CHAPTER II - THEORETICAL BACKGROUND

2.1 INTRODUCTION

Knowledge of electrochemistry is basic need of every researcher in the field of semiconductor-liquid junction solar cells. Perticularly in the solar energy field, the photoelectrochemistry is of vital importance because of its utility in conversion of solar energy into electrical energy or transportable fuel such as hydrogen. Number of review articles on semiconductor electrochemistry have been appeared in literature [1-12] : The needed theoretical background for the understanding of basic electrochemical processes and hydrogen production with semiconductor septum cell is given in the present chapter.

2.2 PRINCIPLE OF SOLAR CELL

When photon of energy, hν greater than the band gap energy Eg of a semiconductor is absorbed, a pair of electron and hole is generated. However, the electron with negative and hole with positive charge attract immediately. As a result, though the electrons and holes are generated within a single piece of semiconductor by the absoption of radient energy one cannot get externally the electrons to flow.

When the semiconductor junction is formed due to the transport of charges across the junction to set the equilibrium i.e. to make the fermi levels at equal energy level, the donors are ionised at the interface within the n-type semiconductor and acceptors are ionised at the interface with P type semiconductor. This give rise to a local field, also called as built in potential V_D. When the light of energy $h\nu > Eg$ is made to incident within this interfacial layer, the pairs of electron and hole are generated and are separated due to the influence of local electric field as shown in Fig.2.1. The n type side of a junction acts as a source of electrons while the p type, as a sink of electrons and when these two sides are connected through an external circuit, the current flows through the external circuit.

2.3 PHOTOELECTROCHEMICAL EFFECT

The photoelectrochemical effect was first observed by Becquerrel in 1839 [13] in which irradiation of electrode/electrolyte system caused to produce a change in electrode potential when the circuit was kept open or change in current flow when circuit was closed. The PEC effect at semiconductor electrolyte interface is a consequence of generation of electron-hole pairs by light absorption at the interface. The PEC effect involves photophysical, photochemical, and electrochemical processes [14].

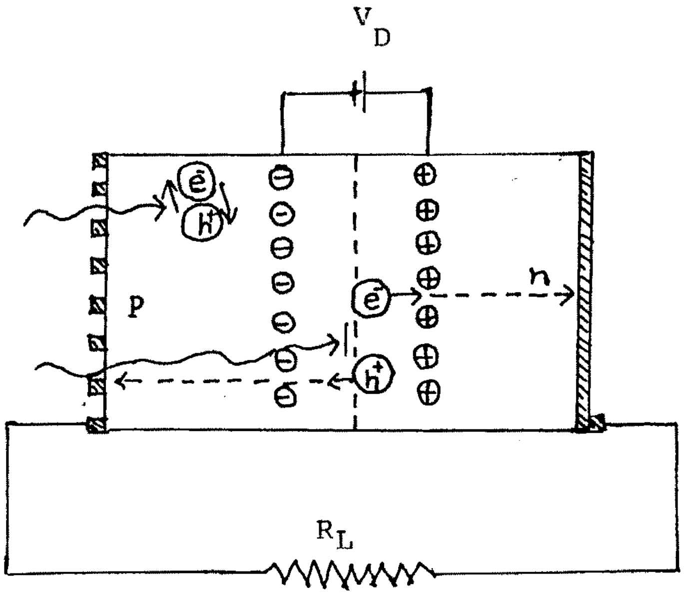


Fig.2.1. P-n junction with influence of local electric field.

2.4 SEMICONDUCTOR-LIQUID JUNCTION SOLAR CELLS (BASIC THEORY)

Photoelectrochemical process can be both photoelectrical and photochemical in nature. When a semiconductor is dipped in a redox solution, it's chemical potential is different from the redox potential Eredox. A new equilibrium is established between the semiconductor and electrolyte solution by rearrangement of charges. This results in a strong field near the junction. This is shown by the bending of bands for a n type semiconductor as illustrated in Fig.2.2(a) when the semiconductor electrolyte junction is illuminated with light having energy greater than the band gap energy, electron-hole pairs are produced in the depletion layer. Charge separation takes place due to local field present at the interface. The probability of annihilation of a hole with an electron is reduced by this field. This condition will be optimum when the light penetration depth is equal to the depletion layer width so that all the light is absorbed in the depletion layer and maximum number of electronhole pairs are produced in it. These separated charges produce a counter charge and under open circuit condition this counter field is maximum. This is the open circuit photovoltage. The conduction band and valence band get shifted due to the counter voltage. The photovoltage is given by the change in fermi levels as shown

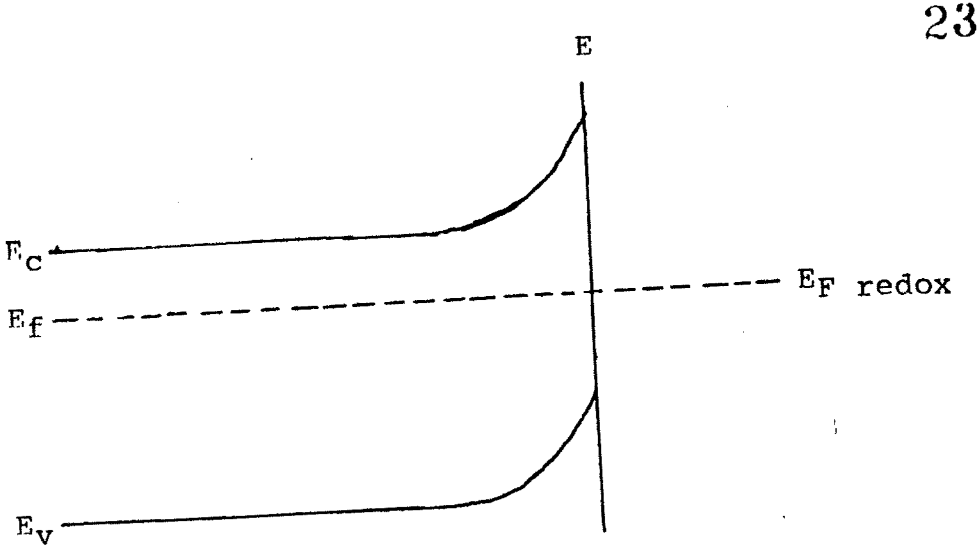


Fig.2.2(a) Bending of bands for a n-type semiconductor

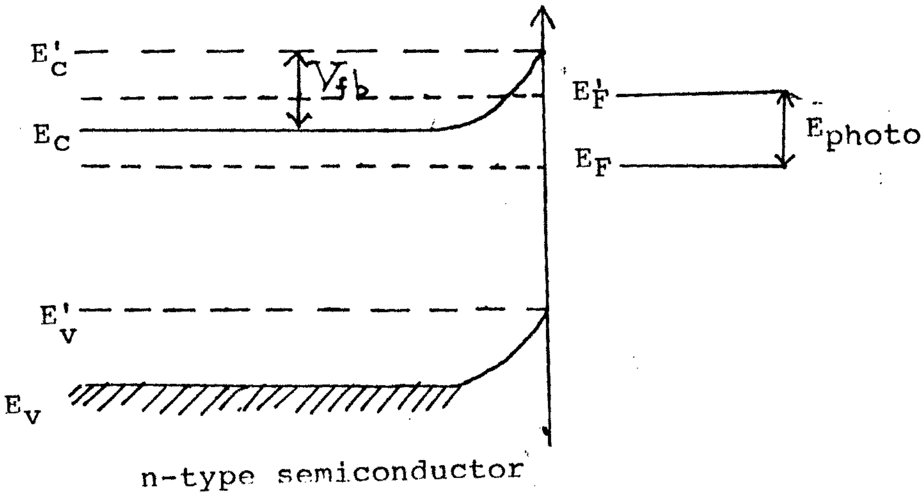


Fig.2.2(b) Shifting of bands as a result of illumination.

in Fig.2.2(b). When a counter electrode is immersed in the electrolyte and connected externally to the semiconductor, the photogenerated electron moves into the bulk of semiconductor and through the external circuit it reaches the counter electrode to reduce an oxidised species in the electrolyte. The hole is pushed to the electrode surface where it oxidizes a species in the electrolyte as shown in Fig.2.3(a).

Fig.2.3(b) illustrates the flow of photocurrent in short circuit condition of semiconductor-electrolyte junction cell for redox couple A/A^+. Fig.2.4 shows the photoelectrochemical cell with an external load resistance in the circuit.

The oxidation and reduction reactions in the photoelectrochemical cell are illustrated as follows.

A process in which the substrance gains an electron is called a reduction reaction [13,15].

$$OX + e^- \rightleftharpoons Red.,\ E^\circ \qquad \text{.... 2.1}$$

where OX and Red. are the oxidized and reduced species and E° is the standard electrochemical potential measured with respect to standard electrode. The reverse process of losing an electron is called an oxidation reaction.

A system in which one species loses an electron

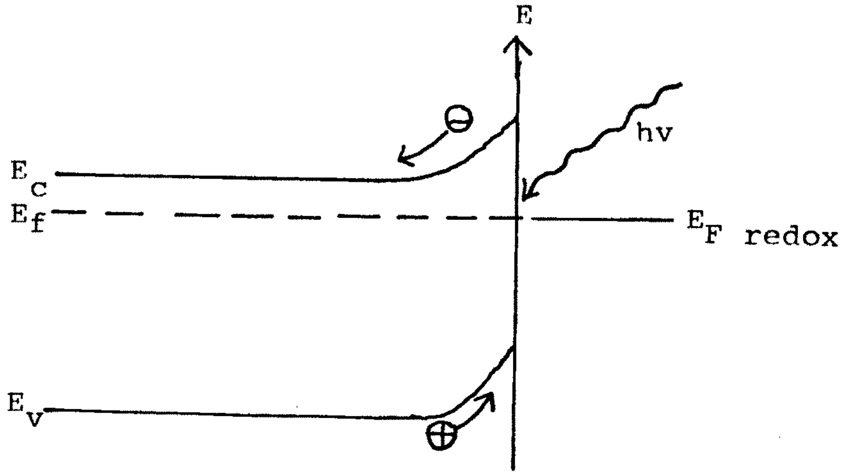


Fig.2.3(a) Transfer of holes and electrons.

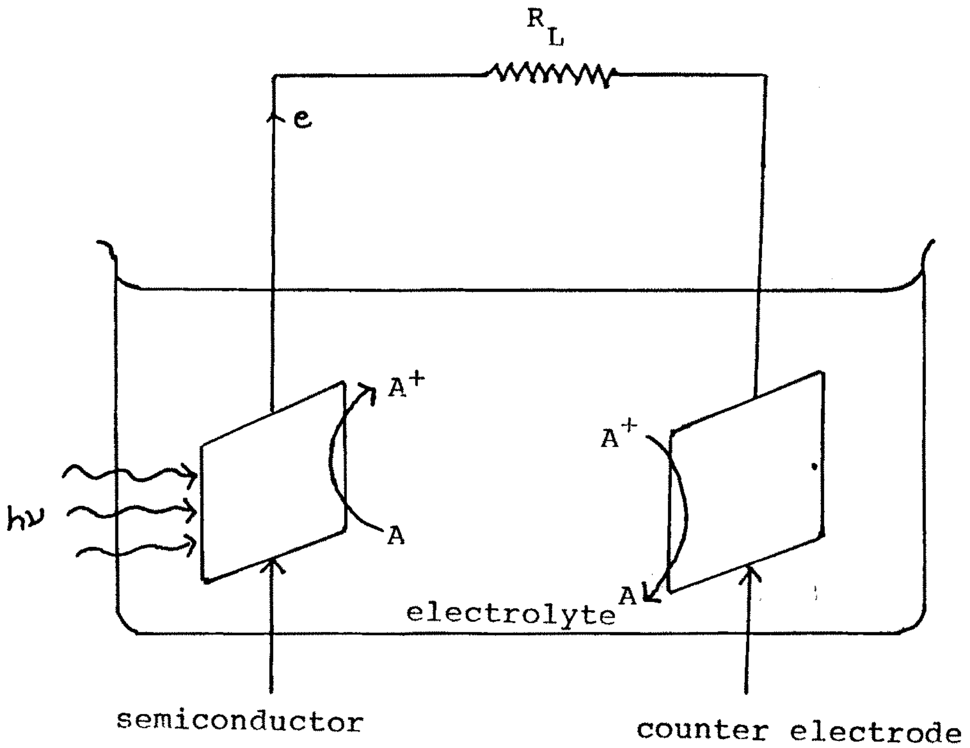


Fig.2.3(b) Photocurrent at short circuit condition.

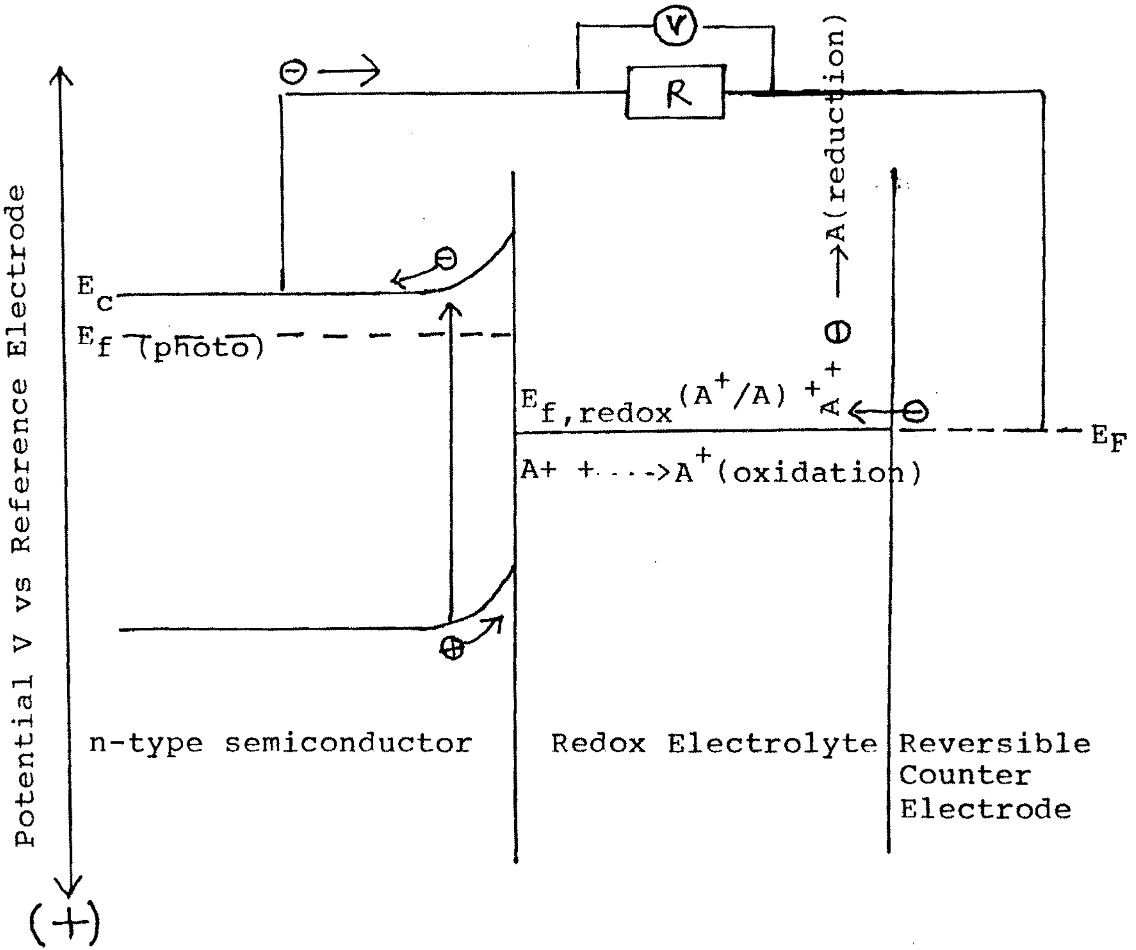


Fig.2.4 A regenerative PEC cell. The interface energetics are illustrated.

and other species gains an electron is called redox system. E°, is the measure of the tendency of the reaction to proceed in a perticular direction and is measure of free energy available. If E° is positive, the reaction proceeds from left to right and when it is negative, the reaction proceeds from right to left.

Gerischer, while deriving an anology with semiconductor physics, has suggested that the oxidized and reduced species may be linked with the conduction band (i.e. an unoccupied electron state) and valence band (i.e. an occupied electron state) respectively [16-17]. A term similar to fermi level E_F of a semiconductor can be defined for a redox couple also and can be abbreviated as E_F, redox. The energy necessary to transfer an electron from reduced species to the oxidized species is analogous to the band gap of a semiconductor. The redox potential is defined as the potential required to transfer an electron from redox species to the vacuum level or vice-versa [18].

The electron energy state in the redox electrolyte is in analogy with the concept of energy state in a solid. One can define the electron energy state in the redox electrolyte by energy change in the reaction.

$$(OX^{+}\ \mathrm{Solv.}) + \bar{e}\infty \longleftrightarrow (\mathrm{Red\ Solv.}) \qquad .... \ 2.2$$

This means that we introduce a free electron from infinity into the solution and let it occupy the lowest electron state in an oxidized species without change of solvation structure. This gives the energy of the unoccupied state. The reverse process gives the energy of occupied state. Because the solvation structure of redox by thermal fluctuation, we get a thermal distribution of energy states in the redox electrolytes.

The probability function for electron states in redox electrolytes as the sum of occupied and unoccupied states is given by [19].

$$D_{redox}(E) = D_{red}(E) + D_{OX}(E) \qquad \text{.... 2.3}$$

which is equivalent to the density of states function in solid

$D_{red}(E)$ and $D_{OX}(E)$ are represented by,

$$D_{red}(E) = C_{red}(E) \cdot W_{red}(E) \qquad \text{.... 2.4}$$

and $D_{OX}(E) = C_{OX}(E) \cdot W_{OX}(E)$ 2.5

Where W_{red} and W_{OX} are given by the thermal distribution functions of ionic configurations with a shape as given in Fig.2.5 and C_{red} and C_{OX} are the concentrations of reduced and oxidized species. These distribution functions have a maximum at the electron level for the most probable configuration of the reduced and oxidized component of the redox couple.

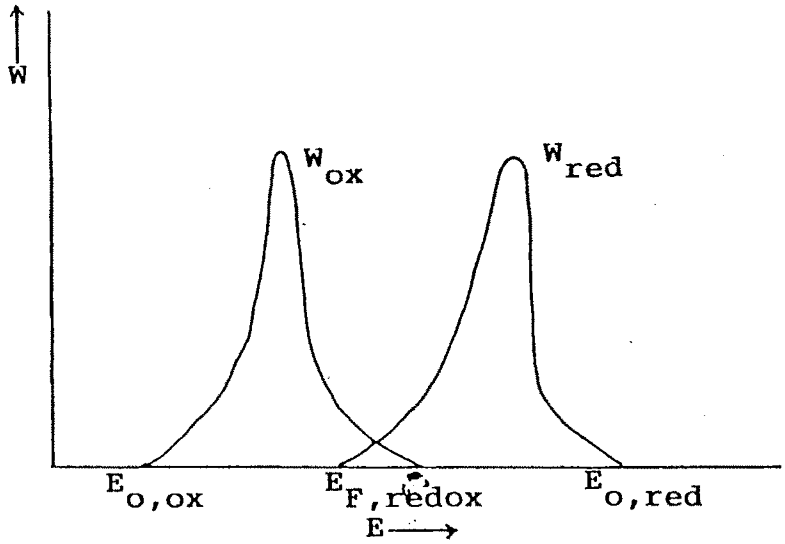


Fig.2.5 Distribution of energy states for ions of a redox system in solution

At equilibrium the occupation of these energy states in redox electrolyte is given by the Fermi distribution function.

$$D_{red}(E) = D_{redox}(E)F,(E-E_{f,redox}) \qquad \ldots.\ 2.6$$

and $D_{OX}(E) = D_{redox}(E)F(E_{f,redox}-E)$ 2.7

E_f, redox is equivalent to the chemical potential of electrons in the redox electrolyte and is related to the mean free energy change, per mole electrons in the redox reaction as

$$E_{f,redox} = E^{\circ}_{f,redox} + KT|n\ C_{red}/C_{OX} \qquad \ldots.\ 2.8$$

2.5 CLASSIFICATION OF PEC CELLS

A photoelectrochemical cell is defined as a device in which one or both half cells exhibit a photoelectrochemical effect. The principle of charge transfer reaction at the semiconductor electrolyte interface forms the basis of various types of PEC solar cells. The photoelectrochemical and solar cells can be categorised according to the net free energy change in the overall system as given below and shown in Fig.2.6.

a) Electrochemical Photovoltaic Cells ($\triangle G = 0$)

It consists of such a redox couple that the total

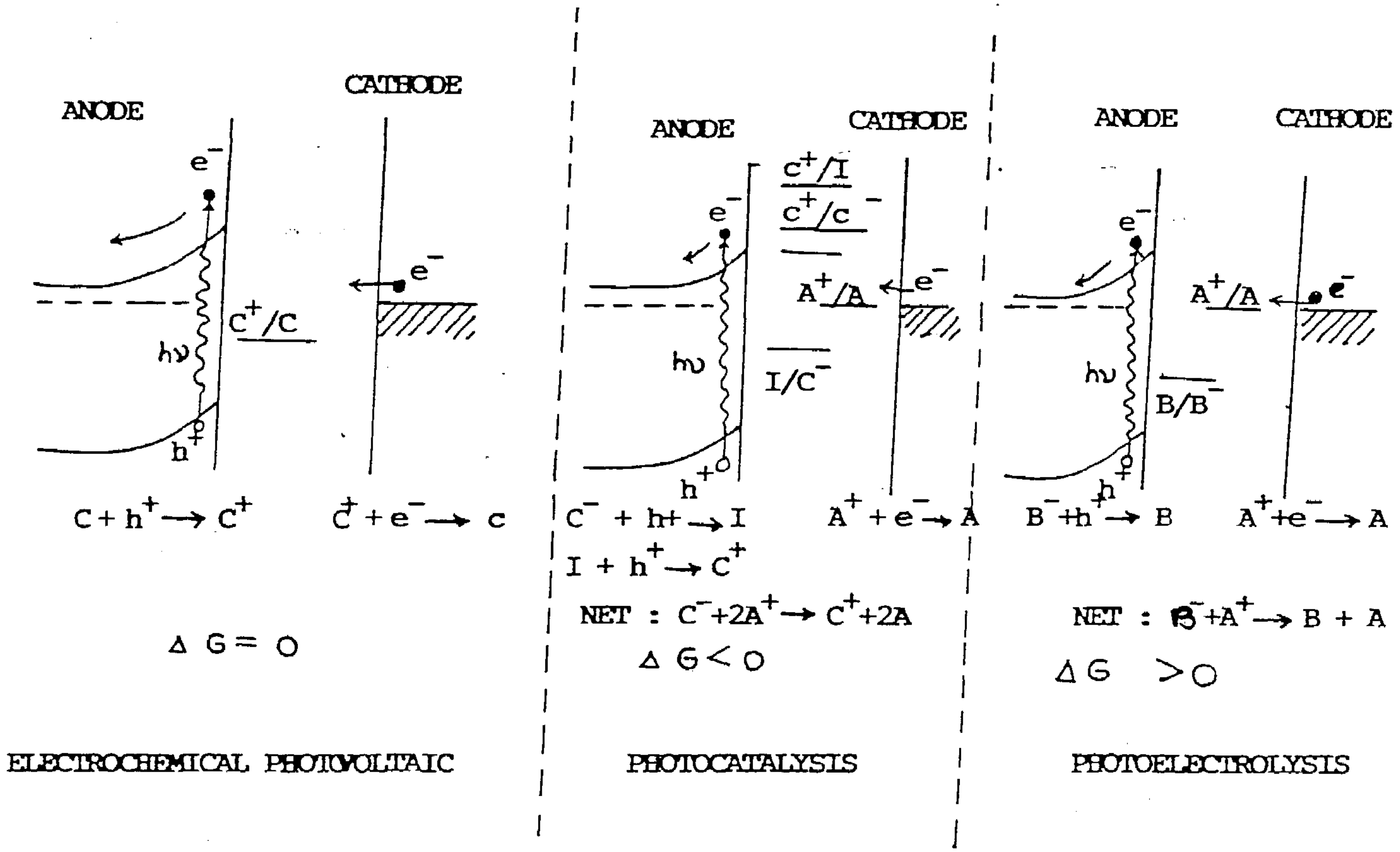


Fig. 2.6 Classification of Photoelectro chemical cells

cathodic plus anodic reactions do not lead to the net chemical change. The electrodes do not participate in the chemical reaction, they only serve as a "shuttle", for the charge transfer mechanism.

At the semiconductor electrode,

$$(\text{red})_{\text{solv.}} + h^{+} \Longleftrightarrow (\text{OX})_{\text{solv.}} \qquad \ldots.\ 2.9$$

At the metal counter electrode

$$(\text{OX})_{\text{solv.}} + \bar{e} \Longleftrightarrow (\text{red})_{\text{solv.}} \qquad \ldots.\ 2.10$$

The above cell is the regenerative type of PEC cell used for direct production of electricity.

(b) Photocatalytic Cells ($\Delta G < 0$)

In these cells two redox couples are present and a net chemical change takes place as given in Fig.2.6. Here $\Delta G < 0$ and the optical energy provides the activation energy for the chemical reaction. One example for photocatalytic cell is

$$N_2 + 3H_2 \xrightarrow{h\nu} 2\ NH_3$$

(c) Photoelectrolysis Cells ($\Delta G > 0$)

Effectively two redox couples are present and a net chemical change takes place in the system. The photoelectrolysis cells and electrochemical storage cells belongs to this category. The general reaction is given in Fig.2.6.

Some examples of reaction for above types are,

$$H_2O \xrightarrow{h\nu} H_2 + \frac{1}{2}O_2$$

$$CO_2 + H_2O \xrightarrow{h\nu} CH_2O + O_2$$

Hence, optical energy is converted in to chemical energy.

The category (b) and (c) are some times termed as photoelectro synthetic cells.

2.6 ENERGETICS OF PHOTOELECTROLYSIS CELLS

The operation of photoelectrolysis cell can be generally explained in terms of electron energy levels in the electrodes and the redox levels of the electrolyte. The semiconductor is characterised by it's fermi energy level which is denoted by chemical potential of electrons in the semiconductor i.e. E_f. However, energy levels of the electrolyte are determined by solvent and ionic species present in the electrolyte and are denoted by redox potential of the redox system. These are shown in energy level diagram. The minimum thermodynamic free energy to cause the water splitting reaction $H_2O \longrightarrow H_2 + \frac{1}{2}O_2$ at standard temperature and pressure is 2.46 eV per water molecule [20] (56.7 K cal/mole) or 1.23 eV per electron transfer. It is the difference between two standard fermi energies.

The positions of the redox levels of the hydrogen water system and of oxygen water system are given [20] as,

$$E_f\ (H_2O/H_2) \Longleftrightarrow E_f^\circ(H_2O/H_2) - KT\ln\frac{aH^+}{a^\circ H^+} + \tfrac{1}{2}KT\ln\frac{PH^2}{P^\circ H_2}$$

and

$$E_f\ (O_2/H_2O) \Longleftrightarrow E_f^\circ(O_2/H_2O) - KT\ln\frac{aH^+}{a^\circ H^+} + \frac{1}{4}\ KT\ln\frac{PO_2}{P^\circ O_2}$$

where $a^\circ H^+$ is standard activity of protons in water and P° is standard pressure of a gas. The operation of a photoelectrolysis cell at equilibrium condition in dark and under illumination is shown schematically in Fig.2.7(a).

In dark at equilibrium, the initial fermi energy level of the semiconductor will be anywhere between the redox energy levels of the redox couple. The exact position is determined by concentration of two redox species. Under illuminated short circuit condition the cell configuration is considered as n-type semiconductor as photoanode and a metal as a cathode. When a semiconductor electrolyte junction is illuminated, electron hole pairs are generated in the depletion region. These electron hole pairs are separated by the electric field created at the interface. The photogenerated holes combined with electrons from redox

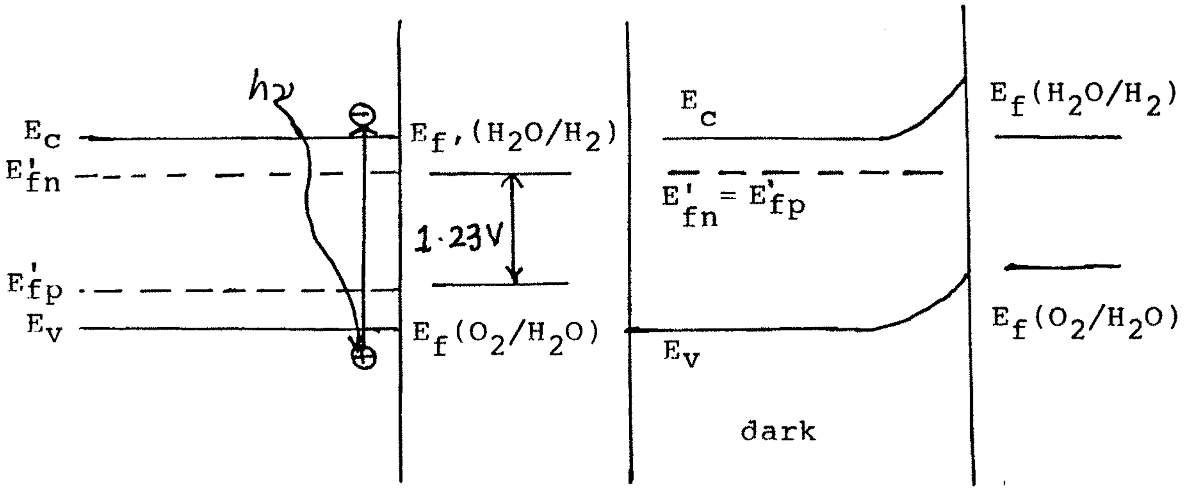
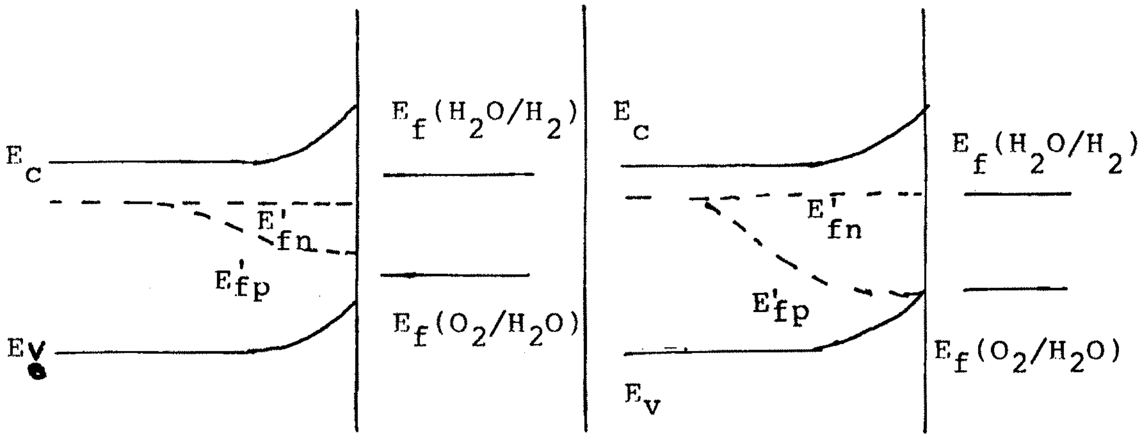


Fig.2.7(a) The minimum condition for water decomposition.



Moderate illumination Intense illumination

Fig.2.7(b) The quazi - fermi levels in an n-type semiconductor at the electrolyte interfaç under various light intensity.

species 'A' at semiconductor electrode surface and photogenerated electrons from conduction band passes to metal cathode via external circuit and used to reduce 'B^+' in the electrolyte. Under open circuit condition the charge separation process gives a maximum counter field which we say as maximum open circuit photovoltage i.e. V_{OC}. This photovoltage is used for current drive in opposite direction which can perform photoelectrolysis. At flat band position, no transfer of electron from metal is possible unless and until the fermi energy is shifted to higher energy level by applying an external bias.

Under steady state illumination, there is no equilibrium condition for energy levels and distribution of electrons and holes. There is increase in electrons and holes due to the new photogenerated electron hole pairs. Ultimately there is change in chemical potential of electron and hole. These new values of chemical potentials are called as quasi fermi energies and are shown in Fig.2.7(b). The current flow through photoelectrolysis cell is as shown in Fig.2.8(a).

Murphy has proposed model systems for photoelectrolysis [21]. His two compartment water photoelectrolysis cell is as shown in Fig.2.8(b). Murphy suggest that if stable photocathode and photoanodes with

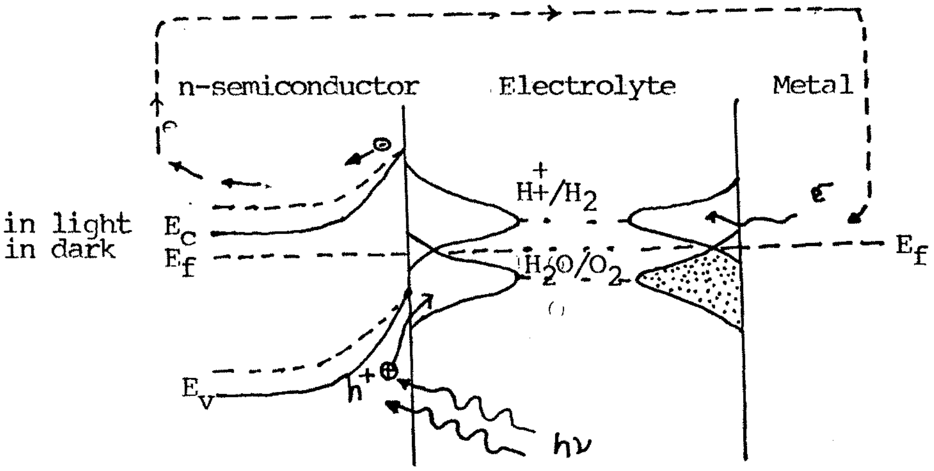


Fig.2.8(a) An energy level diagram of a typical photoelectrolysis cell.

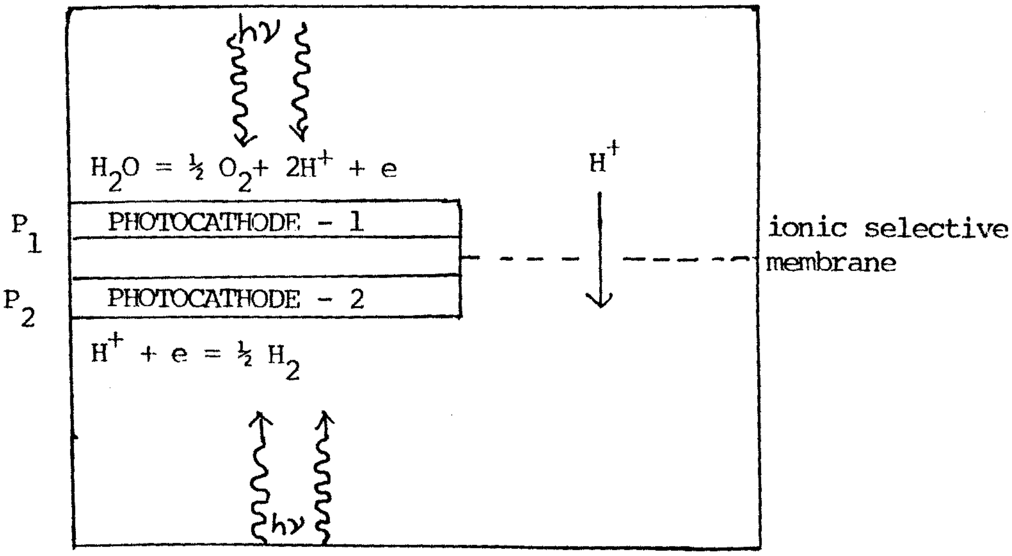


Fig.2.8(b) Schematic representation of two compartment photoelectrolysis cell.

wide spectral response can be found, the photoelectrolysis can be carried out in the two compartment cell where a cation-selective membrane keeps the hydrogen and oxygen gases separated.

2.7 REQUIREMENTS OF PHOTOELECTROLYSIS CELL

Requirements of photoelectrolysis cell are as following.

1. For maximum photoabsoption the band gap energy (Eg) should be atleast 1.8 eV [22].
2. The fermi level of electrons should be above the water| hydrogen redox potential.
3. Fermi level of holes should be below the water|oxygen redox potential.
4. The illumination must be intense enough to split the quasi fermi levels of holes and electrons by more than the decomposition potential.
5. The minimum energy required to split water is that these fermi levels should differ by 1.23 volts, the voltage of decomposition of water.
6. The hydrogen evolving surface must be chemically stable.
7. The coating of the semiconductor electrode must be thin enough to allow free tunneling of photogenerated electrons to ions adsorbed from the solution.

8. The semiconductor surface must be free from species causing recombination.

2.8 SEMICONDUCTOR-ELECTROLYTE INTERFACE

Charge transfer across the semiconductor-electrolyte interface in dark or under illumination results in the flow of current through the junction of electronically (or hole) conducting solids and ionically conducting liquids. This is the key concept in the working of photoelectrochemical solar cells [23].

Theoretical treatment of the semiconductor electrolyte interface has been extensively reviewed by Gerischer [16], Frenud and Gomes [24], Green [25], Myamlin and Pleskoy and Dewald [26,27].

Gerischer [28] has shown that in contrast to metals, the average free energy of electrons in the semiconductors can be changed to a large extend by illumination. Especially the concentration of minority electronic carriers on illumination can differ by order of magnitude from the equilibrium value. Therefore, it is expected that all important chemical and electrochemical effects in semiconductor will be due the large deviation from equilibrium of the minority carriers.

When an electrode is dipped into electrolyte, the excess charge residing on the electrode surface must be exactly balanced by an equal charge of opposite sign on the solution side. This can happen by charge transfer across the electrode electrolyte interface [8,29,30]. For a semiconductor, the charge transfer results in a space charge region in the semiconductor and a Helmoltz double layer and Gouy-chapman layer (diffusion layer) in electrolytes as shown in Fig.2.9(a).

2.8.1 TYPES OF INTERFACE

Interface is defined as boundary between two different materials or two grains of differing orientation of same material. It plays an important role in all modern electronic devices, especially in solar cells. In general following are the types of itnerfaces solid-vacuum, solid-gas, solid-solid, liquid-liquid and a solid-liquid interface. Much literature is available on the metal-electrolyte interface, but very little data are available on semiconductor-electrolyte interface. The properties of the interface depends on the arrangement of particles, the forces between the particles and the ions in an electrolyte. Numerous authers such as Helmholtz, Gouy-chaptman, stern etc. suggested various models for the arrangement of particles at the interface between the electrode and electrolyte.

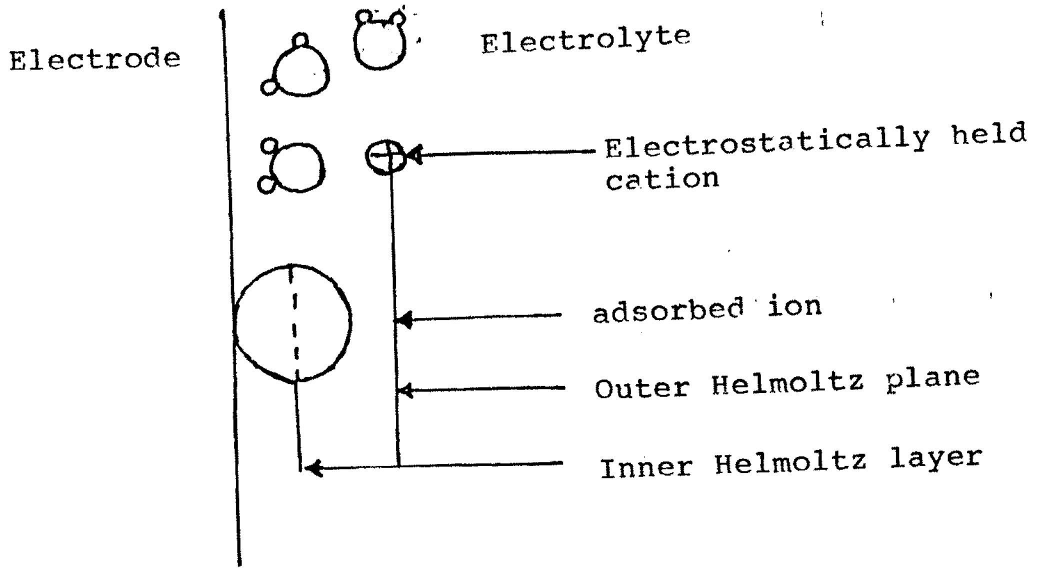


Fig.2.9(b) Relative positions of inner and outer Helmoltz planes of electrode doubble layer.

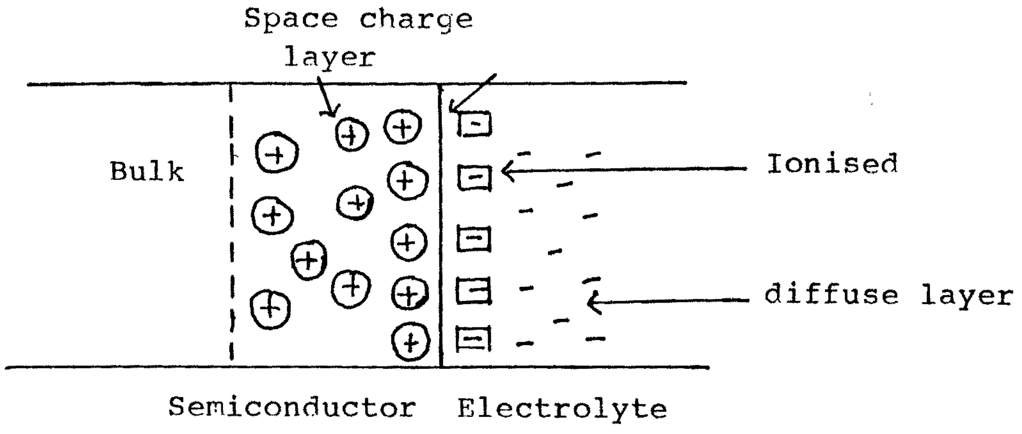


Fig.2.9(a) Charge distribution at the semiconductor electrolyte interface.

2.8.2 SPACE CHARGE REGION IN THE SEMICONDUCTOR

Fermi levels E_f semiconductor and E_f redox are at different levels resulting in electron transfer from semiconductor to electrolyte which establishes the equilibrium. This flow of electrons results in the accumulation of ions in the semiconductor. A strong local electric field is developed and band bending takes place.

The potential drop in the semiconductor space-charge layer depends on the difference between the fermi level of semiconductor and the fermi level of the redox electrolyte, if the former is free from excess charge. The simplified theory of space charge region is well explained by Sze [31].

2.8.3 HELMOLTZ'S DOUBLE LAYER

The electrode-electrolyte system was studied quite earlier in 1879 by Helmholtz revealing the discrete layers at the interface on the solution side. When only electrostatic interaction operates, the ions from the solution side may approach the electrode only so far as their inner solvation shells will allow. The surface array of ions is thus 'cushioned', from the electrode surface by a layer of solvent molecules. The line drawn through the centre of such ions at the distance of closest approach makes the boundary known as the Helmoltz's outer plane. The region within this plane constitutes the compact part of the double layer on the Helmoltz layer.

In other cases, specific adsorption of ions may occur where vander waals and chemical forces participate. Most anions are specifically adsorbed, thereby losing most of their inner hydration shell, but most cations retain their hydration molecules. Specially adsorbed species can evidently approach much closer to the electrode surface. A line drawn through the centres of such species aligned at the electrode surface defines a further boundary within the Helmoltz layer, the so called inner Helmoltz plane. The extent to which the specific adsorption occur is controlled by the nature of the ions in the solution as well as the nature of the electrode material and potential applied on it. Fig.2.9(b) shows relative positions of inner and outer Helmholtz planes of the electrode double layer.

2.9 ENERGY STORAGE WITH SEMICONDUCTOR SEPTUM CELL

In recent years much efforts have been directed towards developing new and better solar energy conversion devices. Recent publications indicate that pigmented bilayer lipid membranes are also of interest in field of solar energy conversion [32-39]. The origion of semiconductor septum (SC-SEP) electrochemical photovoltaic cell is traceable to early studies of the membrane biophysics aspects of photosynthesis for redox reactions. In SC-SEP cells, the semiconductor separates two compartments containing different redox couples. These redox couples can either be oxidised or reduced under illumination. The semiconductor septum cell can be used as an efficient storage cell if the semiconductor septum electrode and electrolyte have properties, listed in Table I and Table II respectively.

2.9.1 PRINCIPLE OF SC-SEP CELL FOR HYDROGEN PRODUCTION

The mechanism and operation of SC-SEP cell for hydrogen production is illustrated in Fig.2.10. The band bendings at the n-CdSe|metal interface are produced by the choice of the electrolyte and metal respectivley whose redox potential and work functions are much greater than that of the semiconductor. Thus, a deplation layer and hence a strong electric field are produced below the n-CdSe surface.

Upon illumination photogenerated holes and electrons (excitons) are produced. The electrons are excited into conduction band and holes are left behind in the valance band (V_B) of the semiconductor. Because of the potential barrier of the space charge region that resutls from the SC|electrolyte junction, light generated electrons and holes are separated. At the left side of the SC-SEP the electrons migrate through the bulk of the semiconductor to

Table I Semiconductor septum electrode

1. The energy of the incident light should be greater than the band gap of the semiconductor.
2. Recombination states must be minimum.
3. The thickness of the bulk of semiconductor must be optimum.
4. Contacts to the semiconductor should be ohmic.

Table II Electrolyte properties requisites for the ECPV cells.

Property	Role
1. Reduction-oxidation potential	Redox reaction to be positioned appropriate to the semiconductor band edges. Electrolyte decomposition limits suitability
2. Electron-transfer rates of OX and red. species	Idealy rapid (reversible) at both semiconductor and counter electrodes. Suitable mass transport conditions.
3. Photo and thermo stabilities	OX, red. and solvent components to have photo and thermal stability through out usable solar spectrum and operational temperature range.
4. Surface compatibility	Noncorrosive to electrode and containment materials. Semiconductor corrosion inhibited if necessary and undesirable surface reactions absent, e.g. adsorption, dissociation, passivation, etc.
5. Optical transparency	Minimum absoption losses for solar energy spectrum.
6. Fluidity	Liquidous range and viscosity to allow convective mixing within temperature extremes.
7. Solubility	OX, red and supporting electrolyte concentration in solvent or liquid matrix to be adequate to reach required current densities.
8. Conductance	Ionic conductance of electrolyte should permit negligible ohmic losses.

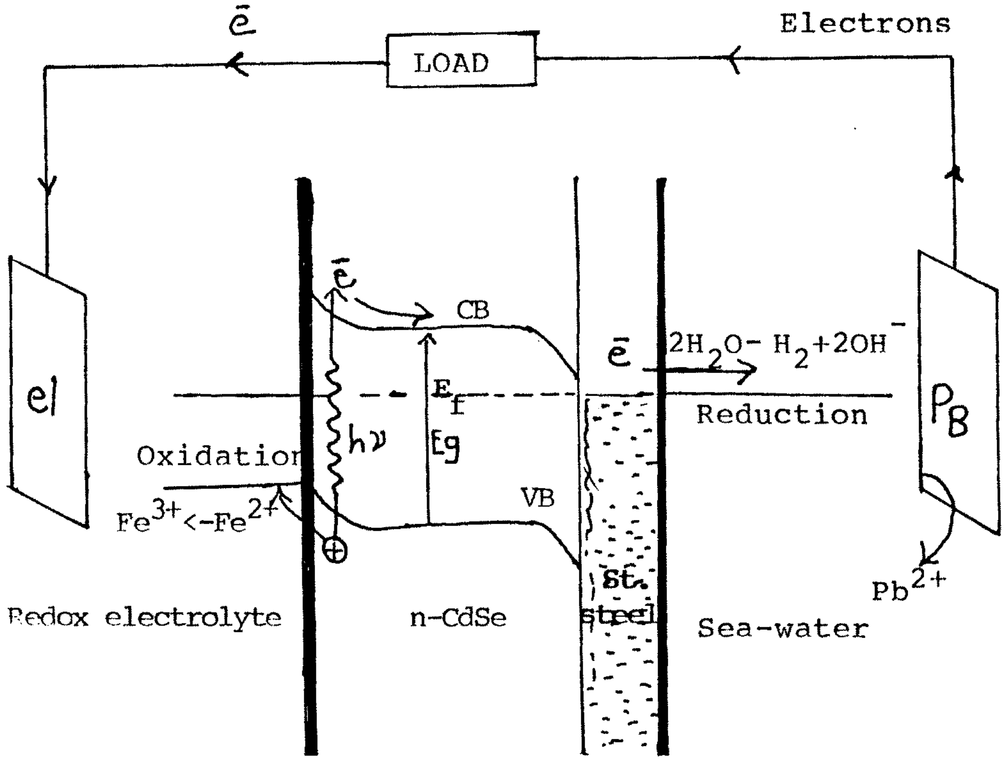


Fig.2.10. The principle of a SC-SEP cell for hydrogen production from sea water.

the metal and to the metal|electrolyte interface and holes move to the opposite interface. The photogenerated electrons reduce adsorbed H^+ ions from aqueous solution to gaseous hydrogen. In the chamber containing Pb electrode and artificial sea water, H_2O is decomposed to OH^- ions and hydrogen. Thus a semiconductor septum of this type functions as transducer, changing light into stored chemical energy of hydrogen via photolysis.

2.9.2 STORAGE IN THE FORM OF ELECTRICAL ENERGY

The semiconductor septum cell under illumination causes generation of electron hole pairs, the electron jumps into conduction band from valence band. The electron further moves towards the bulk of semiconductor and via metallic substrate travels into the other compartment where it is received by the oxidized species, and gets reduced. These oxidized species gets either reduced to lower oxidation state or to metal. These species can again be reoxidized by transferring an electron to the metal electrode in compartment II, in dark, while holes moves towards the surface of the semiconductor and accepted by reduced species present in compartment I, and get oxidized. In dark, these oxidized species accept electrons from compartment II, resulted in the electricity flow through external load.

In general the reactions in compartment I and compartment II can be written as follows :

$$\text{semiconductor} + h\nu \rightleftharpoons e^- (\text{C.B.}) + h^+ (\text{V.B.})$$

$$nS^{2-} + nh^+ \rightleftharpoons S_2{}^{n-} \quad \text{compartment I}$$

$$nM^{n+} + ne^- \rightleftharpoons nM^{n-1} \quad \text{compartment II (dark)}$$

where M denotes various redox species present in compartment II. During charging these reactions shift from left to right and in the opposite direction during discharging. Thus, the system could be charged photoelectrochemically and discharged electrochemically for production of electricity upon demand.

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