

## 3

## Principles of Photo-electrochemistry (PEC)

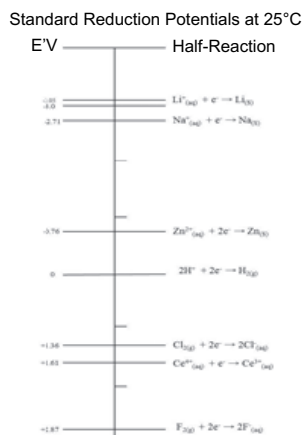
### 3.1 INTRODUCTION

Photo-electrochemistry has gained importance in the last four decades after the announcement by Fujishima and Honda that water can be decomposed using  $\text{TiO}_2$  and solar radiation. The electrolysis of water is a well known phenomenon but not widely used industrially for the production of hydrogen since considerable over-voltages are required to decompose water over the conventional thermodynamic reversible decomposition potential of water that is 1.229 V. The observation that water decomposition involves over-voltage means that the efficiency of the process will be considerably less than one. However if one wants pure hydrogen without the impurity of carbon oxides which are invariably present if hydrogen was obtained from steam reforming of naphtha, then direct electrolysis may be resorted to. Though photo-electrochemistry assumed importance from the point of view of water decomposition or generation of hydrogen from renewable source, water, it has assumed considerable importance today in many areas including the reduction of carbon dioxide as well as synthesis of ammonia from nitrogen which are most challenging propositions.

### 3.2 BASIC ELECTROCHEMISTRY AND SOLID STATE SCIENCE

The study of photo-electrochemistry needs some fundamental knowledge of Electrochemistry and Solid State Physics. However since this monograph basically deals with only photo-electrochemistry and its manifestations, it is not our intention to outline the basis of electrochemistry or solid state physics in any manner. However, since it is necessary that one comprehends the various values of redox potentials and their significance in a concise manner, even with the fear of repetition, the values of standard redox potentials of many of the commonly employed redox couples are given in Table 3.1 and the same is schematically represented in Fig. 3.1.

### 3.2 PHOTOELECTROCHEMISTRY: Principles and Practices



**Figure 3.1** Standard reduction potential at 298 K

**Table 3.1** Standard Reduction Potentials at 273 K for various Redox Reactions

Half Reaction	Standard reduction Potential in Volts
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.05
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.93
$\text{Ba}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ba}(\text{s})$	-2.90
$\text{Sr}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sr}(\text{s})$	-2.89
$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ca}(\text{s})$	-2.87
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.71
$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Be}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Be}(\text{s})$	-1.85
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Mn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mn}(\text{s})$	-1.66
$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	-0.83
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Cr}(\text{s})$	-0.74
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40
$\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.31
$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Co}(\text{s})$	-0.28
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.25

**Table 3.1** (Continued)

<i>Half Reaction</i>	<i>Standard reduction Potential in Volts</i>
$\text{Sn}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Pb}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Pb}(\text{s})$	-0.13
$2\text{H}^+(\text{aq}) + 2\text{e} \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Sn}^{4+}(\text{aq}) + 2\text{e} \rightarrow \text{Sn}^{2+}(\text{aq})$	+0.13
$\text{Cu}^{2+}(\text{aq}) + \text{e} \rightarrow \text{Cu}^+(\text{aq})$	+0.15
$\text{AgCl}(\text{s}) + \text{e} \rightarrow \text{Ag}(\text{s}) \text{Cl}^-(\text{aq})$	+0.22
$\text{Cu}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Cu}(\text{s})$	+0.34
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e} \rightarrow 2\text{OH}^-(\text{aq})$	+0.40
$\text{I}_2(\text{s}) + 2\text{e} \rightarrow 2\text{I}^-(\text{aq})$	+0.53
$\text{MnO}_4^-(\text{aq}) + 2\text{H}_2\text{O} + 3\text{e} \rightarrow \text{MnO}_2(\text{s}) + 4\text{OH}^-$	+0.59
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e} \rightarrow \text{H}_2\text{O}_2(\text{aq})$	+0.68
$\text{Fe}^{3+}(\text{aq}) + \text{e} \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.77
$\text{Ag}^+(\text{aq}) + \text{e} \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Hg}_2^{2+}(\text{aq}) + 2\text{e} \rightarrow 2\text{Hg}(\text{l})$	+0.85
$2\text{Hg}^{2+}(\text{aq}) + 2\text{e} \rightarrow \text{Hg}_2^{2+}(\text{aq})$	+0.92
$\text{Br}_2(\text{l}) + 2\text{e} \rightarrow 2\text{Br}^-(\text{aq})$	+1.07
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e} \rightarrow 2\text{H}_2\text{O}$	+1.23
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e} \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}$	+1.23
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e} \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}$	+1.33
$\text{Cl}_2(\text{g}) + 2\text{e} \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Au}^{3+}(\text{aq}) + 3\text{e} \rightarrow \text{Au}(\text{s})$	+1.50
$\text{Ce}^{4+}(\text{aq}) + \text{e} \rightarrow \text{Ce}^{3+}$	+1.61
$\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e} \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}$	+1.70
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e} \rightarrow 2\text{H}_2\text{O}$	+1.77
$\text{Co}^{3+}(\text{aq}) + \text{e} \rightarrow \text{Co}^{2+}(\text{aq})$	+1.82
$\text{O}_3(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e} \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	+2.07
$\text{F}_2(\text{g}) + 2\text{e} \rightarrow 2\text{F}^-(\text{aq})$	+2.87

Figure 3.1 has some messages for understanding the redox processes from the point of electrochemistry. For any electrochemical processes to be feasible, the net free energy change (standard free energy change) has to be negative which means that the net potential has to be positive since  $\Delta F^0 = -nFE^0$  where  $n$  is the number of electrons transferred in the redox process and  $F$  is the Faraday constant which is the product of charge on the electron  $\times$  Avogadro number  $= 1.6022 \times 10^{-19} \times 6.0221 \times 10^{23} = 96485$  Coulombs/mole ( $= F$  Faraday constant). The feasible half cell reactions should have positive values of potential while the reverse of the reactions are feasible for the processes with negative values of potential. Secondly the two ends of the electrochemical potential scale are represented by the fluorine reduction and

### 3.4 PHOTOELECTROCHEMISTRY: Principles and Practices

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lithium ion reduction. This denotes the magnitude of potentials that can be realized using these redox species.

### 3.3 ELECTRODE-ELECTROLYTE INTERFACE

Photo-electrochemical cells are the simplest devices consisting of a semiconductor and metallic electrodes immersed into an electrolyte and the semiconductor electrode is preferentially exposed to sun light or light irradiation. The semiconductor electrode absorbs the light and creates energetically separated electrons and holes which drive the chemical reaction to evolve chemicals (it will be hydrogen if the electrolyte contains water) or fuels. These simple devices if they can be efficient at least greater than 15% (or capable of over coming the conventional Carnot limitation) can become a source of fuel production device. There are at present, three known methods of converting light into usable energy sources. Among these three, the first one is the remarkable nature's path namely Photosynthesis. Probably this may be the most preferred pathway by which nature provides energy sources for all the living beings on earth. The total solar energy reaching the earth surface per year is approximately  $3850,000 \times 10^{18}$  joules/yr or 120,000 TW. Out of this estimated resource only less than 0.02% will be sufficient to replace the energy requirement now met by fossil fuels and nuclear energy. The total solar energy received by earth is given by  $1366$  watts per square meter ( $\pm 6.9\%$ )  $\times 127,4000,000 \text{ km}^2 = 174 \pm 3.5\%$  peta watts from which at least half (89 PW) reaches the earth surface. The total solar energy reaching the earth in a year is more than twice of all the energy stored in various forms like coal, oil and all other conceivable forms of energy. Possibly the energy utilized in photosynthesis can account for about  $3000 \times 10^{18}$  joules. Thus, it can be seen that only a tiny fraction of the total solar energy is harnessed by the plants, but still this level of energy storage is sufficient to support living systems on earth. It is clear that energy conversion by photosynthesis appears to be a possible means of providing the energy requirements of earth. There are two alternate methods of energy conversion that have been proposed and are being developed for increasing the efficiency of the processes. One of them is termed as Photovoltaics. A photovoltaic cell consists of two different types of solids connected at an abrupt but defined junction. This type of cell promotes the current flow in only one direction in the external circuit and thus produces electrical power. Unlike the photosynthesis, wherein solar energy is utilized to produce fuel, photovoltaics produce electricity directly. This brings us to the concept of electron versus fuel for energy conversion. Which route is better and why can be another debate. There are some distinct advantages of Photovoltaics, like the device can be compact in nature and net efficiency achievable even today is nearly the Carnot efficiency or more and are durable

and can last nearly 20 or more years. The positive features mentioned are only indicative figures and in practice they can be different.

### 3.4 PHOTO-ELECTROCHEMICAL CELLS

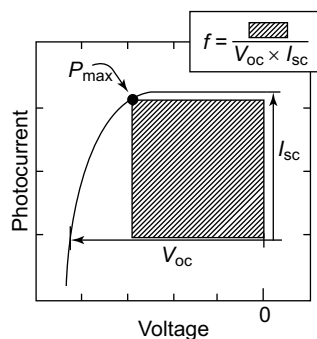
The third possibility is the Photo-electrochemical cells. The main component of the photo-electrochemical cells is the photo-active electrode which is usually a semiconductor. Metals are not so much effective in this operation ( see the chapter on plasmonic photocatalysis where metal particles in the nano state can be active) since the energy levels are continuous (between occupied and unoccupied states) and hence excitation in these systems will lead to fast recombination and hence the net free energy change can not be harnessed. For conventional redox reactions, one is interested in either reduction or oxidation of a substrate. For example consider that one were interested in the oxidation of  $\text{Fe}^{2+}$  ions to  $\text{Fe}^{3+}$  ions then the oxidizing agent that can carry out this oxidation is chosen from the relative potentials of the oxidizing agent with respect to the redox potential of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  redox couple. The oxidizing agent chosen should have more positive potential with respect to  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple so as to affect the oxidation, while the oxidizing agent undergoes reduction spontaneously. This situation throws open a number of possible oxidizing agents from which one of them can be easily chosen. However, in the case of water splitting one has to carry out both the redox reactions simultaneously namely, the reduction of hydrogen ions ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ) as well as ( $2\text{OH}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O} + 1/2\text{O}_2$ ) oxygen evolution from the hydroxyl ions. The system that can promote both these reactions simultaneously is essential. Since in the case of metals the top of the valence band (measure of the oxidizing power) and bottom of the conduction band (measure of the reducing power) are almost identical they cannot be expected to promote a pair redox reactions separated by a potential of nearly 1.23 V. Another aspect is that metals liberate hydrogen preferentially and if these semiconductors can be designed to have enhanced metallic/reducing properties it may be advantageous. But this aspect is not considered in this presentation. Therefore one has to resort to systems where the top of the valence band and bottom of the conduction band are separated at least by 1.23 V in addition to the condition that the potential corresponding to the bottom of the conduction band has to be more negative with respect to  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$  while the potential of the top of the valence band has to be more positive to the oxidation potential of the reaction  $2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}_2$ . This situation is obtainable with semiconductors as well as in insulators. However insulators are not appropriate due to the high value of the band gap which demands high energy photons to create the appropriate excitons for promoting both the reactions. The available photon sources for this energy gap are expensive and again require

### 3.6 PHOTOELECTROCHEMISTRY: Principles and Practices

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energy intensive methods. Hence insulators may not be employed for the purpose of water splitting reaction. Therefore, it is clear that semiconductors are alone suitable materials for the promotion of water splitting reaction. In the operation mode, the semiconductor electrode-electrolyte interface is the key factor and a complete understanding of this interface alone can lead to a successful development of highly efficient photo-electrochemical cells. In some sense, photo-electrochemical cells can be considered as a notional hybrid of photo-synthesis and photo-voltaics since these cells can generate either or both electricity and fuel. However, the development of Photo-electrochemical cells with the desired efficiency appears to be one of the major issues calling the attention of the developers. It is better to comment further between the similarities and also differences between PEC and Photosynthesis and Photovoltaics. Photosynthesis appears to provide remarkable efficiency due to various factors. The essential points of relevance are (i) The absorption of the photon takes place in the chlorophyll dimer or the special pair facilitated by the antenna and chlorophyll pigment. (ii) The excited electron-electron vacancy (hole) pair could normally undergo de-excitation thus releasing the optical energy as heat without producing fuel or electricity. However, in the photo-synthetic reaction centre the separation of the excited electron from its vacancy is achieved by the presence of a series of electron acceptors that are not only strategically located in the protein but could also adjust their redox potentials like in an escalator steps thus positioning the acceptor states suitable for harnessing the energy. (iii) In addition, the presence of a series of electron acceptors makes the electron to move from one species to another thus spatially separating the electron hole farther away thus restricting the thermodynamically feasible recombination of the excited electron and hole thus bringing in a kinetic control. This alone facilitates the use of the excited electron to perform the chemical reactions in photosynthesis and is responsible for fuel production. In the case of Photovoltaics, the free energy gradient caused by the potential energy gradient present at the junction of the two solids is the cause for the flow of electrons or electricity. In the case of photoelectrochemical cells also the driving force is the electrical field gradient that is available at the semiconductor/electrolyte interface and also the interaction of the photon field in the semiconductor adds cumulatively for this field gradient which is responsible for the vectorial transfer of electrons and also for driving the chemical reaction in the electrolyte. Hence, PEC can thus produce electricity, chemical reaction or both. However, PEC can be operated exclusively in the current mode if the reaction that takes place at the counter electrode to the semiconductor electrode (usually a metallic electrode) is simply the reverse of the anodic reaction that takes place at the semiconductor. In this mode of operation (for example the oxygen evolution

and oxygen reduction were to occur at the two electrodes) then the PEC is presumed to operate similar to Photovoltaic cell as an energy conversion device. However, if the energetics of the electrons is suitable it is possible to reduce water to hydrogen at the counter electrode instead of the reduction of oxide ions and this process may be considered as fuel production caused by the use of photon energy and also the electrical field gradient. Depending on the net energetics, it is possible to produce both fuels and also electricity. In this sense the PEC appears to be unique if one were to understand and implement both the process in the same cell. It is necessary therefore to define some specific parameters for the operation of PEC. The term short circuit current ( $I_{SC}$ ) refers to the current that will flow in low resistance ammeter when the two electrodes of PEC are in direct short circuit. The term open circuit voltage ( $V_{OC}$ ) is the maximum Gibbs free energy that can be obtained from the cell and usually measured with a high resistance voltmeter. The term fill factor refers to the maximum power that can be produced by a photo-electrochemical cell. It will be clear that all these three parameters have to be optimized. See for example Fig. 3.2.



**Figure 3.2** *i-V curve to explain the parameters like VOC , ISC and fill factor*

It is also possible that other concurrent reactions can take place in the PEC, like corrosion and passivation processes of the semiconductor electrode can compete with the desired energy conversion process. These dissolution or degradation processes can restrict the life time of the electrodes. Secondly some trap states can be present in the materials which will lead to loss processes for the effective conversion of excited states into energy and thus contribute to the lowering of the conversion efficiency. Third parameter is the electrode-electrolyte interface which may not give rise to a large free energy gradient so that effective charge separation is not achieved at the interface. This is an important component of PEC and deserves careful attention. Even though the focus of this presentation will be on the conversion of solar energy into useful forms of energy like electricity or fuels or both, it is possible to make use of the concept of PEC for the treatment of waste water and for other

### 3.8 PHOTOELECTROCHEMISTRY: Principles and Practices

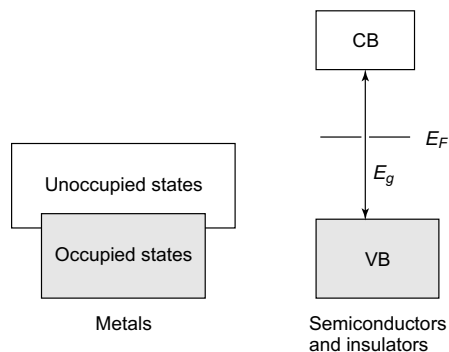
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organic synthetic oxidation reactions. These two aspects will be dealt with in separate chapters.

### 3.5 SELECTION CRITERIA FOR ELECTRODES

It has been stated earlier, that semiconductor materials are commonly employed as electrodes in PECs. It is therefore necessary that one outlines some governing principles of electron transfer in semiconducting materials before one considers the semiconductor-electrolyte interface. Unlike in simple molecular systems, wherein the energy levels take discrete and specified energy values, the energy levels in semiconductors are close together instead of the discrete energy levels and hence give rise to energy bands of allowed energy levels. Normally one mole of any substance will contain Avogadro number of species and hence the frontier orbitals of these systems should consist of multiples of Avogadro number of eigen states, each with double occupancy with paired spins. If the occupied density of states (DOS) overlaps with density of states of unoccupied states, then the material can be considered to possess metallic conduction, which is normally identified by the decrease in conductance value with increase in temperature. However in the case of other materials, the occupied valence band is separated from the usually unoccupied conduction band and depending on the band gap values the materials can be either semiconductors or insulators. This situation is usually depicted in terms of a box type diagram shown in Fig. 3.3, though this is not the real picture arising from three dimensional solids. In the case of semiconductors, the band gap is usually or the order of 0 to 4 eV. A compilation of band gap values of the some of the known semiconductors is given in Table 2. The value of the band gap ( $E_g$ ) has important implications in the application as electrodes in PEC. One is normally interested in the electrochemical potential of the electrons for the redox reactions of interest, the position of the highest occupied state or more precisely the Fermi level (it should be Fermi surface for three dimensional systems) of the solid system on hand. Essentially, one is tempted to denote the Fermi level in the conceived two dimensional box type diagram in between the top of the valence band and the bottom of the conduction band, more precisely considering the energy position where the probability of finding the electron is 0.5. However, the more precise definition should be based on the electrochemical potential of the electrons but since it is a conceived concept, one takes the route of a visual and manageable parameter of probability function. The distribution of electrons in the frontier bands in the solids has to be rationalized in terms of well defined distribution functions containing at least two distinct constants related to energy of the electrons and also to the total number of electrons in the system considered.





**Figure 3.3** *The energy band positions in metals, semiconductors and insulators ( $E_g$  = band gap and  $E_F$  Fermi level)*

There are various ways the energy states of the frontier wave functions (namely the energy states of the valence and conduction bands can be altered by appropriate substitutions in the solid matrix or even the solid matrix can sustain small amounts of alter valent ions and thus can give rise to extra allowed wave functions in the so called forbidden gap which is termed as band gap ( $E-g$ ). Depending on the eigen-value of these allowed wave functions in the forbidden gap, they can be either acceptor states near the top of valence band (mainly contributing to conduction by positive holes and hence called p-type semiconductor). If on the other hand, the added species were to generate allowed energy states very near to the bottom of the conduction band, then these states are denoted as donor states, since these states are usually occupied and hence called n-type semiconductors. The electrical behavior that arises out of the incorporation of the foreign species in a given semiconductor lattice and hence termed as extrinsic semiconductors. However, the energy states namely acceptor and donor states can also be intrinsically generated in a given semiconductor without the addition of foreign altermvalent species and these are termed as intrinsic semiconductors. The statements that have been made so far refer to the single crystals of semiconductors. In the case of amorphous and poly crystalline semiconductors, the additional energy levels can be generated from the inherent defects in them like grain boundaries, trap states and defects. The presentation given is one of the simplest and for more rigorous treatments, it would be good the reader refers to some text book on solid state physics to understand the electronic structure of semiconductor materials.

### 3.6 STRUCTURE AND DYNAMICS OF ELECTRODE/ELECTROLYTE INTERFACE

The primary purpose of this presentation is to examine the structure and dynamics of the electrode-electrolyte interface. When a metal electrode is

### 3.10 PHOTOELECTROCHEMISTRY: Principles and Practices

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immersed in an electrolyte, and since these two systems are in electrical contact, there will be equalization of the Fermi levels in both systems which will result in the transfer of charge. Under these equilibrium conditions, the electrochemical potential of the electrons is conventionally given by the Nernst Equation

$$E_{redox} = E^0_{redox} + (RT/nF) \ln (a_{ox}/a_{red})$$

Where  $a_{ox}$  and  $a_{red}$  stand for the activities of the oxidized and reduced species in the redox couple and  $E_{redox}$  can be identified with the Fermi level in the electrolyte. At this point, one must realize that one is dealing with two scales for energy. The electrochemical scale of energy which is of relevance for PEC assumes that the potential of the standard hydrogen electrode (SHE) as reference value and assigns the value of zero. However, the solid state community has adopted the more reasonable reference value for the energy scale and assigned the zero value for the free electron in vacuum. It is therefore possible now to connect both the electrochemical scale and that of the energy scale with reference to free electron in vacuum as zero by the relationship that the zero of the electrochemical scale (namely the potential of SHE) is at  $\sim 4.5$  eV with respect to the energy of the free electron in vacuum. Now if a semiconductor is immersed in a redox electrolyte, the electrochemical potential (for this discussion it is the Fermi level of the two phases) are different at the interface. A second point to be noted is that the field gradient is varying in some form from the interface to the solution side as well as inside the semiconductor. However in the case metal-electrolyte interface the field gradient is prominent only in the solution side and not very deep within the metallic electrode. In the case of semiconductor-electrolyte interface, equilibration of the interface Fermi levels thus necessitates the flow of charge from one phase to another and hence the eigen values of the allowed energy levels also vary with respect to distance from the interface inside the semiconductor. This variation of the values of allowed energy levels within the semiconductor is usually visualized as band bending. In reality it only shows how the allowed energy levels get altered due to the free charge flow across the semiconductor, this alteration can also be due to the accumulation or adsorption of charged species from the electrolyte on the semiconductor electrode. This redistribution of allowed energy levels in the semiconductor gives rise to build of voltage  $V_{SC}$  ( $Sc =$  space charge) within the semiconductor.

The charge injection as a result of Fermi level equilibration can lead to alteration of the Fermi level in either of the directions (namely it can be more stabilized or can also be more destabilized, though it is conventionally denoted as moving “down” or “up”). Essentially this alteration of the Fermi level can take place till the Fermi level equilibration takes place. The concepts that have

been described so far namely band bending or Fermi level equilibration are not unique to the semiconductor/electrolyte interface and any interface can give rise to readjustment of electronic energy levels if electron transfer is feasible at the interface. However it must re-emphasized that the potential drop or the charge accumulation (may be appropriately charge density change) is mainly concentrated at the surface or at the most few nanometers from the surface (skin depth), which could be due to high electronic conductivity of the metals which cannot support a net electric field within the bulk metal. This is the reason why electrochemists have been successful in explaining the electrochemical electron transfer process at the metal/electrolyte interface in terms of Helmholtz region. In the case of semiconductors the field penetrates inside the semiconductor as in the electrolyte region and this is called **Garrett-Brattain space charge region**. The point of relevance is that the behavior of metal/electrolyte interface is different from that of semiconductor/electrolyte interface. The differences have been examined in terms some kind visualizable equivalent circuits, but it is not yet clear if this description is quite sufficient and adequate. It is realized now that there is a definite region in the semiconductor where the charge distribution is altered because of equilibration. Beyond this region, may be the electro-neutrality condition is holding good. One is concerned with the space charge region or the layers where the charge density alteration exists. The potential distribution in this interface region can be expressed under certain conditions by the equation

$$V(x) = - (e_0 N_D / 2 \epsilon_s) x^2 \text{ where } x (0 \leq x \leq w)$$

In this equation,  $\epsilon_s$  is the static dielectric constant of the semiconductor and  $e_0$  is the electronic charge. The quantitative equation for the value of  $V_{SC}$  is therefore given by

$$V_{SC} = - (e_0 N_D / 2 \epsilon_s) w^2$$

where  $w$  stands for the field penetration depth and in the case of charge depletion it is depletion layer width. It is therefore clear that the value of  $N_D$  (can be considered to be equal to doping level or impurity level. It may be necessary one understands the difference between the concept of doping or dissolution or solid solution formation. The doped species ( in the ionic state) must be accommodated in the crystalline lattice positions while in solid solution this condition need not be satisfied. This implies that only certain species which satisfy conditions like ionic size and extent (read percentage) of doping will have restrictions) which can be in the order of  $10^{16}$  to  $10^{18} \text{ cm}^{-3}$  for the situation of light or heavy doping respectively decides the field penetration depth and this is of the order of 10 to 1000 nm for most of the semiconductors as compared to the typical Helmholtz layer width of 0.4 to 0.6 nm. It is therefore clear that if one were to extend the

### 3.12 PHOTOELECTROCHEMISTRY: Principles and Practices

science of metal/electrolyte interface to semiconductor/electrolyte interface, the layer width has to be considerably reduced. The potential difference across a semiconductor electrolyte can be mathematically written by simple extrapolation of the metal/solution interface as

$$V_t = V_{SC} + V_H + V_G$$

where  $V_t$  denotes the total potential difference between the semiconductor electrode and the counter metallic electrode. It is generally realized that  $V_{SC}$  depends on the nature of the semiconductor and also that of the electrolyte and its magnitude is sometimes difficult to estimate so also that of  $V_H$  and  $V_G$ . Another contributing factor for the uncertainty in the determination of these values is the specific adsorption of the electrolyte on the surface of the electrode. In the case of metallic electrodes this is simpler since there are only one type of surface sites that are available and also the field effects are possibly known while in the case of semiconductor these factors are not yet fully certain and one has to make some striking approximations which may not be representing the true situation existing at the interface. It is necessary that one estimates the extent of so called band bending ( though in reality this is band alteration) which can be assessed by a parameter called the flat band potential  $V_{fb}$ , that is the potential that need to be applied to make the band to be flat. The value of this parameter can be determined from the Mott-Schottky relation which is given by the expression for a n-type semiconductor

$$1/C_{sc}^2 = 2/N_D e_o s [(V - V_{fb}) - kt/e_o]$$

Where  $C_{SC}$  is the semiconductor depletion layer capacitance and this relation itself is derived invoking the Poisson distribution.. It must be noted that  $V_{fb}$  itself depends on many parameters like the specific adsorption of the electrolyte and also the trap states in the semiconductor. When the value of the flat band potential  $V_{fb}$  is known then the Fermi level of the semiconductor is defined. This provides a means to delineate the position of the top of the valence band and also the bottom of the conduction band which essentially correspond to the oxidation and reduction potential of the semiconductor and this also provides a means of estimating the band gap which facilitates the choice of the wavelength of the radiation necessary to make an exciton in a semiconductor. Having identified that the oxidation and reduction capabilities of the semiconductor are associated with the energy positions of the top of the valence band and bottom of the conduction band of the semiconductor, it is seen that the so called band bending associated with the semiconductor/electrolyte interface positions or alters the Fermi level of the semiconductor in the direction for favourable redox reaction. In other words the band bending probably is capable of tracking the redox potential changes that occur in the system. So far we have considered an

ideal semiconductor/electrolyte interface. However in reality semiconductors necessarily have abrupt termination of the lattice and this situation can give rise to co-ordinatively unsaturated positions which are different from that of the species in the bulk of the lattice. The presence of such species in the surface can result in some kind of surface reconstruction of the surface or the unsaturation has to be satisfied by extraneous species. In both these cases, the electronic energy states take discrete values in the forbidden band gap region rather than forming one of the energy levels in the continuously varying with respect to energy valence or conduction bands. Depending on the occupancy of these states, it is possible that these energy levels can exchange charge either with the valence or conduction bands or with the redox electrolyte. If the value of  $V_{SC}$  (that is the band bending in the semiconductor) is not altered with change in the value of the redox potential of the solution redox couple, then the Fermi level is said to be pinned. This extent of Fermi level pinning is reflected from the plot of variation of  $V_{SC}$  (any other parameter equivalent to it) versus  $E_{redox}$ . If the slope of this plot were to be zero then the Fermi level is completely pinned and any other variation with a slope value up to 1 denotes the possible variation in  $V_{SC}$ . It should be noted that the argument given is applicable only for under non-irradiated condition. Under irradiation of the semiconductor, there can be changes in the values of  $V_H$  and also that of  $V_{SC}$  which can complicate and alter the situation. Depending on the magnitude of the values of  $N_D$  and  $\epsilon_s$ , it is possible that the values of  $V_H$  can become sizable fraction of the potential drop exceeding the value of  $V_{SC}$ . The Fermi level pinning can also be associated with the extent of defect states in the crystalline lattice. The charge transfer process of semiconductor/electrolyte interface in the dark follows simple electrochemical principles. Let us consider the electrode/electrolyte under equilibrium conditions. Under these conditions the forward current and the reverse currents exactly balance each other and there is no net current across the interface. If the system sustains a bias voltage, then the net current will flow in either of the directions depending on the number of majority carriers that are generated in the space charge region in the semiconductor. This argument is based on the assumption that the voltage drop essentially takes place in the space charge region and hence one is modulating the population of majority charge carriers only in the surface layers. This situation gives rise to exponential dependence of the current on the applied potential when  $V < 0$  cathodic bias and when  $v > 0$  (anodic bias) the current is independent of the applied potential.

Under these conditions one has to consider the value of  $i_0$  which is conventionally termed as the exchange current density, that is the current that flows at equilibrium when the cathodic and anodic currents exactly balances each other. The value of  $i_0$  should therefore naturally depend on the

### 3.14 PHOTOELECTROCHEMISTRY: Principles and Practices

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concentration of the redox species in solution and also on the extent of band bending, which is dependent on the extent of doping or other alterations that cause a change in the Fermi level in the semiconductor. The magnitude of  $i_0$  is therefore a measure of the rectification that can be realized in the system. In the dark under no illumination condition, there can be hole injection in the VB of the semiconductor. These holes can recombine with electrons either through the surface states or by the occupied states in the space charge region.

Now if the semiconductor is exposed to the radiation of energy equal to or greater than the band gap ( $E_g$ ) then these radiations can give rise to excitation of an electron from the occupied valence band to an unoccupied state in the conduction band. If all these electrons thus excited could be harnessed in the external circuit, then the process can be said to have high quantum efficiency. However there are other concomitant processes that are possible. Essentially they arise due to scattering and also absorption of radiation by the electrolyte and other components of the assembly and these radiations have to be quantitatively assessed for calculating the net quantum efficiency. As stated earlier the number of carriers that are collected in the external circuit versus those that are generated by optical absorption is conventionally termed as quantum yield, it is clear even though one can estimate the conversion efficiency, there are uncertainties in the estimation of the absorption of the photons by the semiconductor alone. Secondly, it is assumed that the photon field and electric field are acting on the semiconductor independent of each other. The validity of this assumption has not been explicitly addressed even though there are indications that there can be photon enhanced field emission. Irradiation of semiconductor results in some kind of charge redistribution in the density of states of valence and conduction bands. The superimposing electric field can give rise distortion of the energy states. Similarly if the charge distribution in the valence and conduction bands are perturbed by the electric field, then the application of the photon field can give rise to altered redistribution and hence the net effect can not be considered to be an algebraic sum of the individual field effects though that is how it is considered mostly so far. It is possible that the extent of band bending and also the extent of effective space charge region might get altered and hence the kinetics of charge transfer process can be generally altered either way.

### 3.7 PERSPECTIVE CONCLUDING STATEMENTS

Having outlined the physics of semiconductor/electrolyte interface necessary for energy conversion processes, it is now possible to briefly comment on the strategies for the choice of semiconductors for PEC applications. What one hopes at this stage is to delineate the semiconductor system that will provide efficient fuel production from decomposition of water. Unfortunately, in spite

of intense research efforts for more than four decades this projection appears to be a distant future due to many obstacles. The competing components are the large band gap or small band gap materials. Large band gap materials show low efficiency and low band gap materials are susceptible for photo-corrosion and other related process like passivation which restrict the life time of the system. The presentation given has shown that the kinetic stability limitation has to be overcome than any apprehension over thermodynamic limitation. The prime factor that is responsible for this situation is the anxiety to utilize maximum extent of solar radiation instead of searching for kinetically compatible reagents to prevent photocorrosion or photopassivation processes. It may be possible or desirable to use non-aqueous electrolytes instead of solvents that promote photocorrosion. Another approach can be to modify the surface of semiconductors with surface enriching co-catalysts instead of substitution or doping. These possibilities have been explored but yet success appears to be far off.

Another approach that has been attempted is to alter the position of the top of the valence band by substitution at anionic positions of the semiconductors with species like nitrogen, phosphorus, sulphur and carbon, or alter the position of the bottom of the conduction band by doping in the cationic positions. These attempts also have provided only a marginal success only. Coupling of the semiconductors is also possibly aimed in this direction only. The focus has been only to show hydrogen evolution in the decomposition of water but it should have been on the realization of stoichiometric evolution of oxygen and hydrogen. Secondly, the search could have been on the surface of the semiconductors which can effectively activate the molecule employed for decomposition. Use of scavenging agents to restrict the photocorrosion has also not yielded the desired level of activity for fuel production. These studies show that the limitation for not achieving desired level of activity does not lie either in thermodynamic parameter barrier or kinetic rate limitation alone but above these two conventionally blamed parameters there is need for some intrinsic evaluation of the required parameters. It has been tempting to identify this parameter with the usual choice of parameters like 'd' electron configuration ( $d^0$  or  $d^{10}$ , band gap value (this is proved to be not true from the studies on band gap engineering studies) or intrinsic bond character, but the truth appears to lie above all these known variables that are amenable for study. It is hoped that the search will continue in the years to come and possibly, the solution is possibly blurred with our polarized vision.

## References

Only typical references alone are given, they are not the selected ones. There are many earlier references

**3.16** PHOTOELECTROCHEMISTRY: Principles and Practices

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