Chapter-1 : Introduction

CHAPTER - 1

INTRODUCTION

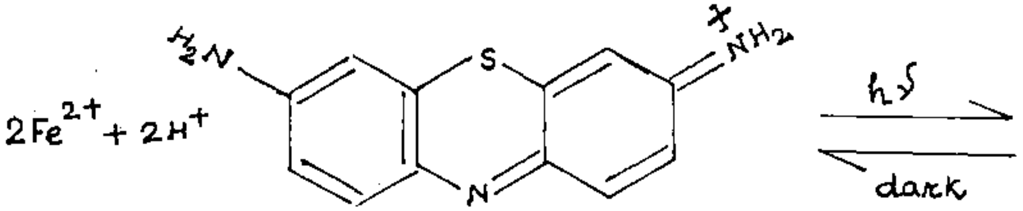
The search for renewable source of energy has led to an increasing interest (1-4) in photoelectrochemical cells because of their possible role as transducers of solar to electrical energy. Although photoelectrochemical studies commenced with the observation of Becquerel (5) in 1839, the mechanism of photo-voltage generation in photosensitive electrodes/electrolyte systems are still at an early stage of development. Two approaches to photoelectrochemical cells are currently available. On the one hand, Albery and Archer (6) have provided a good account of the electrochemical kinetics applying to light sensitive concentration cells containing inert electrodes and two dye couples, one of which is photosensitive. On the other hand, Memming and Kürsten (3,7) have given attention to the reactive intermediates produced by photolysis in such cell electrolytes and proposed that semioxidized and semireduced forms of the fluorescent dye are responsible for the photo induced electrodic electron transfers.

A number of analyses of the general thermodynamic and kinetic aspects of the electrical output of photogalvanic cells have been published (8,9). It is inconvenient to separate such analyses completely from devices specifies. After the discovery over fifty years ago (10,11) that thionine is reversibly photoreduced by Fe^{+2} in acidic aqueous solution, Rabinowitch (12)explored the possibility of utilising the system in the construction of a photogalvanic cell for the solar energy conversion. In the "primitive beaker" cell the electrodes are identical with one illuminated and the other in the dark. The open circuit voltage is ideally the difference in the reversible potentials at the two electrodes. For the iron-thionine system, the concentration of leucothionine is negligible at the dark electrode so that the exchange current is determined entirely by the iron couple. The potential at the dark electrode is given by the Nernst expression in equation 1,

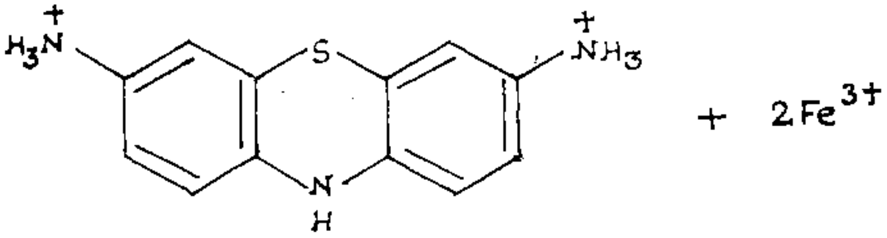
$$E_{dark} = E^{\circ}_{Fe} + 0.058 \log \left([Fe^{3+}]/[Fe^{2+}] \right)_{dark} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where E^{o}_{Fe} is the standard reduction potential of the Fe^{+3}/Fe^{+2} couple and the terms in the square brackets represent the activities of the species. The potential at the illuminated electrode is a complex function and depends on the concentrations of all the redox species at the electrode (13). The expression for this potential can be simplified for an ideal electrode by assuming that the electron transfer rate constants for all the redox species are the same and further simplified by assuming that the photostationary concentration of the half-reduced dye, semithionine, is negligible. The result is equation 2 where $f = F/RT$, F is the Faraday in coulombs, E_{light} is the potential of the illuminated electrode,

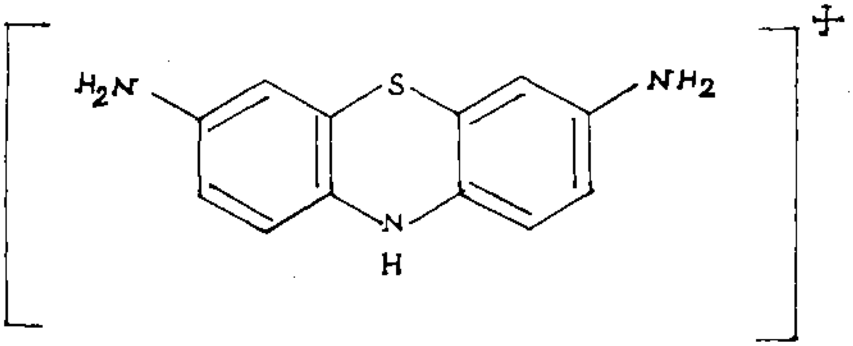
E^{o}_{Fe} is the standard reduction potential of the Fe^{+3}/Fe^{+2} couple,



Thionine, T



Leucothionine, L



Semithionine, S

$E^{o}_{T\rightarrow S}$ is the standard potential for the one-electron reduction of thionine, and $E^{o}_{S\rightarrow L}$ is the standard potential for the one-electron reduction of semithionine. The terms in the square brackets represent the activities of the various species in the photo-stationary state.

$$\exp\left(f E_{light}\right) = \frac{\left[Fe^{3+}\right] \exp\left(f E^{\circ}_{Fe/2}\right) + 2\left[T\right] \exp\left(f E^{\circ}_{T\rightarrow S}/2\right)}{\left[Fe^{2+}\right] \exp\left(-f E^{\circ}_{Fe/2}\right) + 2\left[L\right] \exp\left(-f E^{\circ}_{S\rightarrow L}/2\right)} \quad \ldots \quad (2)$$

The potential of the photo galvanic cell under open circuit photo stationary conditions is equal to $E_{dark} - E_{light}$ as calculated from equation 1 and 2. The current produced by such photogalvanic cell with ideally reversible electrodes depends on composition of the bulk solution in the photostationary state under short-circuit or other conditions of current withdrawal and on the rate of diffusion of charge carriers to the electrodes. This current is related to various system parameters by equation 3, where 'n'

$$i = nFADC/\delta \quad \ldots \quad (3)$$

is the number of redox equivalents per mole of a given charge carrier, F is the Faraday, A is the electrode area, D is the diffusion co-efficient of a given charge carrier, C is the concentration of a given charge carrier in bulk solution under photostationary conditions and δ is the thickness of the diffusion layer. The crucial figure of merit in evaluating the efficiency of solar energy conversion is sun light engineering efficiencies (S.E.E.) as defined in equation 4, for conversion to electrical power or energy.

$$\text{S.E.E} = \frac{\text{electrical power or energy delivered to load}}{\text{incident sun light power or energy}} \times 100 \qquad \ldots \quad \ldots \quad \ldots \quad (4)$$

The totally illuminated thin layer (TI-TL) photogalvanic cell was first described by Clark and Eckert (14) and a number of studies of the behaviour of the iron-thionine (13,15-20) photoredox system in such cells have been reported. In TI-TL cells, at least one electrode is selective; ideally, a selective electrode completely blocks one redox couple while it is completely reversible to the other. Greatest efficiency would be achieved with TI-TL cell in which each electrode was perfectly selective for a different couple.

As mentioned earlier, the simplest system for a photogalvanic (PG) cell, however, consists of two redox couples A, B and Y, Z. The general reaction scheme is as follows;

Solution : $\text{Thionine (A)} + \text{Fe(II)(Z)} \rightleftharpoons \text{Leucothionine (B)} + \text{Fe(III)(Y)}$

Photochemistry : $\text{Thionine (A)} \xrightarrow{h\nu} \text{Semithionine } (A^{*})$

$$\text{Semithionine } (A^{*}) + \text{Fe(II)(Z)} \xrightarrow{k'} \text{Leucothionine (B)} + \text{Fe(III) (Y)}$$

Electrochemistry:

At the illuminated electrode

$$\text{Leucothionine (B)} - e \longrightarrow \text{Thionine (A)}$$

At the dark electrode

$$\text{Fe(III)(Y)} + e \longrightarrow \text{Fe(II)(Z)}$$

For an efficient cell it is obvious that one must avoid the thermal back reaction of B and Y described by the rate constant k'. Hence one of the problems with this type of device is that the homogeneous kinetics may destroy the energetic species B and Y. A crucial requirement for the photogalvanic cell is that the illuminated electrode should be selective. If the illuminated electrode is not selective between B and Y then we will have

$$\begin{array}{ll} & B \pm e \longrightarrow A \\ \text{and} & Y \pm e \longrightarrow Z \\ \hline & B + Y \rightarrow A + Z \end{array}$$

The beastly electrode is merely an efficient catalyst for the back reaction.

The Electrode Kinetics

At the illuminated electrode, we need the A, B couple to be reversible so that B is easily converted to A, but we also require that as far as possible, the conversion of Y to Z is blocked. The electrode will then be close to the standard electrode potential of the A, B couple $E_{A,B}$. Very little B reaches the dark electrode because the illuminated electrode is close to the region where B is generated (10^{-4} cm) as opposed to the dark electrode being far (10^{-2} cm) away. This means that the dark electrode has merely to convert the photo generated Y back to Z at a potential close to the standard electrode potential of the Y,Z couple, $E_{Y,Z}$. In fact if there is little concentration polarization, and if the Y,Z couple is reversible, the dark electrode potential will shift very little when the cell is illuminated. The change in voltage on illumination occurs at the illuminated electrode from the manyfold increase in the concentration of B.

The problem with thionine as a constituent of a photogalvanic cell is that, although its kinetics of reaction has a satisfactory value, its solubility is far too low to achieve an optimum result. Thus it is impossible, using thionine, to achieve the necessary optimum conditions. Attempts have been taken to overcome these problems by using acetonitrile as a solvent. Even so, the solubility is not sufficient. Furthermore, there is another problem in that thionine forms dimers at concentration $\sim 10^{-3}$M. These dimers are inactive from the point of view of the photoredox system, the energy is lost by internal **quenching** in the dimer.

Self Quenching:

A problem with increasing concentration of the dye is that there may be self quenching of Thionine* by Thionine. Moreover, dimer and higher aggretates of dye are shown to undergo efficient internal quenching. As a result absorption of light by ground state thionine dimer resulted in little, if any, transduction to electricity in a totally illuminated, thin layer acidic iron-thionine cell with water as solvent and with a 1.2×10^{-3}M stoichiometric concentration of thionine (21). The most effective materials for use as solar harvesters will be those that absorb strongly in the visible and near-UV regions of the spectrum. Even if all the other characteristics of photogalvanic cells employing thionine were perfectly efficient, such cells would be limited by the fraction of the solar output absorbed by the solution.

It being shame to waste all those potentially perfectly good solar photons, approaches must be taken to improve the absorption characteristics of the medium, especially to the red; there is no lack of chromophores for the UV region. Molecular modification of thionine to methylene blue results in a substantial shift of λ_{max} from 595 nm to 665 nm ($\epsilon_{thionine} = 4.4 \times 10^4$, $\epsilon_{Methylene\ blue} = 5.6 \times 10^4\ M^{-1}cm^{-1}$) (Chapter 3).

In most cases, the intense visible absorption bands and those further to the blue are separated by regions of significantly lower absorbance. In order to utilise those solar photons, sensitizers can be employed to absorb light and transfer energy from the excited state of the sensitizer to the photochemically active species. The requirement is for the energy of the excited state of the donor to be higher than the energy required to reach the populated excited state of the acceptor.

Electrode Selectivity

We now turn from the processes occurring in the bulk of the solution to the kinetics of the electrode reactions. Regardless of the type of photogalvanic cell, efficient electron transfer must occur between photochemically-generated separate charge carriers and appropriate electrodes.

If practical photogalvanic (PG) cells are ever achieved, it appears likely that electrodes selective to particular redox couples will be employed. Selectivity is not, however, the only requirement. In addition, the electrode must not catalyze back reaction of charge carriers on its surface. Such back reaction is equivalent to shorting a circuit in parallel with load. It is vital that the illuminated electrode should discriminate between the photogenerated products, in general B and Y (page 5), or in particular leucothionine and Fe(III). Thus, in the photogalvanic cells the selective electrode separates both B and Y and prevents their recombination. That is why, it is a vital part of the cell. For example, the SnO_2 electrode is more selective to the thionine/leucothionine couple rather than the Fe^{+3}/Fe^{+2} couple, as shown by Clark and Eckert (14). Investigations with different carbon materials as light electrodes have also shown that although the leucothionine oxidation is fast on all types of carbon materials (reticulated vitreous carbon, carbon paste, glassy carbon, pyrolytic graphite and carbon cloth), the Fe^{+3}/Fe^{+2} electron transfer is slow (22). Electrode modification is another approach. Albery and co-workers (23) have found that Pt or SnO_2 electrodes modified with coatings of thionine of upto 20 monolayers could discriminate between photogenerated leucothionine and Fe^{+3} and hence are suitable for an iron-thionine PG cell. Murthy and Reddy (24) have shown that only pyrrole-modified electrodes are more selective to Fe^{+3}/Fe^{+2} rather than to thionine/leucothionine couple. The nature of anions present in the solution also sometimes influences the cell output by possibly altering the rate of thermal bulk reaction. The addition of Triton X-100 micelles also suppressed the thermal back-reactions increasing the power of the cell by a factor of five (22).

Dye-incorporated modified electrode

Clay-modified electrodes have attracted the attention of many electrochemists because of the ion-exchange properties of the clay and because of the unique layered structure of the material (25). Kamat (26) successfully incorporated thionine in the clay films cast on SnO_2 and Pt-electrodes. Though the sunlight engineering efficiency of the photogalvanic cell employing thionine incorporated clay-modified electrode in the present case was very poor (10^{-4} %), such a modified electrode possesses several attractive features:

(1) a high concentration of the photo active dye species can be achieved at the electrode surface.

(2) because of the small thickness of the film, the incident photons are efficiently absorbed by the dye molecules present near the electrode surface.

If the electrochemical experiment is carried out at a modified electrode, the area of the conductive channel can play an important role in defining the type of diffusion behaviour observed. For example, all the parameters accessible to the electrochemist depend upon the competitive exchange reaction as shown for a trivalent/ monovalent exchange reaction.

$$A^{3+} + 3NaX = A^{3+}X_3 + 3Na^+ \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

where A^{3+} is an exchanging trivalent species, NaX is a single clay (montmorillonite) site containing a Na^+ counter ion, and $A^{3+}X_3$ is the clay exchanged with trivalent species. The selectivity coefficient for the exchange is

$$K_{III} = \left[Na^+\right]^3 \left[A^{3+}X_3\right] \Big/ \left[A^{3+}\right] \left[NaX\right]^3 \quad \ldots \quad \ldots \quad \ldots \quad (6)$$

The magnitude of diffusion co-efficient D is directly dependent on the distance, d, between equilibrium sites, and exponentially dependent on $-E/RT$, where E is the activation energy necessary to leave the equilibrium site (27). E is related to K_{III}, or analogously, to K_{II}, for a divalent species. As the energy of interaction between a site and an intercalated molecule increases, the diffusion coefficient diminishes. Also, as the number of sites increases, the distance between sites decreases, so that the distance travelled in any one "hop" is small and the observed diffusion coefficient decreases. The magnitude of concentration, C in modified layer, and formal potential E^o, for any bathing solution are also determined by the value of the slectivity coefficient. Finally, combining expressions for divalent and trivalent exchange with the Nernst equation yield an expression for the shift (ΔE) in the observed formal potential in the film ($E^o_{app.}$) with respect to the solution formal potential ($E^o_{soln.}$) of the couple.

$$\begin{aligned}\Delta E &= E^{\circ}_{app.} - E_{Soln.} \\ &= (RT/nF)\ \ln\left(K_{\underline{II}}/K_{\underline{III}}\ [NaCl]\right) \\ &\qquad + (RT/nF)\ \ln C_{Na} \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (7)\end{aligned}$$

In equation 7, [NaCl] is the number of exchange sites occupied by Na^+ and C_{Na} is the analytical concentration of Na^+, which approximates the equilibrium concentration of Na^+ if the bulk solution volume is large with respect to the volume of the film on the surface of the electrode. If the clay-modified electrode is exposed to a solution containing only the Na^+ electrolyte and a trivalent exchanging complex, the potential shifts positive as a function of the analytical concentration of the trivalent complex, and the total number of exchange sites, if C_{Na} is constant. The shift in potential is a function of the magnitude of the trivalent/Na^+ exchange constant.

The preliminary study of clay-modified electrode has indicated the feasibility of dye incorporated clay films in the photogalvanic conversion of light energy into electricity. Better understanding of the interaction between the clay and the dye is necessary in order to improve the performances of such photogalvanic transducers (26).