# PHOTOELCTROCHEMICAL CELLS

BY

*Dr. G. J. Navathe* *M.Sc., Ph.D.*

(Assist. Professor)

VIVEKANAND COLLEGE, KOLHAPUR (AUTONOMOUS)

DEPARTMENT OF PHYSICS

DATE : 29/11/2019

In its simplest form, a photoelectrochemical (PEC) hydrogen production cell consists of a semiconductor electrode and a metal counter electrode immersed in an aqueous electrolyte. When light is incident on the semiconductor electrode, it absorbs part of the light and generated electricity. This electricity is then used for the electrolysis of water.

## Semiconductor-electrolyte cells advantages

(i) Easy and simple to make,

(ii) Many processing steps of the p-n junction cell are simplified or eliminated;

(iii) Growth of large single crystals is not required, even with crystallites as small as lo-20 micron, a substantial part (70 %) of the efficiency of the single crystal based cell is achieved;

(iv) Since the junction with the liquid forms spontaneously up to contact, irrespective of crystal orientation, randomly oriented crystallites can be used;

(v) The doping and diffusion steps, in which p-n junctions are formed, are eliminated;

(vi) The need for front metallization is eliminated, since the current is carried by the redox couple in solution and the inexpensive counter electrode;

(vii) A transparent epitaxial layer, which is grown to reduce electron-hole surface recombination losses at the surface is not needed or is functionally replacable by simple chemical treatment; and

(viii) AR-coating can be replaced by building a non-reflective structure into the surface of a semiconductor by simple etching.

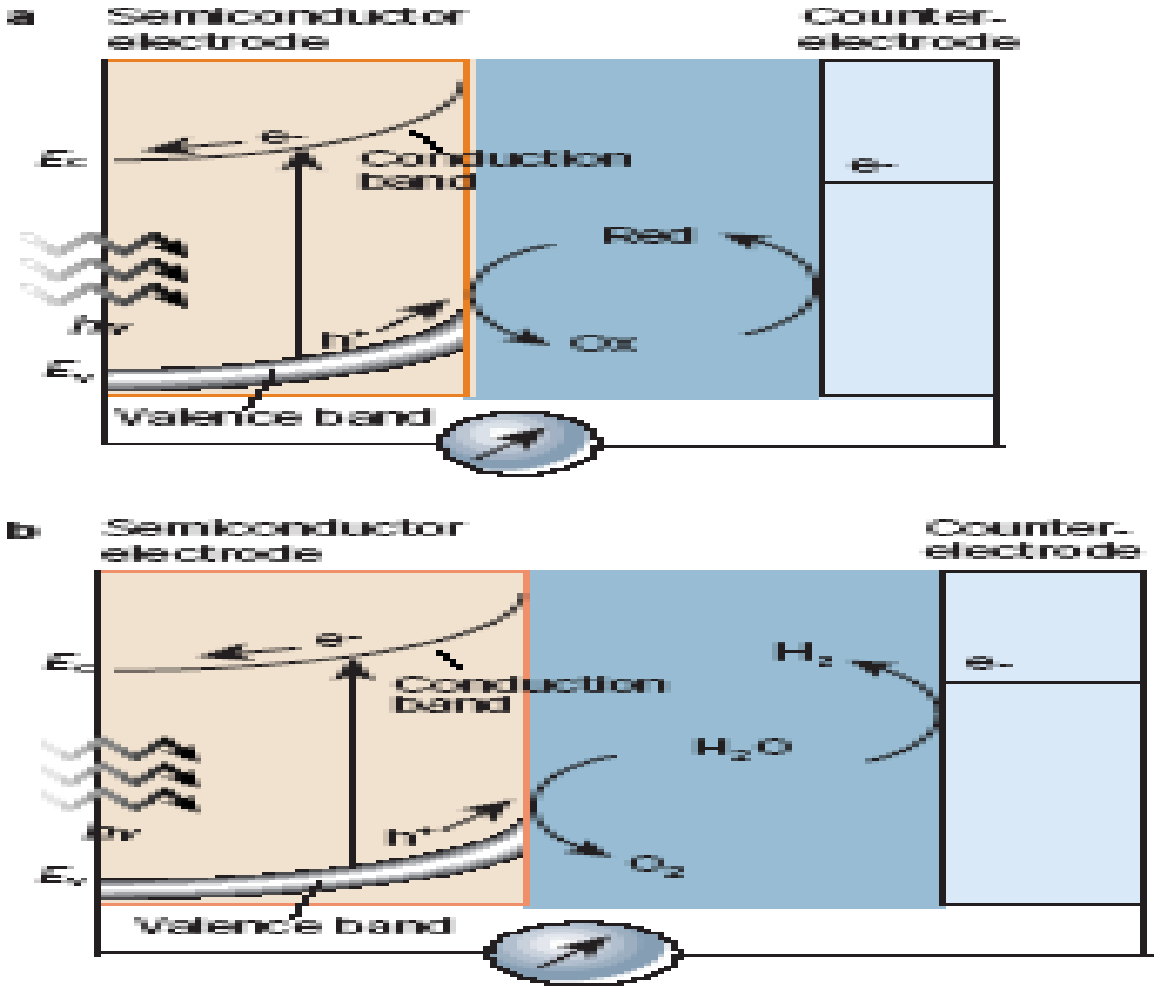
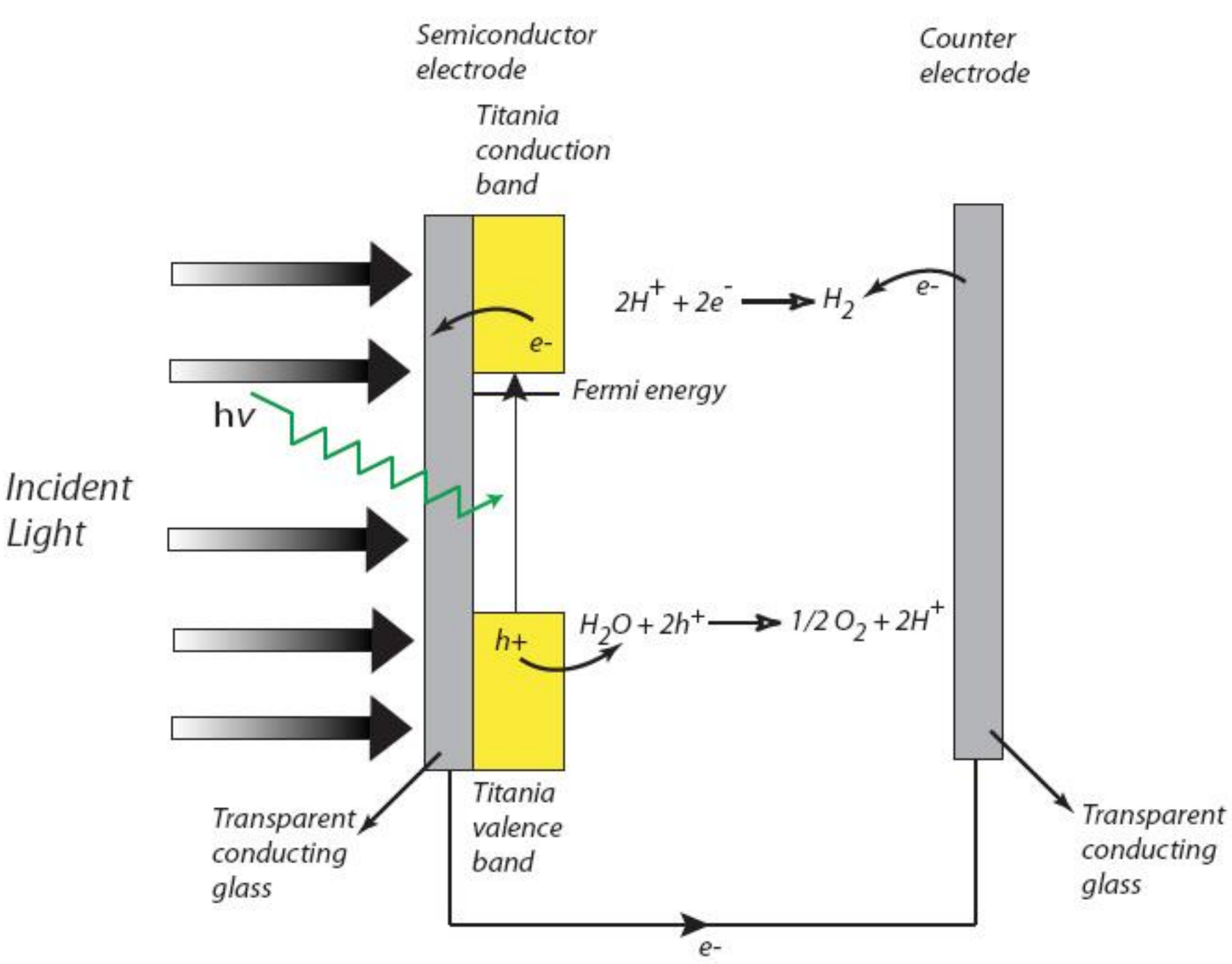
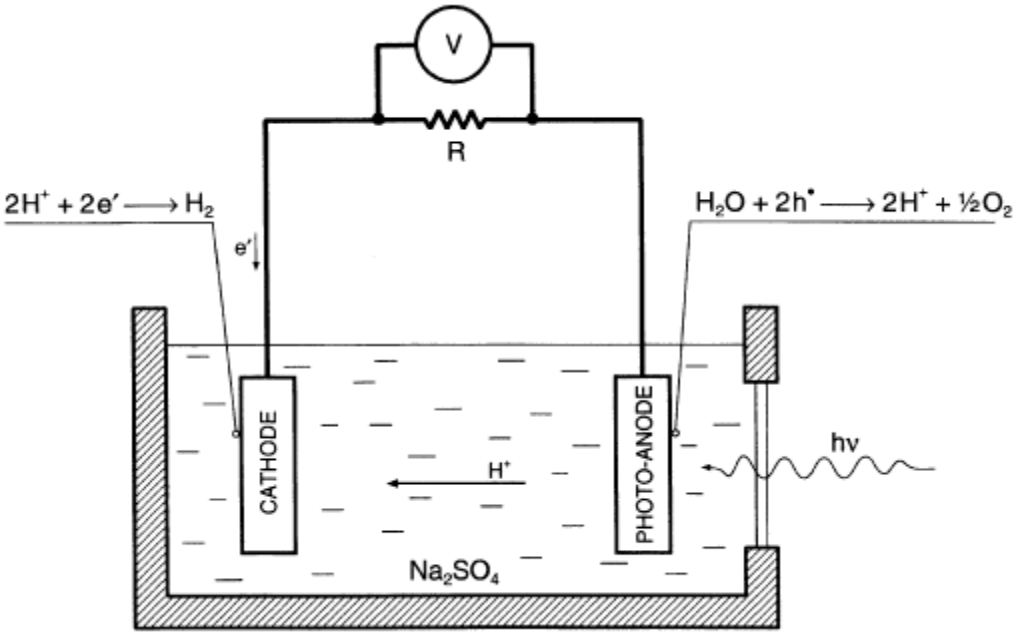



Figure 1 Principle of operation of photoelectrochemical cells based on *n*-type semiconductors. a, Regenerative-type cell producing electric current from sunlight; b, a cell that generates a chemical fuel, hydrogen, through the photo-cleavage of water.


Semiconductor electrode
Counter electrode
Titania conduction band
$2H^+ + 2e^- \rightarrow H_2$
e-
e-
Fermi energy
hv
Incident Light
$H_2O + 2h^+ \rightarrow 1/2\ O_2 + 2H^+$
h+
Titania valence band
Transparent conducting glass
Transparent conducting glass
e-


V
R
$2H^+ + 2e' \longrightarrow H_2$
$H_2O + 2h^\bullet \longrightarrow 2H^+ + \frac{1}{2}O_2$
e'
CATHODE
PHOTO-ANODE
hν
$H^+$
$Na_2SO_4$

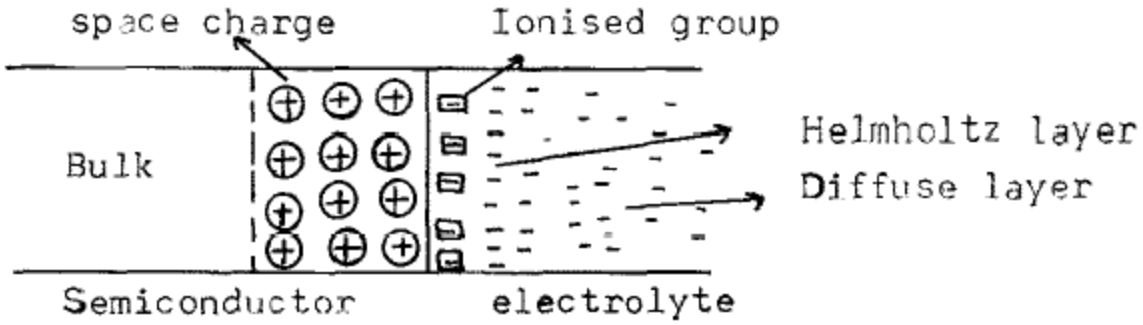



Fig.1a. Charge-distributions at the semiconductor-electrolyte interface.

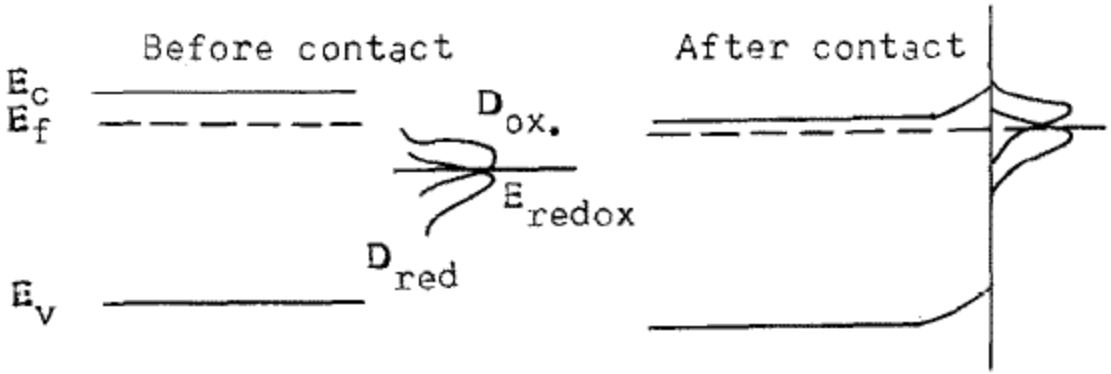
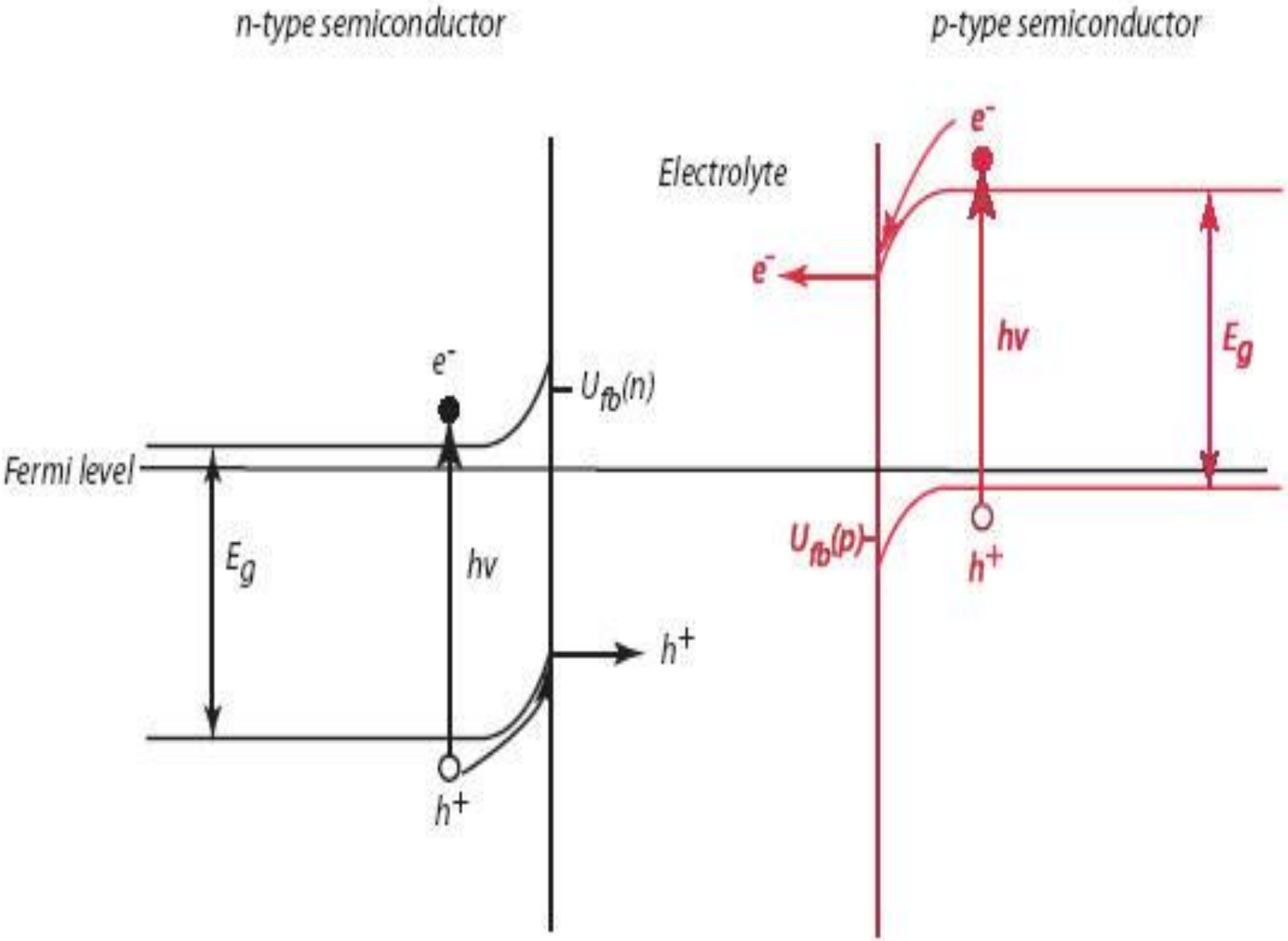



Fig.1b. Electron energy level diagrams for n-semiconductor-electrolyte system before and after coming in contact.


n-type semiconductor
p-type semiconductor
Electrolyte
e⁻
e⁻
hv
Eg
e⁻
Ufb(n)
Fermi level
Eg
hv
h+
h+
Ufb(p)
h+

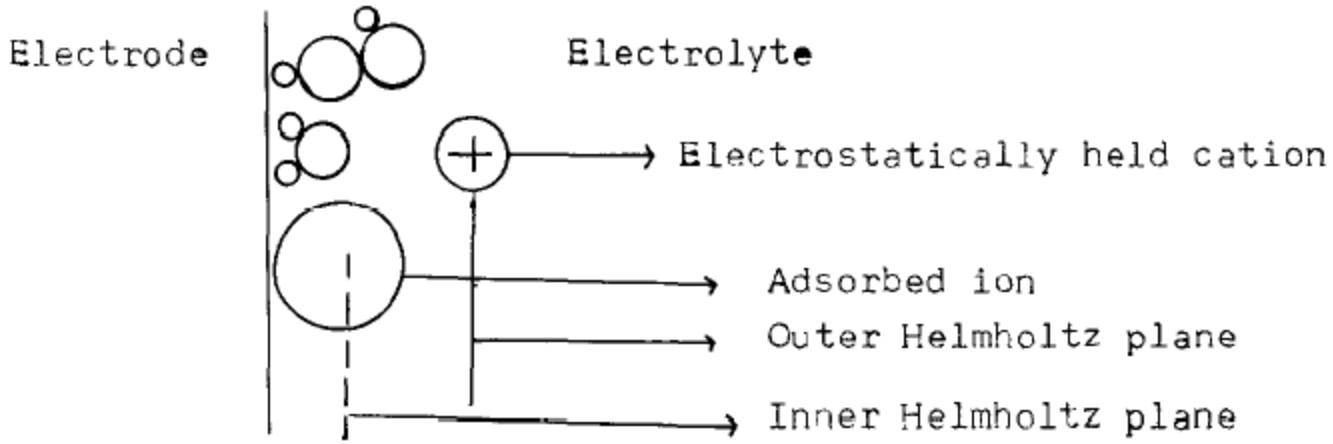



Fig.2a. Relative positions of inner and outer Helmholtz planes of electrode double layer.

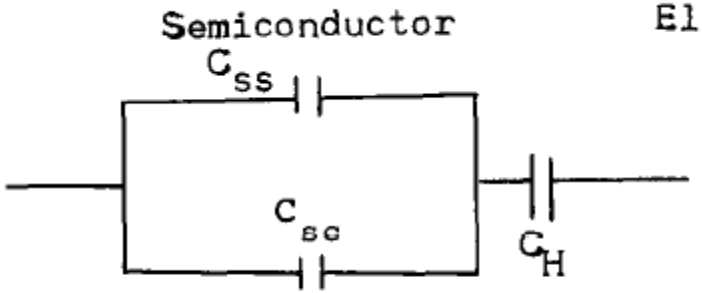



Fig.2b. Equivalent circuit diagram of capacitance formed at semiconductor-electrolyte interface.

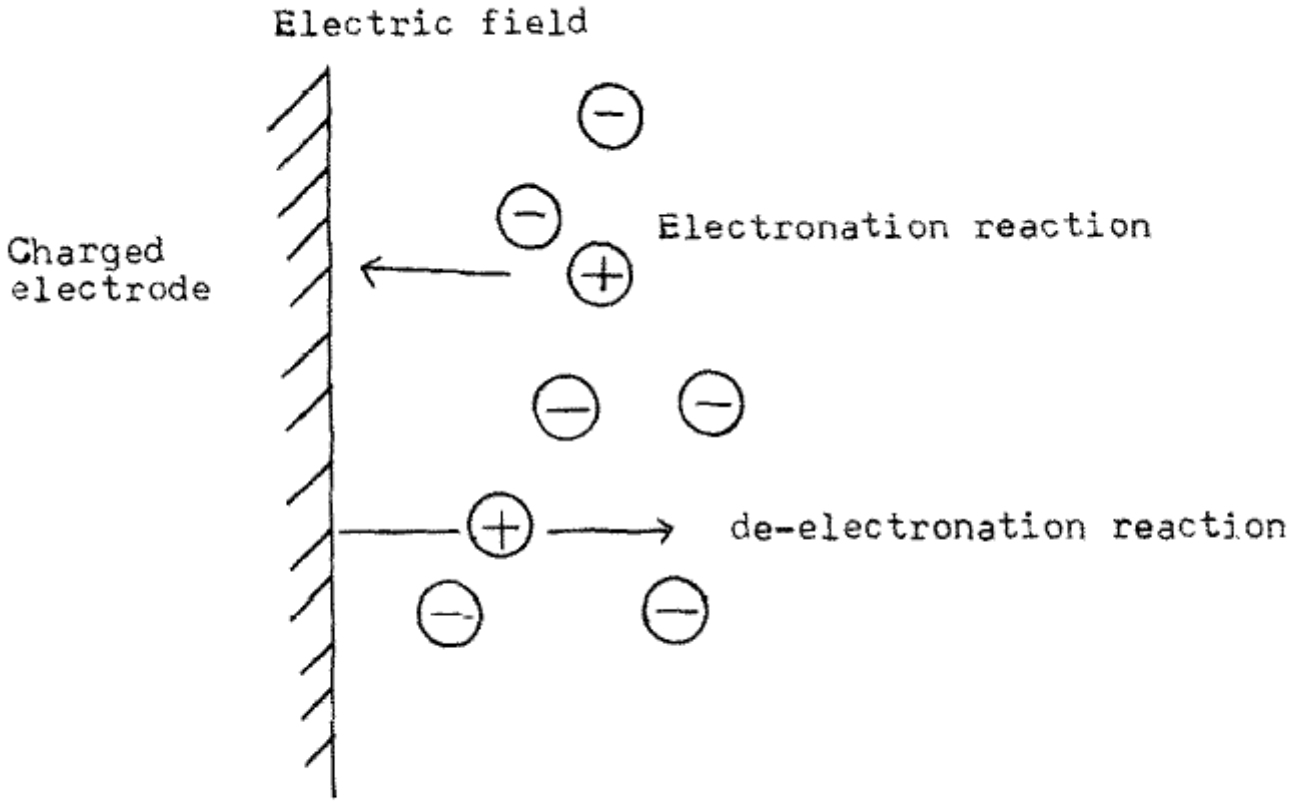



Fig. 3a. Electric field effect on electronation and de-electronation.

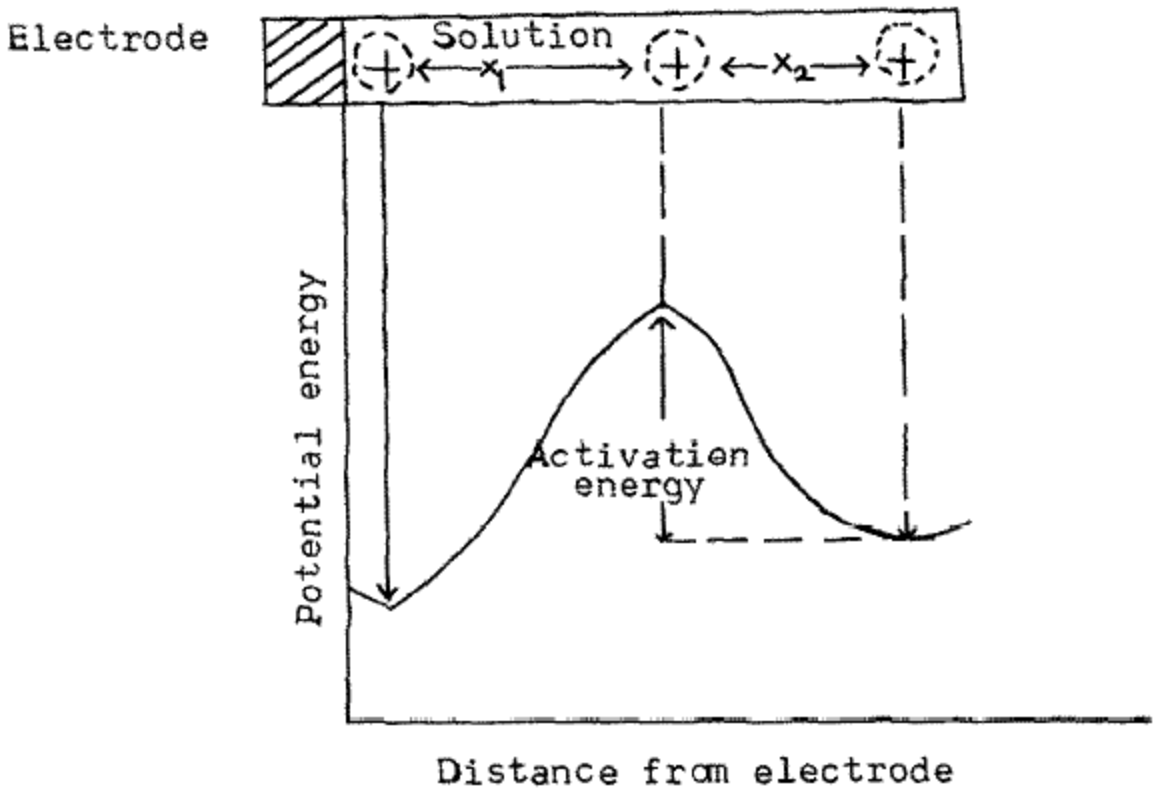



Fig.3b. Construction of a potential-energy-distance profile by consideration of the potential-energy changes produced by varying $x_1$ and $x_2$ .

Table 1. Comparison between p-n junction and S-E junction solar cells ( Ref. 11)

| p-n junction solar cell | S-E junction solar cell |
|---|---|
| Junction type : | |
| p- n<br>Solid-Solid | p-semiconductor-electrolyte<br>n-semiconductor-electrolyte<br>Solid - liquid |
| Potential barrier at the junction | |
| Yes | Yes |
| The barrier is formed due to interdiffusion of majority carriers between p and n region. | The barrier is formed because of transfer of majority carriers from semiconductor to electrolyte. |
| The potential drop on band bending in the two regions of semiconductor is almost equal. | Major potential drop is in semiconductor space charge layer, only a small fraction of the drop is in the electrolyte region. |
| Facilitates flow of minority carriers and inhibits majority flow. | Same as in p-n junction |
| Photo effect | |
| Excess carriers are generated; mutual diffusion of excess photogenerated minority carriers in the two regions gives photovoltage. | Excess carriers are generated; the excess photogenerated minority carriers transfer charge with ions of the electrolyte to give photovoltage or lead to electrolysis. |

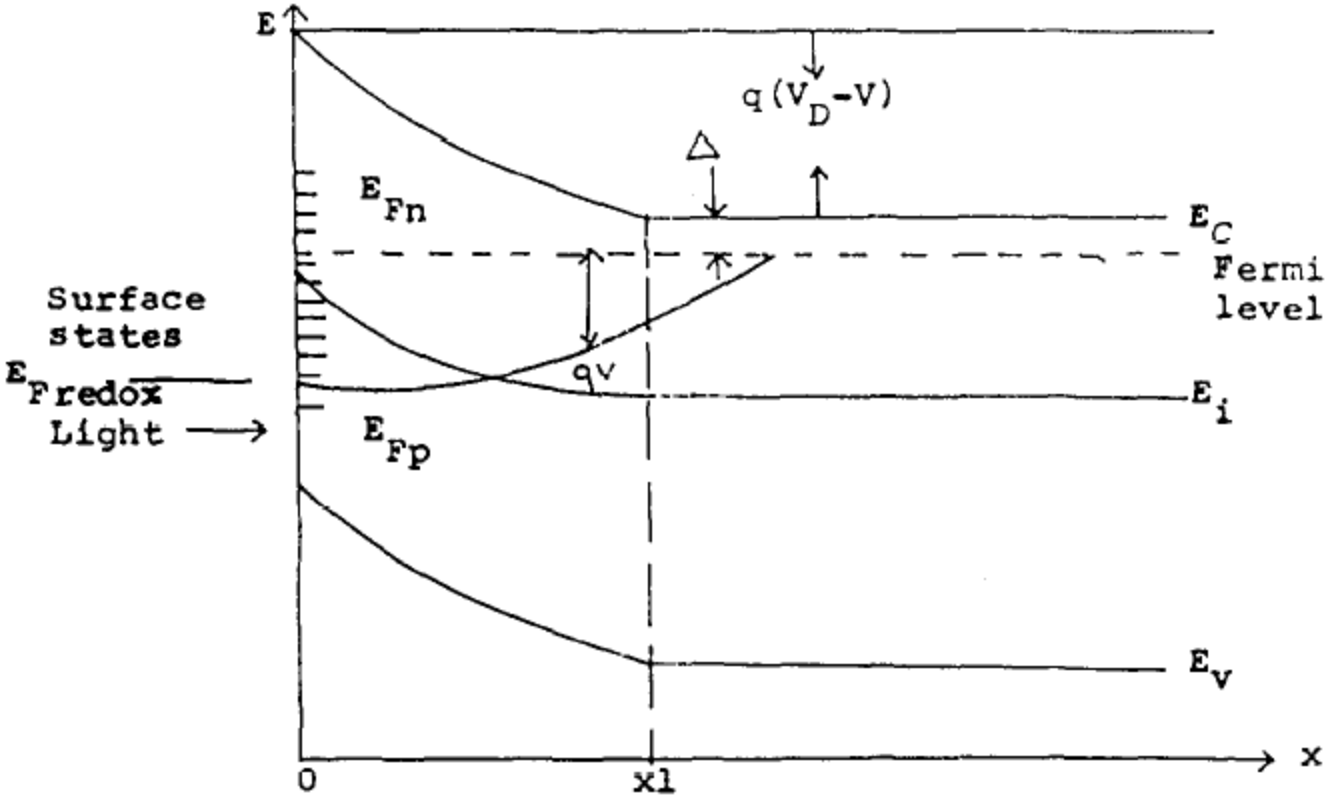
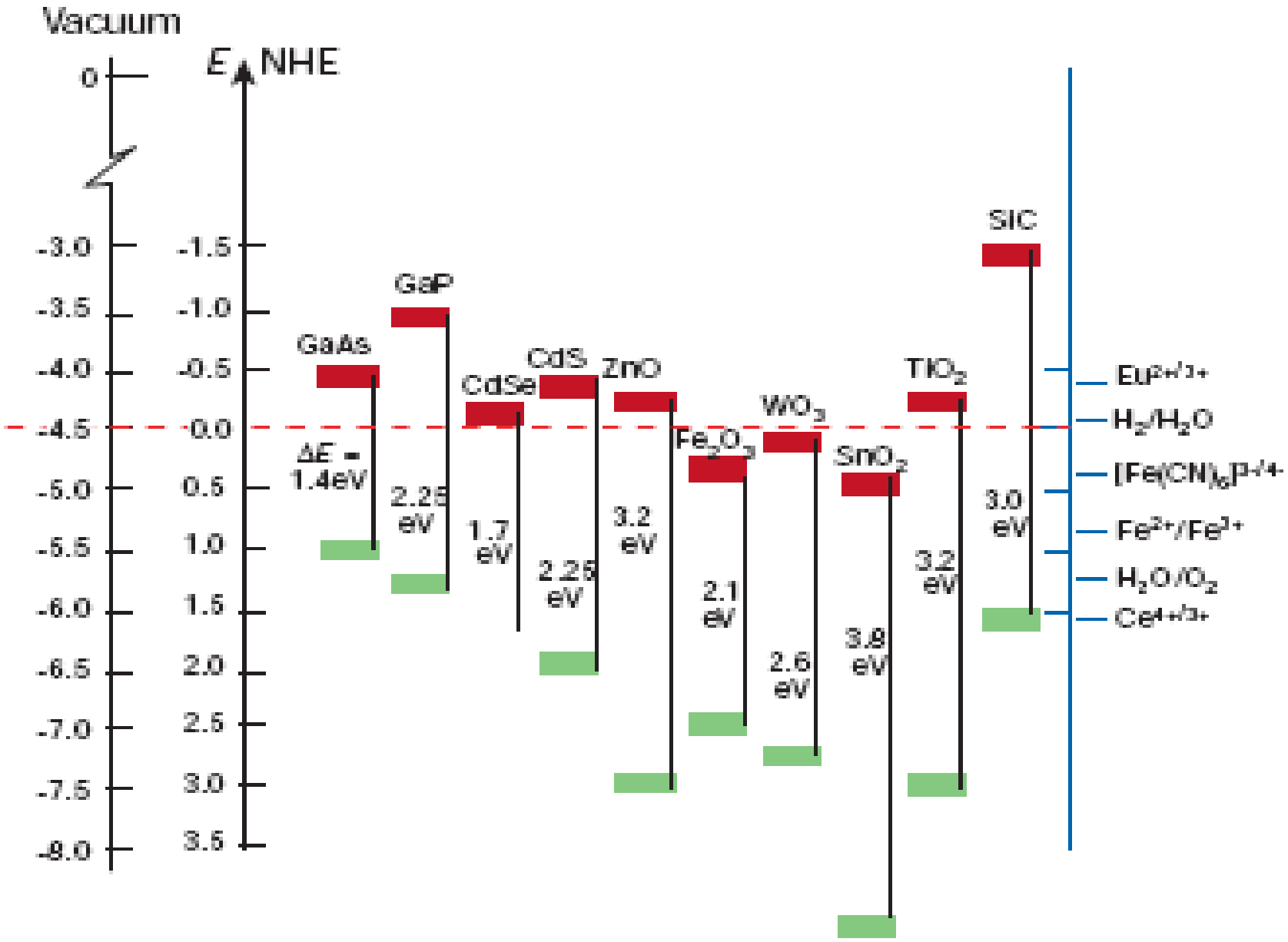



Fig. 4. Electron energy level diagram for an n-type semiconductor-electrolyte photoanode near the semiconductor-electrolyte interface. The photoanode is assumed to be under illumination and a forward bias V is applied, reducing the band bending from $aV_D$ to $q(V_D - V)$. (Ref.31).


Vacuum
E NHE
0
-3.0
-3.5
-4.0
-4.5
-5.0
-5.5
-6.0
-6.5
-7.0
-7.5
-8.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
GaAs
ΔE = 1.4eV
GaP
2.25 eV
CdSe
1.7 eV
CdS
2.25 eV
ZnO
3.2 eV
Fe2O3
2.1 eV
WO3
2.6 eV
SnO2
3.8 eV
TiO2
3.2 eV
SiC
3.0 eV
Eu3+/2+
H2/H2O
[Fe(CN)6]3-/4-
Fe3+/Fe2+
H2O/O2
Ce4+/3+

## 2.5 Efficiency considerations

The photovoltaic devices are threshold devices; i.e. they require a minimum optical energy to activate them. The energy conversion efficiency ($\eta$) of any threshold device is given [11,36] by

$$\eta = \frac{E_{stor} \int_{E_{th}}^{\infty} d(E)\,\phi_o(E)\,dE}{\int_{o}^{\infty} E\phi_o(E)\,dE} \qquad (31)$$

where $E_{th}$ is the band gap of the semiconductor; $\phi_o(E)$ is the number of photons with energy E, d(E) is the fraction of photons absorbed and $E_{stor}$ is cell voltage. An inspection of eqn.(31) indicates that the efficiency would be larger if :

(a) the band gap were high. However, it may be noted that the photodecomposition of semiconductor electrodes limits the conversion efficiency to a maximum of $(E_c - E_D)/Eg$, where $E_D$ is the decomposition energy.

(b) $\alpha(E)$ were high. The expression for $\alpha(E)$ near the band edge is approximately written as

$$\alpha(E) = \frac{A'(h\nu - E_g)^{n/2}}{h\nu} \qquad (32)$$

where A' is a constant and n = 1 or 4 for direct or indirect band gaps respectively. Hence the value of $E_g$ should be small. Both these conditions are in contradiction with each other. Thus $\eta$, of expression 31 would be maximum for some optimum value of $E_g$.

In addition to $E_g$, there are other factors also which affect the efficiency of ECPV cells. These can be summarised as follows [11]:

In addition to Eg, there are other factors also which affect the efficiency of ECPV cells.

(i) physical properties of the semiconductor
(ii) energy losses due to the photoinduced redox reactions
(III) light losses due to absorption in the electrolyte, reflection from semiconductor surface, etc.
(iv) ohmic losses due to absorption in the electrolyte, semiconductor, etc.
(V) losses due to concentration polarisation if the redox process is slow.

The optical to electrical energy conversion efficiency in a semiconductor/liquid junction cell is given by [9]

$$\eta = \frac{(I\ V)_{max}}{P_{input}} \times 100\ \% \qquad (33)$$

where $(I\ V)_{max}$ is the maximum output power.

A parameter namely, fill factor, ff, is defined as

$$ff = \frac{(I\ V)_{max}}{I_{sc}\ V_{oc}} \qquad (34)$$

where $I_{sc}$ and $V_{oc}$ are short circuit photocurrent and open circuit voltage, respectively.

## 3 ELECTROCHEMICAL PHOTOVOLTAIC CELLS

### 3.1 Classification of PEC cells

Considering the changes in chemical energy photoelectrochemical (PEC) cell can be classified as follows [8]:

PEC cells
- $\Delta G = 0$ - ECPV cells
- $\Delta G = 0$ photoelectrosynthetic cells
  - Photoelectrolysis cell (energy storage $H_2O \rightarrow H_2 + 1/2O_2$ )
  - (Photocatalytic cell ($N_2 + 3H_2 \rightarrow 2\ NH_3$)

In ECPV cells, the electrolyte contains only one effective redox couple and the oxidation reaction at the anode is reversed at the cathode. There is thus no net chemical change ( $\Delta G=0$) but the photon energy is converted into electrical energy in this process.

## 3.2 Semiconductor photoelectrodes

An ECPV cell consists of (1) a semiconductor photoelectrode, (2) an electrolyte and (3) a counter electrode. All of these parts play an important role in the ECPV cell formation. The semiconductor photoelectrode is the heart of the ECPV cell; properties such as photovoltaic output, efficiency, spectral response, etc., depend on the nature of the photoelectrode. In general, photoelectrodes in the form of single crystals and polycrystalline films have been employed in ECPV cells. The semiconductor photoelectrode should satisfy the following properties [ 3, 11, 37] :

(i) $h\nu > E_g$; i.e. the energy of the incident light should be greater than the band gap of the semiconductor. Optimum band gap lies between 1.2 to 1.8 eV.

(ii) The absorption coefficient, $\alpha$, of a semiconductor must possess a large value.

(iii) In order to utilize the incident light to generate electricity, the reflection and transmission coefficients must be small.

(iv) The local field generated after the formation of the junction should be strong enough to separate electron-hole pairs effectively.

(v) Recombination states must be minimum.

(vi) The thickness of the bulk of the semiconductor must be optimum.

(vii) Contacts to the semiconductor should be ohmic.

## 3.3 Selection of an electrolyte

Various types of electrolytes have been tried in accordance with ECPV cell requirements. Table 3 shows the types of different electrolytes [38,39]. It is observed that aqueous electrolytes cause surface modifications and hence restrict the use of many semiconductors. Molecular organic or inorganic solvents with supporting electrolytes and mixtures of totally ionic molten salts have been substituted for aqueous electrolytes [40-42].

Table 3. Types of different electrolytes used in ECPV cells (Ref. 38).

| | Class | Redox additive | Supporting electrolyte | Molecular solvent |
|---|---|---|---|---|
| I | Conventional solution | $(red)^{(n.)+}$ | $M^+ A^-$ | Inorganic ($H_2O$ / other); Organic; mixed aq-organic; organic-organic |
| II | Conventional solution | $(red)^{(n-1)+}$ $ox^{n+}$, $A^+$ or $M^+$ | None | As above |
| III | Indifferent molten salts | $(red)^{(n+1)+}$ $ox^{n+}$ | $m^+ A^-$ | none |
| IV | Redox molten | $(red)^{(n-1)+}$ $ox^{n+}$, $A^-$ or $M^+$ | None | none |

Notes : (1) n may commonly range from −2 to + 2.
(2) The cation and anion, $m^+$ and $A^-$ may be multicharged.
(3) Only a one electron charge transfer reaction is represented.

Redox molten salts have the advantage of high energy storage capabilities per volume element and hence are useful as cell materials.

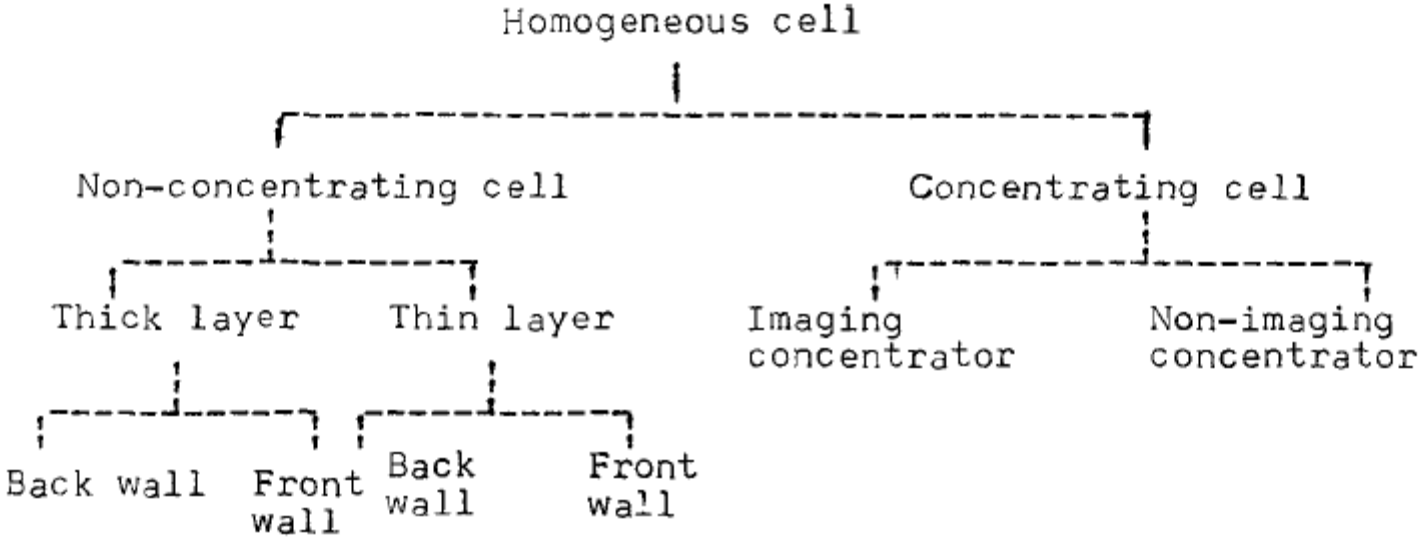
Table 4. Electrolyte properties requisite for the ECPV cells ( Ref. 38 ).

| | Property | Role |
|---|---|---|
| a | Reduction-oxidation potential | Redox reaction to be positioned appropriate to the semiconductor band edges. Electrolyte decomposition limits suitability. |
| b | Electron-transfer rates of ox. and red.species | Idealy rapid (reversible) at both semiconductor and counter electrodes. Suitable mass transport conditions. |
| c | Photo and thermal stabilities. | Ox., red.and solvent components to have photo and thermal stability throughout usable solar spectrum and operational temperature range. |
| d | Surface compatibility | Non-corrosive to electrode and containment materials. Semiconductor corrosion inhibited if necessary and undesirable surface reactions absent, e.g. adsorption, dissociation, passivation, etc. |
| e | Optical transparency | Minimum absorption losses for solar energy spectrum. |
| f | Fluidity | Liquidous range and viscosity to allow convective mixing within temperature extremes. |
| g | Solubility | Ox., red. and supporting electrolyte concentration in solvent or liquid matrix to be adequate to reach required current densities. |
| h | Conductance | Ionic conductance of electrolyte should permit negligible ohmic losses. |
| i | Toxicity and reactivity to environment, cost. | Preferably low, dependent on application. |

## 3.4 Counter electrodes

A counter electrode is the third part of the ECPV system. In a regenerative process, the electrolyte species are oxidised at the photoanode and are again reduced at the counter electrode, giving no net change in the electrolyte composition. Requirements of counter electrodes for use in ECPV cells are : chemical inertness with the electrolyte, non-polariability and low cost.

Counter electrodes should be inert; i.e. they should not form any new compound by reacting with the electrolyte, otherwise, they will change the electrolyte composition as well as the counter electrode properties. The non-polarised electrode is one which allows free and unimpeded exchange of electrons or ions across electrode-solution interface [25]. When a charge crosses an ideal reversible electrode, the electrochemical change takes place with such rapidity that the equilibrium situation is restored instantaneously. Thus a non-polarised counter electrode will allow all the applied voltage to appear across the semiconductor-electrolyte interface.



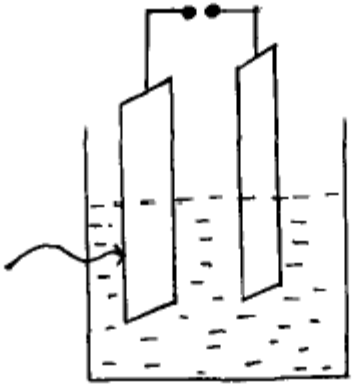



Fig. 10. A homogeneous ECPV cell.

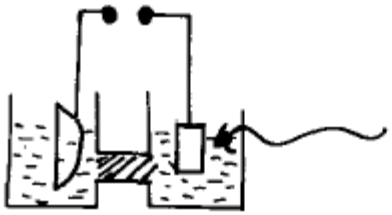


Fig. 11. A heterogeneous ECPV cell.

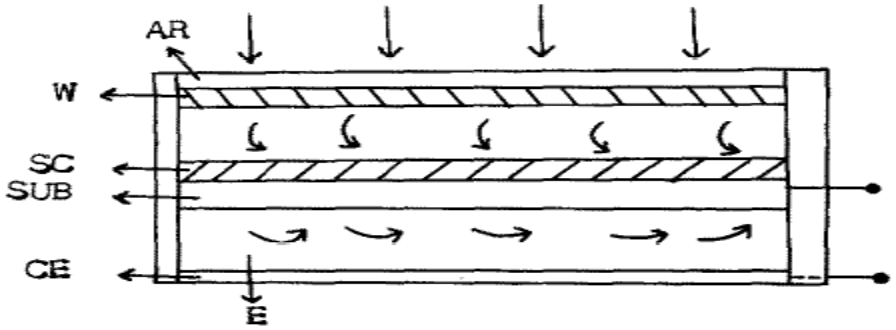



Fig. 12. Side view of a design for thick wall cells (Ref.58) AR - antireflection coating, W - window, SC - Semiconductor, SUB - substrate, E - redox couple, CE - counter electrode.

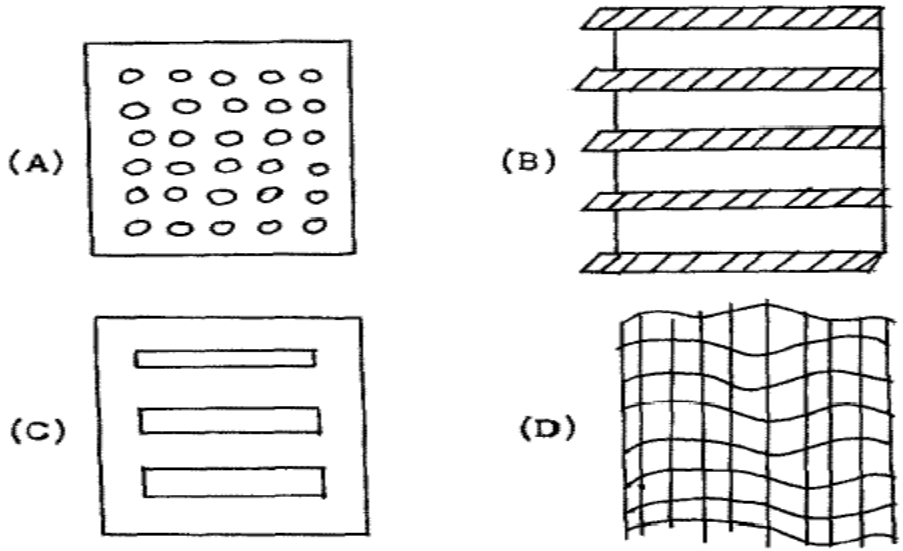



Fig. 13. Different types of matrix of small holes for photoelectrode.

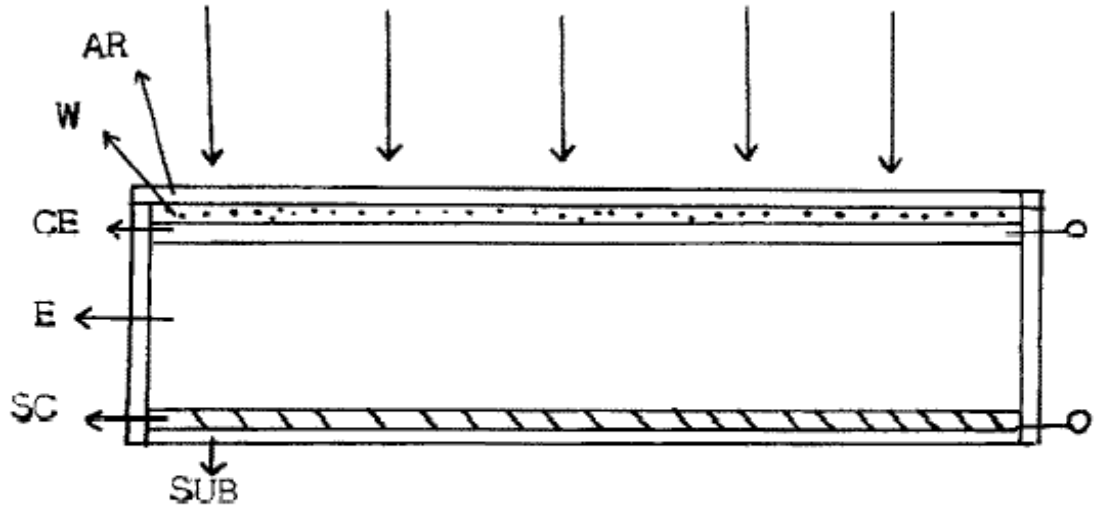



Fig. 14. Side view of a flat plate cell with a transport counter electrode. This design may be either thick or thin layer.



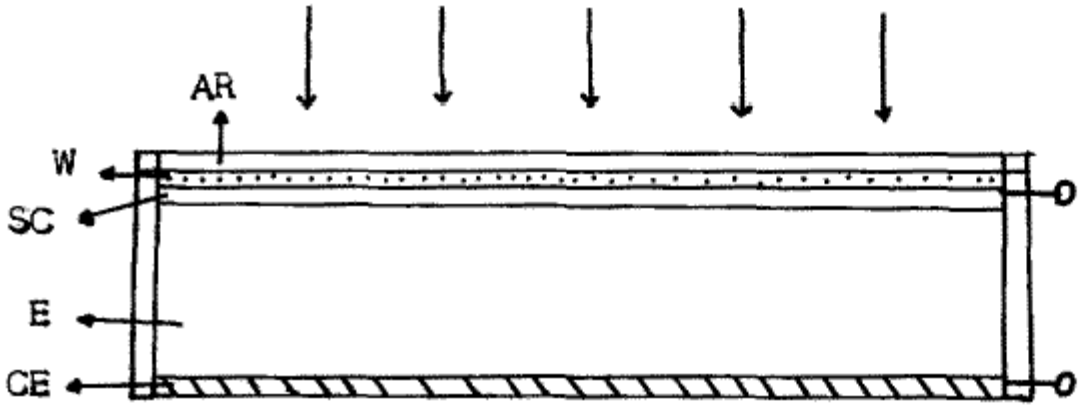



Fig.15. Side view of backwall illumination cell. This design may also be thick or thin layer.

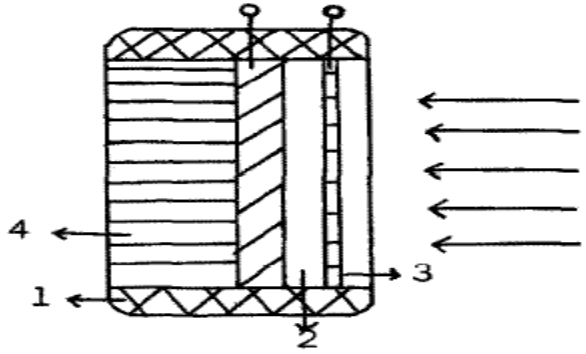



Fig. 16a

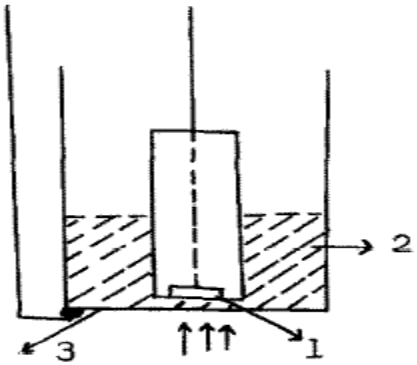



Fig. 16b

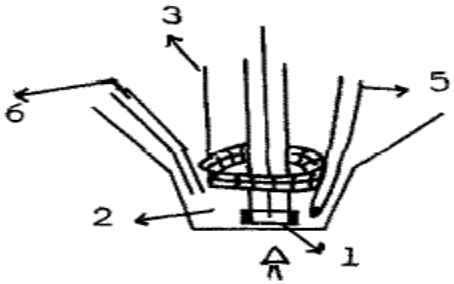



Fig. 16c

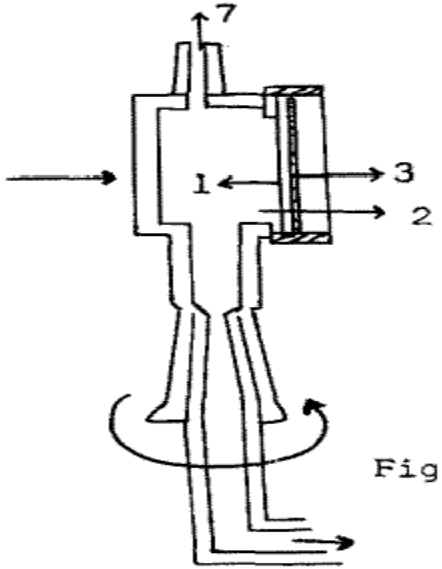



Fig.16d

Fig.16a - 16d. Modified cell configurations used by various workers (Ref.15,56,60,61 respectively).
(1) semiconductor electrode (2) redox electrolyte,
(3) counter electrode (4) support seal (5) Luggin capillary
(6) Ar gas (7) nitrogen gas.

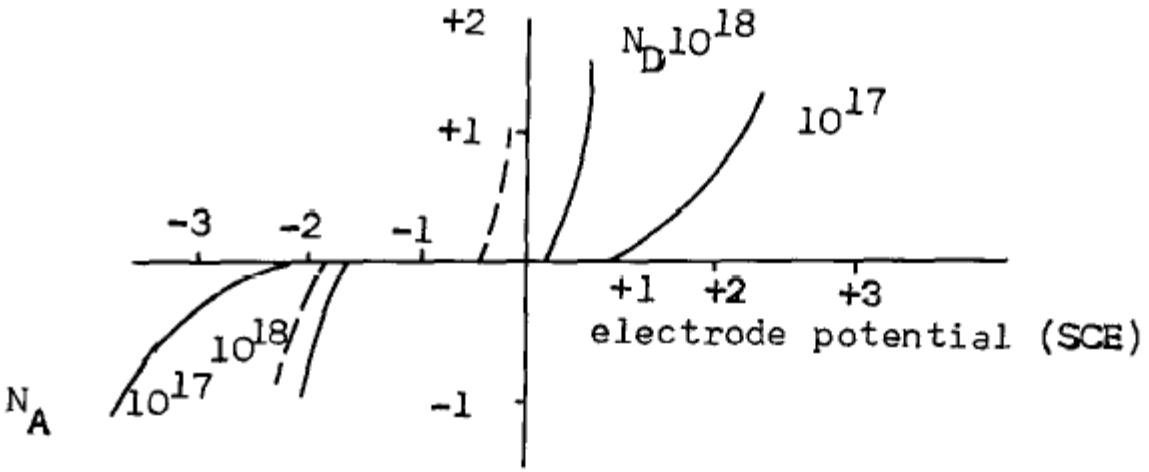



Fig.19. Typical current potential (I-V) characteristics for GaAs electrodes in 1N NaOH electrolyte (Ref.67). The effect doping concentrations is also demonstrated in figure. ——— n type and --- p type.

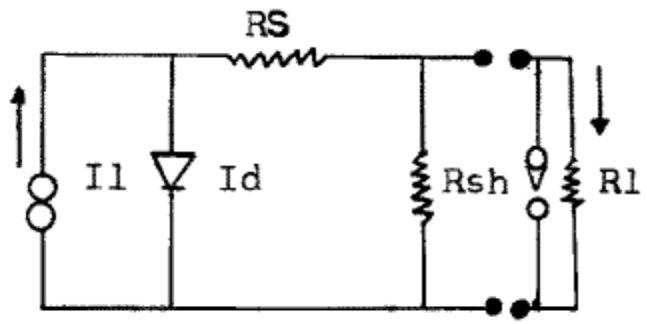
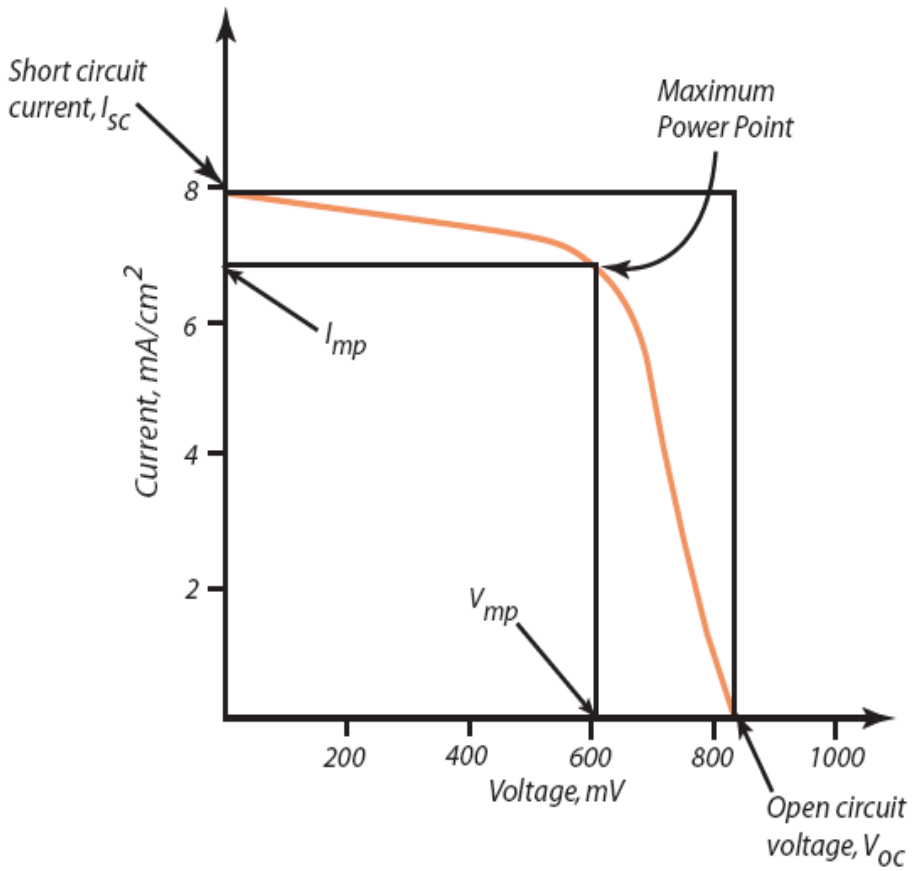



Fig.21. Equivalent circuit diagram for an ECPV cell (Ref.31,32).




$I_{mp}$ and $V_{mp}$ are maximum power current and voltage, respectively.

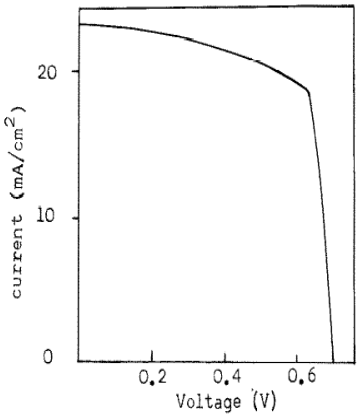



Fig.20. Typical photovoltaic output curve for n GaAs/ 0.8 $K_2Se$ - 0.1M $K_2Se_2$ - 1M KOH/C cell (Ref.69). The maximum efficiency achieved is 12 %.