CHAPTER - II

Theoretical Background of Solar Energy Conversion

The conversion of solar energy into electrical energy is considered as an important alternative in the present energy crisis. The conversion using semiconductor is based on the production of additional charge carriers; for example, electrons in n-type and holes in p-type semiconductors with the help of incident solar radiation. The solid state devices (utilizing solid-solid junction, eg. solar cells) and photo-electrochemical devices (utilizing solid-liquid junction) are the two options available for solar energy conversion. This chapter deals with the theoretical considerations related to the chemistry and physics of the solar radiation absorption and its conversion to electricity.

2.1 The Solar Cell

Solar cells are designed to convert, at least some portion of the light energy falling on it into electrical energy. The development of the solar cell stems from the work of the French physicist A.C. Becquerel in 1839, who discovered the photovoltaic effect. The voltage developed when a light fell upon the solid electrode in an electrolyte solution is called photovoltaic effect. Since then, a significant research has been carried out by various researchers generating various kinds of solar cells with various efficiencies. By the late 1980s silicon cells, as well as those made of gallium arsenide, with efficiencies of more than 20 percent had been fabricated. In 1989, a concentrator solar cell achieved an efficiency of 37 percent due to the increased intensity of the collected energy. In general, solar cells of widely varying efficiencies and cost are now available.

The modern solar cells are based on p-n junction of two semiconductors with a very large light-sensitive area. The photovoltaic effect causes the cell to convert light directly into electrical energy. This occurs in the three layers of p-n junction device. The top layer of the
junction device uses photon energy to generate a pair of electron-hole (exciton). The middle layer absorbs the exciton and separates them at p-n junction. The last layer is the back junction, i.e., p-type semiconductor where holes are concentrated and swiped off externally under applied bias. The n type semiconductor thus acts as anode while p type semiconductor acts as cathode. The former is an all solid-state device which has been developed to an advanced level. Today’s cells are reported to function with 15-18% efficiency. The cost of silicon-based photovoltaic devices has been brought down by innovations in silicon production technology.

2.2 Photo-electrochemical Cell

A semiconductor electrode and an inert electrode immersed in suitable redox electrolyte constitute this cell. When a light of photon fall on the surface of the semiconductor, an electron-hole pairs are generated in the semiconductor. This pair is separated in a semiconductor-electrolyte junction easily. The photo-electrochemical mode of conversion nowadays is attracting a great deal of interest due to many advantages over the conventional solid-solid junction cell [1-3]. The PEC cell is said to be a regenerative or liquid-junction photocell. The solid-solid junction fabrication is not an easy task, since a fabrication of ideal junction is highly difficult, this ultimately limits the efficiency of the solar cells. However, junction fabrication in PEC cells is very easy, since the junction is easily formed just by immersing even a polycrystalline material (instead of a single crystal) in redox electrolyte. The PEC cell was first introduced by Gerischer in 1960 and since then has been subject of intensive research [4]. Many semiconductors have been studied in a variety of redox electrolytes. The solar energy conversion efficiency, though poor, the research on these cells has greatly enhanced our understanding of semiconductor–electrolyte inter phases, since this conversion route is easy to setup and cheap to fabricate the device.
The semiconducting materials are important material that can really ‘allow’ the photon energy to be converted to other forms. The basic properties of these semiconductors have to be clearly understood in order to gain further insight into the electrochemical kinetics of charge transfer at semiconductor - solution interfaces. It may be pointed out that metals are totally unstable for light energy conversion because their excited electronic states have extremely short lifetimes, and the energy is rapidly dissipated as heat.

The PEC devices have to compete with highly efficient photovoltaic devices. PEC cells like other conventional batteries, involve electrochemical oxidation and reduction processes with the necessary charge transfer made to occur at two electrodes (semiconductor and metal) solution interfaces, making the flow of electrons unidirectional. The redox species may be generated in situ by the incidence of light (as in photogalvanic cells). The photo-electrochemical cell involves the charge transfer process at the semiconductor-electrolyte interface. The electron or hole transfer through the solution of redox species occurs by electronation and de-electronation processes. Thus the redox system is a combination of two species; one losses electron and other gains electron. These redox species are usually counter part of the same species and differ by one or more electron content. For the production of electricity directly from solar energy in the PEC cells, semiconductor electrodes are so chosen that the effect of incident light energy is felt directly on the semiconductor material. This makes available electrons for reduction or holes for oxidation of the species in solution. [5,6]. The semiconductor electrode can be combined with a counter electrode made up of a metal or another semiconductor material so that both the oxidation and reduction processes occur at the appropriate electrodes and electrons flow in the external circuit. The semiconductor materials with the large band gaps (~3.0 eV)
promotes a very few number of electrons from the valence band to the 
conductance band while material with smaller band gaps are not stable in 
water and are useless in harnessing of photons of solar energy. The proper 
use of solvents redox potentials etc are important in working with the PEC 
devices.

2.3. The Theory of a PEC cell

The basics involved in PEC cell is the electrical energy generation 
(i.e., generation of electrical charges, electrons and holes) at a 
semiconductor-electrolyte interface and their circulation via external 
circuits. The corresponding redox reaction occurring at respective electrode 
help in movement of charge carriers.

2.3.1 The Band Structure

The band structure of a semiconductor is the key parameter in solar 
to electrical conversion. In solids, the energy level of an atom transforms 
into an energy band. If an energy band is completely filled it is called 
valence band (VB). The next higher band which may be partially filled or 
completely empty is called conduction band (CB). The difference between 
the minimum of highest energy band (bottom of the conduction band) and 
the top of the valence band is called, band gap ‘Eg’. The electrons in 
conduction band are loosely bound is called band gap, and by giving a 
small energy they can be made to move through the crystal and thus cause 
current.

\[ Eg = Ev - Ec \]  

...(2.1)

Where, Ev is valence band and Ec is conduction band. If the 
conduction band of a solid is partially filled or overlaps on the valence 
band, it is a conductor. If the conduction band is empty and the energy gap 
is large between the conduction and valence band, it is an insulator (bad 
conductor). If the conduction band is empty and the energy gap is small, by
some process covalent bonds can be broken and a few electrons can leap into conduction band; these solids are semiconductors.

![Fig 2.1 Conductor, Insulator and Semiconductor](image)

The conduction band (CB) and valence band (VB) position of several semiconductors studied in the context of the PEC are shown in fig 2.1 a, b and c. The $E_g$ (band gap) is essentially the same for a material, either as an n-type or as a p-type semiconductor. The $E_c$ and $E_v$ are independent of doping and are mostly independent of the redox systems if they do not interact too strongly with the semiconductor. The larger the band gap, the smaller is the wavelength of incident light required for exciting the electrons from the VB to the CB. The oxide semiconductors are less prone to corrosion in water but have large band gaps. Photo corrosion occurs when the holes created on illumination tend to oxidize the semiconductor material. It has been shown that, in the presence of appropriate redox species, the holes will oxidize preferably the solution species. Thus, the semiconductor material is stabilized against photo-corrosion. For efficient
charge transfer at the semiconductor-solution interface, the electron acceptor or donor level must be close to the $E_C$ or $E_V$ respectively.

2.3.2 The Electronation and De-electronation

As mentioned earlier, power is generated by using an oxidation-reduction reaction at a semiconductor-electrolyte interface and the corresponding reduction-oxidation process at a different counter electrode. When an incident light falls on the semiconductor material it results in a difference in the number of mobile excess charge carriers of opposite sign i.e. the electrons and holes. It is therefore necessary to understand the properties of the semiconductor-electrolyte interface and the electrochemical reactions. Electronation and de-electronation reactions are highly reversible in the electrochemical sense and the kinetics of charge transfer are not a limitation for the energy conversion process. In PEC cell, electron/hole transfer across the semiconductor-electrolyte interface occurs by electronation (gain of electrons) and de-electronation (loss of electrons) processes taking place in the solution species. Thus a redox system is a combination of two species; one lose electrons and other gains, which are usually counterpart of the same species and differ by one or more electron content. A few reports are available which deal with the charge transfer across the interface [4, 5]. Gerischer [6] suggested that the reduced and oxidized species may be linked with valence and conduction band respectively. Similar to Fermi level in solid-solid junction, a Fermi level in solid-liquid junction cell can be defined as the electrode potential of the redox, $E_{F,\text{redox}}$. A potential required to transfer an electron from the redox species to a vacuum level or vice versa is called as redox potential. The transfer of the electron to or from the solution can take place only in the energy region of the conduction band and the transfer of hole in the region of the valence band. Such transfer occurs between the two states having the same energy, one occupied and other empty. The energy necessary to transfer an electron from reduced species to oxidized species is analogous

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to a band gap of a semiconductor (Figure 2.2 a) shows the influence of electronic excitation on electron transfer process. The nature of charge carrier is different in the two phases. In solid counterpart of the junction, the charge is electronic, while in liquid counterpart, it is ionic in nature. In solid phase, the environment seen by electron is an electron cloud moving under the periodic potential of positively charged ions and fixed ionic core while in liquid phase, the ion moves with an ionic cloud of opposite charge with or without change in salvation core. In a PEC cell, these two distinctly different phases are brought in intimate contact. In the bulk of semiconductor, the charge carriers are under the influence of isotropic forces.

![Diagram](image)

**Fig. 2.2 a) Electron transfer process across interface b) Qualitative discretion of charge distribution across interface**

While inside the electrolyte the net force on ions is zero. At interface, the ions are under the influence of two forces, one due to ions of the electrolyte itself and other due to electrons of the semiconductor electrode. This type of anisotropy at the interface (in contrast to bulk) results in the new type of arrangement of solvent dipoles, ions of the electrolyte and electrons of the semiconductor, called as electrification of the electrode/electrolyte interface which is shown in (Fig. 2.2 b).
The anisotropy of force in the beginning, makes the charge carrier to accumulate near the surface. When there is sufficient build up of charges on both the sides; the electrical forces at the surface overpower the barrier resulting into the flow of charges. This potential gradient at the interface region acts as a barrier for the further flow of the charges. The potential gradient is high at the surface and gradually decreases as we move away from it. This gives rise to the formation of a double layer.

Extensive study of solid state devices shows that a maximum energy conversion efficiency (30%) is possible with semiconductors having a band gap of about 1.6 eV.[7]. GaAs which can be made both n-type and p-type is one of the most suitable candidates. As high as 23% efficiency has been reported when both electrodes are single crystals while 16% is reported for the cheaper silicon/ polycrystalline thin films. High efficiencies are possible if losses are occurring due to recombination of electron-hole pairs.

2.3.3 Semiconductor -Electrolyte Interface

The semiconductor-electrolyte interface is different from the metal-electrolyte interface in which there is not only a Helmholtz potential drop on the solution side (double layer) but also within the space charge region of the semiconductor [8,9]. This is due to the lower carrier densities in semiconductors. When a semiconductor electrode is dipped into an electrolyte solution containing redox electrolyte, the additional charges present on the electrode surface must be exactly balanced by an equal charge of opposite charges on the solution sides. This is observed only when there is a charge transfer across the electrode-electrolyte interface [10-12]. An equilibrium is established due to charge with a potential drop, $U_{SE}$, in the space charge region below the semiconductor surface, leading to a certain bending of the energy bands. The redox system is characterized by its standard potential referred to the standard hydrogen electrode. However a vacuum level is chosen as a reference point in this study, as is
common in the study of solids. The $E_{\text{redox}}$ is a Fermi level $E_F$ and the point of reference is shifted up by 4.5 eV. [13].

A photo-electrochemical cell (PEC) is based on the junction between a semiconductor (either n or p-type) and an electrolyte, generally liquid, containing a suitable redox couple. At equilibrium, the Fermi level of the semiconductor (which is the electrochemical potential of electrons) equalizes the Fermi level of the redox couple (which is the Nernst potential). This induces band bending with formation of a depletion layer at the interface [2,14-17]. The energy schemes and band bending for n-type and p-type semiconductors in junction with a redox couple in solutions are illustrated in Figure 2.3a.

**Fig 2.3 (b and c) Fermi level diagram**
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This difference in energies, allows the electron transfer from semiconductor to electrolyte. This flow of electrons results in the accumulation of ions on the semiconductor. A strong local electric field developed in such manner will result in band bending. The magnitude of this potential drop in the semiconductor space charge region depends upon the difference between the energies of the two Fermi levels [18]. Under equilibrium condition, the band bending presents an effective barrier to the flow of majority charge carriers. Figure 2.3 b and c shows the energy band structures for n-type and p-type semiconductor respectively after establishing the contact with redox electrolyte. The charge transfer process results in a depletion region inside the semiconductor and a Helmholtz double layer and Gouy-Chapman diffused layer in the electrolyte.

2.3.4 The Flat Band Potential and the Mott Schottky Plot

Another important parameter in PEC is the flat band (FB) potential of the semiconductor-electrolyte system. It is possible to remove the band bending shown in figure 2.3 b & c so that CB and VB levels are straight. An externally applied potential E can remove the band bending and the following relation holds good.

\[ E_{FB} = E_{\text{redox}} - E \]  

...(2.2)

The FB potentials have been experimentally determined and vary with the composition of the redox system in solution. It also varies with the composition of the redox system in solution and solution pH in the case of some semiconductors (oxide semiconductors) and are independent of the pH in the case of others, e.g. MoSe₂. The FB potential shows a small variation with temperature and is generally obtained using the Mott-Schottky equation [19,20].

\[ \frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_o N_D} [V - V_{FB} - (kT/e_o)] \]  

...(2.3)

Where, \( C \) - capacitance measured, \( \varepsilon_o \) - permittivity of free space,
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\(\varepsilon\) - dielectric constant, \(V_{FB}\) - flat band potential and \(V\) is the applied potential. The intercept of the linear portion of a line on the X-axis of the plot \(1/C^2\) versus \(V\) gives the \(E_{FB}\). With most semiconductors, \(E_{FB}\) is independent of the frequency of the alternating voltage superimposed in the experimental determination of the capacitance. The slope of the linear region can be used to calculate the carrier density \((N_D)\) of the semiconductor according to the above expression.

The FB potential can be determined by using other methods as well. It is observed that with n- type semiconductors, in particular, the photo-oxidation of a redox solution species sets in at this potential, an anodic polarization of the semiconductor. Knowing the \(E_{FB}\) one can determine the \(E_{CB}\) or \(E_{VB}\) with the help of the expression;

\[N_D = N_C \exp[-(E_C-E_F)/kT]\] \(\ldots(2.4)\)

Where \(N_D\) is the donor density, \(N_C\) is the density of states in the CB, \(K\) is the Boltzmann constant, \(T\) is the absolute temperature, and \(E_F\) is the Fermi level. The energy scheme of a semiconductor electrolyte interface looks very similar to that of a semiconductor-metal Schottky junction. The nature of the photo effect is identical in both cases.

Electron-hole pairs are created by light and separated by the electrical field. The highest possible photo-potential depends on the band bending below the semiconductor surface obtained at equilibrium in the dark. Hence a redox system whose Fermi level \(E_{red}\) is close to the \(V_B\) of an n-type semiconductor must be chosen to achieve maximum band bending. If the semiconductor is having band gap about 1.6 V, a high energy conversion can be expected.
2.3.5 Charge Transfer Phenomena

2.3.5.1 The Charge Transfer in Dark

The charge transfer process occurs across the electrode/electrolyte interface by the movement of positively charged ions from the solution side to the electrode, they can also jump back in the reverse directions so that there can occur both electronation and de-electronation. A positive ion moves against the field direction in an electronation reaction, while in de-ele-lectronation it will move in the direction of field which is shown in figure. 2.4 (a) If the positive ion is to be activated through a potential difference of magnitude $\beta\Phi$ in electronation reaction, then it has to be activated by $(1-\beta\Phi)$ in de-electronation, where $\beta$ is symmetry factor and $\Phi$, a potential through which ion passes. The net current density is given by the following equation;

$$i = i_0 \exp \{[(1-\beta\Phi)vF/RT]-\exp(-\beta vF/RT)} \quad \text{(2.5)}$$

The equation 2.5 is the famous Butler–Volmer relation [21]. The equation shows the dependence of current density across interface on the potential ‘$\nu$’. A small variation in $\nu$ produces a large change in current density. In the electrode/electrolyte systems, a hill shaped potential barrier is present even in the absence of electric field as shown Fig. 2.4 b. This barrier is related to the atomic movement during bond stretching which is prerequisite for processes such as chemical reaction and the diffusion of atoms/ions. The electric field modifies the existing potential barrier such that only a fraction of the input electrical energy $qv$, turns in to the change of activation energy and hence in the rate expression. This is because the atomic movement necessary for the system to reach a barrier peak is only a fraction of the total distance over which potential barrier extends.
2.3.5.2 The Charge Transfer in Light

When a semiconductor-electrolyte interface is illuminated, the electron-hole pairs are generated in the depletion region of the PEC cell and are separated by the electric field at the interface [22,23]. This charge separation process results in a generation of a counter field which is maximum at the open circuit condition and is indicated as $V_{oc}$. This photo voltage acts as driving force for electrons to move from semiconductor to counter electrode, whereas the holes are captured by species in electrolyte to undergo oxidation reaction. The whole redox reaction occurring can be written as;

Red (solv) + h$^+$ $\leftrightarrow$ Oxi (solv.) (at semiconductor electrode) ...(2.6)

Oxi (solv) + e$^-$$\leftrightarrow$ Red (solv.) (at counter electrode) ...(2.7)

The electrode acts as a shuttle in charge transfer reaction. For n-type of semiconductor material in contact with electrolyte under illumination with a forward bias voltage (V). The various electronic processes is taking
place are depicted in Fig 2.5. The quasi fermi levels for electron ($e_{fn}$) and for holes ($e_{fp}$) in the depletion region are assumed to be flat so that the difference between them can be taken as;

$$-qu = e_{fn} - e_{fp} \quad \quad \quad (2.8)$$

The assumption that $u>v$ represents the fact that the minority carrier concentration under illumination is greater than that in dark. For holes to flow from semiconductor surface to an electrolyte, $u$ is defined as,

$$[\exp (qu/kt)] = p(w)/p_o \quad \quad \quad (2.9)$$

Where, $p(w)$ is the hole concentration at the depletion layer edge ($x=w$) and $p_o$ is the equilibrium hole concentration in bulk of semiconductor under dark condition. It is assumed that most of the applied voltage appears across the semiconductor depletion region. Thus the series resistance of a cell should be negligible and an electrolyte concentration should be high such that $c_h > c_{le}$. The depletion layer width under this circumstance is given by;

$$w = w_o(v_d - v_o)^{1/2} \quad \quad \quad (2.10)$$

Where $w_o = [2e_e\varepsilon_o/qn_d]$, $\varepsilon_o$ is the dielectric constant of the material, $\varepsilon_o$ is the permittivity of the free space, $n_d$ is the donor concentration and $v_d$ is the equilibrium band bending voltage. If $s_t$ be the surface transfer velocity, $s_r$ -the surface recombination velocity, $\Phi_\gamma$ - the incidence photon flux (after allowing the losses due to reflection and absorption by electrolyte) $\alpha$- the light absorption coefficient and $w$ is the width of depletion region, the minority carrier flux due to hole injection can be given by;

$$j_i = (s_t/s_r) \{\Phi_\gamma [1-\exp (\alpha-w)/(1+\alpha t)]\} \quad \quad \quad (2.11)$$
Fig. 2.5  The electron energy level diagram for n-s/e interface under illumination and biasing voltage ‘v’.

The direction of $j_i$ is opposite to the photo generated flux and is the photo generated current of the working PEC cell flowing from semiconductor electrode to electrolyte [24].

2.3.6 Electron hole Recombination

The efficiency of a PEC cell is zero when the rate of recombination is equal to that of photo generation. Radiative recombination losses are generally very small. Radiationless recombination involving surface states which is responsible for major losses. These states are induced by extraneous chemical impurities or by atoms of the semiconductor itself, for example atoms which are less tightly bound in the lattice. These loosely bound atoms are encountered in the bulk, at defects (dislocation), and occur in plenty at grain boundaries and the surface [25]. The recombination rate, $S_r$, depends on $V$ and is given by;

$$S_r = \sum \delta_{ij} N_{e,i}^i N_{n,j}^j \quad \ldots(2.12)$$
Where,

\[ N_e^i \] - the electron population at the \( i \)th state,

\[ N_n^j \] - the hole population in the \( j \)th state,

\[ \delta_{ij} \] - the cross-section for their recombination.

The states \( ij \) are due to the splitting caused during the formation of bonding and antibonding orbitals. The weak bonding causes smaller splitting between bands. The recombination current is a function of the electrode potential, since the \( N_e^i \) and \( N_n^j \) depend on the energy difference between the Fermi level and the surface state responsible for recombination. The potential at which the recombination current becomes equal to the photo-generated current defines the limit of the achieved \( V_{oc} \).

When this limit is reached, the \( V_{oc} \) no longer depends on the \( E_0 \), i.e. redox in solution and we have Fermi level pinning. When the recombination current is high, a loss in \( ff \) is observed. A lower \( I_{sc} \) is also attributed to recombination effects. The correlation between high recombination rates and weak chemical bonds has been proved from studies with layered semiconductors such as \( \text{MoSe}_2 \), \( \text{MoS}_2 \), graphite, are naturally occurring lubricant consisting of layers in the crystalline state. These layers can slip past each other. These compounds have Van-der Waals planes in which all the surface atoms are bound strongly. The binding in the direction perpendicular to these planes is weaker. Recombination of electrons and holes were shown to be very rapid at ‘step’ with planes perpendicular to the surface. The solar energy conversion efficiency is also found to be higher if the semiconductor material is free from step free.

The recombination cross-section is larger when the spacing between the states is small and when surface states are present in the middle of the band gap. In large band gap semiconductors, e.g. \( n-\text{TiO}_2 \), surface combination losses are not significant. Further even if the surface states are as much as 0.5 eV below the conduction band or above the valence band,
the gap to be crossed by the recombining holes and electrons will be more than 2 eV. On the other hand, with ideal semiconductors \((E_g = 1.4 \text{ eV})\), the gaps between states differing by 0.5 eV from the conduction band and valence band will be only 0.3 eV. Recombination is easier and happens more often. Energy from this radiationless process is transformed to the mechanical energy of lattice vibration.

A 10% conversion efficiency of the cell n–WSe\(_2\)/ KI, KI\(_3\) / C has been reported when perfectly smooth Van-der Waals planes of layered WSe\(_2\) are used. A more recent paper reports 18% efficiency with n- WSe\(_2\), prepared using SeCl\(_4\) as carrier gas. A 7.2% efficiency was reported for the cell n–CdS/Na\(_2\)S, S, NaOH/C where a light assisted ion exchange produces a layer of CdS on the surface. The layer thickness is about 10 Å. There is very little recombination loss since the \(E_g\) of CdS is 2.4 eV. (CdSe, \(E_g\) is 1.6 eV). The ingredient of the solution is thus responsible for increased chemical bonding on the surface owing to the photo assisted reaction with the semiconductor surface. Mild air oxidation or anodization of the semiconductors is also found to reduce the recombination rates.

2.3.7 Cell Efficiency Parameters

The following are the parameters that govern the efficiency of a PEC cell.

2.3.7.1 Maximum-Power Point

A Solar/PEC cell may operate over a wide range of voltages (V) and currents (I). By increasing the resistive load on an irradiated cell continuously from zero (a short circuit) to a very high value (an open circuit) one can determine the maximum-power point, that is, the load for which the cell can deliver maximum electrical power at that level of irradiation.

\[
V_m \times I_m = P_m \quad \text{(in watts)} \quad \ldots(2.13)
\]
2.3.7.2 Energy Conversion Efficiency

A semiconductor electrode has a threshold for light absorption which is ideally a band gap of the material. The photon energies below this threshold value are not absorbed. For the activation of the PEC cell, only the photons having energy above the band gap may be utilized. The conversion efficiency (\( \eta \)) is given by [22,24],

\[
\eta = \frac{E_g \delta \{ \alpha (E) N (E)/ E N(E) \} dE}{dE} \quad \text{(2.14)}
\]

Where, \( E_g \) is the band gap, \( \alpha (E) \) is the fraction of photon absorbed, \( N (E) \) is the number of photon incident having energy \( E \). The various factors such as ohmic loss, light absorption in the solution etc. are neglected. The above equation was suggested for large value of band gap and high absorption coefficient. If the band gap as well as absorption coefficient is high, the efficiency will be higher. The \( \alpha (E) \) [24] near band gap is,

\[
\alpha (E) = A (h\delta - E_g)^n / h\delta \quad \text{(2.15)}
\]

Where, \( A \) is constant and \( \eta \) takes value of \( \frac{1}{2} \) or 2 and suggest the type of transition. \( n = \frac{1}{2} \) for direct type of transition and \( n = 2 \) for indirect type transition. To obtain \( \alpha (E) \) value higher, the value of ‘\( E_g \)’ must be low. Thus the equations 2.14 and 2.15 are contradictory. Fig. 2.6 shows maximum efficiency at the value of \( E_g = 1.2-1.4 \) eV.

In practice, the energy conversion efficiency (\( \eta \)) of any solar to electrical conversion cell is the percentage of power converted (from absorbed light to electrical energy) and collected, when a cell is connected to an electrical circuit. This term is calculated using the ratio of \( P_m \), divided by the input light irradiance under "standard" test conditions (\( E \), in W/m\(^2\)) and the surface area of the solar cell (\( A_c \) in m\(^2\)).

\[
\eta = \frac{P_m}{E \times A_c} \quad \text{(2.16)}
\]
On a clear day, the solar radiation at the equator is about 1000 W/m². Hence, the "standard" solar radiation known as the "air mass 1.5 spectrum" has a power density of 1000 watts per square meter. Thus, a solar cell having 1 m² of surface area and 12% efficiency in full sunlight at solar noon (at the equator) during March or September equinox will produce approximately 120 watts of peak power.

2.3.7.3 The Fill Factor

Another defining term in the overall behavior of a cell is the fill factor (FF). This is the ratio of the maximum power point divided by the open circuit voltage and the short circuit current.

\[
FF = \frac{P_m}{V_{oc} \times I_{sc}} = \frac{\eta \times A_c \times E}{V_{oc} \times I_{sc}} \quad \text{(2.17)}
\]

Where, \(I_{sc}\) and \(V_{oc}\) are short circuit current and open circuit voltage respectively. \(P_m\) is the maximum power delivered by cell, \(\eta\) is efficiency. The fill factor should be low in PEC cell with high internal resistance. The maximum open circuit voltage attainable from a PEC cell would be,

\[
V_{oc} = V_{Redox} - V_{fb}. \quad \text{(2.18)}
\]

Thus ultimate efficiency also depends upon \(V_{Redox}\).

2.3.7.4 Quantum Efficiency

The Quantum efficiency refers to the percentage of absorbed photons that produce electron-hole pairs (or charge carriers). This is a term intrinsic to the light absorbing material, and not the cell as a whole (which becomes more relevant for thin-film solar cells). This term should not be confused with energy conversion efficiency, as it does not convey information about the power collected from the solar cell.

2.4 Parameters Controlling the Efficiency of a PEC Cell

The concept of operation of a PEC cell is technologically appealing since the solid/liquid junction is easily obtained simply by immersing the
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semiconductor electrode into the liquid electrolyte. The selection of semiconductors having suitable band gap values is of prime concern. The efficiency of a PEC cell depend upon band gap (E_g), photo corrosion, recombination rates of photo generated holes and electrons in the bulk at the surface and at grain boundaries, the absorption of light by the electrolyte, the internal cell resistance, the electrode kinetics of the charge transfer process, and the stability of the semiconductor material in the solution environment [26,27]. The polycrystalline nature of the film materials are the important parameters to be studied for establishing a stable, high efficiency PEC cells.

2.4.1 Band Gap

As discussed in earlier section, the efficiency is proportional to V_oc x I_sc x ff. The V_oc increases with E_g , while I_sc increases with the fraction of the photons absorbed and hence with intensity. The theoretical maximum efficiency is 30% for a band gap of 1.5eV with light of 960 nm. A high theoretical efficiency of 50% seems possible with junction of multiple semiconductors, each absorbing a part of the solar spectrum. CdTe, GaAs and InP are ideal semiconductors in this respect. An efficiency of 12% has been realized with single-crystals of n-GaAs, while CdSe (1.7eV), CulnS_2 (1.5eV) and Si (1.13V) give a lower efficiency of 5%. TiO_2 (3.00eV), SrTiO_3 (3.2eV) and CdS (2.4eV) have large band gaps and do not have the appropriate band levels, therefore yield efficiencies ranging from 2-3%. Thus for higher conversion efficiencies, the semiconductors must have a band gap in the range 1.1-1.6 eV.

2.4.2 Photo Corrosion

The photo generated minority charge carriers in solution may oxidise or reduce the n-type or p-type semiconductor. This is called photo-corrosion, which rapidly degrade the life of PEC. To prevent such photo
corrosion effect, two main routes can be used, one which is based on a kinetic approach and the other based on a material selection approach.

The first route is pursued with the choice of suitable electrolyte compositions in order to make the rate of transport of the photo-generated minority carriers to the redox couple much faster than that of photo corrosion. In such cases, even if the photo corrosion process is thermodynamically favored, its rate is made negligibly small so that semiconductor electrode becomes kinetically stable.

The material approach is directed to the selection of semiconductor materials whose optical transitions do not involve bonding orbitals, thus having promise of good stability against photocorrosion. This condition appears to be fulfilled by layered semiconductors (e.g. molybdenum and tungsten chalcogenides) and by using ternary semiconductors.

2.4.3 Absorption and Reflection of Light

The absorption of light by the redox electrolytes depends on the intensity of color of the solution and the volume and size of the cell. The colorless electrolytes will not involve losses due to absorption. The \( \text{S}_2^{2-} / \text{S}^{-2} \) electrolyte system absorbs at 470 nm, while that of \( \text{I}^- / \text{I}_3^- \) at 570 nm. The loss due to absorption of light is about 2 ± 10% Å. The \( \text{V}^{3+} / \text{V}^{2+} \) redox couple absorbs weakly in the whole range of visible light. The cell \( \text{p-InP/V}^{3+/2+} \text{HCl/C} \) which has shown 11.5% efficiency would have had a 14% efficiency in the absence of absorption.

The reflection losses cannot be eliminated since antireflection coating cannot be applied at the solution interface. Surface modifications by coating will alter electrode kinetics. The Etching of submicron hills in semiconductor can help in reducing the reflection losses.
2.4.4 Electrode Kinetics

In a photovoltaic device, increased intensity of radiation can increase the \( V_{oc} \). In a PEC cell, a sluggish mass transfer can limit the effects of sunlight. A limiting current is present but it is more often solution–diffusion controlled rather than light-intensity controlled. The photocurrent must become ultimately limiting since the number of electrons (holes) generated by light is limited by the intensity of incident light and the band gap of the semiconductor. A slow diffusion of ions in solution is due to the high viscosity of the medium and ion-solvent interaction. A less conducting solution increases the internal resistance of the cell and lead to poorer efficiency. High concentration of the redox system without a supporting electrolyte, if possible are recommended.

Charge transfer electrode kinetics may not alter the \( V_{oc} \) but may reduce \( I_{sc} \). The fill factor, is however, invariably reduced. If the rate of recombination of holes and electrons exceeds the rate of reduction by electrons and that of oxidation by holes, the efficiency is bound to become poorer. Generally, one electron processes which are highly reversible at the semiconductor–solution interface are chosen to avoid the effects of slow kinetics of charge transfer and chemical reactions in the overall electrode processes.

2.4.5 The Polycrystalline Materials

All solar cells require a light absorbing material contained within the cell structure to absorb photons and generate electrons via the photovoltaic effect. The materials used in solar cells tend to have the property of preferentially absorbing the wavelengths of solar light that reach the earth surface. However, some solar cells are optimized for light absorption beyond Earth's atmosphere as well. Many currently available solar cells are configured as bulk materials that are subsequently cut into
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wafer form and used. The other materials are configured as thin-films (inorganic layers, organic dyes, and organic polymers) that are deposited on supporting substrates.

The various thin-film technologies currently being developed to reduce the amount (or mass) of light absorbing material required in creating a solar cell. This can lead to reduced processing costs of bulk materials (in the case of silicon thin films) and also tends to reduce energy conversion efficiency. Many multi-layer thin films have efficiencies above those of bulk silicon wafers. Cadmium telluride is considered as an efficient light-absorbing material for thin-film solar cells. Compared to other thin-film materials, CdTe is easier to deposit and more suitable for large-scale production. Despite the toxicity of CdTe-based solar cells, this evolved as the only technology (apart from amorphous silicon) that can be delivered on a large scale.

The grain boundary is the weak bond region in a polycrystalline material. The recombination problems are not severe with large band gap semiconductors for the reasons mentioned earlier. Similar efficiencies have been reported for polycrystalline n - TiO₂ (produced by flame oxidation of titanium) or n-CdS (by anodization of cadmium) and single crystals of the same material. On the other hand, the efficiencies of small band gap semiconductors are reduced by an order of thousand when polycrystalline materials are used instead of single crystals.

Chemisorption in some cases (e.g. chemisorptions of Ru ³⁺ at boundaries of 3-4 μ grains of n- GaAs films) increases the efficiency of the cell. The strong bonds are formed when an impurity is adsorbed strongly so that the splitting of the states becomes large enough to prevent recombination. It is sufficient that the impurity diffuses into the grain boundaries of the top several thousand angstroms (<10⁻⁵ cm) of the polycrystalline material. This is easily achieved even at room temperature
by doping of the semiconductor in the appropriate solution. The efficiency also depends on grain size. Larger changes are observed in I–V curves with grains of size 3–4 μm.

### 2.4.6 Stability of Semiconductor Electrodes

Most semiconductors can either be oxidized by holes in the valence band, or reduced by accumulation of electrons in the conduction band forming either soluble or insoluble products. Some materials may even undergo both types of photo-decomposition. Examples, CdS photo-decomposes into Cd$^{2+}$ ions and molecular sulphur, and ZnO into Zn$^{2+}$ ions and molecular oxygen. The holes generated in the process are responsible for these photo-corrosion. The surface of the semiconductor can get modified by such processes and the modified surface can catalyze hole–electron recombination. When the thickness exceeds a critical value (larger than the distance the carriers can tunnel through) the transport of holes to the electrolyte may get inhibited. The overall effect is a decrease in energy conversion efficiency.

The water oxidation of CdS can also occur if hole concentration reaches a sufficiently high value at the surface. However, this is considered energetically less favorable than the decomposition of CdS.

The presence of the redox couple [Fe(CN)$_6$]$^{4-}$ as electrolyte, in spite of the $E_0$ redox level being below that of the decomposition potential of CdS, can reduce photo corrosion of the semiconductor. This is attributed to the high reversibility of the one- electron process of [Fe(CN)$_6$]$^{4-}$ being oxidised to [Fe(CN)$_6$]$^{3-}$ involving a much lower activation energy. A general recommendation is that only those redox couples be selected which satisfy the following condition;

$$E_{\text{redox}} > E_{\text{decomp}}$$

Examples given in the literature indicate that the oxidation of the solution species will effectively compete (for the holes) with that of the
semiconductor material if the Fermi energy level of the redox species is not at the valence band but somewhat above it. This observation implies that surface states are involved. The electrons are transferred from the redox species to the surface states, and then recombine with the holes of the valence band.

If surface states are present, holes may move towards the surface and rupture a surface bond. The remaining electron is then no longer in the valence band but in an energy state a little above it. As soon as another hole is trapped, the next bond may be broken and surface atoms get dissolved. This second step may be prevented if an electron is quickly transferred from the redox species to the surface atom with a broken bond. The bond is then restored. This stabilization consists actually of a partial dissolution followed by a regeneration process.

Corrosion of photo anodes can be avoided if irradiation is restricted to a level indicated by the rate of hole consumption by the redox couple. In addition to charge transfer, mass transfer also plays a role in the latter process. Hence mechanical agitation or flow of the electrolyte can result in faster hole consumption by the redox species. A large concentration of the oxidizable form of the redox species will also lead to lower photo corrosion of semiconductor material. In the cell n GaAs/K$_2$Se, K$_2$Se$_2$, KOH/C photo corrosion is prominent up to 0.1 M selenide concentration and becomes negligible at 0.2 M concentration.

MoS$_2$, MoSe$_2$ and WSe$_2$ are typical layered dichalcoagenide semiconductors where, the Van der-Waals planes are much more corrosion-resistant than the other planes. These semiconductors are also more stable than other semiconductors with similar band gaps (1.1 – 1.6 eV). This stability is associated with stronger bonding at the surface which reduces the density of hole traps. Further the electrons are excited into bands formed by nonbonding rather than antibonding orbitals of the
transition metals. The Cl\(^{-}\) can even be oxidized to Cl\(_2\) by these semiconductors without these being corroded.

The p-type semiconductor used as cathode is generally less prone to corrosion, owing to cathodic protection. Irradiation causes transport of electrons to the solution interface preventing oxidative corrosion. Reductive corrosion has been observed with p-InP and p-GaAs.

Photocathode stability is further improved by the formation of passivating oxides under mild anodization. The cell p-InP/VCl\(_3\), VCl\(_2\), HCl/C gives an efficiency of 11.5% with little corrosion of p-InP.

### 2.4.7 Natural Resistance

The natural resistance to electron flow in a cell decreases the cell efficiency. These losses predominantly occur in three places; in the bulk of the semiconductor material, in the top layer of thin film and at the place of electrical contacts. The resistance associated with PEC includes series resistance and the shunt resistance. For an efficient cell, the series resistance should of the order of few hundred ohms while shunt resistance should be about few kilo ohms.

### 2.4.8 Temperature

The solar/PEC cells work best at low temperatures, as determined by their material properties. All cell materials lose efficiency as the operating temperature rises. Much of the light energy shining on cells becomes heat, so it is good to either match the cell material to the operation temperature or continually cool the cell.

### 2.5 Advantages and Disadvantages of PEC Devices

The followings are the advantages and disadvantages of PEC devices [28].

#### 2.5.1 Advantages

1. They are regenerative and their solution composition remains unchanged.
2. The major advantage is that the semiconductor–electrolyte junction is achieved immediately on immersion of the semiconductor in the solution. Since doping and diffusion are not involved, random orientations and shunting do not pose major problems. Doping and diffusion are also not required with metal-semiconductor (Schottky) junctions.

3. A wide variety of semiconductors and redox electrolytes are available for investigation.

4. Unlike in photovoltaic devices, antireflection coating of semiconductors is not required in PEC cells.

5. Colorless electrolytes can be used to minimize bulk absorption losses. Commonly used redox couples like $S^{2-}/S_2^{2-}$ and $I^-/I^3-$ lead to about 20% loss of useful solar photons.

6. Electro catalysis can be utilized to improve the electrode kinetics of the charge transfer process and consequently the efficiency of energy conversion.

### 2.5.2 Disadvantages

1. Photo corrosion of the semiconductor by holes is a serious problem. Oxides are corrosion of the semiconductor by holes is a serious problem. Oxides are corrosion-resistant but have a wide band gap. Hence the energy of incident illumination has to be higher while using to them. Non-aqueous media may prove useful in this chapter.

2. Recombination of holes and electrons lead to poorer efficiency. Chemical impurities are mainly responsible for this, and appropriate chemical treatment has to be carried out to meet the situation.

### 2.6 Toxicity Considerations

The perception of the toxicity of ZnHgTe is based on the toxicity of elemental mercury, a heavy metal that is a cumulative poison. The Scientific research carried out in National Renewable Energy Laboratories
(NREL) in the USA, has shown that the release of mercury to the atmosphere is quite lower than those of CdTe-based solar cells and silicon based thin-film solar cell technologies. The quantity of Hg present in a thin film is few milligrams, not in term of elemental but highly stable compound form. This compound is having its melting point more than 800 degree.

2.7 Conclusion

The PEC utilizing semiconductor- electrolyte cells are promising systems for solar energy conversion. The studies carried out have helped in understanding in detail the physics and chemistry of semiconductors and the interfaces. The PEC cells are easy to set up and are cheap. There is no problem of lattice mismatch as the junction is formed easily. The doping is not required. The major obstacle that PEC, like solar cell faces is the problem of recombination of charge carriers at grain boundaries. A new generation of cells in which the semiconductor surface is covered by chemically formed films is being looked into in this context. Now a days semiconductor coated with a sensitizer dye which functions as a mediator has been successfully reported. The PEC cells are still promising since post-depositive treatments and measures adopted may help to improve the cell efficiency.
References: