
CHAPTER 12
INTRODUCTION TO PHOTOELECTROCHEMICAL (PEC)
SOLAR CELLS

12.1 INTRODUCTION

The interest in solar energy as well as in other renewable sources of power was aroused by the so called oil or roughly, energy crisis of the 1970s. According to experts' estimates, fossil fuels will suffice only for a limited period, it is believed that the reserves of oil may exhaust somewhere around the year 2000 and those of gas, by the year 2015. Besides, burning of fossil fuels (particularly, coal) appreciably pollutes the environment and may, among other things, give rise to the so called

"greenhouse effect" if the concentration of carbon dioxide in the atmosphere exceeds a certain critical value. Self release of energy contained in fossil fuels also disturbs the earth's heat balance, this holds for atomic energy as well.

The use of solar energy, on the contrary will not change the heat balance of the earth, because its conversion and consumption by men are "built in" in the natural process of conversion of radiant energy of the sun into heat; the latter dissipates in space surrounding the earth. The solar energy conversion process is "ecologically clean", inexhaustible and in particular waste free. These facts permitted us to affirm with certainty that solar energy will occupy its place in the energy balance of the future.

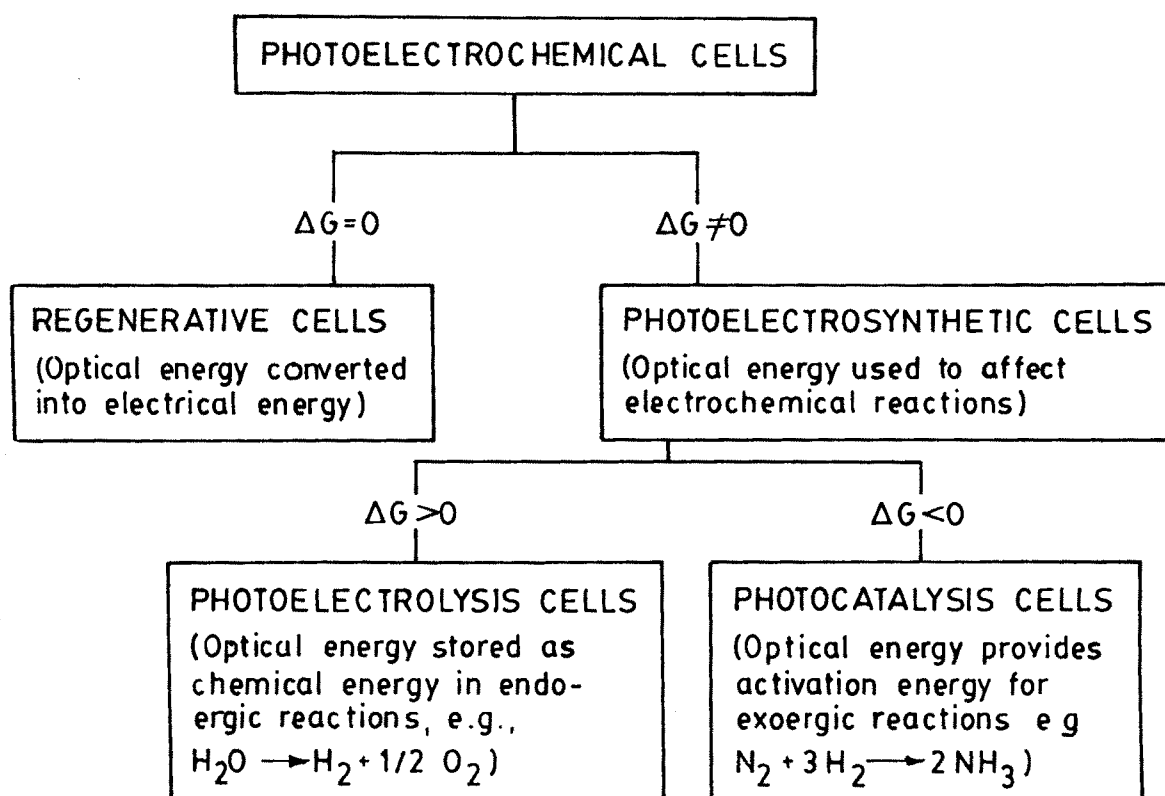
Among the several ways of collecting solar energy, the photovoltaic, the photochemical, the photoelectrochemical, the photothermal and the photosynthetic are some of the better known routes to achieve energy conversion. Out of these methods the idea of converting solar energy directly into chemical or electrical energy by the use of photoelectrochemical systems has rapidly gained popularity in recent years.

A photoelectrochemical [PEC] cell is defined as a cell in which the irradiation of an electrode in contact with an appropriate electrolyte produces a change in the electrode potential with respect to a 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].

Nozik [2] has proposed the following classification for photoelectrochemical cells [Fig. 12.1]. According to this classification, all cells are divided into :

1. regenerative photoelectrochemical cells, also known as "liquid junction solar cells" or "electrochemical photovoltaic cells", in which the Gibb's free energy G of the electrolyte solution does not vary, and
2. photoelectrosynthetic cells in which the Gibb's energy of the electrolyte solution changes when in operation.

In the present work attention has been mainly focussed on the regenerative photoelectrochemical solar cells. A historical account of the development of semiconductor electrochemistry is summarised in Table 12.1.



Classificationⁿ of photoelectrochemical cells
(according to Ref.[2])

Fig. 12.1

Table 12.1 Historical account of the development of photoelectrochemistry

Sr. No.	Name of the study	References
1.	First observation of photo-effect at silver halide electrodes in aqueous solutions	Becquerel [3]
2.	Beginning of semiconductor electrochemistry study of elemental semiconductors (Si, Ge)	Brattain and Garrett [4]
3.	First comprehensive experimental studies CdS, CdSe and other binary semiconductors	Williams [5]
4.	Development of models for semiconductor electrolyte interface energetics	Green [6] Myamlin and Pleskov [7], Gerischer [8]
5.	Ability of TiO_2 to oxidise water under reverse bias conditions	Body [9]
6.	Report of the first photo-electrolysis cell to decompose using TiO_2 photoanodes	Fujishima and Honda [10]
7.	Concept of semiconductor liquid junction solar cell.	Gerischer [11]
8.	SrTiO_2 the first semiconductor to photoelectrolyse water without externally applied bias voltage	Wrighton et al. [12] Mavroides et al. [13,14] Watanbe et al. [15]
9.	Concept of p-n photo electrolysis cells	Yoneyama et al [16], Nozik [17-20]

Table 12.1 (contd.)

10.	Study of semiconductors in non-aqueous solvents	Frank and Bard [21]
11.	Stable semiconductor-liquid junction solar cells based on CdX (X = S, Se, Te) and aqueous polychalcogenide electrolytes	Ellis et al. [22,23], Hodes et al. [24] Miller and Heller [25]
	Photoelectrochemical systems with energy storage	Hodes et al. [24]
12.	Visible light sensitization of large band gap oxides by doping with transition metal ions.	Ghosh and Maruska [26]
13.	Layered dichalcogenide semiconductor for PEC cells.	Tributsch [27,28]
14.	Importance of thermodynamic and kinetic considerations	Gerischer [29], Bard and Wrighton [30]
15.	Chemical derivatization of semiconductor electrode surfaces	Wrighton et al. [31]
16.	High efficiency (12 %) GaS liquid junction solar cells (surface modified by Ru ³⁺ ion adsorption).	Parkinson et al. [32] Heller et al. [33]
17.	High efficiency thin film electrodes in PECs	Heller et al. [34] Hodes [35]
18.	Effect of surface states, concept of Fermi level pinning and inversion layer model	Bard et al. [36], Wrighton et al. [37] Kautek and Gerischer [38] Turner et al. [39].

Table 12.1 (contd.)

19.	High efficiency (11.5 %) of p-InP semiconductor liquid junction solar cell	Heller et al. [40]
20.	High efficiency (12 %) p-InP based solar photo-electrolysis cell	Heller and Vadimsky [41]
21.	High efficiency based n-WSe ₂ PEC cell (14 %)	F.R.F. Fan et al. [42]
22.	Liquid-junction solar cells based on electrocodeposited films	Chandra et al. [43]
23.	A 17 % efficient n-WSe ₂ PEC solar cell	Prasad et al. [44]
24.	A 22 % efficient semiconductor (n-WSe ₂) / liquid junction solar cell	Campet et al. [45]
25.	A 9.05 % efficient p-WSe ₂ PEC solar cell	Agarwal et al. [46]

Number of research articles [3-46] have been written on this field of photoelectrochemical conversion. Recently two monographs one on photoelectrochemical solar cells [47] and the other on photoelectrochemistry and photovoltaics of layered semiconductors [48] have been written. First monograph [47] introduces the subject of photoelectrochemical conversion from fundamentals and deals with all the recent developments in the field. Whereas second [48] 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 behaviour of PEC solar cells, description of a p-n junction vis-a-vis a semiconductor electrolyte interface is given below. The concepts developed here will be used later in the fabrication of PEC solar cells with DVT grown WS_2 single crystals.

12.2 ELECTROLYTE - SEMICONDUCTOR CONTACTS

The points of resemblance and difference between p-n junction solar cells and photoelectrochemical solar cells are summarised in Table 12.2.

Table 12.2 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	
(b) Solid-solid		(b) 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 is 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 photo-generated 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.	

Similar to the metal semiconductor contacts, there is a charge transfer taking place, when an electrolyte and a semiconductor are brought into contact, until a potential difference, known as "Galvani Potential", is established at equilibrium. The region inside the electrolyte which is in contact with the semiconducting crystal is made up of

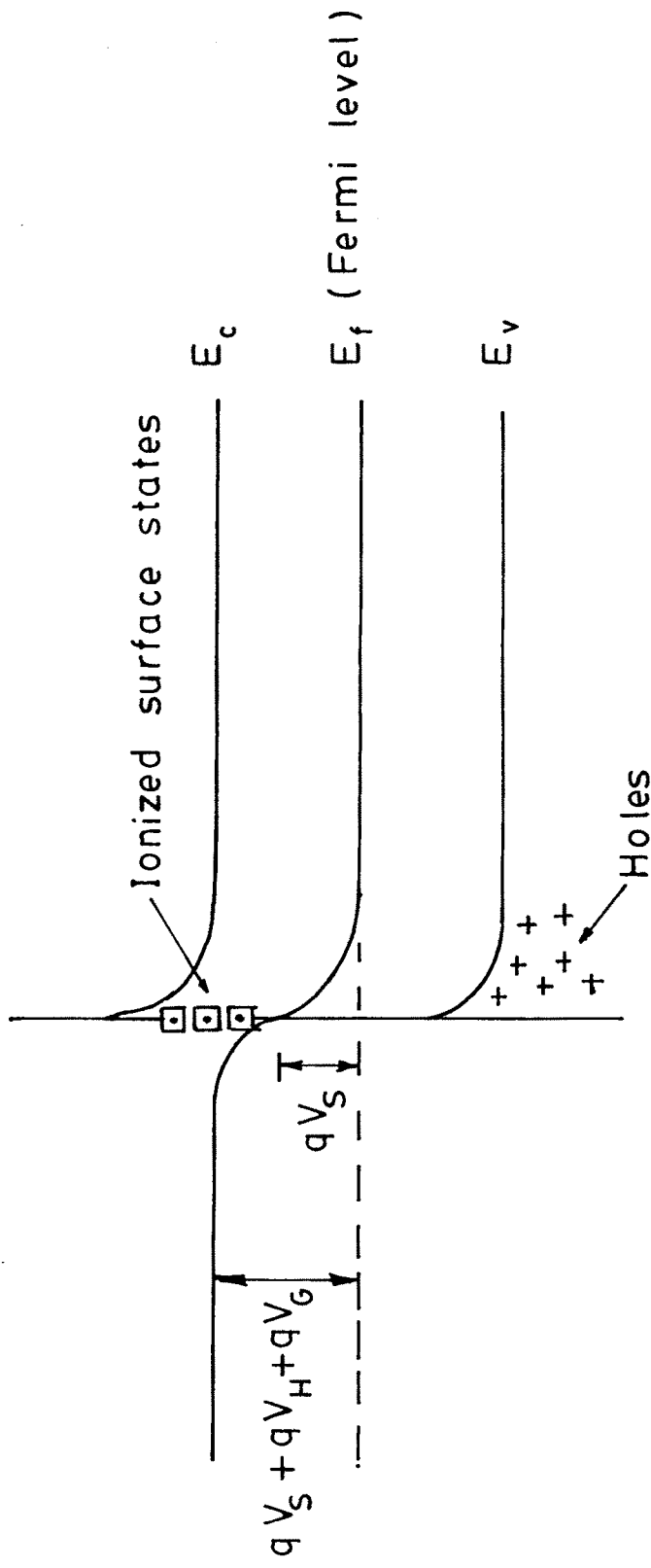
- (a) The Helmholtz region formed by a layer of ions in the electrolyte, firmly held to the semiconductor at the interface V_H , and
- (b) A more diffuse mobile space charge region extending into the electrolyte (the Gouy region) V_G .

Region (a) is sometimes called the inner Helmholtz layer and (b) the outer Helmholtz layer. The Gouy region is generally thin because of the high ion concentration, and the potential across this region is small because its permittivity is much larger than that of the semiconductor and of the Helmholtz region. So the Galvani potential is mainly the sum of the potential across the Helmholtz region and across the space charge region in the semiconductor. The Helmholtz region (here it refers to inner Helmholtz layer) is a fixed layer of one or two atomic diameter (or molecular diameter) in thickness corresponding

to the ions absorbed by the particles in the semiconductor, to which they owe their charges. The diffuse space charges in the Gouy region usually are excess ions of charges opposite to those in space charge region in the semiconductor as shown in fig. 12.2.

12.3 SEMICONDUCTOR - ELECTROLYTE JUNCTION : CONVENTIONAL PICTURES

All phenomena associated with photoelectrochemical system are based on the formation of a semiconductor electrolyte junction when an appropriate semiconductor is immersed in an appropriate electrolyte. The junction is characterised by the presence of space charge layer in the semiconductor adjacent to the interface with the electrolyte. A space charge layer generally develops in a semiconductor upon contact and equilibrium with a second phase whenever the initial chemical potential of the electrons is different for the two phases. For semiconductors, the chemical potential of the electron is given by its Fermi level. For liquid electrolytes, the chemical potential is determined by redox potential of the redox couples present in the electrolyte. These redox potentials are also identified with the Fermi level in the



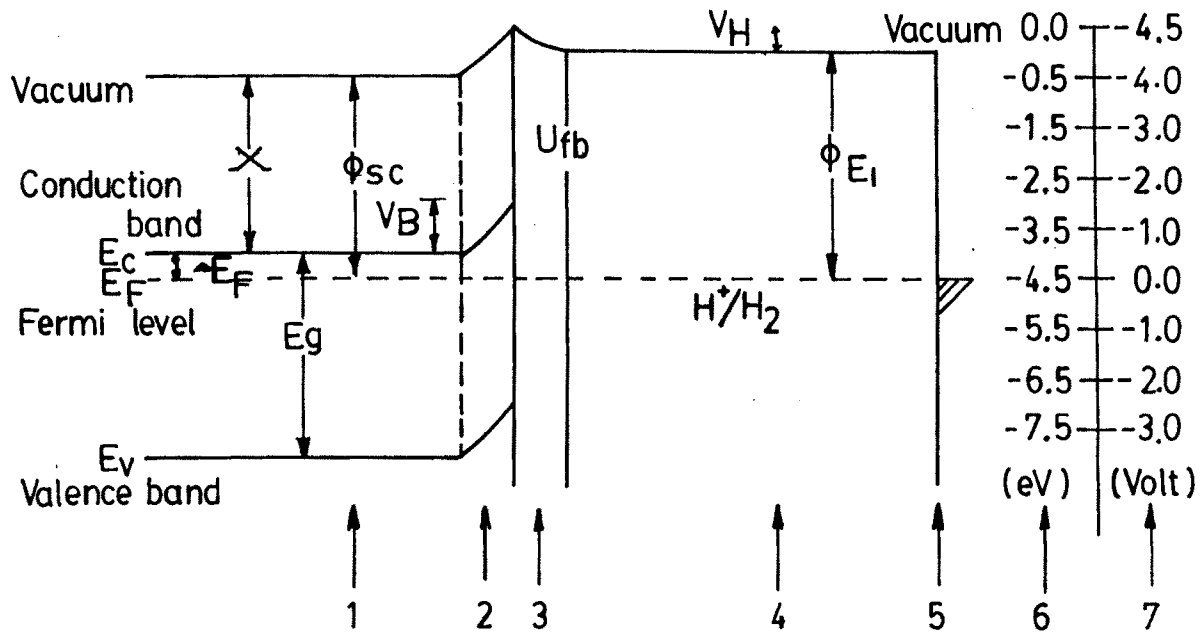
Space charge region in the semiconductor

fig. 12.2

electrolyte.

If the initial Fermi level in an n-type semiconductor is above initial Fermi level in the electrolyte (or any second phase), then equilibration of the two Fermi levels (or chemical potentials) occurs by transfer of electrons from semiconductor to electrolyte. This produces a positive space charge layer in the semiconductor (also called a depletion layer since the region is depleted of majority charge carriers). As a result, the conduction and valence bands are bent upwards, establishing a potential barrier against further electron transfer into the electrolyte (Figure 12.3). An inverse but analogous situation occurs with p-type semiconductors having an initial Fermi level below that of electrolyte.

As pointed out earlier in section 12.2, a charged layer also exists in the electrolyte adjacent to the interface with the solid electrode - the well known Helmholtz layer. An important consequence of this layer for semiconductor electrode is that it markedly affects the band bending that develops in the semiconductor when it equilibrates with the electrolyte. Without this layer the band bending would simply be expected to equal the difference in initial Fermi levels between the two phases (i.e. the difference between their respective work



- | | |
|--------------------------------------|--|
| 1 n-Type semi conductor electrode | H^+/H_2 Electrolyte redox couple |
| 2 Depletion layer | V Helmholtz layer potential drop |
| 3 Helmholtz layer | E_g Band gap |
| 4 Electrolyte | X Electron affinity |
| 5 Metal electrode | ϕ_{sc} Work function |
| 6 Solid state scale (eV) | U_{fb} Flat band potential |
| 7 Electrochemical scale (NHE)(volts) | ϕ_{E_1} Electrolyte work function |
| | V_B Band bending |

fig. 12-3

functions). However, the potential drop across the Helmholtz layer modifies the net band - bending as shown in Fig. 12.3. In this figure, the energy scales commonly used in solid state physics and electrochemistry are shown for comparison. In the former, the zero reference point is vacuum, while in the later it is the standard redox potential for the hydrogen ion-hydrogen (H^+/H_2) redox couple. It has been shown [8,11] that the effective work function of Fermi level for the standard H^+/H_2 redox couple at equilibrium is -4.5 eV with respect to vacuum. Hence, by using this scale factor, the energy levels corresponding to any given redox couple can be related to the energy levels of the valence and conduction bands of the semiconductor electrode.

To make the connection between the energy levels of the electrolyte and the semiconductor, it is necessary to introduce the flat-band potential U_{fb} as a critical parameter characterising the semiconductor electrode. The flat band potential is the electrode potential at which the semiconductor bands are flat (zero space charge in the semiconductor). It is measured with respect to a reference electrode, usually either the standard normal H^+/H_2 redox potential (NHE) or the standard calomel electrode (SCE). Hence the band bending is given by

$$V_b = U_e - U_{fb} \quad (12.1)$$

where U_e is the electrode potential (Fermi level) of the semiconductor. At equilibrium in the dark, U_e is identical with the potential of the redox couple in the electrolyte.

The effect of the Helmholtz layer on the semiconductor band bending is contained within the flat-band potential. This important parameter is a property of the semiconductor bulk and the electrolytes, as seen from the following relation,

$$\begin{aligned} U_{fb} \text{ (n.h.e.)} &= (\chi + \Delta E_F + V_H) - 4.5 \\ &= (\phi_{sc} + V_H) - 4.5 \end{aligned} \quad (12.2)$$

where χ is the electron affinity of the semiconductor,

ϕ_{sc} is the work function of the semiconductor,

ΔE_F is the difference between the fermi level and majority carrier band edge of the semiconductor,

V_H is the potential drop across the Helmholtz layer, and 4.5 is the scale factor relating the H^+/H_2 redox level to vacuum.

12.4 MOTT SCHOTTKY RELATION

The capacity of a space charge region is defined

as,

$$C_{sc} = \frac{dQ_{sc}}{dU_{sc}} \quad (12.3)$$

The space charge (Q_{sc}) vs potential (U_{sc}) dependence can be derived from the Poisson equation

$$\frac{d^2U_{sc}}{dx^2} = - \frac{\rho(x)}{\epsilon\epsilon_0} \quad (12.4)$$

in which the total charge $\rho(x)$ is given by

$$\rho(x) = e [N_D - N_A - n(x) + p(x)] \quad (12.5)$$

The charge is determined by all mobile carriers [electrons, $n(x)$ and holes $p(x)$] and by ionized donors N_D and acceptors N_A . The electron and hole densities n_s and p_s at the interface are related to the carrier density n_0 and p_0 in the bulk of the material by the Boltzmann equations :

$$n_s = n_0 \exp \left(- \frac{eU_{sc}}{kT} \right) \quad (12.6a)$$

$$p_s = p_0 \exp \left(+ \frac{eU_{sc}}{kT} \right) \quad (12.6b)$$

If equilibrium between electrons and holes exists throughout the whole semiconductor then

$$n_o p_o = n_s p_s = n_i^2$$

in which n_i is the inversion concentration, mostly a very low value for large band gap semiconductors decreasing exponentially with the band gap.

Integrating the Poisson equation and using equations (12.3), (12.5) and (12.6) one obtains an exact relationship between space charge capacity C_{sc} and U_{sc} . This equation is rather complex [49] and will not be discussed here. In the exhaustion region (i.e. $n_s < n_o$ for n-type and $p_s < p_o$ for p-type) this equation simplifies to

$$\frac{1}{C_{sc}^2} = \left(\frac{2}{\epsilon \epsilon_o N_D e} \right) \left(U_{sc} - \frac{kT}{e} \right) \quad (12.7)$$

This relation is known as Mott Schottky relation and has been used in the next chapter to obtain the flat band potentials of photoelectrodes prepared from DVT grown WS_2 crystals in different electrolytes.

12.5 PHOTOINDUCED CHARGE TRANSFER REACTIONS

When the semiconductor electrolyte junction is

illuminated with light, photons having energies greater than the semiconductor band gap are absorbed and create electron-hole pairs in the semiconductor. Photons absorbed in the depletion layer produce electron hole pairs that separate under the influence of the electric field present in space charge region. Electron-hole pairs produced by absorption of photons beyond the depletion layer will separate if the minority carriers can diffuse through the depletion layer before recombination with the majority carriers occurs.

The photoproduction and subsequent separation of electron-hole pairs in the depletion layer cause the Fermi level in the semiconductor to return towards its original position before the semiconductor-electrolyte junction was established, i.e. under illumination, the semiconductor potential is driven towards its flat-band potential. Under open circuit conditions between an illuminated semiconductor electrode and a metal counter electrode, the photovoltage produced between the electrodes is equal to the difference between the Fermi level in the semiconductor and the redox potential of the electrolyte. Under close circuit conditions, the Fermi level in the system is equalised and no photovoltage exists between the two electrodes. However, a net charge flow does exist. Photogenerated minority

carriers in the semiconductor are swept away to the surface where they are subsequently injected into the electrolyte to derive a redox reaction. For n-type semiconductors, minority holes are injected to produce an anodic oxidation reaction, while for p-type semiconductors, minority electrons are injected to produce a cathodic reaction. The photogenerated majority carriers in both cases are swept towards the semiconductor bulk, where they subsequently leave the semiconductor via an ohmic contact, traverse an external circuit to counter electrode, and are then injected at the counter electrode to derive a redox reaction inverse to that occurring at the semiconductor electrode.

12.6 COMPARISON OF PEC SOLAR CELLS WITH CONVENTIONAL PHOTOVOLTAIC DEVICES

In the fabrication of typical PEC devices, many processing steps required for conventional 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 12.3. The fabrication steps which could be eliminated for a PEC device are as follows :

- (a) deposition of the grid structure
- (b) deposition of an antireflection coating

Table 12.3 Comparison of components in a fabrication sequence for PEC cells and p-n junction silicon solar cells

PEC Cell	p-n junction silicon solar 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

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

Additional steps required in a PEC cell fabrication 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 photoelectrodes.

It has been shown by Weaver et al [50] that significant reduction in cost for the fabrication of a PEC device (relative to solid state solar cells) are expected inspite of the above additional processing steps.

In addition to the reduction in cost, PEC devices can also be used to store energy in the form of conventional fuels.

12.7 PARAMETERS NECESSARY FOR CHARACTERISATION OF PEC SOLAR CELLS

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

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})

Open circuit voltage (V_{oc})

The voltage measured across the electrodes when there is no load in the circuit is termed as the Open circuit voltage (V_{oc})

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)

Fill Factor (FF)

Ideally a solar cell should have $V_{mp} = V_{oc}$ and

$J_{mp} = J_{sc}$. However, various loss mechanisms operating within the cell make it deviate from the ideal behaviour. The term used to express this departure is known as the "fill factor" (FF) defined by

$$FF = \frac{J_{mp} V_{mp}}{J_{sc} V_{oc}}$$

J_{sc} is the short circuit current density and

V_{oc} is the open circuit voltage

where J_{mp} = current density at maximum power point

V_{mp} = voltage at maximum power point.

Efficiency (η)

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

$$\begin{aligned} \eta &= \frac{V_{mp} \times I_{mp}}{P_{in}} \\ &= FF \times \frac{V_{oc} \times I_{sc}}{P_{in}} \end{aligned}$$

where P_{in} is the solar power input

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

where J_{mp} = current density at maximum power point

$$= \frac{I_{mp}}{\text{area}}$$

12.8 SUITABILITY OF MATERIALS FOR PEC SOLAR CELLS

Some basic requirements for the materials suitable for solar cells are as follows :

- (i) Materials should show high conversion efficiency and long term stability under operation.
- (ii) Should possess a band gap which closely matches the solar spectrum. They should be inexpensive and readily available.
- (iii) Should be capable of undergoing phototransitions in the visible spectral region, which however should not break chemical bonds.
- (iv) Should leave the bonding situation in the semiconductor electrode, surface unchanged so that they could be free from photodecorrosion.

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CAPTIONS TO THE FIGURES

Fig. 12.1 Classification of photoelectrochemical cells
(according to Ref. [2]).

Fig. 12.2 Space charge region in the semiconductor.

Fig. 12.3 Energy level diagram and energy scales for
semiconductor-electrolyte junctions.