Chapter-II

CHEMISTRY OF PHOTOCURRENT ELECTRODE-ELECTROLYTE INTERFACE
2.1 Introduction

In recent years, semiconductor-electrolyte cells have been attracting a great deal of interest in the field of solar energy conversion.\textsuperscript{1-3} They are simple to make as compared to conventional p-n junctions or Schottky barrier cells which require highly pure semiconductor materials prepared under stringent controlling conditions. For the semiconductor-electrolyte cells, solar energy conversion efficiencies up to $\approx 12\%$ have been achieved, which are comparable to those obtained from conventional solid state photovoltaic devices. Photoelectrochemical devices have an additional inherent advantage that either electricity or useful chemical species with potential applications can be produced at the interface whereas only direct electricity generation occurs with solid state photovoltaic cells. These devices are simple to construct and mainly consist of two electrodes, one metallic and other semiconducting. Photoelectrode which is immersed in electrolyte and then exposed to sunlight, converts solar radiations into electrical energy by creating delocalized charges with high yield. The electron-hole pair gives the redox species. The charge transfer process across a photoelectrode-electrolyte interface in dark or in light results in the current flow through the junction.

In this chapter, mainly the chemistry of the photoelectrode-electrolyte interface is discussed in detail. The photoelectrode i.e. semiconducting material is discussed with the help of band theory. In order to understand the mechanism of charge transfer across the junction, the energy levels, both in electrolyte and semiconductor are considered. The process involved in junction formation is discussed with reference to space charge layer, Helmholtz double layer, Gouy Chapman layer and the Butler-Volmer relation for charge transfer mechanism. The differential capacitance and Mott Schottky plots for the charge transfer mechanism of semiconductor at electrolyte interface both under illumination and in dark are studied. Theoretical and practical conversion efficiency considerations are also mentioned.
2.2 Concept of Semiconductor

Solid materials are classified according to the population of electrons among the energy bands viz. metals, semiconductor and insulators. If a completely filled band has a partially filled band lying just above it in a material, it will show metallic conduction. If the band is completely filled, the applied field cannot impart any change in electron movement as no empty state is there to accommodate the electron with changed energy. The next empty band lies far above and cannot be reached by the electrons of filled band. Such materials will be insulators. The bands are separated by an energy gap, called band gap (or forbidden band) ‘Eg’ devoid of energy level

\[ E_g = E_v - E_c \]

Where, \( E_v \) is valence band and \( E_c \) is conduction band energy. If the forbidden energy gap is narrow, at temperature \( T>0 \) K, it may be possible for some electrons from full band to have sufficient thermal energy to jump into higher empty band. As a result, movement of charge carriers is possible because of availability of empty states. This type of material is called as semiconductor.

Partially filled band can also result from the overlap of completely filled band with an empty band. The formation of energy bands in metal, insulator and semiconductor are shown in Fig. 2.1

Semiconductors are mainly classified into two groups

1) Intrinsic semiconductor
2) Extrinsic semiconductor

1) Intrinsic Semiconductor

When the energy band gap is sufficiently narrow, some of the electrons occupying states at the top of the valence band may gain thermal energy sufficient to transfer to empty states in conduction band and such electrons can contribute to conductivity of the material. Because the temperature, at which conductivity becomes appreciable, depends on the crystal structure, such crystals are properly called intrinsic semiconductor. The density of conduction electrons in a semiconductor increases with temperature so that its
conductivity also increases. The Fermi level lies exactly at the middle between the conduction and valence band in an intrinsic semiconductor.

\[ E_F = \frac{1}{2} (E_v + E_c) \] \hspace{1cm} \text{2.2}

For intrinsic semiconductors at higher temperature continuous thermal agitation exists, which results in the excitation of electrons from valence band to conduction band and leaves an equal number of holes in the valence band. The process is balanced by recombination of electrons in the conduction band with holes in the valence band. At room temperature, the intrinsic carrier density is small. Intrinsic carrier density increases rapidly with temperature. At high temperature, thermal generation can be dominant process of carrier generation. Because of this thermal effect, the carrier concentration becomes equal to the background concentration at the intrinsic temperature. Below intrinsic temperature, the carrier concentration is relatively temperature independent. Above intrinsic temperature, it rises exponentially with temperature.

2) Extrinsic semiconductor

In real crystals, there always exist impurities or defects giving rise to new energy levels in the band gap. Crystals usually contains some foreign atoms, which may be present in interstitial or substitutional solid solution. These atoms have valence electrons, which are bound to their nucleus by force differing from those binding such electrons in the other atoms. In terms of band model, this means that there are energy levels present in the crystal which different in energy. If the electrons occupying this energy level can contribute to conductivity in a crystal, then such a crystal is called an extrinsic semiconductor. If the substitutional impurity atoms have five or more valence electrons, they are said to “donate” excess of electrons to the crystal. It increases the concentration of electrons in the conduction band without generating any extra holes in the valence band. Since the electron concentration is greater than hole concentration, the former become the majority carrier. The energy of these levels is usually somewhat less than the energy level at the bottom of the conduction band, electrons being the
majority carrier, it is called as n-type semiconductor. If the impurity atoms have three or less valence electrons, they can “accept” electrons. The energy level so called acceptor level is usually slightly higher than the level at the top of valence band. An electron from the valence band can be easily excited to this localized level leaving a hole in the valence band. This itself does not generate any electron in the conduction band. The majority carriers are holes. These types of extrinsic semiconductors are known as p-type semiconductors.

The band diagram of the different types of semiconductors is shown in Fig. 2.2

When a semiconductor is doped with donor or acceptor impurities, impurity energy levels are introduced. A donor level is defined as being neutral if empty and negative if filled by an electron. The conductivity of doped semiconductors is then much higher than that observed for intrinsic semiconductor. The position of the Fermi level depends upon the relative values of the effective masses of the electron and the hole. If effective mass of electron is greater then effective mass of hole then, it move downwards, in the contrary cases, it moves upwards.4-6
Fig. 2.1: The band structure and Fermi level of
a) a conductor
b) an insulator
c) a semiconductor.

Fig.2.2: Band diagram for (a) n-type semiconductor and
(b) p-type semiconductor
2.3 Description of Electrolyte

The electronic properties of the electrolyte have already been studied by Marcus and Gerischer. According to them, oxidized and reduced species present in the electrolyte do not have the same energy due to different degree of solvation. The oxidized species are acceptors, which corresponds to the empty electronic levels, while the reduced species are donor, which corresponds to the occupied electronic levels.

The distribution of electronic levels of the redox system is schematically depicted in following Fig.2.3

![Energy diagram of an electrolyte](image)

**Fig.2.3: Energy diagram of an electrolyte**

As shown in equation 2.3 the electronic structure is concentration dependent, thus a concentration change induces a shift of the redox potential ($E_{\text{redox}}$). This is described by the well-known Nernst equation;

$$E_{\text{redox}} = E_{\text{redox}}^0 + \frac{RT}{zF} \ln \left( \frac{C_{\text{Ox}}}{C_{\text{Red}}} \right) \hspace{1cm} 2.3$$

Where, $E_{\text{redox}}^0$ is the standard redox potential, $C_{\text{Ox}}$ and $C_{\text{Red}}$ are the concentrations of the oxidized and reduced species respectively, R the gas constant, z the number of electrons involved in the reaction and F Faraday constant.
2.4 Photoelectrode-Electrolyte Interface

2.4.1 Introduction

To study the operation of photoelectrochemical cell in detail, we must examine the energy level diagram of electrolyte and photoelectrode. The simple photoelectrochemical cell consists of a semiconductor electrode dipped in an appropriate electrolyte to form the junction to be illuminated by solar energy. When n-type semiconductor having energy ‘Eg’ immersed in an appropriate electrolyte (the principles for p-type materials are generally the same) the electrochemical potential of electrons in semiconductor electrode is represented by its Fermi level and in the liquid electrolyte containing a redox couple, by its redox potential. A redox couple implies two-electroactive species in the solution, one being the electron donor and other acceptor. The transfer of electric charge produces a region on each side of the junction where the charge distribution differs from the bulk materials, and this is known as space-charge layer. This layer provides the initial Fermi levels of two phases, which are different.

When the photoelectrode is immersed in an electrolyte, electron transfer takes place at the interface until the Fermi levels in two phases are equal. In this case, electron from the photoelectrode is transferred to the solution, which results in the photoelectrode positively charged. This charge is distributed in the space-charge region near the surface. The valence and conduction band edge are bent as a result of the formation of space charge region, establishing a potential barrier against further transfer of electrons into electrolyte. The direction of the field is such that holes generated in the space charge region move towards the interface and excess electrons move towards the bulk. The width of the space charge is given by

\[
W = (2 \frac{\varepsilon_s \varepsilon_0 V_B}{e N_D})^{1/2}
\]

Where, \(V_B\) is the extent of band bending in depletion layer. \(e\) is electronic charge, \(N_D\) is donor charge density in the photoelectrode, \(\varepsilon_s\) is dielectric constant of photoelectrode materials; \(\varepsilon_0\) is the permittivity of free space.
Similarly, a charged layer (Helmholtz layer) also exists in the solution side of the interface, which is made up of ions that are charged opposite in sign to the charge in depletion region. The width of the Helmholtz layer is of the order of few Å.

The energy levels of photoelectrode and the electrolyte are related via a parameter known as flat band potential ($V_{fb}$). It is the electrode potential at which the conduction and valence bands are flat. $V_{fb}$ is influenced by the specific absorption of ions from the electrolyte on the surface of photoelectrode. At equilibrium in the dark, the electrode potential ($E_F$) is equivalent to the potential of redox couples ($V_{redox}$). The extent of band bending is given by

$$V_b = V_{redox} - V_{fb} \quad \text{---------------------2.5}$$

This is the driving force for the separation of electron-hole pair.

When a photon of energy greater than $E_g$ is absorbed in the semiconductor, electron-hole pairs are created, which are separated by the electric field formed in the space charge barrier. The minority carriers (holes for n-type) move towards the semiconductor-electrolyte interface and produce an anodic oxidation reaction. The majority carriers (electron for n-type) move towards the semiconductor bulk and subsequently to the counter electrode through an extended circuit, where they produce a cathodic reduction reaction. The possible reaction in addition to recombination after the absorption of light is

$$P^+ (\text{surface}) + R \rightarrow O \quad \text{---------------------2.6}$$

$$e^- (\text{space charge}) \rightarrow e^- (\text{bulk}) \quad \text{---------------------2.7}$$

And/or

$$P^+ + \text{Photoelectrode} \rightarrow \text{decomposition of photoelectrode} \quad \text{----------2.8}$$

It is evident that the stability of photoelectrode in photoelectrochemical cells depends directly on the minimization of the reaction 2.8 and at present, it seems to be bottleneck in efficient photoelectrochemical cell conversion of solar energy.
When the photoelectrode is immersing in an electrolyte, the photoelectrode obtains a charge density. The photoelectrode become positively charged compared to the solution due to loss of electron from the surface. This electron goes into the electrolyte decreasing the total cation concentration. At the interface, an electrical double layer consisting a sheet of positive charge at the surface of electrode and a sheet of negative charge next to it in the solution or vice versa. The overall charge neutrality occurs when
\[ q_s = q_l \]

Where, \( q_s \) and \( q_l \) are the charges near the semiconductor and electrolyte side of the interface respectively. This interface can be classified into two groups

a) an electrolyte side of the interface

b) the semiconductor side of the interface

2.4.2 An Electrolyte Side of the Interface

Helmholtz assumed that the charged layer of the ions form sheath at the dipped side of the photoelectrode surface as shown in Fig.2.4. The model suggests that the

![Fig.2.4: Energy level diagram for p-type semiconductor-electrolyte](image)

  a) before contact
  b) after contact
Photoelectrode-electrolyte interface is similar to parallel plates of a condenser, charged oppositely as shown in Fig. 2.5. The term ‘double layer’ thus originates and almost all the potential is assumed to be dropped across this double layer of width $\delta H$. The ‘$\delta H$’ is initially assigned to be independent of the voltage applied to the electrode. If ‘$dQ$’ is the charge on the capacitor and ‘$dV$’ is the potential drop across the layer, then the differential capacitance is given by

$$C = \frac{dQ}{dV} = \frac{\varepsilon_s \varepsilon_0}{\delta H}$$

Where, $\varepsilon_s$ is the dielectric constant of photoelectrode material, $\varepsilon_0$ is the dielectric constant of free space. This voltage independency of capacitance is however, against the experimental observations.

Gouy and Chapman$^8$ suggested that the electrode surface on which charges have accumulated may be considered as large central ion exerting a planar electrostatic field on solution side of the interface. The differential capacitance of layer is dependent on the voltage and concentration. The diffused layer is known as Gouy layer, which is shown in Fig. 2.6(a). The force falls off slowly as we move deep in the bulk solution. The charge distribution in Gouy layer decays exponentially with distance as shown in Fig. 2.6(b). According to Poisson’s equation;

$$\Phi_x = \phi_0 \exp (-L_G x)$$

Where, $\Phi_x$ is the potential at any distance $x$ in the electrolyte, $\phi_0$ is the potential at $x = 0$ and $L_G$ is the Gouy layer thickness (or Debye length). It is found that 1) the charge density distribution in the Gouy layer decays exponentially with distance in electrolyte, 2) the thickness of Gouy layer varies inversely with square root of the ionic concentration 3) the differential capacitance of the Gouy layer is both voltage and concentration dependent.

Stern$^9$ noted that the ions being of finite size, keep minimum distance of approach to the photoelectrode surface. Thus, a layer neither abrupt nor diffuse but combination of the two. The situation is as shown in Fig.2.7 (a). According to Stern, the interface distribution is divided into two layers such as dense layer & diffused layer. In dense layer, the ions stick to
the electrode and potential variation is linear, whereas a diffused layer is formed as a result of opposing tendencies of attractive columbic force and discarding thermal fluctuations, where the potential decays exponentially, as shown in Fig.2.7(b). The Stern model does not explain explicitly how the ions adhere to the

Fig.2.5: A Semiconductor-electrolyte interface
(Helmholtz-Perrin model)

a) Helmholtz double layer
b) Electrical equivalence
c) Potential distribution.
Fig. 2.6: Semiconductor-electrolyte interface (Gouy-Chapman model)

(a) Schematic Charge Distribution.

(b) Potential Distribution in Electrolyte
electrode. The probable reason may be due to hydrated electrode surface and “stripping off” the solution. This means pushing some water molecules away so that the ion can come in close contact with the electrode. The ions so ‘sitting’ are called “contact adsorbed ions” and locus of all such contact adsorbed ions form the inner Helmholtz plane (IHP). The solvated ions are in the outer Helmholtz plane (OHP) as shown in Fig. 2.7(c). The IHP consisting of water dipoles and adsorbed ions, forms a dense sheet near the electrode surface. The water molecules form a saturated dielectric layer with dielectric constant equal to 6. The OHP consisting of solvated ions at a distance of their closest approach to the electrode surface, hence OHP consists of partially orientated water molecules with dielectric constant between 6 and 78. A mean value of 42 is usually used. The region with IHP and OHP constitutes the compact part of Helmholtz double layer. The specific adsorption of ion, which is responsible for formation of layer, is controlled by the nature of ions in solution as well as the nature of the electrode material and potential applied to it. This observation is correct at low ion concentration. At higher concentration, the screening charge cloud assumes a layered structure. Liu has developed a lattice gas model suggesting the ions and solvent molecules as the hard sphere of almost equal radii, forming parallel layers near to planar electrode. The lattice parameter is chosen as the distance of closest approach of the two molecules. Liu’s model gives a reasonable description of the properties of electrolyte in the interface region and is better than all the other approaches.

2.4.3 Photoelectrode Side of the Interface

Brattain and Garret first reported the systemic investigations of the photoelectrode material-electrolyte interface and much informative data is now available with detail, regarding the photoelectrode electrolyte interface. The rearrangement of electrons and ions at the interface are due to anisotropic force at the photoelectrode–electrolyte interface and charge transfer across the interface. The charge distribution across the metal and semiconductor junction are different because
Fig. 2.7: A Semiconductor-electrolyte interface (Stern model)

a) A Schematic charge distribution

b) Potential distribution

c) Position of inner & outer Helmholtz planes.
i) There are two types of charge carriers (electrons and holes) in semiconductors but in metals electrons are the only charge carriers.

ii) The charge carrier density in semiconductor is of the order of $10^{16}$ to $10^{19} \text{ cm}^{-3}$ while in the metals it is $10^{28} \text{ cm}^{-3}$.

iii) For metals, the charge carriers are at the surface, while for semiconductor they form a space charge layer within the semiconductor near the interface.

On the semiconductor side of the junction, the nature of the band bending depends on the position of the Fermi level in the solid. If the Fermi level of the electrode is equal to the flat band potential, there is no excess charge on either side of the junction and the bands are flat. If electrons accumulate at the semiconductor side, one obtains an accumulation layer. Such a layer leads to downward bending of a band for an n-type semiconductor and upward bending of a band in case of p-type semiconductor. If the surface becomes depleted of majority charge carriers then space charge layer is called as depletion layer. If the charge distribution is such that the minority charge carriers concentrate at the surface greater than that of bulk, the space charge layer is called an inversion layer, which leads to a large upward band bending in n-type and downward band bending in p-type semiconductor. Fig.2.8 illustrates n-type materials where electrons are the mobile charge carriers. Fig. 2.9 shows p-type semiconductors, where holes are the mobile charge carriers.

2.4.4 Surface State and Surface Adsorbed Ions

The potential and the charge distribution at the photoelectrode-electrolyte interface are affected by the surface states and surface adsorbed ions. The surface states are essentially the result of non-periodicity of the lattices at the boundary, which lead to the formation of electronic states localized at the interface. The adsorption of foreign atoms or ions can also generate the surface states. The resulting model of photoelectrode-electrolyte interface consists of i) diffused charge layer in the semiconductor indicating surface states and surface adsorbed ions ii) Helmholtz layer and iii) Gouy layer. The surface states are roughly classified into two groups a) Short
Fig. 2.8: Energy levels at the interface between an n-type semiconductor and an electrolyte; (a) flat band potential (b) accumulation layer (c) depletion layer (d), inversion layer.

Fig. 2.9: Energy levels at the interface between an p-type semiconductor and an electrolyte; (a) flat band potential (b) accumulation layer (c) depletion layer (d), inversion layer.
relaxation time: $10^{-3}$ down to $10^{-6}$ s (intrinsic) b) Long relaxation time: 1s (extrinsic). The surface states can be populated or depopulated by changing the electrode potential.

Due to the presence of surface states, a layer of depleted conductivity is formed below the surface. Under these circumstances, the space charge layer is a property of the material itself and not particularly sensitive to work function, which may be brought in contact with surface. The presence of surface states also plays a role in the interpretation of contact potential measurements across p-n junctions.\textsuperscript{18-20}

2.4.5 The Differential Capacitance and Mott-Schottky Plots

Neglecting the contribution from surface states and the surface adsorption as a first approximation, the simplest electrical equivalence of a semiconductor-electrolyte interface can be considered as the series of combination of the capacitance due to three layers, such as space charge capacitance ($C_{SC}$), Helmholtz capacitance ($C_H$) and Gouy layer capacitance ($C_G$). Hence, the total capacitance ($C_T$) is given by Chan\textsuperscript{11}

$$\frac{1}{(C_T)} = \frac{1}{C_{SC}} + \frac{1}{C_H} + \frac{1}{C_G} \quad \text{equation 2.12}$$

For moderately concentrated electrolyte, the value of Helmholtz capacitance and Gouy layer capacitance can be neglected, as a result, the capacitance is only due to space charge layers. A model to account the behavior of the surface states can be incorporated into an equivalence circuit of the interface as shown in Fig. 2.10. Each of the surface states is represented as a series combination of a capacitance (C) and a resistance (R). The surface states are in parallel with each other and with the semiconductor space charge capacitance ($C_{SC}$). The total capacitance of the electrode is therefore

$$C_{SC} = \sum C_i \quad \text{equation 2.13}$$

This network of parallel capacitance is in series with the bulk resistance ($R_s$) of the photoelectrode material, the double layer capacitance ($C_{dl}$) and the solution resistance ($R_{sol}$) between the semiconductor and reference electrode. The Faradic process, if any, can be short across $C_{SC}$ and $C_{dl}$ as represented by Z. The double layer capacitance is far greater than $C_{SC}$ i.e. $C_{dl} \gg C_{SC}$ and
hence can be ignored.\textsuperscript{15,16} Thus, the measurement of differential space charge layer capacitance provides an important and convenient tool to analyze the photoelectrode-electrolyte interface. Neglecting the effect of surface states in this case and assuming high ionic concentration of the redox couple and fully ionized nature of the donors and the acceptors, the space charge layer capacitance is given by;

\[
\frac{1}{C_{SC}^2} = \frac{2}{\varepsilon_s \varepsilon_0 q N_D} (V - V_{fb} - \frac{KT}{q})
\]

Where, \(\varepsilon_s\) is the dielectric constant of the photoelectrode material, \(\varepsilon_0\) permittivity of free space, \(N_D\) is the donor concentration, \(V\) is the applied electrode potential, \(V_{fb}\) is the flat band potential. The above equation is a Mott-Schottky equation. According to it, a plot of \(1/C_{SC}^2\) versus \(V\) should be a straight line intersecting on voltage axis giving the flat band potential (\(V_{fb}\)) and slope of that line giving donor concentration. A typical Mott-Schottky plot for n-type and p-type semiconductor is shown in Fig. 2.11. The Mott-Schottky plot determines the type of majority carriers and the band bending, \(V_b\), which is the maximum open circuit voltage obtainable from photoelectrochemical cell. The \(V_b\) is related to \(V_{fb}\) as;

\[
V_b = \frac{((E_f \text{ redox}/q) - V)}{-----------------------------2.15}
\]

Where, \(E_f \text{ redox} = (4.5 \cdot V_{NHE} + qV_{\text{redox}})\)

The depletion layer width (\(w\)) and the position of the band edge can be determined from the equation

\[
W = \left(2 \frac{\varepsilon_s \varepsilon_0 q N_D}{V - V_{fb} - \frac{KT}{q}}\right)^{\frac{1}{2}}
\]

The Mott-Schottky behavior is an ideal behavior for the photoelectrode-electrolyte interface. The deviations from the ideal behavior of the interface are due to following reasons.\textsuperscript{21-22}

1) Geometrical factors such as the edge effect, non-planar interface, surface roughness.

2) Non-uniform doping.

3) Presence of both donor and acceptor impurities.

4) Presence of deep donor and acceptor levels.
5) An extra contribution to total capacitance due to a) presence of an oxide film b) Helmholtz layer capacitance c) ionic adsorption on the surface. d) acid-base equilibrium at the interface.

Fig. 2.10: An equivalent circuit diagram for semiconductor-electrolyte interface showing the presence of surface state and surface adsorbed ions.

Fig. 2.11: A typical Mott-Schottky plot for n and p type GaAs (1 M H$_2$SO$_4$)
The presence of surface states gives very complicated structure of Mott-Schottky Plots, since they can exchange the carrier with either of the bands or to both by electrostatic coupling.

2.5 Charge Transfer Mechanism of Photoelectrode-Electrolyte Interface

2.5.1 Under Illumination

When a semiconductor-electrolyte interface is illuminated, the electron-hole pairs are generated in the depletion region and are separated by an electric field at the interface. This charge separation process results in generation of a counter field, which is maximum at the open circuit condition & is indicated by Voc. This photovoltage acts as driving force for electrons to move from semiconductor to counter electrode, whereas the holes are captured by reduced species in electrolyte to undergo oxidation reaction. The whole redox reaction can be written as:

\[
\text{Red (solv)} + h^+ \leftrightarrow \text{Ox (solv)} \quad \text{At semiconductor electrode} \quad \text{--------2.17}
\]

\[
\text{Ox (solv)} + e^- \leftrightarrow \text{Red (Solv)} \quad \text{At counter electrode} \quad \text{-------------2.18}
\]

The electrode acts as a shuttle in charge transfer reaction. N-type semiconductor in contact with an electrolyte under illumination with a forward bias voltage (V) is shown in Fig.2.12. The quasi-Fermi levels for electron (Efn) and for hole (Efp) in the depletion region are assumed to be flat. If U is the separation between them then,

\[
qU = Efn - Efp \quad \text{---------------------------------------------2.19}
\]

It is believed that \( U > V \) because minority carriers concentration under illumination is larger than its concentration in dark. For holes to flow from semiconductor surface to an electrolyte, U is defined as

\[
[\exp(qU/kT)] = P(w)/Po \quad \text{-----------------------------------2.20}
\]

Where \( P(w) \) is the hole concentration at the edge of the depletion region and \( Po \) is the equilibrium hole concentration in the bulk of the semiconductor in dark. 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
Fig. 2.12: a) Effect of electric field on Electronation and de-electronation reaction. b) Potential energy profile.
concentration should be high such that $C_H > C_{sc}$. The depletion layer width ($w$) under these conditions is given by:

$$w = w_o (V_D - V_o)^{1/2}$$

Where $w_o = \left[\frac{2\varepsilon_s\varepsilon_0}{qN_D}\right]$, $\varepsilon_s$ is the dielectric constant of the material and $\varepsilon_0$ 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, $S_r$ is the surface recombination velocity; $\Phi$ is the incident photon flux after allowing the losses due to reflection and absorption by electrolyte. $\alpha$ be the light absorption co-efficient and $w$ is the width of depletion region, the minority carrier flux due to hole junction can be given by

$$J = \frac{S_t}{S_r} \Phi \left\{1 - \exp\left[\frac{\alpha - w}{1 + \alpha t}\right]\right\}$$

The direction of generated photocurrent is from semiconductor electrode to electrolyte.\(^{16,22,24}\)

### 2.5.2 Under Dark

Under suitable values of the valence band, conduction band and redox energies, the charge may be transferred from electrolyte to semiconductor or vice versa. The ionic species will be reduced or oxidized at the respective electrode. They can also jump back in the reverse directions so that there can occur oxidation and reduction. If a positive ion moves against the field direction in a reduction reaction, it will move in the direction of field in oxidation. This is shown in Fig.2.13. If the positive ion is to be activated through a potential difference $\beta \Delta \Phi$ in reduction reaction, then it has to be activated by $(1 - \beta \Delta \Phi)$ in oxidation, where $\beta$ is symmetry factor and $\Phi$ is a potential through which an ion passes. The net current density can be given by the Butler-Volmer equation.\(^{25}\)

$$I = I_o \left\{\exp\left[(1 - \beta) V_F/RT\right] - \exp\left(-\beta V_F/RT\right)\right\}$$

The equation shows the dependence of current density across interface on the potential $V_F$. A small variation in $V_F$ 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. 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 \((1- \beta)\) of the input electrical energy \((qV)\) turns into 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 the potential barrier extends.

Fig. 2.13: The electron energy level diagram for n-S/E interface under illumination and biasing voltage ‘V’
2.6 Efficiency (\(\eta\))

The ratio of maximum output power to the input power is called as conversion efficiency.

\[
\eta\% = \frac{\text{Maximum output power}}{\text{Input power}} \times 100
\]

From the input power source, the photon energy less than the band gap of the semiconductor electrode is not absorbed. The photons having energy higher than the band gap are useful for the creation of electron-hole pairs in photoelectrochemical cell.

The conversion efficiency (\(\eta\)) is given by

\[
\eta = \frac{\int \{ \alpha(E) N(E)/E \} dE}{\int \{ \alpha(E) N(E)/E \} dE}
\]

Where, \(\alpha(E)\) is the fraction of photon absorbed, \(N(E)\) is the number of photons incident having energy \(E\). The various factors such as ohmic losses, light absorption in the solution etc. are neglected. The above equation suggests that if value of band gap as well as absorption coefficient is high, the efficiency will be higher. \(\alpha(E)\) near band gap is approximately as

\[
\alpha(E) = A (hv-Eg)^n / hv
\]

Where \(A\) is constant, \(n = \frac{1}{2}\) or 2, suggest the type of transition. \(n = \frac{1}{2}\) for allowed direct type of transition and \(n = 2\) for indirect type transition. In order to obtain higher \(\alpha(E)\), the value of band gap ‘\(Eg\)’ should be small. The above equations are contradictory. Hence efficiency should be maximum at some optimum value of \(Eg = 1.2-1.4\) eV as shown in Fig. 2.14. From the figure it is seen that theoretical efficiency of a regenerative cell is expected to be near about 25%.

Another parameter fill factor (\(ff\)) is defined as

\[
ff\% = \frac{\text{Maximum power output}}{V_{oc} I_{sc}}
\]

Where, \(V_{oc}\) and \(I_{sc}\) is the open circuit voltage and short circuit current respectively. The fill factor should be low in photoelectrochemical cell with high internal resistance. The maximum open circuit voltage attainable from
a photovoltaic cell would be

\[ V_{oc} = V_{\text{redox}} - V_{fb} \]

Thus efficiency also depends upon \( V_{\text{redox}} \).

Fig. 2.14: Optical conversion efficiency at AM1 sunshine

1- Theoretical conversion efficiency
2- Estimated optical conversion efficiency
References


8) A. Gouy, J. Physique, 4 (1910) 457.

9) D.L. Chapman, Phil. Mag., 26 (1913) 475.


