CHAPTER I

**THEORETICAL BACKGROUND OF SEMICONDUCTOR AND ELECTROLYTE INTERFACE**

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* 1. **Introduction**

A relatively recent but well-developed subfield of electrochemistry is semiconductor electrochemistry. In particular, photochemistry examines the processes started by electrically excited molecules as a result of solar energy absorption in the visible and near ultraviolet parts of the spectrum. Its varied uses in lithography, PCB fabrication, photostabilizers, photochromic sunglasses, lasers, etc. are what make it relevant. Understanding chemical reactions, forms of energy transmission, and the complex structure of matter is made easier by the fundamental study of excited states of molecules with nano and pico second reaction kinetics (1-4). The study of the photophysical and photochemical processes involved in the conversion and storage of solar energy is now being aided by science and technology. 1–7. The most effective chemical method for converting solar energy is known as photoelectrochemical cells (PECs). These cells can be designed to either produce electricity or store chemical fuel, or both, making them a mix of photovoltaics and photosynthesis. These devices are easy to build and frequently only have two electrodes—one metallic and the other semiconducting—that are submerged in an electrolyte and exposed to light (Figures 1–7). The semiconducting electrode can effectively absorb sunlight, produce delocalized charges, effect the separation of these charges with high yield, and produce an electrical current that results in energy conversion using an intriguing method that will be discussed in chapter. Light is absorbed and excites electrons when it strikes a semiconductor electrode.

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**1.2 Mechanism Of The Charge Transfer Across The Semiconductor / Electrolyte (S / E) Interface**

Under appropriate valence and conduction band energies and electrolyte redox couple selection, an electron can be transmitted either from an electrolyte to the semiconductor electrode or from the electrode to the electrolyte. At the appropriate electrodes, the ionic species will be reduced or oxidized.

**1.2.1 The charge transfer in dark**

Consider the passage of ions from the solution side to the electrode and back to comprehend the charge transfer process across an electrode / electrolyte contact in the dark. There is both decline and increase.

A++ e- → D ----(1.1)

and oxidation

D → A++ e- ----(1.2)

reactions /1,4,9,10/. If a positive ion moves in the opposite direction of the field in a redox reaction, it moves in the opposite direction of the field in an oxidation process. Figure 2.9 (a) illustrates this. Furthermore, if a positive ion must be activated via a potential difference. in a reduction reaction, it must be activated via the remainder (1-) in an oxidation reaction, where is the symmetry factor and is the potential through which an ion passes. As a result, the rates of reduction and oxidation reactions, as well as their relative current densities, may be determined. As a result, the net current density is / 3,9 /.

I = I0 {exp [(1-β) V.F / RT] -exp (-βV.F) / RT}. --- (1.3)

Equation (2.18) is a famous Butler - Volmer relation / 3,4,9-12 It demonstrates the relationship between the applied voltage, V, and the current density through a semiconductor/electrolyte interface. Changes in V cause huge changes in I. Even in the absence of an electric field, there is a hill-shaped barrier in the electrode/electrolyte system, as shown in fig. 2.9 (b). This barrier is caused by atomic motions in bond stretching, which is required for processes like as chemical reactions and atom and ion diffusion. The electric field adjusts the existing potential barrier so that only a fraction (1-) of the input electrical energy (qV) changes the activation energy and thus the rate expression. This is due to the fact that the atomic movements required for the system to approach a critical barrier are only a fraction of the overall distance covered by the potential barrier.

X1

X2

Activation Energy

Solution

Electrode

Charged

Electrode

Oxidation

Reduction

Electric Field

**1.2.2 Charge transfer in the presence of light**

When a S / E interface is illuminated, photo generated carriers in the depletion zone are separated by an electric field at the interface / 1,3,4 /. The charge separation process produces a counter field, which is greatest at the open circuit condition known as Voc. The electrons are dragged from the semiconductor to the counter electrode by the photovoltage, while the holes are captured by an electrolyte. The overall reaction can be written as

Red (solv) + h+ → OX (solv)  (At semiconductor electrode)

and

OX (solv) + e- → Red (solv) (At counter electrode).

An electrode has no effect on the process and solely serves as a shuttle or charge transfer mechanism. Consider an n-type semiconductor in contact with an electrolyte in the presence of illumination and a forward voltage, V. Figure 1.1 shows a schematic of an electron's energy level diagram.

q

EFp

EFn

Eg

Ei

Ev

E

Δ(VFb-V)

Ec

Redox

Surface State

EFp

Light

Xo

W

X

Fig. 1.1 Electron energy level diagram for an n-type seconductor photoelectrode near the S/E interface under illumination and forward bais voltage, v reducing the band bending from qVd to q(Vo - V)

In the depletion zone, the quasi Fermi levels for electrons (EFn) and holes (EFp) are considered to be flat. If U represents the distance between them, then

EFn - EFp = qU.

The assumption that U >>V illustrates the fact that the concentration of minority carriers under illumination is greater than its concentration in the dark. In order for a hole flux to flow from the semiconductor surface to an electrolyte, U is defined as

exp (qU / KT) = P (W) / P0 --- (1.5)

where P (W) is the hole concentration at the depletion region's edge (X = W) and P0 is the equilibrium hole concentration in the semiconductor's bulk in the dark. Because the majority of the applied voltage occurs across the semiconductor depletion area, a cell's series resistance should be minimal and the electrolyte concentration should be high enough that CH > Csc. In such cases, the depletion layer width (W) is

W = W0(VD-V0)1/2

where W0 = [2 εs ε0  / q ND] --- (1.6)

where s is the semiconductor's dielectric constant, o is the permittivity of free space, ND is the donor concentration, and VD is the equilibrium band bending. If St is the surface transfer velocity, Sr is the surface recombination velocity, 0 is the input photon flux, is the light absorption coefficient, and W is the depletion area width, then the photo flux may be calculated as

j1= (St / Sr ) [ φ0{1-exp (∝ - W) / (1+ ∝t) }]. --- (1.7)

This is the usable photogenerated current of a solar cell, flowing from the semiconductor electrode to the electrolyte / 2-4,11 /.

**1.3 PEC Classification**

The charge transfer process at the semiconductor / electrolyte interface is the foundation of photoelectrochemical solar cells. A counter electrode, in addition to the semiconductor electrode, is an equally vital component of a solar cell that aids in the reduction process. PECs are classified into three types based on the net free energy (G) change in the whole system: i) electrochemical photovoltaic cells, ii) photoelectrolysis cells, and iii) photocatalytic cells.

**i) Electrochemical photovoltaic cells (Δ G=0).**

These cells are made up of such a redox pair that the overall cathodic + anodic reactions do not result in a net chemical change, i.e. G=0 [Fig. 2.11(a)]. The electrodes do not participate in the chemical process; instead, they operate as a "Shuttle" for the charge transfer mechanism and are employed for direct electricity production. The following are the many processes involved in the electrochemical conversion (for n-type semiconductor): / 1-4,11,12 /.

1. Light absorption by the semiconductor in the bulk and in the space charge region.

hν e-+ h+ ( i.e. creation of electron - hole pairs).

2. In space charge layer, separation of electron - hole takes place

esc- e- bulk

hsc+ h+ (photoelectrode surface).

3. In bulk, electron – hole recombination takes place

e-+ h+ heat in the semiconductor.

4. At the surface of a semiconductor, hole reacts with the redox species and

semiconductor.

h+ + (red)solv (ox)solv

h+ + semiconductor photodecomposition.

5. At the counter electrode, reduction of the redox species takes place

e- + (ox)sol (Red)solv.

6. Surface recombination at the electron-hole traps.

esc- etr -

h+surf htr+

etr- + htr - Heat at the semiconductor surface.

**ii) Photoelectrolysis cells (Δ G > 0).**

This form of cell employs two redox couples, and a net chemical change occurs in the system by turning optical energy into chemical energy [fig. 2.11(b)]. This sort of reaction is

**iii) Photocatalytic cells (Δ G < 0).**

iii) Photocatalytic cells ( G 0).

Similar to above, two redox couples are present in these cells, resulting in a net chemical change [Fig. 2.11(c)]. The optical energy acts as a catalyst for the chemical process. One example is N2 + 3H2 2NH3 ---(1.10).

Photoelectro synthetic cells are another name for categories (ii) and (iii).

N2 + 3H2  2NH3 ---(1.10)

A C

h+

C+ h+ C+ C++e- C

ΔG=0

(a) Electrochemical photovoltaic cell

hν

EF, redox

C- + h+ I , I+ h+ C+ , A+ + e- A,

Net C- + 2A+ C+ + 2A ,ΔG<0.

( c) Photocatylitic cell

Fig 2.11 Energy level diagram and cell reactions for different types of photoelectrochemical cells.

C+/I

C+/C

A+/A

I/C-

h+

e-

e-

hν

A+/A

B / B-

B- + h+ B+  A++ e- A

Net B- + A+ B + A , ΔG>0

(b) Photoelectrolysis cell

e-

e-

h+

hν

**1.4 Efficiency Considerations.**

The solar cell efficiency is defined as

η % = x 100 . …..(1.11)

Output power

Input power

The quantum efficiency ηq is defined as

Number of photoelectrons flowing per unit area

ηq = .…(1.12)

Number of incident photons with energy hν per unit area

Because the solar cell is a threshold device, requiring just a little amount of optical energy to activate, its efficiency is limited by the band gap of the semiconductor utilized. The influence of band gap, ambient absorption, lighting, reflection losses, and other factors on the efficiency of a p-n junction photovoltaic solar cell has been studied by Loferski / 13 /. These findings may be used to photoelectrochemical solar cells with a few changes that account for extra photoelectrochemical processes. The conversion efficiency in the simplest PEC, when losses due to Ohmic resistance, over potentials, light absorption in the solution, and so on are ignored, is given by

η = …(1.13)

Eg 0∫∞ α (E).N(E).dE

0∫∞ E.N(E).dE

where Eg is a semiconductor's optical band gap, N(E) is the number of photons with energy E, and (E) is the proportion of photons absorbed. According to equation (1.13), the efficiency would be greater if: a) the band gap, Eg, is big. It should be noted, however, that the photodecomposition of semiconductor electrodes restricts the conversion efficiency to a maximum of (EC - ED) / Eg, where ED is the decomposition energy / 1,3,11,14 / and b) (E) is high. Near the band edge, the expression for (E) is roughly expressed as

A (hν-Eg)n/2

α(E) = …(1.14)

hν

where A is a constant and n is either 1 or 4 for direct or indirect band gaps. As a result, the value of Eg should be tiny. Both of these requirements are in conflict with one another. Thus, for some ideal value of Eg, expression (1.13) would be greatest. It goes without saying that the ideal band gap should be approximately 1.4 eV. Other elements that impact the efficiency of PECs, in addition to Eg, are as follows:

1) Physical features of the semiconductor,

2) Energy losses owing to photoinduced redox processes;

3) Light losses due to electrolyte absorption, reflection from the semiconductor surface, and so on.

4) Ohmic losses owing to electrolyte, semiconductor, and other resistances.

5) Concentration polarization losses if the redox process is delayed. Both (4) and (5) can be reduced by minimizing the distance between the counter electrode and the photoelectrode. Furthermore, electrolyte agitation may aid in lowering concentration polarization by improving redox species transport to the corresponding electrodes. To avoid light absorption in the electrolyte (condition 3), a clear electrolyte would be preferred.

Considerations such as (2) and (4) place further constraints on the selection of Eg. Furthermore, the net energy available should be adequate to overcome losses as well as drive the redox reactions, i.e. h= Eg = (Energy necessary to drive the redox reaction) + losses owing to over potential, ohmic resistance, etc.

**1.5 Strategies For Design Of The PEC’s**

The following considerations should be considered while developing an effective PEC cell.

1. The redox pair must be transparent to light; otherwise, many photons will not be able to reach the semiconductor electrode, resulting in a drop in efficiency.

2. Ionic species involved in redox reactions should be diffusion restricted. As a result, churning the electrolyte may enhance efficiency.

3. A counter electrode should have the following characteristics: i) a low over potential for redox reactions to occur, and ii) a broad area for lowering concentration polarization.

4. Cell efficiency varies with temperature.

5. The semiconductor electrode should be resistant to dissolution, photocorrosion, and electrochemical corrosion. Surface modification of semiconductor electrodes aids in the stability and efficiency.

**Table 1.1 Qualitative comparison between a p-n junction cell and a PEC cell.**

|  |  |
| --- | --- |
| **p-n junction solar cell** | Photoelectrochemical solar **(PEC) cell** |
| Junction type p-n | p / electrolyte or n / electrolyte |
| Solid-solid | Solid-liquid |
| **Potential barrier at the junction** Yes | Yes |
| The barrier is produced as a result of majority carrier interdiffusion between the p- and n- regions. | The barrier is produced as a result of majority carrier transfer from a semiconductor to an electrolyte. |
| The potential drop or band bending in the two semiconductor areas is about identical | The majority of the potential drop occurs in the semiconductor space charge layer, with only a minor portion of the drop occurring in the electrolyte area. |
| Minority carrier flow is facilitated while majority carrier flow is inhibited. | The same as a p-n junction. |
| Photoeffect Excess carriers are produced as a result of the photoeffect. Photovoltage is produced by the mutual diffusion of excess photogenerated minority carriers in the two locations. | Excess carriers are produced.  Excess photogenerated minority carriers exchange charge with electrolyte ions, resulting in photovoltage or electrolysis. |

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