CHAPTER : 8

AN INTRODUCTION TO BASIC PRINCIPLES OF PEC SOLAR CELLS

8.1 INTRODUCTION :

Mankind has regarded SUN as the biggest source of energy. Solar energy coming down to the earth's surface per year is approximately ten thousand times the world wide energy consumption per year. Harnessing solar energy has therefore, attracted the attention of the scientists, technologists, economists, sociologists and politicians. Much effort has therefore been directed towards developing new and better solar energy conversion devices.

A high degree of sophistication has been achieved in the fabrication of p-n junction solar cells. However, a challenging problem in solar energy research is solar energy storage. In 1970s, an alternative strategy was suggested in which a solid-liquid junction was used. In 1972, Fujishima and Honda used this junction to photoelectrolyse water and thus obtain hydrogen, which is a transportable form of energy. In 1975, Gerischer used this junction for direct conversion of solar energy into electricity. In this thesis, use of solid-liquid junction has been made to take up the strategy adopted by Gerischer i.e. direct conversion of solar energy into electricity.

The photoelectrochemical conversion of solar energy is attractive because there is an opportunity of solar energy storage in form of fuel, which is easily transportable. Photoelectrochemical cell is generally referred as the PEC cell.

A photoelectrochemical (PEC) solar cell is defined as a cell in which the irradiation by light of appropriate frequency of an electrode in contact with a suitable electrolyte produces a change in the electrode potential with respect to reference electrode (under open circuit

conditions) or produces a change in the current flowing in the galvanic cell containing the electrode (under short circuit conditions) [1].

Number of research articles [2 - 54] has been written on the field of photoelectrochemical conversion of solar energy. In the present decade two monograms one on PEC cells [55] and the other on photoelectrochemistry and photovoltaics of layered semiconductors [56] have been published. First monogram [55] introduces the subject of PEC conversion of energy from fundamentals and deals with all the recent developments in the field whereas second [56] describes various aspects of the layered semiconductors, e.g. their interfacial characteristics, optical to electrical (chemical) conversion parameters, photoconversion and surface modification, surface electronic properties, quantum size effects and materials preparation.

In order to develop the concepts needed for studying the behavior of PEC solar cells, description of a p-n junction vis-à-vis a semiconductor electrolyte interface is given below. The concepts developed here will be used later in the study of partial replacement of selenium by sulphur on photoresponse of PEC solar cells fabricated with DVT (Direct vapour transport) grown WSe$_2$ single crystals.

8.2 PHOTOCONVERSION :

Photons are the quanta of electromagnetic radiation. Traditionally, photoconversion is taken as a process through which the visible electromagnetic radiation is converted into electrical energy. In general, the photoconversion process involves interaction of these photons with materials, which give rise to

(1)   Photoemission from metallic surfaces and

(2)   Photoeffects in semiconductors

Upon photoirradiation of semiconducting material and subsequent absorption of this radiation in the semiconductor, following processes may result

(1)   Excitation of electrons from valence band to the conduction band.

(2)   Excitation of electrons from and to the impurity atoms.

(3)   Excitation of electrons to higher energy states in the same band.

(4)   Excitation of excitonic states.

(5)   Excitation of phonons.

With one or more of the above kind of processes occurring, two kinds of photoeffects; namely - photoconductive and photovoltaic have generally been recognised. It may be pointed out that it is the photovoltaic effect, which is at the root of the liquid junction solar cells.

8.3   SEMICONDUCTOR - ELECTROLYTE INTERFACE :

The points of resemblance and difference between p-n junction solar cell and PEC solar cell are summarised in Table 8.1.

The equilibrium concentration of carriers and hence the chemical potential of n-type semiconductor (for example) and the electrolyte are originally different when they are brought in contact with each other. As a result transfer of electrons takes place from the conduction band of the semiconductor to the ionic species in the electrolyte. Accepting these electrons, the ionic species near the interface get reduced. The reaction can be given as
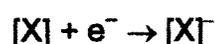
$$[X] + e^- \rightarrow [X]^-$$

Table 8.1 : Comparison of p - n junction and Photoelectrochemical cells

p - n junction solar cells	Photoelectrochemical solar cells

JUNCTION TYPE

(a) p - n	(a) p - electrolyte, n - electrolyte
(a) Solid - Solid	(a) Solid - Liquid

POTENTIAL BARRIER AT THE JUNCTION

(a) Yes	(a) Yes
(b) The barrier is formed due to inter - diffusion of majority charge carriers between p- and n - region	(b) The barrier is formed because of the transfer of majority carriers from semiconductor to electrolyte
(c) The potential drop or band bending in the two regions of semiconductor is almost equal	(c) Major potential drop in semiconductor space charge layer, only a small fraction of the drop is in the electrolyte region
(d) Facilitates flow of majority carrier and inhibits majority carrier flow	(d) Same as in p - n junction

PHOTOEFFECT

(a) Excess carriers are generated	(a) Excess carriers are generated
(b) Mutual diffusion of excess photogenerated minority carriers in the two regions give photovoltage	(b) The excess photogenerated minority carriers transfer charge with ions of the electrolyte to give photovoltage or lead to electrolysis

This process continues till the equilibrium is set up when the chemical potentials of the semiconductor and the electrolyte become same and no further flow of electrons from the semiconductor to the electrolyte takes place. As a result of this charge transfer, the semiconductor region near the interface gets depleted of electrons, giving rise to a positively charged space charge layer. Corresponding to this layer at the interface, there is a sheath of negatively charged ions in the electrolyte, which is known as the Helmholtz layer. The ion density in the Helmholtz layer is high and gradually decreases as the distance in the electrolyte from the interface increases. Thus this layer in general is diffused rather than discrete in nature. The diffused nature of this layer is due to the fact that the preferential electrostatic force responsible for building up of the Helmholtz layer decreases with increasing distance towards the electrolyte from the interface. The denser layer within the sheath of ions in the electrolyte is known as the first Helmholtz layer or simply the Helmholtz layer whereas the ions in the diffused part from an outer or second Helmholtz layer normally termed as Gouy layer. The ions in this layer are somewhat mobile though restricted compared to the ions in the interior of the electrolyte. At equilibrium, the energy bands in the semiconductor are bent upward and fermi levels of the semiconductor and redox level of the electrolyte align. The general structure of the n-type semiconductor electrolyte interface and the corresponding energy band diagram are shown in Fig. 8.1.

Thus the complete picture of the semiconductor electrolyte interface can be summarised as

1. Diffused space charge layer in the semiconductor (plus surface states, adsorbed ionic species).

2. Helmholtz layer.

3. Diffused ionic layer (Gouy layer)

1. Space charge layer
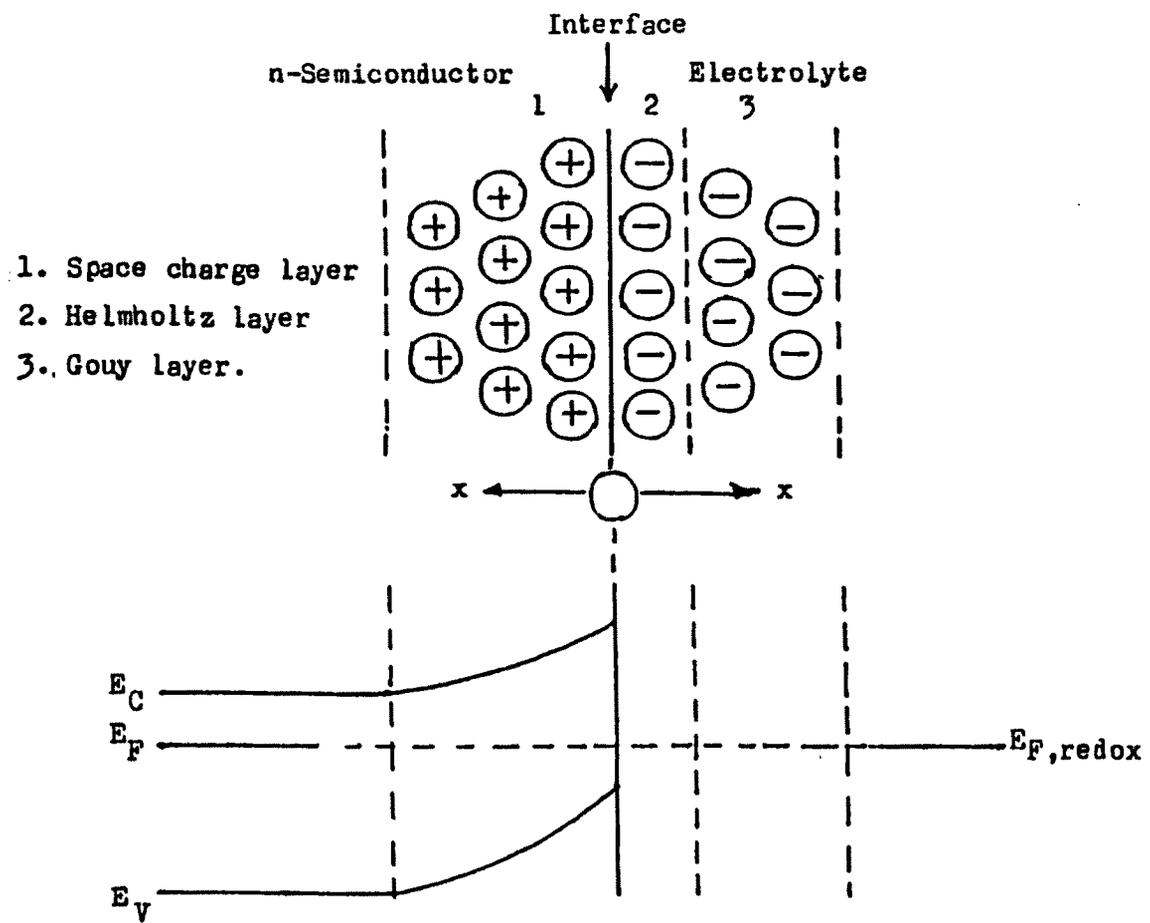2. Helmholtz layer
3. Gouy layer.

Fig. 8.1 General structure of n-semiconductor-electrolyte interface along with corresponding energy band diagram at equilibrium.
   (1) Space charge layer
   (2) Helmholtz layer
   (3) Gouy layer

The distribution of charge and potential are given in Fig. 8.2. The total charge in the semiconductor side of the interface is

$$q_s = q_{sc} + q_{ss} + q_{ads}$$

where q_s = total charge

q_{sc} = charge in the space-charge region

q_{ss} = charge due to surface states

q_{ads} = adsorbed charge

The electroneutrality condition demands that

$$q_s = q_{el}$$

where q_{el} is charge in the electrolyte.

The distribution of potential across the interface is given in Fig. 8.2(c). The total interface potential, ϕ_{Ga} (Galvanic potential) can be written as

$$\phi_{Ga} = \phi_{sc} + \phi_G + \phi_H + \phi_{ss}$$

where ϕ_{sc} is potential across the space charge layer

ϕ_G is potential across the Gouy layer

ϕ_H is potential across the Helmholtz layer, and

ϕ_{ss} is potential across the surface states.

But we know that, for continuity of electric vectors

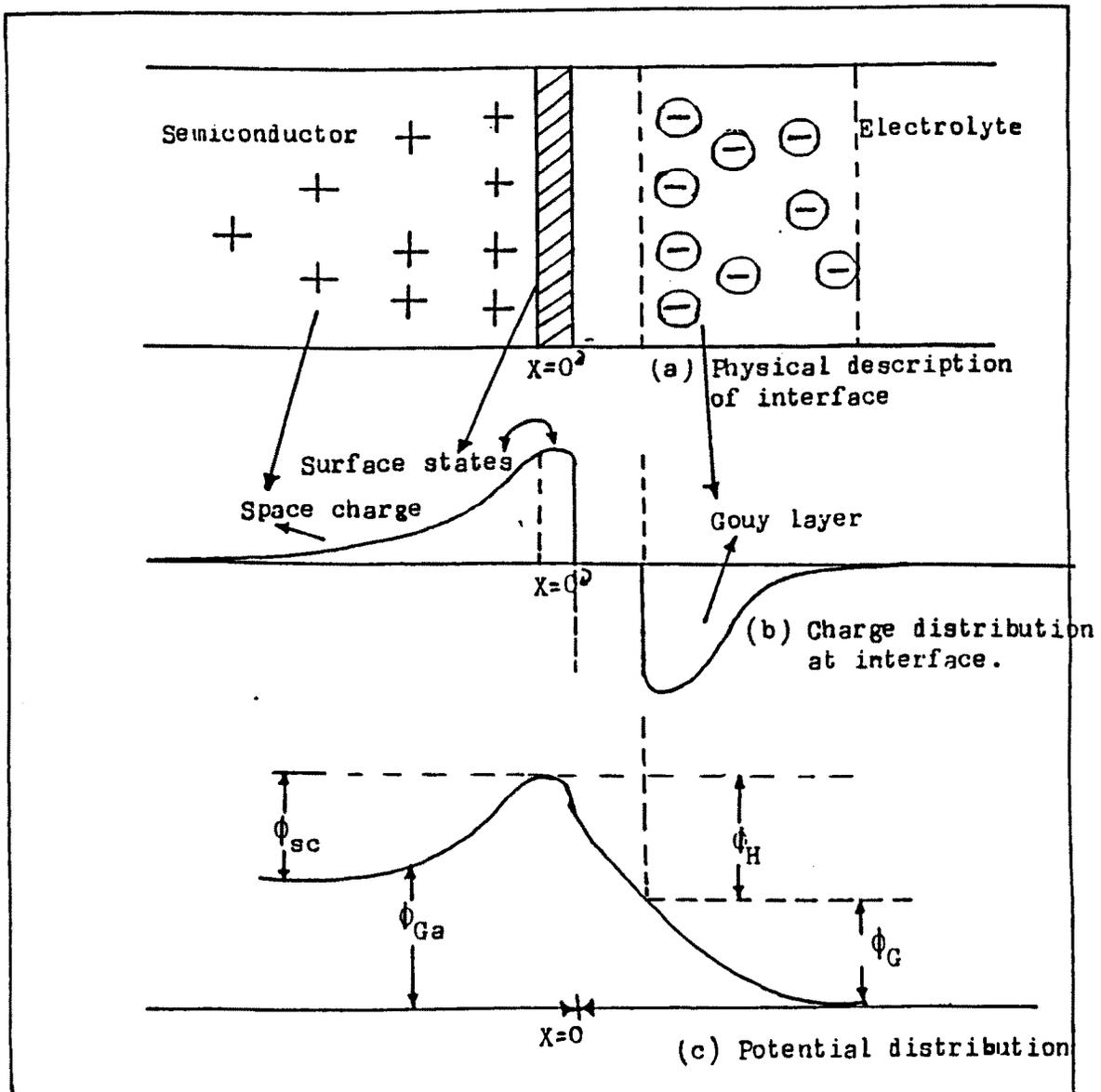$$\varepsilon_s E_s = \varepsilon_H E_H = \varepsilon_G E_G$$

Fig. 8.2 Charge and potential distribution at the semiconductor-electrolyte Interface.

Also as L_D, L_H and L_G are Debye lengths in the semiconductor, Helmholtz and Gouy regions respectively, then

$$E_{sc} = \frac{\phi_{sc}}{L_D} \ , \ E_H = \frac{\phi_H}{L_H} \ \text{ and } \ E_G = \frac{\phi_G}{L_G}$$

The differential capacitance is defined as

$$C_{sc} = \frac{\varepsilon_s \varepsilon_0}{L_D} \ , \ C_H = \frac{\varepsilon_H \varepsilon_0}{L_H} \ \text{ and } C_G = \frac{\varepsilon_G \varepsilon_0}{L_G}$$

The simplest electrical equivalent of a semiconductor - electrolyte can be regarded as a series combination of these capacitors. The total capacitance is given by

$$\frac{1}{C} = \frac{1}{C_{sc}} + \frac{1}{C_H} + \frac{1}{C_G}$$

8.4   SPACE CHARGE CAPACITANCE AND MOTT SCHOTTKY PLOT :

The relation between the space charge capacitance and the space charge potential is represented by well known Mott-Schottky equation as

$$\left(\frac{1}{C_{sc}}\right)^2 = \frac{2}{\varepsilon_0 \, \varepsilon_s \, e \, N_D} \left(\phi_{sc} - \frac{kT}{e}\right)$$

where C_{sc} is space charge capacitance

ε_0 is permeability

ε_s is dielectric constant of semiconductor

e   is charge of electron

N_D is donor density

ϕ_{sc} is space charge potential

k   is Boltzmann constant

T   is absolute temperature

According to this equation $(1/C_{sc})^2$ versus ϕ_{sc} plot is a straight line. However, ϕ_{sc} cannot be measured directly, generally, in electrochemistry electrode potentials are measured against a reference electrode (usually a Normal Hydrogen Electrode (NHE)).

The measured potential difference V corresponds to

$$V = \phi_{sc} - \phi_{NHE}$$

for $\phi_{sc} = 0$, there is no band bending corresponding to a flat band situation. Suppose the flat band potential is V_{fb} and the electrode potential is V then the Mott-Schottky equation can be written as

$$\left(\frac{1}{C_{sc}}\right)^2 = \frac{2}{\varepsilon_0 \varepsilon_S e N_D}\left(V - V_{fb} - \frac{kT}{e}\right)$$

Therefore, a plot of $(1/C_{sc})^2$ versus electrode potential (V) will be a straight line.

8.5   SOME APPLICATIONS OF MOTT SCHOTTKY PLOTS :

1.   Type of semiconductor :

The signs of the slope of $(1/C_{sc})^2$ versus V plots would be different for n and p-type semiconductors. A positive slope indicates

n-type semiconductor whereas a negative slope indicates p-type semiconductor.

2. *Flat band potential and donor density :*

The intercept on the voltage axis of the $(1/C_{sc})^2$ Vs V plot gives flat band potential (V_{fb}) and the slope of the straight line gives donor density N_D.

3. *Band Bending :*

Band bending V_b can be obtained as

$$V_b = \frac{E_{f,redox}}{e} - V_{fb}$$

where $E_{f,redox}$ is the fermi level associated with a particular redox species given by

$$E_{f,redox} = -(4.5eVNHE + eV_{redox})$$

4. *Depletion layer width :*

The majority carrier depletion layer width, W, can be calculated from the following relation knowing the values of V_{fb} and N_D

$$W = \left[\frac{2\varepsilon_0\varepsilon_s (V - V_{fb} - kT/e)}{eN_D} \right]^{\frac{1}{2}}$$

5. *Positions of Band edges :*

The electron and hole density in the conduction and valence bands are given by

$$n_0 = N_c \, e^{-(E_c - E_F)/kT}$$

$$p_0 = N_v \, e^{-(E_F - E_v)/kT}$$

where N_c and N_v are density of states respectively for conduction and valence bands and E_c and E_v are respectively the conduction and valence band edges. The above equations give

$$E_c = E_f - kT \ln (n_0/N_c) \text{ and}$$

$$E_v = E_f + kT \ln(p_0/N_v)$$

For a semiconductor electrode in contact with an electrolyte at equilibrium.

$$E_f = E_{f,redox}$$

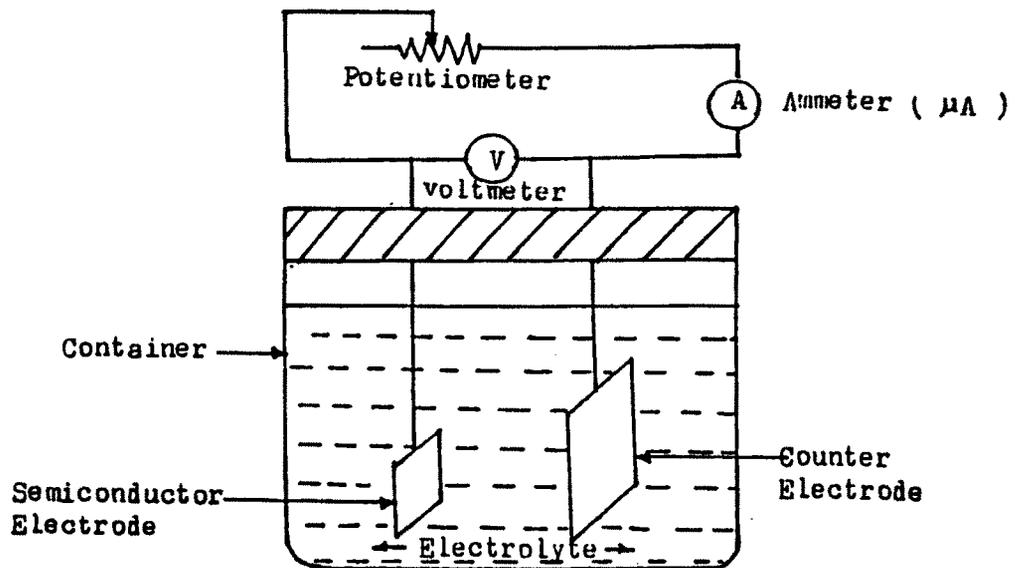Since $E_{f,redox}$ is known E_c and E_v can be obtained.

With the help of all these values obtained from Mott-schottky plots, a complete location of various energy levels for the semiconductor photoelectrodes of WSe_2 and WSSe PEC solar cells will be described in the next Chapter 9.

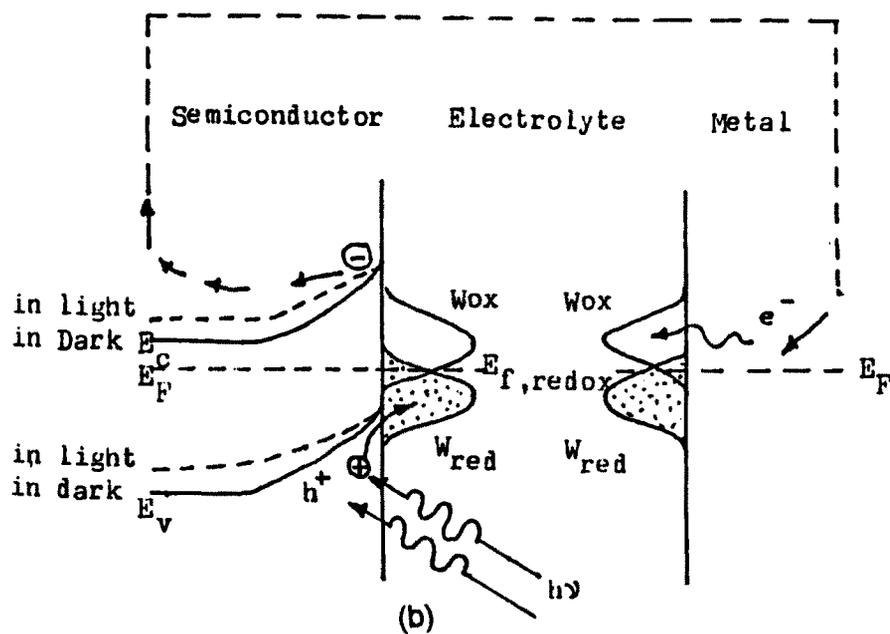## 8.6 PRINCIPLES OF DIFFERENT PHOTOELECTROCHEMICAL SOLAR CELLS :

Two phenomena can happen in a semiconductor electrolyte system under photoexcitation or illumination - (1) The electrolyte species, may be excited to higher energy states; or (2) the semiconductor absorbs the photons, which results in the enhancement of charge carriers in it through the generation of electron hole pairs. The first phenomenon leads to photogalvanic cells while the second phenomenon leads to photoelectrochemical cells. It is the second phenomenon, with which we are concerned in this thesis.

The principle of charge transfer reaction at the semiconductor electrolyte interface forms the basis of various types of photoelectrochemical solar cells. In addition to the semiconductor electrolyte interface, incorporation of a counter electrode in the electrolyte to complete the electrical circuit gives the desired photoelectrochemical solar cell. A typical cell is shown schematically in Fig. 8.3. Illumination results in the generation of electron-hole pairs, their separation in the space charge layer, lowering of the depletion layer barrier and subsequently the hole flux crossing the interface to be captured by the reduced ionic species of the electrolyte increase. On short circuiting, the electron is driven via the external circuit towards the metal counter electrode where it participates in the reduction reaction of the oxidised species. The various types of photoelectrochemical solar cells can be categorised according to the net free energy change in the overall system as given below (see Fig. 8.4).

(a)   Electrochemical photovoltaic cells ($\Delta G = 0$)

Potentiometer

(A) Ammeter (μA)

(V) voltmeter

Container

Semiconductor Electrode

Counter Electrode

← Electrolyte →

(a)

Semiconductor   Electrolyte   Metal

in light
in Dark E_C
E_F
W_{ox} W_{ox} e^-
$E_{f,redox}$ E_F

in light
in dark E_V
h^+
W_{red} W_{red}

$h\nu$

(b)

Fig. 8.3(a) Schematic diagram of a PEC system.
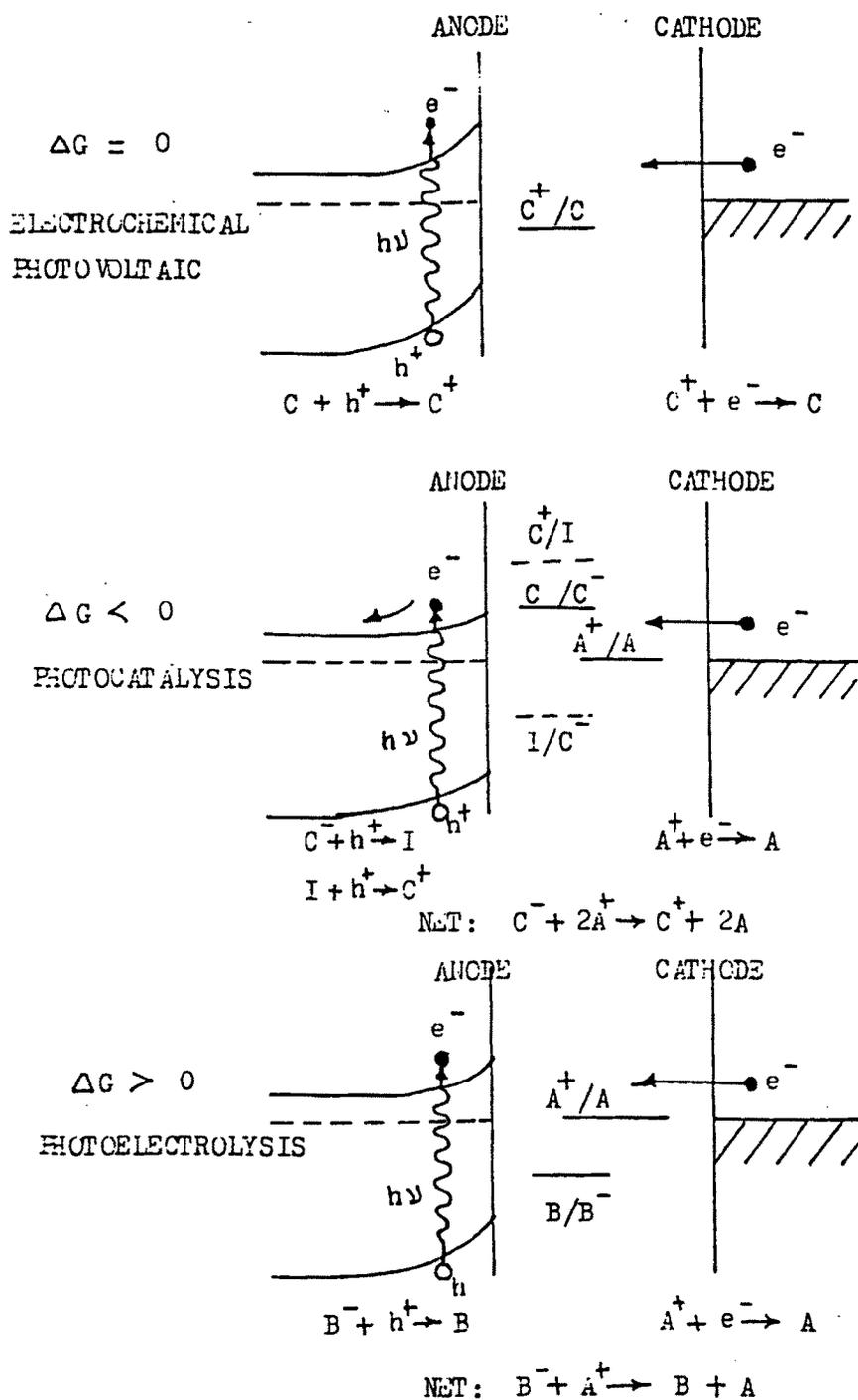(b) Energy band diagram for a PEC cell based on an n-type semiconductor as the photoelectrode.

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ANODE   CATHODE

$\Delta G = 0$

ELECTROCHEMICAL
PHOTOVOLTAIC

e$^-$

C^+/C

hν

h$^+$

e$^-$

$C + h^+ \longrightarrow C^+$ $C^+ + e^- \longrightarrow C$

ANODE   CATHODE

C^+/I

C^-/C^-

$\Delta G < 0$

PHOTOCATALYSIS

e$^-$

A^+/A

e$^-$

hν

I/C^-

$C^- + h^+ \longrightarrow I$ $A^+ + e^- \longrightarrow A$
$I + h^+ \longrightarrow C^+$

NET: $C^- + 2A^+ \longrightarrow C^+ + 2A$

ANODE   CATHODE

$\Delta G > 0$

PHOTOELECTROLYSIS

e$^-$

A^+/A

e$^-$

hν

B/B^-

h$^+$

$B^- + h^+ \longrightarrow B$ $A^+ + e^- \longrightarrow A$

NET: $B^- + A^+ \longrightarrow B + A$

**Fig.8.4 Energy level diagram and cell reaction for different types of
photoelectrochemical solar cells.**

It consists effectively of such a redox couple that the total cathodic plus anodic reactions do not lead to a 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

$$(red)_{solv} + h^+ = (ox)_{solv}.$$
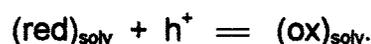
At the metal counter electrode

$$(ox)_{solv} + e^- = (red)_{solv}$$
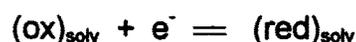
The above cell is the usual regenerative type used for direct production of electricity, with which we shall be concerned in the present work. (Chapter - 9).

(b)   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 some electrochemical storage solar cells belong to this category. The general reaction is given in Fig. 8.4. Some examples of reaction for the above type are

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

$$CO_2 + H_2O \xrightarrow{\;h\nu\;} CH_2O + O_2$$
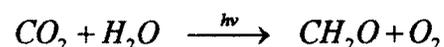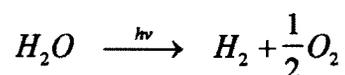
Hence, the optical energy is converted into chemical energy.

(c)   In these cells also such redox couples are present that a net chemical change takes place as given in Fig. 8.4. Here $\Delta G < 0$ and the optical energy provides the activation energy for the chemical reaction. One example of photocatalytic cell is :

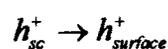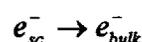$$N_2 + 3H_2 \xrightarrow{\ h\nu\ } 2NH_3$$

8.7   PRINCIPLE OF ELECTROCHEMICAL PHOTOVOLTAIC SOLAR CELL :

The various steps involved in a PEC cell fabricated with a n-type semiconductor can be summarised as follows :

(1)   Light absorption (in space charge and bulk)

$$e^- + h^+$$
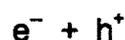
(2)   Electron-hole separation in space charge layer

$$e^-_{sc} \rightarrow e^-_{bulk}$$

$$h^+_{sc} \rightarrow h^+_{surface}$$

(3)   Electron-hole recombination in bulk

$$e^- + h^+ \rightarrow \text{heat (in semiconductor)}$$

(4)   Semiconductor surface holes react with redox species.

$$h^+ + (red)_{solv} \rightarrow (ox)_{solv}$$

(5)   Semiconductor surface holes may react with the semiconductor bands itself

$$h^+ + \text{semiconductor} \rightarrow \text{semiconductor photodecomposition}$$

This has to be avoided.

(6) Reduction of relevant redox species at the counter electrode

$$e^- + (ox)_{solv} \rightarrow (red)_{solv}$$

(7) Surface recombination at electron-hole traps

$$e_{sc}^- \rightarrow e_{tr}^-$$

$$h_{surface}^+ \rightarrow h_{tr}^+$$

$$e_{tr}^- + h_{tr}^+ \rightarrow \text{heat (at semiconductor surface)}$$
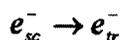
Obviously, this lowers the efficiency of the solar cell.

8.8 ADVANTAGES OF PEC SOLAR CELLS OVER THE SOLID STATE PHOTOVOLTAIC CELLS :

The important advantages of a PEC solar cell over the solid state cells in general can be summarised as follows :

(1) The great ease with which the semiconductor/liquid junction can be formed.

(2) Since the photosensitive junction in a PEC is extremely abrupt compared to the solid state counterpart and one side of the junction is practically transparent to the solar spectrum, more of the incident light is absorbed within the region of high electric field at the interface where charge carriers are more efficiently separated and collected.

(3) The simple formation and the abruptness of the photosensitive semiconductor/liquid junction make the use of polycrystalline material in PECs feasible [23 - 24, 57 - 64].

(4) Many processing steps required for solid state solar cells e.g. (p-n junction) are either simplified or completely eliminated. A comparison

of the two cases is shown in Table 8.2. The fabrication steps, which would be eliminated for a PEC device, are as follows :

(a)   deposition of the grid structure

(b)   deposition of an antireflection coating

(c)   high temperature processing of the semiconductor substrate for junction formation by doping.

Additional steps required in a PEC cell fabrication sequence relative to p-n junction devices are the following :

(a)   injection of an electrolyte containing suitable redox species.

(b)   fabrication of counter electrodes

(c)   insulation of the back surface of the photo electrode.

(5)   In situ energy storage is possible with some PEC cells [65] and thus can accomplish in one stage, which the photovoltaic cell/storage battery combination can accomplish in two

(6)   In an electrochemical photovoltaic cell, the band bending may be increased by adjusting the redox potential (V_{redox}) of the electrolyte, thus increasing the attainable open circuit voltage. In comparison, the open circuit voltage (barrier height) in a Schottky type cell is generally independent of the metal work function because of the Fermi-level pinning [35].

(7)   It has been elegantly shown [66] that significant reduction in cost for the fabrication of a PEC device (relative to solid cells) are expected in spite of the additional processing steps outlined in (4) above.

Table 8.2 : Comparison of components in a fabrication sequence for PEC cells and p – n junction solar cells.

PEC cell	p – n junction silicon cell
* Electrolyte injection	* Antireflection coating
* Counter electrode fabrication	* Front contact metallization
* Plastic insulation on rear surface of photoanode	* Transparent epitaxial layer
* Photoanode fabrication (e.g. thin film deposition)	* Growth of silicon single crystals
	* Encapsulation

8.9 PARAMETERS NECESSARY FOR CHARACTERISATION OF PEC SOLAR CELL :

The performance of a photovoltaic or PEC device can be described by the following measurements :

(a)   the short circuit current

(b)   the open circuit voltage

(c)   the maximum power

(d)   the fill factor

(e)   the efficiency

(a)   The short circuit current (I_{sc}) :

The current measured directly across the electrodes in the absence of any load in the circuit is referred to as the short circuit current I_{sc}

(b)   Open circuit voltage (V_{oc}) :

The voltage measured across the electrodes when there is infinite load in the circuit is termed as the open circuit voltage V_{oc}.

(c)   Maximum power (P_m) :

The product of current and voltage gives the output power i.e.

$$P_{out} = V \times I$$

for a particular load resistance value, this output power will be maximum. This point is referred as the maximum power point and the value is called the maximum power (P_m).

(d) Fill Factor (FF) :

Ideally a solar cell should have $V_{mp} = V_{oc}$ and $I_{mp} = I_{sc}$ however, various loss mechanisms operating within the cell make it to deviate from the ideal behaviour. The term used to express this departure is known as the "fill factor" (FF) defined by

$$F.F = \frac{J_{mp} \times V_{mp}}{J_{sc} \times V_{0c}}$$

where J_{sc} is the short circuit current density

J_{mp} is the current density at maximum power point and

V_{mp} is the voltage at maximum power point.

Efficiency (η) :

The theoretical conversion efficiency of a solar cell at the maximum power point is given by

$$\eta = \frac{V_{mp} \times I_{mp}}{P_{in}} = \frac{F.F \times V_{oc} \times I_{sc}}{P_{in}} \times 100\%$$

where P_{in} is the solar power input or

$$\eta = \frac{V_{mp} \times J_{mp}}{P_{in}}$$

where $J_{mp} = I_{mp}/Area$.

8.10 REQUIREMENTS FOR FABRICATION OF EFFICIENT PEC SOLAR CELLS :

Essentially a PEC solar cell consists of

(I)   semiconductor photoelectrode

(ii) an electrolyte, and

(iii) a counter electrode

All these parts play an important role in deciding the better performance of the PEC solar cell. The requirements, which these parts should meet for the efficient PEC solar cell, are detailed below :

(I)   Semiconductor photoelectrode :

Semiconductor photoelectrode is the heart of a PEC solar cell. For the achievement of good performance it should satisfy the following requirements:

1.   The optical absorption coefficient of semiconductor photoelectrode material should be high.

2.   The band gap (E_g) of the photoelectrode material should be optimum so as to match with maximum span of solar spectrum $(E_g = 1.2$ to 1.8 eV$)$.

3.   It should be of direct band gap type with high optical absorption coefficient.

4.   The diffusion length for minority carriers should be as long as possible.

5.   The width of the space charge layer must be large.

6.   Photoelectrode should be stable in the electrolyte and should not get corroded during illumination.

7.   Thickness and area of the photoelectrode should be large enough to absorb all the incident radiation.

8.   The lattice mismatch and thermal mismatch between two materials should be small.

9.   Series resistance R_s should be as small as possible and shunt resistance R_{sh} should be large enough. Ideally $R_s = 0$ and $R_{sh} = \infty$.

10.   Cost of the material manufacturing process and efficiency should be acceptable.

In addition to the above requirements the parameters as e.g. film thickness, grain size and grain boundaries should be controlled for polycrystalline thin films.

(ii)   Electrolyte :

Another important parameter in PEC solar cell is the electrolyte. Electrolyte consists of the oxidised and reduced species. These species are ionic species, which help in transferring the photogenerated holes from photoelectrode to counter electrode.

Requirements of properties of the electrolyte, which PEC solar cell should satisfy, are listed below :

1.   The charge transfer rates due to redox system at both semiconductor and counter electrode should be high or effective.

2. The electrolyte should have minimal optical absorption.

3. Oxidised species, reduced species and solvent components should have photo and thermal stability throughout usable solar spectrum and operational temperature range.

4. Oxidised species, reduced species and supporting electrolyte concentration in solvent should be adequate to reach required current densities.

5. Ionic conductance of electrolyte should permit negligible ohmic losses.

6. Electrolyte should not react with the semiconductor electrode and should be non-corrosive to the electrode and container material.

7. Cost, toxicity and environmental aspect should be preferably low.

(iii) Counter Electrode :

A counter electrode is the third part of the PEC solar cell. The requirements of counter electrode for better performance in PEC solar cell are as follows :

1. The counter electrode should not react with electrolyte i.e. it should be chemically inert.

2. The counter electrode must be electrically active i.e. the charge transfer between the counter electrode and redox species in the electrode must be fast.

3. The area of the counter electrode must be larger than that of the semiconductor electrode. This improves the collection efficiency

and avoids the concentration polarisation.

4. When a counter electrode is immersed into the electrolyte, the half cell potential of the semiconductor electrode should match with the half cell potential of the semiconductor electrode.

5. Counter electrode should have low over potential for the reduction reaction.

6. Counter electrode must be cheaper, platinum and graphite are more widely used. Many counter electrode materials have been evaluated electrochemically by Allen and Hickling [67].

8.11 CONCLUSIONS :

The detailed understanding of the general principles of photoelectrochemical solar cells developed in this Chapter will be used in studying the effect of partial replacement of selenium by sulphur on photoresponse in tungsten diselenide based PEC solar cells to be described in the next Chapter (i.e. Chapter 9).

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