handful of them appear to be promising. For application in Dye Sensitized Solar Cells (DSSC) the most studied systems are  $\text{TiO}_2$ ,  $\text{ZnO}$  and tin oxide [2]. Unfortunately all these three systems are wide band gap semiconductors and absorb only UV radiation which is only about 5-8% of the total solar radiation.

Secondly the conversion efficiency,( photon to electricity) is also governed by the process of recombination which is the predominant mode of decay when excitation is carried out in the semiconductor itself. It appears therefore, necessary that some kind of charge injection is resorted to. This may be possible if the excitation by photon is carried out in another system and the excited electron takes occupancy in the conduction band states of the wide band gap semiconductor so that the electron can be moved in the external circuit. The auxiliary system where photo-excitation is taking place is termed as the sensitizer. It is therefore clear that the sensitizer has to fulfill some specifications. The important ones are:

- i. the system chosen should be capable of absorbing light in visible and infra red region of the solar spectrum.
- ii. the energy state of the electron on excitation in the sensitizer should be on par or suitable with that of the conduction band of the semiconductor so that charge injection can be feasible
- iii. the sensitizer employed should be capable of being dispersed on the semiconductor so that the photon absorption can be maximized
- iv. the sensitizer should be stable under strong illumination conditions since electron excitation may ultimately after electron transfer lead to an oxidized form of the sensitizer and it should be capable of easily reduced by the shuttled electron from the counter electrode
- v. the sensitizer should be stable on the semiconductor surface (good adhesion). It is therefore appropriate to note that the sensitizers may be any substance that can absorb low energy photons (visible and IR region) and also is capable of providing the electrons in the external circuit to draw the power.

There are various motivations for including this chapter in this monograph. We list them as follows:

- (i) This technology is threatening to be a viable for the conversion of solar energy into electricity for nearly 20 years now.
- (ii) Efficiency of this type of solar cell has been consistently improving over the years either from the point of utilizing major portion of the solar radiation by appropriate choice of the dyes (the HOMO and LUMO levels of the dye could be altered to suit the available solar radiation) and/or their suitability with the semiconductor which is being sensitized.
- (iii) Various structural modifications of the dye are feasible and also tried.
- (iv) The cost of these solar cells has been considerably reduced with respect to time.
- (v) As of now, these devices appear to be environmentally acceptable and the available infrastructure may be able to sustain this technology
- (vi) These devices may be universally accepted, and
- (vii) Above all, market penetration is possible.

In view of these reasons, in recent years there have been a number of perspective articles and reviews on this topic [only selected ones in 3-7]. It is a fact that vast literature is already available on this topic, as this topic is very contemporary and hence it is necessary to assess the scientific and technological developments at periodical intervals so that one does not miss out the important advances that are taking place in such an application area. The contents of this chapter therefore will be focusing on the various possible sensitizers that have been already examined for DSSC applications as well as other relevant aspects of this emerging technology. It may be appropriate at this stage to draw the comparison with the natural photosynthesis. Both DSSC and photo synthesis make use of photon absorption by a molecular dye (it is chlorophyll a and b in the case of photosynthesis). The excited electron is transferred effectively in the case of photosynthesis since it is an escalator type redox species and hence most of the excited electrons are effectively transferred and utilized in the reduction reaction. In photo synthesis the excited electron gets transferred to a variety of species so that effective and efficient electron transfer can take place to the species undergoing reduction. In essence, in photosynthesis after initial photo-excitation the electron takes appropriate energetic position in terms of reduction potential so as to be suitable for the species undergoing reduction. Such a situation is not realizable in the case of laboratory driven reduction processes since one has only fixed value redox couples and hence effective transfer of electron and thus efficient reduction of carbon dioxide could not realized in the laboratory. However, in the case of DSSC, the excited electron has to be transported via the conduction band of the semiconductor and hence it is necessary to match the LUMO level of the molecular dye employed for sensitization and that of the bottom edge of the conduction band of the semiconductor. In addition, the electron mobility in the semiconductor has to be high enough so that fast electron transfer takes place without the concurrent recombination process. This similarity makes the DSSC to be considered as a form of bio-mimicry. However it should be emphasized that the efficiency of DSSC cannot reach the levels of efficiency of photosynthesis. The basic principles of photosynthesis will be outlined in a separate chapter.

## 1.2 Configuration of a Dye Sensitized Solar Cell

There are various forms of Photo-electrochemical cells (PEC). Some of these forms are considered in this book. Among them, Dye Sensitized Solar Cells (various abbreviations are employed in the literature the prominent ones are DSSC, DSC or DYSC) are the prominent ones. These cells are simpler in construction compared to solid state solar cells. The first cell was constructed by Michael Gratzel and Brian O'Regan in 1991 [8]. Dye sensitized solar cells (DSSC) have been claimed to be promising for energy conversion to electricity with the possibility of low fabrication cost, easy manufacturing feasibility and fairly high efficiency. In general, the conversion efficiency is less than that of the best thin film cells, but this could be compensated in terms of price/performance ratio which could be as much favourable as that of fossil fuel to electricity generation and hence these types of cells can be expected to be possible mode of energy converters in the near future. If one were to combine an electron rich semiconductor (n type) with an electron deficient semiconductor (p-type) then one can

visualize the transfer of electrons from n to p due to the difference in the electrochemical potential of the electrons in the two semiconductors. This shuttling of the electron (partly formed by photo-excitation in n type semiconductor) in the external circuit is made use of to derive energy so that the electron returns back to the n semiconductor in the valence band as it was in the original state before photo-excitation. Therefore, the harnessing of energy is related to the extent to which one can make use of the photons for increasing the electrochemical potential of the electrons. This manifests itself in the extent of the available number of appropriate energy photons and also the absorption capacity of the semiconductor employed. The origin of the dye sensitized solar cells is in this direction meant to increase the extent of photon absorption (as dyes are good photon absorbers) and possibly also favours smooth transport of the electrons through the conventional semiconductor namely  $\text{TiO}_2$  in the external circuit. Configurationally, dye sensitized solar cells consist of conventional semiconductor (usually  $\text{TiO}_2$  which is the work horse semiconductor for photo-electrolysis) and a counter metallic (Pt) electrode usually in supported mode to reduce the extent of requirement of the noble metal. However, the oxide semiconductor has a surface coating of the dye (mostly mimicking chlorophyll in the leaves). This coating can be achieved in a variety of ways like dipping the semiconductor in a solution of the dye whereby the dye molecules are adsorbed on the semiconductor by probably covalent bonding. However other variations of the loading of the dye on the semiconductor can also be pursued. These include loading the dye with appropriate binder, preparing the electrode ( in this case it functions as anode) materials from semiconductor oxide and the dye from a slurry. Improvements in the stability of DSSC have also been achieved in alternate use of the plasticized polymer electrolyte instead of the conventional  $\text{I}_3^-/\text{I}^-$  system. For an elementary description of the dye sensitized solar cells, readers are referred to the site [http://www.science20.com/mei/blog/dye\\_sensitized\\_solar\\_cell-75581](http://www.science20.com/mei/blog/dye_sensitized_solar_cell-75581).

### 1.3 Sensitizers

It may be appropriate if one makes some comments on the sensitizers (not necessarily dyes alone) normally employed in DSSC since this is the central part of these cells. In a sense, they are the real converters of photon energy into electrons which are injected into the semiconductor to be passed on to the counter electrode for the reduction reaction. A variety of substances have been employed probably taking the clues from the natural photosynthesis process. The type of molecules that have been tried include a variety of ruthenium based complexes like  $\text{cis Ru(L)}_2(\text{NCS})_2$  where L is bipyridine carboxylic acid, or  $\text{RuL(NCS)}_3$  where L is a tripyridine carboxylic acid or  $\text{RuL}_3$ , [9] or the corresponding analogs of Os [10] (These species give rise to intense (in the visible region) metal-to-ligand charge transfer (MLCT) bands with a favourable energetics for possible activation-less charge injection into the semiconductor. In essence, several organic [11] and inorganic compounds have been investigated for the sensitization of the semiconductor which include chlorophyll derivatives [12], porphyrins [13], phtalocyanines [14,15], platinum complexes [16,17], fluorescent dyes [18], carboxylated derivatives of anthracene [19], polymeric films [20], and coupled semiconductors [21,22] with lower-energy band-gaps, natural dyes like anthocyanin [23] from black rice, carotenoid [24] from erythrina and

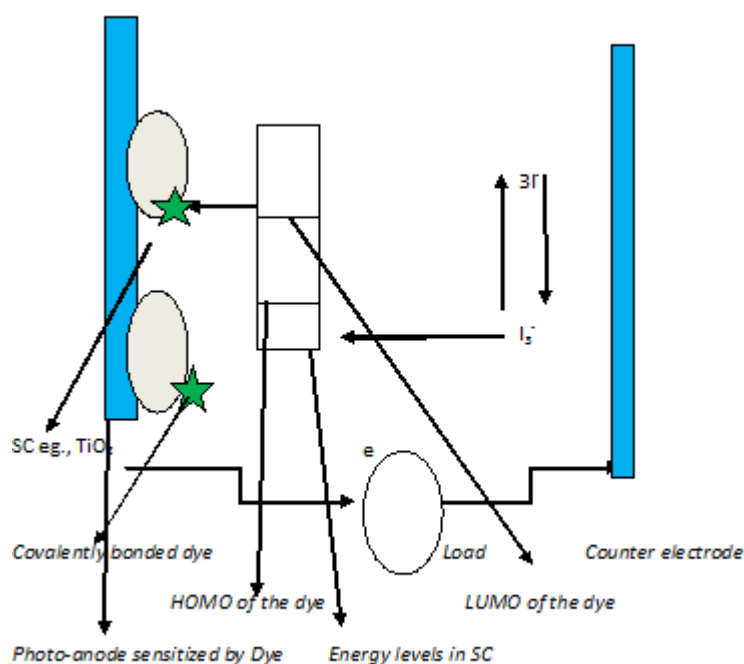


Figure 1.1: Schematic diagram of a dye sensitized solar cell. The photo-anode consists of semiconductor usually TiO<sub>2</sub> and occasionally, ZnO or other semiconductors to which the dye is covalently attached and the photon absorption by the dye gives rise to electron injection into the semiconductor conduction band from where it is transported in the external circuit through the load to the cathode which is conventionally carbon supported metal system which injects the electrons to carry out the reduction reaction in the tri-iodide/iodide couple I<sub>3</sub><sup>-</sup> / I<sup>-</sup>. Other couples or electron shuttles can be employed to facilitate the electron reinjection into the dye. A variety of electrolytes have been employed.

chlorophyll from *variegata*, rose bengal, porphyrin complexes especially that of zinc [25], inorganic species like copper diselenium, [26], and iodide (doped in ZnO)[27], and organic dyes without the metal ions. A complete listing of 86 sensitizers that have been tried and their characteristics are given in a recent book [28]. In recent years a number of other possibilities are being examined. The relevant data on these systems are briefly given in Table in the appendix to this chapter. Based on cost considerations, attempts have been made to use metal free dyes for DSSC applications. However, these systems exhibit lower efficiencies as compared to the metal containing dyes. [3, 4, 29-31]. It may be useful to place some general remarks on the dyes or essentially on the types of sensitizers conventionally employed in DSSC in terms of materials selection and logistics for consideration.

- (i) . The sensitizers conventionally provide the excited electrons to the semiconductor and hence they should be stable enough in the oxidized state

such that it will return to the original state by electron injection from the cathode. This means that the dyes chosen should be capable of providing electrons of suitable energy so that the electrons can be injected into the conduction band of the semiconductor employed. This brings a condition that the energy of the excited electron in the dye must match at least with bottom of the conduction band of the semiconductor.

- (ii) Since the electrons are directly injected into the conduction band of the semiconductor from the excited state of the sensitizers, the hole-electron recombination within the semiconductor does not take place or at least less likely.
- (iii) The choice of the semiconductors are based on the spectral region where the absorption of photons can take place and it is usually preferred to extend the absorption region as low energy as possible namely to visible and IR region. Hence the molecular structures of the sensitizers are chosen such that they will have absorption in the spectral region of the choice.
- (iv) Since sensitizers (for this presentation it can be read as dyes) and the semiconductor are in electrical contact, there can be alterations of the electronic energy levels at the interface and it is preferable that the electron energy state in the sensitizers must be on par with that of the energy of the bottom of the conduction band of the semiconductor. This means that the energy band positions must be suitably altered at the semiconductor/sensitizer interface. This brings us to a limitation that the sensitizers chosen should be such that their energy levels of the excited electrons should be capable of stabilizing the bottom of the conduction band edge. This is usually termed as moving the bottom of the conduction band edge downwards or negative conduction band shift due to favourable dipolar field exerted by the sensitizer to the semiconductor. This may be at variance to conventional metal ion containing sensitizers like heteroleptic Ru(II)-dyes for which an opposite dipole effect has been reported thus increasing the value of the open circuit voltage,  $V(OC)$  [32].
- (v) In a recent publication, [33] there has been an attempt to use an inverse sensitized photocathode in combination with the conventional sensitized photo-anodes (where electron injection was conceived to take place) so as to increase photon to electron yield several times as compared to the conventional n-DSCs. This type of tandem pn-DSCs may be one of the possible alternatives however, it should be remarked that the available dyes for p-DSC are till now poor performers and hence there is a need to develop new systems which can function in this mode. These authors claim that the donor-acceptor dyes, studied as photo-cathodic sensitizers, comprise a variable-length oligothiophene bridge, which provides control over the spatial separation of the photo-generated charge carriers.
- (vi) It is appropriate that some comments are also available in the nature and structure of the sensitizers that have been tried for DSSC. The logic for the selection of sensitizers must be (i) the required excitation energy must fall in the IR or visible region so that most part of the solar spectrum can be used. It means one has to have a fair idea of the available solar

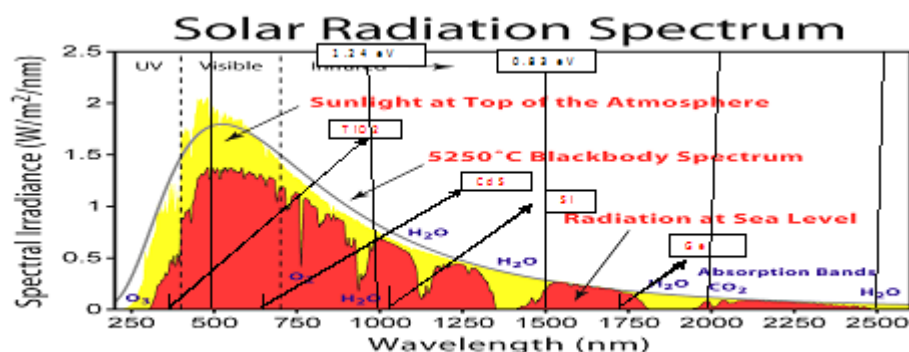


Figure 1.2: The typical solar spectrum with relevant details marked in terms of energy and some typical semiconductor absorption maximum

spectrum which is shown in Fig.2. (ii) The chosen sensitizer should be capable of covalently bonded to the semiconductor employed.

- (i) As mentioned elsewhere, there must be appropriate energetic position of the conduction band of the semiconductor which must be overlapping with the excited state energy of the electron in the sensitizer.
- (ii) The hole electron recombination within the sensitizer should be minimum, this can be achieved to an extent from smaller size (length in case of polyene dyes) of sensitizers or in other words the electron path in the dye system should be as short as possible so that the electron is injected into the semiconductor before recombination takes place.
- (iii) The sensitizers in the excited state should not prefer the de-excitation route through intermolecular interaction with the acceptor species in the electrolyte.
- (iv) The dyes in general used in DSSCs tend to degrade over time, thus leading to decreased efficiency and also the life time of the dyes are also limited and hence needs replacement of costly dyes. Attempts are being made to enhance the life time of the dyes in DSSCs in a variety of ways [34, 35] and it is hoped that the stability problems may eventually be overcome in the near future.
- (v) Even though it is generally claimed that the DSSCs are affordable in terms of cost, it is to remarked that most of the contemporary DSSCs use complexes of the relatively rare metals like ruthenium or osmium and other noble metals as sensitizing species which may not be amenable for large scale applications. Research efforts are made for designing alternate dyes including metal-free organic and natural dyes [36-38]. However, it should be remembered that metal free and natural dyes are generally show lower efficiencies as compared to the metal containing dyes [6, 38, 39-42].
- (vi) The reported efficiencies of dyes sensitized solar cells are in the range of 5-11%. This is lower than most other solar cells like solid state photo-voltaics. DSSCs with metal free sensitizers show lower efficiencies in the

range of 5%. The reason for this may be that metal free dyes may show high molar extinction coefficients ( $50,000-20,000 \text{ M}^{-1}\text{cm}^{-1}$ ) but narrow range of absorption ( $\Delta\lambda \approx 250 \text{ nm}$ ) while metal containing dyes may show low molar absorption coefficient ( $5000-20,000 \text{ M}^{-1}\text{cm}^{-1}$ ) but fairly broad absorption spectra ( $\Delta\lambda \approx 350 \text{ nm}$ )[43]. The overall conversion efficiency of the dye sensitized cell is normally estimated from the measured values of photocurrent measured at short circuit current,  $I_{SC}$ , the open circuit photo-voltage,  $V_{oc}$ , the fill factor of the cell (ff) and the intensity of the incident light ( $I_S$ ) and is given as  $=[I_{Ph} \cdot V_{oc} \cdot (\text{ff})]/I_S$ . The search for the type of dyes employed for sensitization has centred around the following points: The dyes normally employed in DSSCs have good capacity to convert a photon into an electron almost around 80%. This limitation can indicate that the DSSC based arrays may have to be sufficiently larger than solid state photovoltaic arrays to produce the same amount of power. However this disadvantage is offset by the lower cost and greater construction flexibility of DSSCs. Any improvement in efficiency will make DSSCs to be competitive to other types of energy conversion devices. Since DSSCs employ a liquid electrolyte, its operation at lower temperatures will be of still lower efficiency and also will lead to other problems due to freezing of the electrolyte.[44] Even though alternatives that would prevent the freezing problem are being considered, it is unlikely that DSSCs will probably be suitable for cold climates in the near future. The net conversion efficiency of the DSSC depends on the dynamics of the various processes that take place in the cell. Unfortunately all the possible processes in a DSSC are not of the same time scale and hence some processes proceed faster than others and hence the net conversion efficiency does not reach high and desirable levels. Secondly the electron has to be transported from the excited state of the dye to the conduction band of the semiconductor and there-from it is transported in the external (load) circuit to the cathode where it reduces the charge carriers which regenerate the dye from its oxidized state. Generally the diffusion length of the electron generally controls this process and the diffusion length is given by the equation,  $L_n = (D_n \tau_n)^{1/2}$  where  $D_n$  is the diffusion coefficient of the electron,  $\tau_n$  is the life time of the electron. It is therefore necessary that we know the time scales of the various processes that take place in a DSSC. Some estimates of these times are given in terms of the values of rate constants in Table 1.

The second important parameter of concern is the life time of the dye and various governing criteria have been evolved either in terms of number of cycles ( a figure 50 million cycles is claimed) or in terms of time of continuous exposure ( this is of the order of 1000s hours) before the dye degradation sets in. (iii) There is always a concern on the nature of the dye with respect to the electrolyte medium employed. If the electrolyte medium is aqueous then the dyes chosen should have hydrophobic character so that they will be fairly well anchored on the semiconductor electrode. (iv) For improving the stability of the DSSC (either with respect to temperature or chemicals) solid state gel or polymer gel electrolyte or melt of multiple salts have been employed. These studies showed some improvements in terms of efficiency, however, improving the efficiency alone cannot be



Specific electron transfer process in DSSC	Values(ranges)of rate constant in $\text{sec}^{-1}$
Electron excitation in the dye	$10^8 - 10^{10}$
Electron transfer from excited state of the dye to the semiconductor (electron injection)	$10^{10} - 10^{12}$
Back electron transfer from semiconductor to the dye	$10^6 - 10^7$
Electron transfer from semiconductor to external circuit	$10^0 - 10^2$
Oxidized state to the reduced state in the electrolyte at the cathode	$10^8 - 10^9$
Direct electron transfer in the electrolyte at the anode	$10^8 - 10^1$

Table 1.1: Values (in ranges) of the rate constants (in  $\text{sec}^{-1}$ ) for the various electron transfer process in a dye sensitized solar cell

considered as a sole criterion for designing DSSCs. (v) Designing of appropriate dyes for DSSCs (either with or without metal linkages) has been made by a variety of ways. The main factors considered in these studies include the HOMO-LUMO energy gap in the dye (usually estimated through semi-empirical quantum mechanical calculations like DFT or variations thereon [45], the estimation of the life time or properties (dipole moment) of the excited states of the dye and other relevant spectroscopic properties. (vi) In order to increase the light harvesting in DSSCs electron relay dyes have been employed where in the excitation takes place in energy relay dye from which the transfer takes place by Foster energy transfer process to the sensitizing dye. This architecture permits broader spectral absorption, increase in the amount of the dye loading and gives rise to flexible design features for the DSSCs. An increase of nearly 25% (vii) The degradation of the dye and the long term durability of the DSSCs are other factors of concern and it has been briefly mentioned above. Conventional photon induced de-carboxylation or decomposition may take place and it is possible that one can devise methods to restrict this kind of degradation. However, it should be remembered that the dye molecules are in the presence of relay species which can be  $\text{I}^-/\text{I}_3^-$  (alternatively  $\text{Br}^-/\text{Br}_3^-$ ) or other amine in the electrolyte and these can also induce (or at least promote) the degradation of the dye. Since the DSSCs cannot be operated without these kinds of electrolyte media, more attention is needed on the dye degradation process[[46].

## 1.4 The semiconductor Electrode

The commonly used anode material is based on  $\text{TiO}_2$  ( $\text{ZnO}$  is also employed and a variety of other materials are also employed [47-58]) for the following reasons. (i) The energetics of the conduction band of  $\text{TiO}_2$  is well established and hence the appropriate dye could be employed so that the electron transfer from the

excited state of the dye can be facilitated. This transfer probably restricts the recombination of the electron with the hole generated. (ii) Since this transfer has to take place between the dye and the semiconductor, the dye should be capable being adsorbed on the semiconductor and also the coverage ( $\theta$ ) by the dye on the semiconductor should be almost near to 1, since otherwise, the photon will be absorbed or scattered (loss) by the semiconductor. (iii) The semiconductor employed must be amenable for surface modification so that the dye molecule can be easily anchored on the surface and also the excitation energy (the difference between HOMO and LUMO levels of the dye) can be suitably modulated so that the absorption range can be extended to visible and even to IR region of the solar spectrum.[59]

## 1.5 Electrolyte

The electrolyte and the medium to be used in DSSC generally control the potential of the positive electrode. In any form of electrochemical cells, the electrolyte has a significant role in the electron transfer since the medium permits the diffusion of the redox species forth and back to the counter electrode. Generally, high conversion efficiencies are reported in DSSCs in which electrolyte is an acetonitrile solution of iodine ions ( $I^-/I_3^-$ ). The physical properties of the organic medium in this case acetonitrile (like melting/boiling point and the decomposition potential) control the concentration (due to evaporation at higher temperatures or decomposition due to potential) and hence causes drop of conversion efficiency at higher temperatures or with long-term use. Alternate methodologies have also been tried like sealing the electrolyte (that controls the evaporation loss) solidification of the electrolyte or employing solid electrolytes like CuI or CUSCN, Conductive polymers like polypyrrole, low molecular weight materials like triphenyldiamine or amorphous organic compounds. At this moment, the selection of electrolyte does not seem to attract much attention though there are sporadic reports on the use of alternate electrolyte medium.

## 1.6 Counter electrode

The counter electrode acts as the conduit for the return of the electron to the dye. Since the electrolyte can be corrosive, it is essential that the material of the counter electrode is fairly corrosion resistant, and is also capable of reducing triiodide to iodide ion. The appropriate material can be conductive glass electrode having a dispersion of Pt. However carbon electrodes and conductive polymers can also be the alternate choices. However, these materials cannot come up to Pt in terms of the reduction rate.

## 1.7 Packaging of the DSSCs

It is known that this technology is threatening to be commercially viable for a number of years in recent times. This means a neat packaging of this technology must be in place if this technology were to be adopted for energy conversion process. Since packaging may lead to efficiency loss, it is necessary to encapsulate DSSC appropriately like in optical nanofibers [60,61] Various single cell

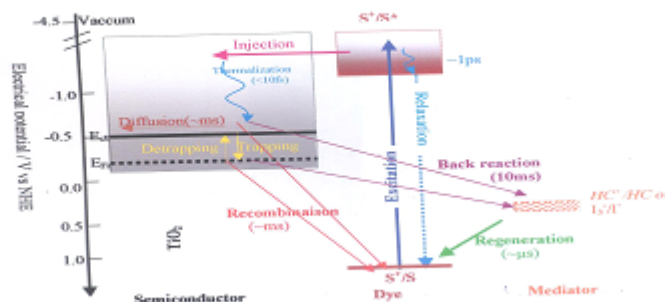


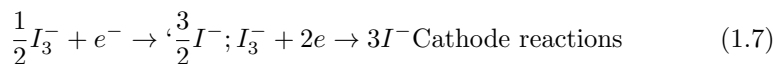
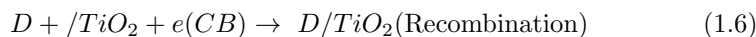
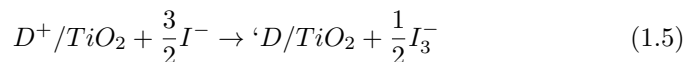
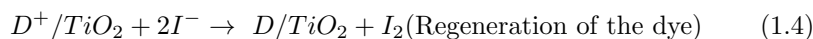
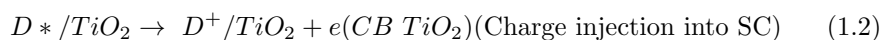
Figure 1.3: Schematic representation of the various possible process for the generation, transfer, recombination of the electron that is electron transfer processes occur in parallel and in completion in DSSC [reproduced from ref.64]

configurations for long term stability and also for grid connection possibilities are being examined with plastic substrate [62,63]

## 1.8 Possible Routes for Electron Transfer in DSSC

The values of rate constants of for electron transport in DSSC have already been considered in an earlier section. It is essential that one considers the dynamics of this transport both from the points of view of electron transport feasibility and also the flexibility. This section addresses these aspects in some detail. A pictorial representation of the various possible processes for the electron excitation, de-excitation, electron injection, transport, recombination, and utilization in regeneration is given in Fig.3. The photon is absorbed by the dye and the electron is excited from the HOMO level of the dye to the LUMO level of the dye. The excited electron from the LUMO level of the dye is injected into the conduction band of the semiconductor. This injection rate constant is assumed to be of the order of  $5 \times 10^{13} \text{s}^{-1}$  for perylene derivatives [64] and it is of the order of  $4 \times 10^{14} \text{s}^{-1}$  for Ru complexes. It is also assumed that the injection rate of the electrons from the sensitizer to the semiconductor is of the same order of magnitude in both electrolyte and solid state solar cells. However it should be remarked that the transfer rate may depend on the density of states in the conduction band of the semiconductor and also the symmetry of the wave functions that constitute the electronic states in the conduction band of the semiconductor. The excitation in the dye takes place in femto-second time scale while the charge injection from the excited state dye  $D^*$  to the conduction band of the semiconductor (typically in  $\text{TiO}_2$  (CB) takes place in sub-pico second time scale. This statement of the time scales is based on the assumption that the excited state dye does not undergo intra-molecular relaxation which not only can alter the time scale of electron injection but also may complicate the injection process itself. The electrons in the semiconductor can be thermalized by lattice collisions and phonon emissions in the time scale of femto-seconds. If

the relaxation of the excited state dye takes place in the time scale of nanoseconds, then the efficiency of electron injection process in the semiconductor can become nearly unity. In this case the excited state dye has to be regenerated by the iodide ions from the mediator. This process will be in the domain of microsecond. This regeneration may prevent the recombination of the electron from conduction band of the semiconductor with the HOMO level of the dye which could be in the range of mill-second time scale. This favourable time scales facilitate the electron percolation and the capture of the electron by the oxidized relay namely  $I_3^-$  which takes place in millisecond or higher time scales. The processes that take place in a DSSC are given in the form of equations below:



It may be appropriate if some general remarks are made on the statements made in this section

- (i) The electron transfer routes outlined in equations 1-6 are only indicative of the various possibilities. It should not be considered exhaustive since the possibilities like the trapping of the electrons in defect or surface states of the semiconductor, and other possible electron transfers with impurities and other species present in the system are not considered and they can also contribute for the loss of efficiency.
- (ii) The life times that are given are indicative and they may not be exact. In addition the life times given are for pure species namely the time indicated for the excitation in the dye is when the dye is in the isolated state while in the experiments the dye will be in the adsorbed on the semiconductor and hence the time required for excitation can be different. This could be due to the fact that in the adsorbed state, the molecular structure of the dye molecule might have changed depending on how and with what functionalities the dye molecule is adsorbed on the semiconductor. Similar arguments may hold good for the mediator species as well.
- (iii) Even though the reactions are shown in a sequence, the process can take place in a competitive and also concurrent manner thus accounting for the loss in efficiency.
- (iv) The other parameters on which the rate of electron injection depends include the length of the spacer between the electron donor and acceptor, the density of acceptor states in the semiconductor, the interaction between the dye and the semiconductor (already mentioned).The total electron

transfer rate is related to the density of states (DOS) at the appropriate energy relative to the bottom of the conduction band edge of the semiconductor, the reorganization energy and the temperature  $T$ . The electron injection in the semiconductor depends on the magnitude of DOS in the semiconductor in the conduction band. When the dye is adsorbed on the semiconductor (most probably through functional groups (like carboxyl groups in the dye) the electron transfer essentially takes place between the  $*$  orbital of the sensitizer dye and the conduction band energy levels (which is essentially the unoccupied  $d$  states of the transition metal in the semiconductor for example  $Ti$   $d$  states). Since the density of states in the conduction band of the semiconductor can be large (of the order of Avogadro number) the electron injection into the semiconductor takes place at a higher rate compared to the relaxation from the excited state to the ground state (that is relaxation through emission). It may be realized that this electron injection is the key for the higher efficiency and hence the choice of the semiconductor and the dye should be such that the energetic positions of the conduction band of the semiconductor and the energy of the excited state are appropriately matched.

- (v) The injected electron is transported through the semiconductor to the back contact and this could be slower in the nano-crystalline semiconductor as compared to single crystal dye sensitized semiconductor.
- (vi) The recombination of the electron with the excited state of the dye can occur over a time period of picoseconds to millisecond. This wide time scale arises due to the charge trapping possibilities by the localized surface states in the semiconductor. In addition the photon field may alter the energy states of the semiconductor (thus altering the position of the quasi Fermi level) and thus may favour the occupancy of the trap states.
- (vii) The electron transport can also be controlled by the composition of the electrolyte employed and also the applied potential.
- (viii) The recombination is also dependent on the nature and structure of the dye employed.

In the operation of DSSC, the regeneration of the dye is an important step. The life time of the cationic form of the dye can be of the order of milliseconds in the presence of pure solvents and can be altered by the nature of the electrolyte. The most widely employed redox system is  $I^-/I_3^-$ . The regeneration of the dye depends on the concentration of iodide ions. The relative energetic positions of the mediator and dye decide the open circuit potential achievable. Till now  $I^-/I_3^-$  redox system is the best electrolyte for DSSC. Efficiency of more than 11% with acetonitrile based electrolyte and 8% and long term stability with other low volatile electrolyte have been reported.[65-68]. Other ionic liquids with fairly ionic conductivity have also been examined like pure imidazolium  $I^-/I_3^-$  [69 - 73]. Quasi solid electrolytes by gelation with aliphatic gels, polymer and even nano particles have also been examined for DSSC application.[74-78]. Other redox couple that has also been tried is  $Br^-/Br_3^-$  [79]. In addition hole conductors like  $CuSCN$ ,  $CuI$ , organic hole conductors like triaryl amines, polymer hole conductors like poly(3-alkyl thiophene, polyaniline) have also been tried in DSSC.[80-88].

## 1.9 Current Voltage Characteristics of DSSC

The standard illumination on a DSSC is usually referred as AM 1.5 with an intensity of  $1000\text{W}/\text{m}^2$  also referred to as 1 sun. This spectrum corresponds to sunlight that passes through the atmosphere 1.5 times longer than when the sun is directly overhead. The current voltage characteristics of DSSCs are monitored under standard illumination conditions by varying the external load from zero value (short circuit condition) to infinite load (open circuit condition). A parameter called fill factor is defined as follows:

$$FF = J_{powermax} \times V_{powermax} / J_{SC} \times V_{OC} \quad (1.8)$$

The solar cell efficiency is given by the ratio of the power generated and power of the incident light

$$\eta = P_{out} / P_{in} = (J_{SC} \times V_{OC} \times (FF)) / P_{in} \quad (1.9)$$

Another parameter of relevance is the Incident Photon to Current Conversion Efficiency (IPCE) which denotes how efficiently the light of a particular wavelength is converted into current and is given by the expression

$$IPCE = h \times c / \lambda \times J_{SC} \text{mA}/\text{cm}^2 / q / P_{in} \text{mW}/\text{cm}^2 = 1240 J_{SC} \text{mA}/\text{cm}^2 / \lambda_{nm} \cdot P_{in} \text{mW}/\text{cm}^2 \quad (1.10)$$

The parameter Absorbed Photon to current conversion efficiency (APCE) denotes how efficiently the absorbed photons are converted into current, the IPCE and APCE are related to each other through light harvesting efficiency (LHE), Transmittance (T) and Absorbance (A) according to the following equation

$$APCE(\%) = [IPCE(\%) / LHE(\%)] \times 100 LHE = 1 - T \text{ and } T = 1 - 10^{-A} \quad (1.11)$$

IPCE itself can be expressed as

$$IPCE(\%) = LHE \times \Phi_{inj} \times \eta_{reg} \times \eta_{cc} \quad (1.12)$$

Where  $(\Phi_{inj})$ ,  $(\eta_{reg})$ , and  $(\eta_{cc})$  denote the quantum yield of charge injection, dye regeneration and charge collection efficiency respectively. The efficiency of a DSSC can also be examined from another point of view. Essentially the efficiency of DSSC depends on how many photons are converted and collected in the external circuit in the form of electrical power. This conversion efficiency (IPCE)( $\lambda$ )(incident photon to current efficiency) depends on three factors namely, the light harvesting efficiency (LHE) which denotes the number of photons absorbed by the dye, the electron injection efficiency  $(\Phi_{inj})$  which is a measure of how many absorbed photons result in injection of electrons into the semiconductor, (this probably accounts for the return of the excited of the dye to the ground state) and charge collection efficiency  $\eta(c)$  (probably accounts for the loss in the semiconductor itself without transfer to the external circuit).

$$IPCE(\lambda) = LHE(\lambda) \times \Phi_{inj} \times \eta_c \quad (1.13)$$

All of three processes in the DSSC are kinetic in nature and hence their efficiency is determined by how fast they occur relative to competing processes like de-excitation of the dye, electron loss in the semiconductor and processes internal to the system. One has to therefore consider the essential characteristics of the dye since the photon to electron conversion critically depends how best the dye absorbs the photon.

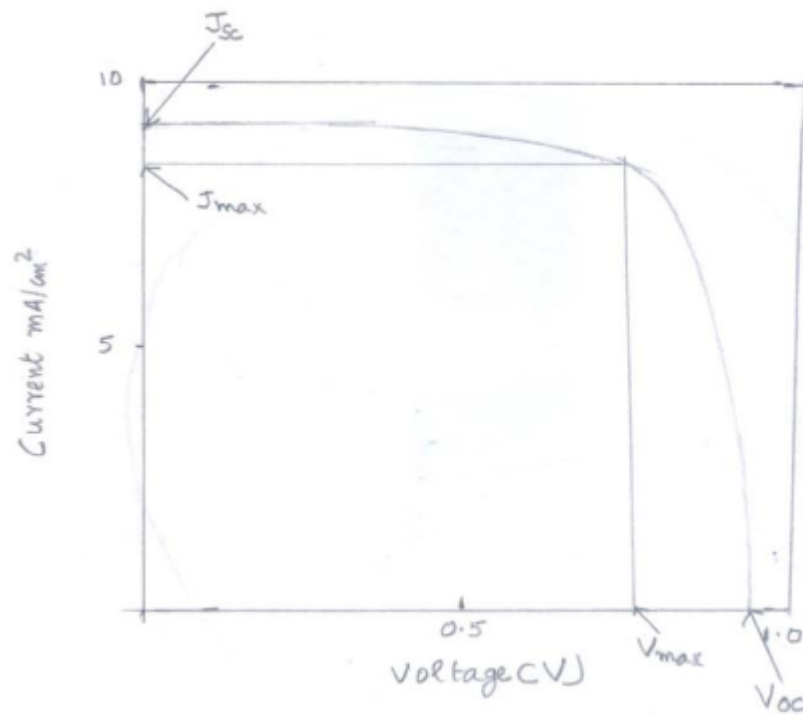


Figure 1.4: Typical representation of current Voltage characteristics of a DSSC denoting the short circuit current ( $J_{SC}$ ), open circuit voltage  $V_{OC}$  Current at maximum power point ( $J_{max}$ ) and voltage at maximum power point ( $V_{max}$ )

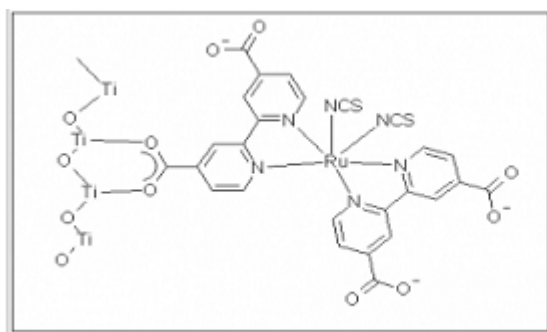


Figure 1.5: Typical and possible bonding scheme of the ruthenium based dye with the TiO<sub>2</sub> surface is shown

## 1.10 Dye Characteristics

In this section, the important characteristics of the dye will be considered in addition to what has already been discussed in the section on sensitizers (sub-section 3) The light harvesting dye is clearly the crucial and central component of the DSSC design. These dyes need to fulfill several functions: adsorption onto metal or semiconductor surface, its absorption spectrum must overlap effectively with the solar spectrum, the dyes should be capable of injecting electrons efficiently into metal oxide and must be stable for many cycles. These aspects have been already outlined. Adsorption of the dye onto the metal oxide surface is normally facilitated by inclusion of a functional substituent that will adsorb readily. In the case of metal complexes like ruthenium species, ligands which have capacity to bind to the metal ions, are preferred, the well studied ligands are those containing carboxyl-substituted ligands. The possibility of adsorbing the ruthenium complex on TiO<sub>2</sub> surface is shown pictorially in Fig 5. It is given as an example for the process of adsorption and one can visualize alternate modes of adsorption of the dye on the semiconductor surface. In the table given in the appendix to this chapter the typical listing of the sensitizing species so far employed and their structures are given. It may be conceived that these species will be adsorbed on the semiconductor surface (TiO<sub>2</sub>, or ZnO or any other semiconductors) through the functional groups contained in them. The spectral absorption of the dye or adsorbed sensitizer should be such that it overlaps with the solar spectrum so that as much of the sun's energy as possible is utilized in exciting the sensitizer. Most of the dyes or sensitizers normally employed in DSSCs absorb in the visible and near infrared region (in the region 400 to 700 nm), capturing about half the available power and a third of the available photons from the solar radiation. The ruthenium complexes which are currently employed as sensitizers have a limitation in that their extinction coefficients (approximately  $2 \times 10^4 M^{-1} cm^{-1}$ ) are comparatively low. This means that one must have sufficient number of sensitizers adsorbed on the semiconductor surface thus necessitating the metal oxide semiconductors have to be prepared with very high surface areas. It is expected that normally efficiencies of greater than 15% is preferable, the designed DSSCs will have to absorb about 80% of light between 350 to 900 nm. In order to extend the spectral



region, complexes of osmium has been examined in place of ruthenium, which extended the absorption further into the low energy red region and enhanced the response of the cell to light relative to the ruthenium analogues. The charge transfer transitions in osmium are more intense than in ruthenium complexes. Organic dyes have also been used successfully as seen from the data given in the table in the appendix. For facile electron transfer from the excited state of the dye to the semiconductor, it is necessary that the energy of the excited state of the dye is suitable with respect to the bottom of the conduction band of the semiconductor so that energetically the electron transfer process will be a downhill process in addition the electron injection process into the semiconductor must be faster than the relaxation process in the excited state of the dye by luminescence or non-radiative decay. It has been pointed out elsewhere in this presentation the relative time scale of each of these processes. In the case of ruthenium species, the injection takes place in the time scale of femto second while the decay process is taking place leisurely in the sub-picosecond time scale. However as pointed out earlier, it is necessary to assess if these time scales determined in the molecular scale will be applicable to the adsorbed state.[89]. Nevertheless, the very fact that fairly efficient DSSCs are available supports these contentions, it is necessary that caution is required in ensuring that efficiency of the DSSCs is not reduced by other design factors of the cell. One way of ensuring that the dye or sensitizer absorbs sufficiently in the red region, one has to lower the LUMO level of the dye or sensitizer, but this option has to be carefully considered since this lowering cannot be done in such way that the LUMO is lower than the conduction band of the semiconductor and also the position of LUMO level should be such that facile electron injection will take place without considerable activation barrier. In a recent publication, the group from Stanford has coupled luminescent chromophores which absorb high energy photons and pass their energy to the sensitizing dyes. These options possibly can show some improvement in the net efficiency. [43].

## 1.11 Semiconductor Material

After the successful injection of the electron into the semiconductor, the electron should be transported in the external circuit through the load to the working electrode. Semiconductors like TiO<sub>2</sub> or ZnO are the common material employed in DSSCs. The normal criterion for the choice of the type of semiconducting material is that they must be relatively inert, cheap, and must be amenable for flexible and scalable synthesis with high surface area. The factors that contribute to the choice of anatase form of TiO<sub>2</sub> as the choice of the semiconductor are: (i) Anatase has a higher band gap (3.2 eV) as compare to rutile (3.0 eV). Hence the anatase phase absorbs limited range of the solar spectrum and the remaining region is available for absorption by the sensitizer. (ii) The recombination of the electron with the hole in the valence band is slower than it has been observed with Rutile form. It must be remarked that the multilayer semiconductors with varying nm sized particles have been advocated as best materials from the point of view increasing the exposed surface area which could sustain considerable layers of the sensitizer molecules so that improved photon absorption condition could be ensured. The time taken for the electron to percolate through the external circuit to the transparent conducting electrode is of the

order of 100s of microseconds. Even though this time scale is longer, it is lower than the conduction band dye recombination or other conduction band decay process within the semi conductor. In order to effectively transfer the electron in the external circuit it will be advantageous to employ one dimensional nano tubes or nano rods rather than bulk materials. These configurations can be expected to facilitate vectorial transfer of charge [90]. . This aspect may be addressed in the future [90]

## 1.12 Electrolyte and Regeneration

The electrolyte contains the redox couple, which regenerates the oxidized dye  $D^+$  which was formed by the injection of electron from the dye to the semiconductor layer. The redox couple should be efficient enough at reducing the dye cation ( $D^+$ ) back to the original state for another cycle, but should not intercept or capture the electrons being injected. The most commonly employed redox couple for this electron transfer is tri-iodide/iodide ( $I_3^-/I^-$ ) system for the transfer of electron from the conduction band of the semiconductor to the oxidized form of the dye or sensitizer. Even though the time scales of this electron transfer process in the tri-iodide/iodide couple may be favourable for the DSSC application, the redox chemistry of tri-iodide/iodide couple is not very well understood even now. This places some restrictions in the selection of appropriate dyes as sensitizers. One of the alternate possibilities may be to use solid state redox couples. This may allow the use of higher concentrations of the redox couple and possibly can extend the applicability of the device.

## 1.13 Summary

Dye-sensitized solar cells is receiving considerable attention in recent times and threatening to be one of the possibilities for alternative renewable energy provider. The principle of operation is to harvest light efficiently by a sensitizer and pass on the energy to a semiconductor surface, which connects to an external circuit generating current. The light harvesting dye is regenerated by mean of a suitable redox couple. It appears that each of the process steps in DSSC like the electron excitation, electron injection into the semiconductor, electron transport in the external circuit, the redox species that facilitates the back transfer of the electron to the sensitizer, and the times scales for each of these processes can offer a wide variety of options and examining them and making an appropriate combination appears to be the job on hand in this exciting area.