**CHAPTER I**

**THEORETICAL BACKGROUND OF SEMICONDUCTOR AND ELECTROLYTE INTERFACE**

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**Introduction**

A recent yet well-established area of electrochemistry is semiconductor electrochemistry. In specifically, photochemistry looks at the processes that electrically energized molecules start as a result of solar energy absorption in the visible and near-ultraviolet range. It is important because of the several uses it has in lithography, PCB manufacture, photo stabilizers, photo chromic eyewear, lasers, and other areas. The basic investigation into states of excitement of compounds having nano and pico second reaction times facilitates comprehension of the chemical reactions, transfer of energy mechanisms, and the complex structure that makes up matter (1-4). Technological advances and science are helping us understand the photophysical and photochemical processes that are involved in converting and storing solar energy more and more. Photo electrochemical cells (PECs) are the most effective chemical method of absorbing solar energy (see figs. 1–7). These types of cells integrate photovoltaics and photosynthesis and may be utilized to generate energy, retain chemical fuel, or both. The only two electrodes in these straightforward to manufacture devices—one metallic and the other semiconducting—are commonly submerged in an electrolyte and exposed to light (Figures 1–7). Using an intriguing method that will be covered in depth in the chapter, the semiconducting electrode may efficiently absorb sunlight, create decentralized costs, cause the division between these ions via elevated production, and generate a current of electricity resulting in an energy transfer. The interaction of light with a semiconductor electrode excites and absorbs electrons.

Photoelectrochemical cells (PECs) are the most efficient method of capturing solar energy. These cells combine photovoltaic’s and photosynthesis and can store chemical fuel, generate energy, or both. The only two electrodes in these straightforward to manufacture devices—one metallic and the other semiconducting—are commonly submerged in an electrolyte and exposed to light (Figures 1–7). The semiconducting electrode may effectively absorb sunlight, form decentralized costs, accomplish the division between these charged through elevated production, and generate a current of electricity resulting in power transformation utilizing an interesting approach that will be detailed in the chapter. The interaction of light with a semiconductor electrode excites and absorbs electrons. The main issues in semiconductor photoelectrochemistry. It will be essential to study a number of fundamental ideas from the fields of solid-state physics and photoelectrochemistry, which are summarized in this chapter, in order to comprehend the features of the semiconductor/liquid interface.

**1.2 The Semiconductor / Electrolyte (S / E) Interface Charges Transfer Mechanism**

Assuming the correct valent for conductivity energy for electrolytes galvanic pair choosing, an electron's charge can be transported via a fluid to the semiconductor electrodes or through the electrode to the electrolyte. At the appropriate electrodes, the species of ion can be diminished or oxidised.

**1.2.1 The dark charge transfer**

Consider the movement of protons through the solution's sides towards the electrodes back to the solution to comprehend how electricity moves at an electrodes/electrolyte interface under darkness. There is both a decrease and a rise.

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, 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.

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

A well-known Butler-Volmer link / 3, 4, 9–12 yields formula (2.18). It shows how a semiconductor/electrolyte interface's densities of current and applied voltage, V, relate to one another. V's changes significantly impact me. The electrode/electrolyte system exhibits a hill-shaped obstacle regardless of the lack or a field of electricity, as can be seen in Fig. 2.9 (b). Molecular motions in bond stretching, that are essential for reactions involving chemicals, atom and ion transport, form this barrier. The current prospective hurdle is changed by the magnetic field, which affects the energy of activation and subsequently the rate expression, such that only a tiny portion (1- ) of the electrical signal (qV) has an influence. This is due to the fact that the atomic movement needed for the structure to reach an important obstacle only makes up a small portion of the entire distance that that the possible obstacle must cover.

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

When an S/E interface is lighted, an electric field at the interface / 1, 3, 4 / separates photo-generated carriers in the depletion zone. The charge separation process's counter field is greatest at the open circuit state known as Voc. While the electrolyte absorbs the holes, the photovoltage draws electrons to move through the semiconductors into the opposite electrode.

The general response might be stated as

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

and

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

An electrode only acts as a shuttle or charge transfer mechanism and has no impact on the process. Think about an n-type semiconductor in an electrolyte-contact situation with lighting and a forward voltage of V. An energy level diagram for an electron is depicted schematically in Figure 1.1.

A typical electron level of energy graph of a semiconductor of the n type photoelectrode at the S/E contact including backward sensing potential plus sunlight, and a band bend form qVd to q(Vo - V) is shown in Figure 1.1.

The quasi-Fermi levels for electrons (EFn) and holes (EFp) are considered to be flat in the depletion zone.

qU = EFn - EFp.

if U accurately anticipates their separation. The presumption that U >>V shows the reality that minority carriers are more concentrated in bright areas than in shadowy ones. U denotes the amount of whole flux expected to transfer from the outermost layer of a semiconductor to the solution.

As defined by U,

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

Here P0 represents the ideal light amount throughout the bulk of the dark semiconductor and P (W) is the hole density at the evaporation region's border. Because the semiconductor depletion area gets the majority of the applied voltage, the cell's serial resistance ought to vary as little as possible and the level of electrolytes must is sufficient that CH exceeds Csc. In these circumstances, the loss of barrier thickness (W) is

W = W0 (VD-V0)1/2

Where W0 = [2 es e0 / q ND] --- (1.6)

Here, ND denotes the quantity of donation concentration, o the corresponding empty space permittivity, s the value of the dielectric constant of the semiconductor, and VD the state of equilibrium group stretching. If the surface's transmission speed is St, the recombination surface rate is Sr, the input photon flux is 0, and the depletion area width is W, the photo flux may be determined.

j1= (St / Sr ) [ f0{1-exp (µ - W) / (1+ µt) }]. --- (1.7)

This is a solar cell's useful photogenerated current, which is flowing from the electrolyte to the semiconductor electrode (see Figure 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 (D 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 semiconductors): / 1-4,11,12 /.

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

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

2. The separation of the electron-hole occurs in the space charge layer.

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, the 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 (D 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 (D G < 0).

iii) Photocatalytic cells ( G 0).

Similar to the 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)

**1.4 Efficiency Considerations.**

The effectiveness of a photovoltaic cell can be described by

Power of output

Input power

h % = x 100. …..(1.11)

Number of photoelectrons flowing per unit area

The quantum efficiency hq is defined as

Number of incident photons with energy hν per unit area

hq = .…(1.12)

The solar cell's efficiency is constrained by the semiconductor's band gap since it is a threshold device that only needs a small quantity of optical energy to activate. Loferski / 13 / investigated the impact between bands discrepancy, environmental digestion, light, reflecting expenses, and other factors on p-n junction-based photoelectric cell effectiveness. With a few adjustments that take into account additional photoelectrochemical processes, these findings might be used to photoelectrochemical solar cells. If electromagnetic opposition, over potentials, absorption of light in the solution itself, and additional inefficiencies are included, the overall conversion effectiveness in the most basic PEC can be calculated as

Eg 0∫∞ a (E).N (E).dE

0∫∞ E.N (E).dE

h = … (1.13)

Where N (E) is the quantity of photons with energy E, (E) is the proportion of absorbed photons, and Eg is the semiconductor's spectral band gap. Efficiency increases if: a) the band gap, Eg, is considerable, according to equation (1.13). While ED is the decomposition energy / 1,3,11,14 / and b) (E) is big, semiconductors electrode the photodecomposition limits the efficiency of conversion to an amount of (EC - ED) / Eg. The formula for (E) is frequently approximated at the band edge as

A (hn-Eg) n/2

hn

A (E) = … (1.14)

For direct or indirect band gaps, n is either 1 or 4, and A is a constant. Therefore, the value of Eg should be very small. These two needs are incompatible with one another. Thus, equation (1.13) would be the best for a certain ideal value of Eg. About 1.4 eV should be the optimal band gap. In addition to Eg, the following factors also affect the effectiveness of PECs: 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) If the redox process is postponed, there are losses in concentration polarisation. Both (4) and (5) can be reduced by closing the space between the opposing filament and the photoelectrode. Furthermore, by enhancing the transfer of redox species to the appropriate electrodes, electrolyte agitation may help reduce concentration polarisation. A transparent electrolyte would be desired in order to prevent light absorption in the electrolyte (condition 3).

Factors such as (2) and (4) further limit the decision to select Eg. As demonstrated by the equation h=Eg= (Energy necessary to drive the redox reaction) + losses owing to over potential, ohmic resistance, and so on, the net energy should be adequate to drive the redox reactions and overcome losses.

**1.5 Strategies for the Design of the PEC**

The following factors should be tackled while constructing an effective PEC cell.

1. The redox pair must be light transparent; otherwise, many photons are going to be prevented to reach the semiconductor electrode, resulting in a decrease in efficiency.

2. Diffusion should be controlled to ionic species that engage in redox processes. In consequence, spinning the electrolyte could boost competence.

3. An opposing electrodes must have a small excess possibility of oxidative activities and a large surface for reducing concentration polarization.

4. The impact of temperature on cells varies.

5. The semiconductor electrode must be resistant to electrochemical, photochemical, and dissolution corrosion. Surface alterations to semiconductor electrodes improve the device's reliability and effectiveness.

**Table 1.1 Comparisons of a PEC cell with a p-n junction cell qualitatively.**

|  |  |
| --- | --- |
| solar cell with a p-n junction | Photoelectrochemical solar (PEC) cell |
| Type of junction p-n | either a p- or n-electrolyte |
| Solid-solid | Solid-liquid |
| Potential obstacle at the intersection Yes | Yes |
| Majority carrier interdiffusion between the p- and n-regions causes the barrier to form. | The barrier is produced when the majority of the carriers are transported from a semiconductor to an electrolyte. |
| In the two semiconductor regions, the band bending or potential drop is nearly equal. | 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. | identical to a p-n junction. |
| Photo effect The photo effect results in the production of extra carriers. The mutual dispersion of surplus photogenerated minority carriers at the two places results in the production of photovoltage. | There are too many carriers created.  Photovoltage or electrolysis are produced when excess photogenerated minority carriers exchange charge with electrolyte ions. |

Photo effect

Excess carriers are produced as a result of the photo effect. 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.

This branch of photochemistry includes actions that begin with electrically excited molecules as a result of solar energy absorption in the visual and electromagnetic spectrum parts of the electromagnetic spectra.

These simple devices typically consist of two electrodes—one metallic and one semiconducting—that are submerged in an electrolyte and exposed to light (Figures 1–7). The semiconducting electrode is capable of successfully absorbing solar energy, producing delocalized charges, effecting the separation of these charges with high yield, and producing an electrical current that results in energy conversion using an exciting method that will be described later in the chapter. Light absorbs and excites electrons when it comes in contact with a semiconductor electrode.

These straightforward gadgets typically comprise of two electrodes, one metallic and the other semiconducting, dipped in an electrolyte and exposed to light (Figures 1–7). It is possible for the semiconducting electrode to effectively absorb solar energy, generate delocalized charges, carry out high-yield charge separation, and generate an electrical current that results in energy conversion through an intriguing procedure that will be covered in more detail later in the chapter. Light is absorbed and activates electrons when it comes in contact with a semiconductor electrode. main challenges in semiconductor photoelectrochemistry. It is necessary to first be familiar with a variety of fundamental ideas in the disciplines of solid-state physics and photoelectrochemistry, which will be discussed in this chapter, in order to fully understand the characteristics of the semiconductor/liquid interface.

Under the proper pit and conductivity energy and electrolytic redox pair selections, a proton may be transported from the semiconductor cathode to a solution of electrolytes via the electrode's surface itself. Cationic molecules are going to be reduced or oxidized by the suitable electrodes.

Consider the movement for protons between the solution's end towards the electro back to the solution to understand how charges move over an electrical/electrolyte interface in darkness. Both a decrease and an increase are seen.

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