CHAPTER 1

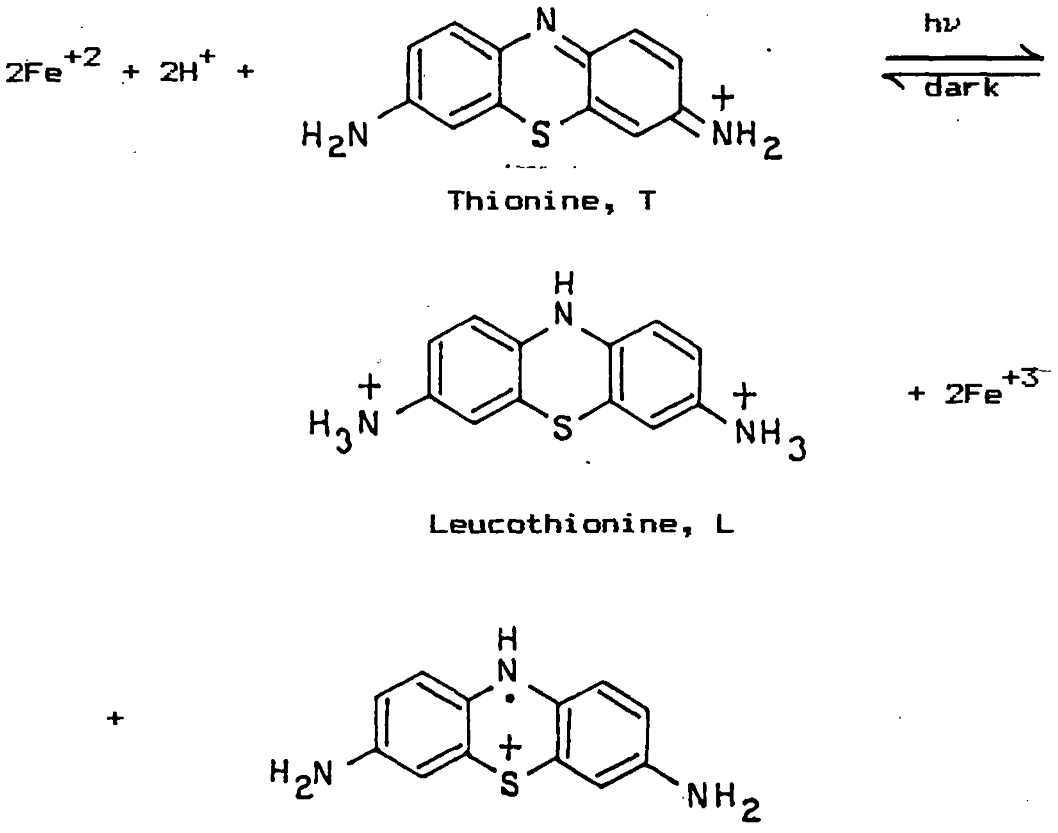
INTRODUCTION:

In recent years there has been an increasing interest in systems which enable the conversion of solar energy into electrical or chemical energy (1-4). Many types of systems have been proposed and studied experimentally, the fundamentals of which extend from solid state physics to photo-electrochemistry. For most of the systems considered excitation of an electron by absorption of a photon is followed by charge separation at an interface. It follows that the different fields involved (photovoltaics, photo-electrochemistry, photogalvanics, etc.) have several essential aspects in common. Although photo-electrochemical studies commenced with the observation of Becquerel (5) in 1839, the mechanism of photovoltage generation in photosensitive electrode / electrolyte systems are still at an early stage of development.

A mumber of analyses of the general thermodynamic and kinetic aspects of the electrical output of photogalvanic cells (PG) have been published (6,7). It is inconvenient to separate such analyses completely from devices specifies. After the discovery over sixty years ago (8,9) that thionine is reversibly photoreduced by Fe^{+2} in acidic aqueous solution, Robinowitch (10) explored the possibility of utilizing 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 the leuco-thionine 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 Nerst expression,

$$E_{dark} = E^{0}_{Fe} + 0.058 \log ([Fe^{+3}]/ [Fe^{+2}])_{dark} \qquad (1)$$

Where E^{0}_{Fe} is the standard reduction potential of the $[Fe^{+3}]/[Fe^{+2}]$ couple and the terms in the square brackets represents 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 (11). 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 columbs, E_{light} is the potential of the illuminated electrode, E^{0}_{Fe} is the standard reduction potential of the Fe^{+3}/ Fe^{+2} couple.



Thionine, T

Leucothionine, L

Semithionine, S

$E^0_{T\to S}$ is the standard potential for the one electron reduction of thionine, and $E^0_{S\to L}$ is the standard potential for the one electron reduction of the semithionine. The terms in the square brackets represent the activities of the various species in the photostationary state.

$$\exp(fE_{light}) = \frac{[Fe^{+3}]\ \exp(fE^0_{Fe/2}) + 2[T]\ \exp(fE^0_{T\to S}/2)}{[Fe^{+2}]\ \exp(-fE^0_{Fe/2}) + 2[L]\ \exp(-fE^0_{T\to S}/2)} \qquad (2)$$

The potential of the PG cell under the open circuit photostationary condition is equal to the $E_{dark} - E_{light}$ as calculated from equation 1 and 2. The current produced by such PG cell with ideally reversible electrodes depends on the composition of the bulk solution in the photostationary state under the short circuit or the 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 is the number of redox equivalents per mole of a given charge carrier, F is the Faraday,

$$i = nFADC/\delta \qquad (3)$$

A is the electrode area, D is the diffusion coefficient of a given charge carrier, C is the concentration of given chagre 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

$$\text{S.E.E.} = \frac{\text{Electrical power or energy delivered to load}}{\text{Incident Sun light power or energy}} \times 100 \qquad (4)$$

The totally illuminated thin layer (TI-TL) PG cell was first described by Clark and Eckert (12) and a number of stydies of the behaviour of the iron-thionine (11, 13-18) photoredox system in such cells have been reported. In TI-TL cells, atleast 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 . Unfortunately, in homogeneous solution, thermal back reaction of electron transfer also takes place. This dissipation of free energy constitutes a considerable problem in the use of iron-thionine cell for practical purposes. However, the following reaction scheme adequately summerizes the whole process, including the relevant recombination reaction :

Solution :

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

Photochemistry :

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

$$\text{Semithionine (A*)} + \text{Fe(II) (Z)} \longrightarrow \text{Leucothionine (B)} + \text{Fe(III) (Y)}$$

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. Hence one of the problems with this type of device is that the honmogeneous kinetics may destroy the energetic species B and Y. A crucial requirement for the PG cell is that the illuminated electrode should be selective. If the illuminated electrode is not selective between B and Y then we will have

$$B \pm e \longrightarrow A$$

and

$$Y \pm e \longrightarrow Z$$

$$\overline{}$$

$$B + Y \longrightarrow A + Z$$

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 as opposed to the dark electrode being far 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 many fold increase in the concentration of B.

The problem with thionine as a constituent of a photogavanic 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 made to overcome these problems using non-aqueous organic solvents. Even so, the solubility is not sufficient. Various substitution in the thionine molecule may increase the solubility to a great extent. Moreover, there is another problem that thionine forms dimers and higher aggregates at concentration above 10^{-5} 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 aggregates of the 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 (19). Thus, the most effective materials for use as solar harvesters will be those that absorb strongly in the visible and near UV region 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 is, therefore, necessary to improve the absorption characteristics of the medium as well. Molecular modification of thionine to methylene blue results in a substantial shift of λ_{max} from 595 nm to 660 nm ($\epsilon_{thionine} = 6.16\times10^{4}$, $\epsilon_{methyleneblue} = 7.2\times10^{4}M^{-1}Cm^{-1}$) (chapter 3)

In most cases, the intense visible absorption bands and those further to the blue are separated by region of significantly lower absorbance. In order to utilize 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 occuring in the bulk of the solution to the kinetics of the eletrode reactions. Regardless of the type of the ptotogalvanic cell, efficient electron transfer must occur between photochemically generated separate charge carriers and appropriate elctrodes.

If practical photogalvanic cells are ever achived, 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 catalize 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, B and Y (page.6) in general, or in particular leucothionine and Fe (III). Thus, in the PG cells the selective electrodes separate both B and Y and prevent 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 (12). 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 (20). Electrode modification is another approach. Albery and coworkers (21) have found that Pt and 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 (22) have shown that poly pyrrole modified elctrodes are more selective to Fe^{+3}/ Fe^{+2} rather than to thionine/leucothionine couple. Moreover, molecular modification of thionine must also affect the thermal back reaction to a great extent. The rate constants for the methylene blue system are always larger than those for the thionine system and the PG outputs for the Fe^{+2}-methylene blue system are less than those from the Fe^{+2}-thionine system. The additon of Triton X-100 micelles also suppressed the back reactions increasing the power of the cell by a factor of five (20).

Dye Incorporated Modified Electrode :

Not satisfied with electrode surfaces that passively accept or provide electrons or content with elctrode surfaces that actively accelerate or hinder certain elctron transfer reactions chemists in the last 20 years have turned to designing chemical structures on electrode surfaces that redefine the chemical and physical microenvironment in which heterogeneous electron transfer reactions occur (23). Inherent in many inorganic materials (e.g. clay, zeolite etc.) are pores, channels, or layer spacings of molecular dimensions. These molecular gateways impart a selective screen, so that differentiation results on the basis of molecular size or shapes of solutes. Further discrimination arises if fixed charged sites are part of the inorganic lattice, producing an ionic filter as well. In these senses, the inorganic layer can "act" as a passive discriminator, allowing, e.g., preconcentration of an analyte or reactant (24).

Kamat (25) successfully incorporated thionine in the clay films cast on SnO_2 and Pt electrodes. Though the sunlight engneering efficiency of the PG cell employing thionine incorporated clay modified electrode in the present case was very poor (10^{-4}%), such a modified electrode possesses several attractive features :

(i) a high concentration of the photoactive dye species can be achieved at the electrode surface.

(ii) 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.

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

Where A^{+3} is an exchanging trivalent species, NaX is a single clay (smectite) 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,

$$K_{III} = [\ Na^{+}]^{3}\ [\ Al^{3+}\ X_3\ ]\ /\ [\ A^{3+}]\ [\ NaX\ ]^{3} \qquad (6)$$

The magnitude of the diffusion coefficient 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 (26). 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 the 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^0, for any bathing solution are also determined by the value of the selectivity coefficient. Finally, cobining expressions for divalent and trivalent exchange with the Nerst equation yield an expression for the shift (ΔE) in the observed formal potential in the film (E^0_{app}) with respect to the solution formal potential ($E^0_{solution}$) of the couple

$$\Delta E = E^0_{app} - E^0_{solution}$$

$$= (RT/nF) \ln (K_{II}/K_{III}) [NaCl]) + (RT/nF) \ln C_{Na} \qquad (7)$$

where, [NaCl] is the number of exchange sites occupied by the 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 the clay modified electrode has indicated the feasibility of dye incorporated clay films in the photogalvanic conversion of light enrgy into electricity. Recent reviews on the material science aspects of zeolites and the use of clays and zeolites to coat electrodes have included the discussions on the use of and interest in zeolite layers on electrodes too. However, better understanding of the interaction between the dye and both clay and zeolite is necessary in order to improve their performances viz, PG transducers (25)