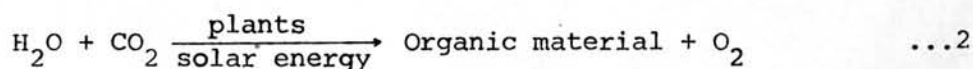


## CHAPTER II

### DIRECT SOLAR ENERGY CHEMICAL REACTIONS



The outstanding example of chemical production in nature is photosynthesis. It is the key process in life and as developed by plants can be simply represented as



In the past photosynthetic products have accumulated in the form of coal, oil and gas, fuelwood, food, fibres and chemicals. Each year plant photosynthesis fixes about  $2 \times 10^{11}$  tons of carbon with an energy content of  $3 \times 10^{21}$  J, even though the photosynthesis process is operating at only a 0.1 % efficiency, while total incoming solar radiation is about  $3 \times 10^{24}$  J per year on the earth's surface<sup>(13)</sup>

Unfortunately reserves of the fossil fuel are being depleted rapidly, it seems necessary now to look how photosynthesis fits into the biosphere and how we could possible construct artificial systems.

In plants, the oxygen from water decomposition is released to the atmosphere while the hydrogen is used for reduction of carbon dioxide to carbohydrate (via Eq.2). According to the burden of so many limiting factors (internal and external) for plant photosynthesis operation, the possible duplicated process is the photodecomposition of water, giving hydrogen gas molecules. Many investigators have produced hydrogen by light-activated water decomposition using the photoelectrochemical cells

(see chapter IV). Recently carbon dioxide reduction has also been demonstrated for organic compounds (formaldehyde, methanal, etc.) by photoelectrocatalytic cells.

## 2.1 General Principles

### 2.1.1 The Solar Spectral Distribution

The raw energy input solar photochemical processes is sunlight outside the earth's atmosphere. Wherever, upon entering the earth's atmosphere, certain regions of the spectrum are strongly absorbed the solar spectral distribution at the earth's surface is considerably different from the AM 0 radiation, which has a total irradiance of  $1353 \text{ Wm}^{-2}$ . AM 0 refers to the intensity and spectral distribution of sunlight outside the earth's atmosphere; AM 1.0 to the sunlight at the zenith. Under the best conditions, only about 75 % of the AM 0 radiation reaches the earth's surface : about  $1.01 \text{ kWm}^{-2}$  (13)

The spectral energy distribution is not exactly equal to that of a black body at the effective temperature, 5800 K, and approximates more closely, but still not exactly (Figure 2.1.1). Molecules in the earth's atmosphere, absorb solar radiation, forming isolated lines throughout the spectrum. But in certain parts of the infrared region there are absorption bands of atmosphere water vapour and, to a lesser extent,  $\text{CO}_2$  and other gases such as  $\text{O}_2$ ,  $\text{N}_2\text{O}$  and  $\text{O}_3$ , and these produce heavy absorption. From figure 2.1.1, most of the radiation lies between  $0.3 \mu\text{m}$  (the near ultraviolet) and  $2.5 \mu\text{m}$  (middle infrared), and about one-half falls in the range  $0.4$  to  $0.7 \mu\text{m}$  which is in the visible range, Later, this will be seen to be important when selective absorbers are considered, the variation in

the spectral distribution of sunlight under various condition affects the fraction of solar energy available for direct conversion processes.

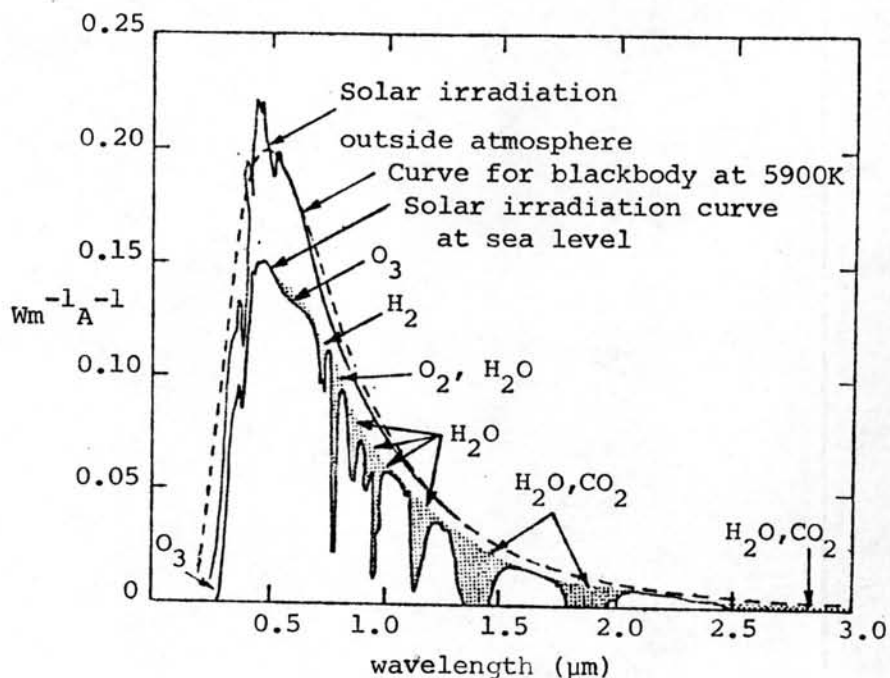


Figure 2.1.1<sup>(63)</sup> Spectral distribution curves related to the sun; shaded areas indicate absorption, at sea level, due to the atmospheric constituents shown.

### 2.1.2 Limits on the Conversion of Light Energy to Chemical Energy.

Direct solar energy conversion systems are threshold devices in which there is a minimum energy, called the band gap energy,  $E_g$  (with a corresponding maximum band gap wavelength  $\lambda_g$  by  $E_g = hc/\lambda_g$ ), which can initiate the photochemical processes. Hence, it is important to know what fraction of the incident solar power is available at the band gap energy. The result is shown as a curve in Figure 2.1.2a. It is a common misconception of many scientists that  $\eta$  represents the maximum fraction of solar power that can be converted to electricity or chemical energy. Bolton<sup>(12)</sup> published the quantitative evaluation of  $\eta_E$ , if  $N_s(\lambda)$  is the incident solar

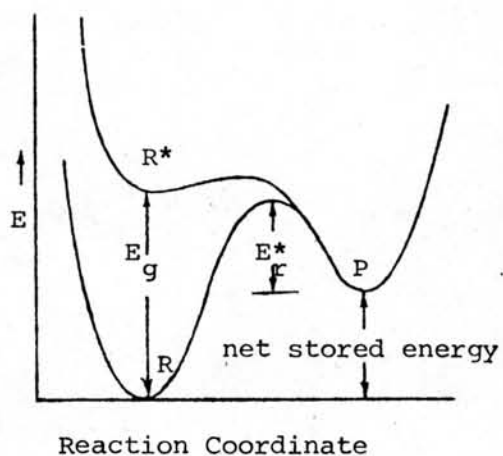


Figure 2.1.2a Energy profile for a general endergonic photochemical reaction  $R \rightarrow P$ .  $E_g$  is the bandgap energy corresponding to the minimum energy gap between the excited state  $R^*$  and the ground state  $R$ .  $E_r^*$  is the back reaction  $P \rightarrow R$ . (12)

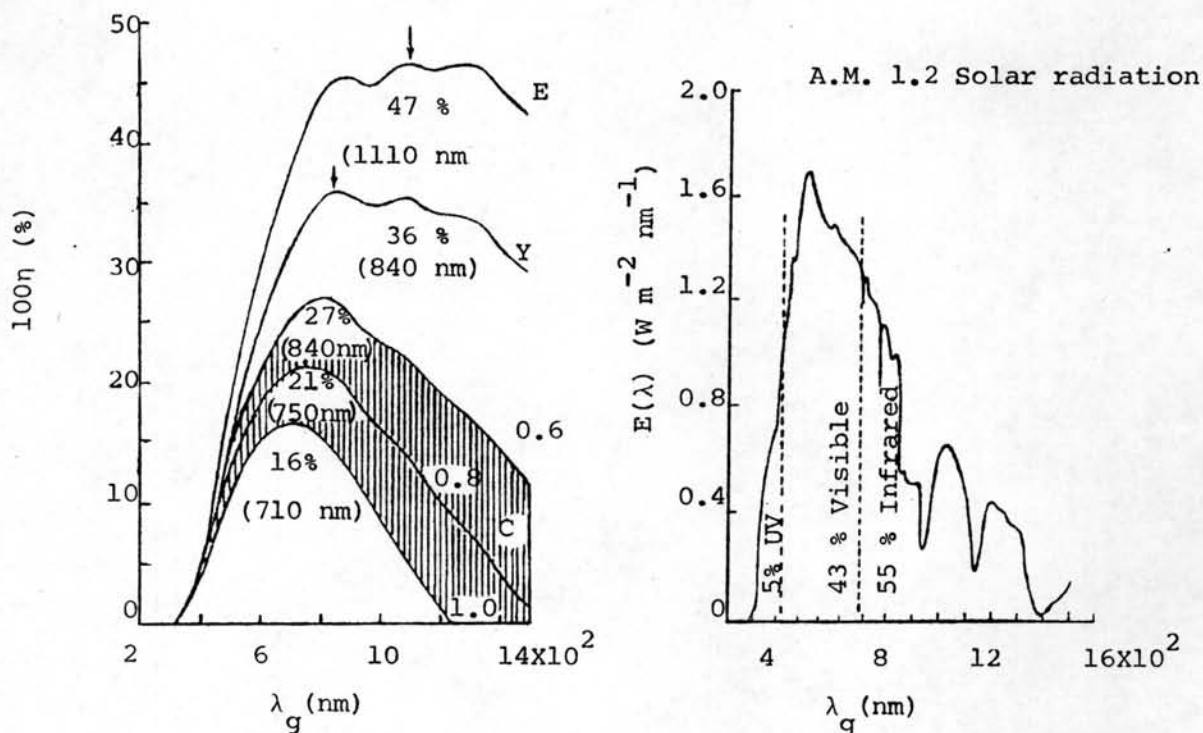


Figure 2.1.2b Plots of the efficiencies  $\eta_E$ ,  $\eta_Y$ , and  $\eta_C$  as a function of the wavelength  $\lambda_g$  corresponding to the energy gap  $E_g$ . The distributions have been calculated for AM 1.2 solar radiation. Note that these curves have been calculated for an ideal absorber in which the absorption coefficient  $a(\lambda)$  is 1.0 for  $\lambda \leq \lambda_g$  and 0 for  $\lambda > \lambda_g$ . (13)

photon flux in the wavelength band from  $\lambda$  to  $\lambda+d\lambda$  (in photon per square meter per second per nanometer) and  $\alpha(\lambda)$  is the absorption coefficient of the absorber, then the absorbed flux of photons with  $\lambda < \lambda_g$  is given by

$$J_e = \int_0^{\lambda_g} N_s(\lambda) \alpha(\lambda) d\lambda \quad \dots 2.1.2a$$

The available solar power  $E$  (in watts per square meter) at the band energy is thus

$$E = J_e \cdot hc/\lambda_g \quad \dots 2.1.2b$$

where  $h$  is Planck's constant, and  $c$  is the speed of light. Then the fraction  $\eta_E$  of the incident solar power available to initiate photochemistry is

$$\eta_E = E / \int_0^{\infty} E(\lambda) d\lambda \quad \dots 2.1.2c$$

Many investigators have treated the problem of thermodynamic and kinetic limits on the conversion of light to chemical energy. Ross and Hsiao<sup>(12)</sup> derived the maximum thermodynamic photochemical power yield possible while was then

$$Y = J_e \cdot \mu_{\max} / N_0 \quad \dots 2.1.2d$$

where  $\mu_{\max}$  was the maximum chemical potential;

$$\mu_{\max} = N_0 hc/\lambda_g + RT \ln \int_0^{\lambda_g} N_s(\lambda) d\lambda - RT \ln(2\pi n^2 kT/h\lambda_g^2),$$

$N_0$  is Avogadro's number,  $n$  is the refractive index of the medium, and  $k$  is the Boltzmann constant. The maximum thermodynamic efficiency is given by

$$\eta_Y = Y / \int_0^{\infty} E(\lambda) d\lambda \quad \dots 2.1.2e$$

However, the requirement of energy storage imposes an additional kinetic requirement, thus for consideration of the limits on energy storage, Bolton developed a kinetic argument. From Figure 2.1.2a, the conversion of  $R^*$  to  $P$  must be an exergonic reaction so that an activation energy  $E_r^*$  for the back reaction was established otherwise, the state  $P$  would have no stability for

storage energy. If the photochemical step was first order, he could apply unimolecular rate theory to calculate  $E_r^*$  (in electron volts)

$$E_r^* = -(kT/q) \cdot \ln(h/kT\tau) \quad \dots 2.1.2f$$

where  $q$  is the charge on the electron and  $\tau$  is the lifetime of the primary products assuming that the only reaction possible is the back reaction.

The creation of this activation barrier must be done at the expense of the excitation energy, and the loss was constant and independent of  $\lambda_g$ . Thus he defined a chemical yield  $C$ ,

$$C = E \cdot \eta_{\text{chem}} \quad \dots 2.1.2g$$

and

$$\eta_{\text{chem}} = \Delta G/E_g$$

where  $\Delta G$  is the net free energy storage in the photochemical step. Then

$$\eta_C = C / \int_0^{\infty} E(\lambda) d\lambda = \eta_E \cdot \eta_{\text{chem}} \quad \dots 2.1.2h$$

The quantities of the efficiencies  $\eta_E$ ,  $\eta_Y$  and  $\eta_C$  were plotted as curves E, Y and C respectively in Figure 2.1.2b. The ideal maximum value of  $\eta_E$  as a function of  $\lambda_g$  was calculated from Eq 2.1.2c. For the ideal assumption,  $\alpha(\lambda) = 1$  for  $\lambda \leq \lambda_g$  and  $\alpha(\lambda) = 0$  for  $\lambda > \lambda_g$ ,  $\eta_E$  had a maximum value of 47 % at 1110 nm for AM 1.2 (a bright sunny day near noon). The  $\eta_Y$  of Eq. 2.1.2e, under conditions where there is no net storage of energy, the chemical potential ( $\mu$ ) will have its maximum value  $\mu_{\text{max}}$ . The quantity  $\eta$  was plotted as curve C in Figure 2.1.2b, assuming that  $E_r^* - E_p^C = 0.6$  eV, 0.8 eV and 1.0 eV, the curve maximize at 27 % for 840 nm, 21 % for 750 nm and 16 % for 710 nm.

However, there are other loss factors to be considered which vary according to the device, Botton gave the practical estimate for solar energy conversion efficiency by equation<sup>(13)</sup>

$$\eta_{\text{storage}} = \eta_{\text{abs}} \cdot \eta_{\text{c}} \cdot \eta_{\phi} \cdot \eta_{\text{coll}}$$

where  $\eta_{\text{abs}}$  was fraction of light, with  $\lambda \leq \lambda_g$ , which was absorbed by the device,  $\eta_{\text{c}}$  was the chemical conversion efficiency,  $\eta_{\phi}$  was the quantum yield for the conversion process, and  $\eta_{\text{coll}}$  was the fraction of product of product produced that can be collected and stored. Using the optimistic values of  $\eta_{\text{abs}} = 0.75$ ,  $\eta_{\phi} = \eta_{\text{coll}} = 0.9$ . Botton came to the conclusion that  $\eta_{\text{storage}}$  was unlikely to be much greater than 12-13 %. This figure should not be discouraging because photosynthesis, which must be considered a very useful process, has a net efficiency of 6 % under ideal conditions and 1 to 3 % under actual field conditions (see 2.3.2).

### 2.1.3 Some Possible Fuel-Generation Reactions

There are many possible redox reactions that could be used to store solar energy, it would be more desirable, from a practical standpoint, to generate a fuel this is already in use from fossil fuel sources. Thus, Botton<sup>(12)</sup> demonstrated a limited of definition of a fuel as any reduced chemical substance producted as a result of an endergonic reaction which, on reaction with oxygen, released the stored chemical energy.

A general reaction producing a fuel F was hence written as



One of the important requirement is that the reactants may be cheap and readily available. Naturally, constituents of the atmosphere and liquid water fill this requirement admirably. Table 2.1.3 lists most of the

Table 2.1.3 Some endergonic fuel generation reactions starting with  $N_2$ ,  $CO_2$  and  $H_2O$  (12)

Reaction	$\lambda_{\max}$		$\Delta E^\circ$ (V)	$n^a$	$\Delta G^\circ$ (kJ mol $^{-1}$ )	$\Delta H^\circ$ (kJ mol $^{-1}$ )	$\lambda_{\max}$	
	one (nm) <sup>b</sup>	photosystem (nm) <sup>b</sup>					two (nm) <sup>b</sup>	photosystem (nm) <sup>b</sup>
$H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$	611		1.23	2	237	286	611	877
$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g)$	581		1.33	2	257	283	581	845
$CO_2(g) + H_2O(l) \rightarrow HCOOH(l) + \frac{1}{2}O_2(g)$	543		1.48	2	286	270	543	804
$CO_2(g) + H_2O(l) \rightarrow HCHO(g) + O_2(g)$	576		1.35	4	522	563	576	840
$CO_2(g) + 2H_2O(l) \rightarrow CH_3OH(l) + \frac{3}{2}O_2(g)$	616		1.21	6	703	727	616	881
$CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$	667		1.06	8	818	890	667	932
$N_2(g) + 3H_2O(l) \rightarrow 2NH_3(g) + \frac{3}{2}O_2(g)$	629		1.17	6	678	765	629	895
$CO_2(g) + H_2O(l) \rightarrow \frac{1}{6}C_6H_{12}O_6(s) + O_2(g)$	607		1.24	4	480	467	607	872

$n^a$  is the number of electrons that should be transferred in an electrochemical reaction for the reaction as written.

$b$   $\lambda_{\max}$  is calculated from Eq. 2.1.3c.



endergonic fuel-generation reactions that use nitrogen, carbon dioxide and water as reactants.

It is significant that the potential difference  $\Delta E^{\circ}$ , which in electron volts is the potential energy stored per electron transferred, is between 1.06 V and 1.48 V for all the reactions in Table 2.1.3.

Thus the requirements for the photochemical energy storage are about the same for each of these reactions. In the last two columns of the table, the threshold wavelengths are calculated from

$$\lambda_{\max} = nNohc\eta_{\text{chem}}/\Delta G \quad \dots 2.1.3b$$

where  $n$  is the number of photons that must be absorbed to carry out the overall reaction and  $\Delta G$  is the free energy change in the reaction. Bottom assumed that 0.8 eV must be lost in each photochemical step, then  $\eta_{\text{chem}}$  would be given by

$$\eta_{\text{chem}} = \Delta G/(\Delta G + 0.8 nqNo.) \quad \dots 2.1.3c$$

For example of the last reaction in the table, the photosynthetic reaction (see 2.3)  $\lambda_{\max}$  of two photosystems operating in series are 670 and 700 nm, eight photons are used to drive the reaction instead of four. Now  $\lambda_{\max}$  is 872 nm (from Table 2.1.3), which leave of the tree plenty of scope for an absorber at 700 nm. Therefore, if you wish to have an efficient energy storage reaction which will utilize the abundant photons in the visible region of the solar spectrum, it is likely that more success will be achieved if attention is given to photochemical processes employing two coupled reactions so that two photons are used for every electron transferred in the ultimate reactions.

#### 2.1.4 General Requirements for the Photochemical Reactions

Many authors have considered the general requirements for photochemical solar conversion and storage reactions. In summary, they are:

- i. The photochemical reaction must be endothermic.
- ii. The process must cyclic.
- iii. Side reactions leading to the irreversible degradation of the photochemical reactions must be totally absent.
- iv. The reaction should be capable of operating over a wide bandwidth of the ultraviolet, visible and near infrared portions of the solar spectrum, with a threshold wavelength well into the red or near infrared.
- v. The quantum yield for the photochemical reaction should be as high as possible.

In addition, there are some requirements that apply particularly to photochemical storage reactions:

- vi. The back reaction must be extremely slow under ambient conditions to permit long-term storage, but should proceed rapidly under special controlled catalytic conditions or at elevated temperatures, to release the stored energy when needed.
- vii. The products of the photochemical reactions should be easy to store and transport.
- viii. The reagents and any container material should be cheap and the reaction should be unaffected by oxygen.

At present, the natural photochemical storage systems that meet nearly all of the above requirements is photosynthesis, however, certain photoelectrochemical cell and photocatalytic cell, satisfy the requirements

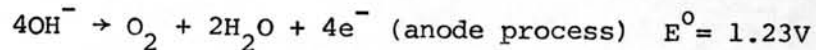
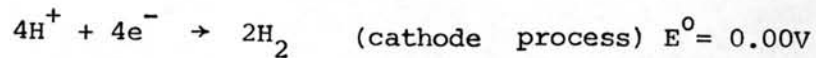
for direct conversion to chemicals. In addition, the photovoltaic cells such as the silicon and GaAs cells, they are the most satisfactory for direct conversion to electricity (see Appendix A.2)

## 2.2 Some Man-made Photochemical Reactions

### 2.2.1 H<sub>2</sub> production

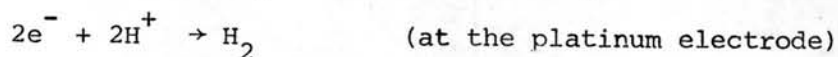
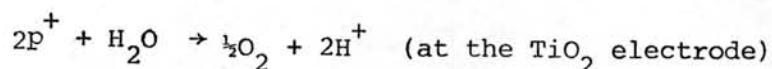
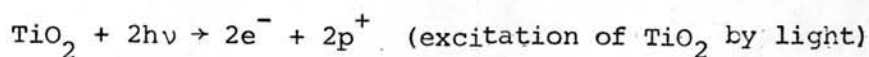
There are many ways<sup>(16)</sup> to produce hydrogen commercially, and electrolysis of water is a well-known method. In all, the external source applies a difference in voltage (potential) across the electrodes, which is necessary to cause electrons to flow properly in the aqueous electrolyte to allow electrolysis (see Appendix A.3). The theoretically required potential difference is 1.23 V, with aqueous solution as the electrolyte, but it has been found that about 1.5 V is necessary for continuous satisfactory operation.

In this way, it is easier to understand that oxidation-reduction (redox) reactions that occur at the electrodes are primarily affecting component of the water electrolyte. This situation can be represented, as discussed by Wrighton<sup>(17)</sup>,



The last formula listed above is a standard representation (at 25°C and pressures of P<sub>O<sub>2</sub></sub>, P<sub>H<sub>2</sub></sub> of 1 atm) of electrolysis of water. This difference of 1.23 V is equivalent to the energy of radiation with a wavelength of approximately 1000 nm<sup>(31)</sup>. Therefore, if the energy of light is used effectively in an electrochemical system, it should be possible to decompose water with visible light. In 1972 two Japanese researchers, Fujishima

and Honda, began to describe a novel type of electrochemical photocell ( see chapterIV) which decomposed water in this way. They had connected a wafer of n -type titanium dioxide ( $\text{TiO}_2$ ) to a platinum counterelectrode, both of which were immersed in an aqueous electrochemical cell. They then exposed the  $\text{TiO}_2$  electrode to an emission of light, thus causing a photovoltage to occur in the cell sufficient to dissociate water into hydrogen and oxygen, without the applications of any external voltage, according to the following schemes: (31)



The overall reaction is



The main significance of this finding and their subsequent work was the resulting possibility that a similar, more developed, cell may be able to split water with solar insolation as the sole energy input. The achievement of such a device would allow for large-scale, inexpensive, reliable production of hydrogen. They demonstrated the production of hydrogen under sunlight with an electrochemical photocell (Figure 2.2.1a) with thin film  $\text{TiO}_2$  electrodes in 1975. (33) From Figure 2.2.1b, they estimated the energy conversion efficiency of the photocell to be more than 0.4 %. The calculation of efficiency is not clear in this paper, but another report of this efficiency was discussed and then assumed the solar intensity to be only  $40 \text{ mW/cm}^2$ . (36)

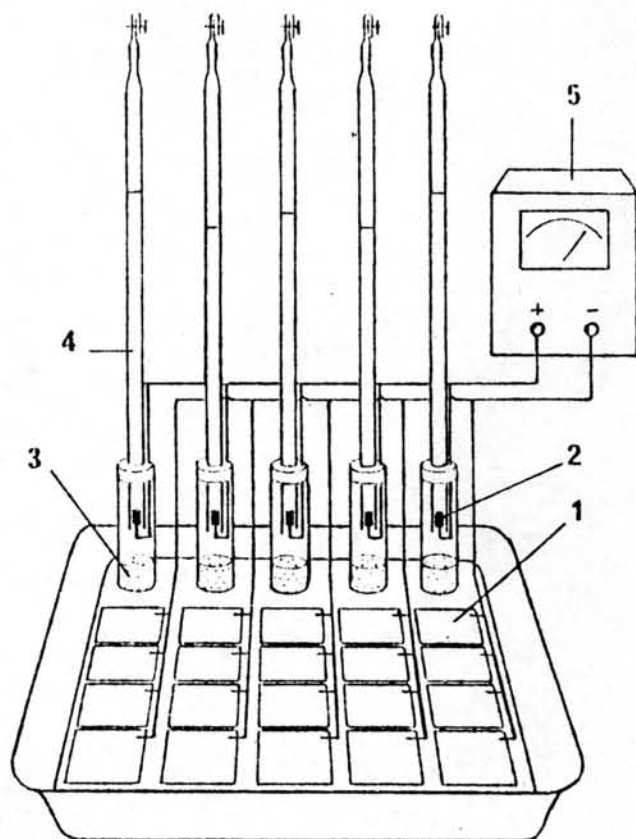


Figure 2.2.1a The geometric arrangement of the electrochemical photocell.

- (1) Anodes coated with titanium dioxide film,
- (2) platinum black cathodes,
- (3) agar salt bridges,
- (4) gas burettes,
- (5) ammeter.

Anolyte : 1M NaOH,  
 catholyte = 0.5M H<sub>2</sub>SO<sub>4</sub>

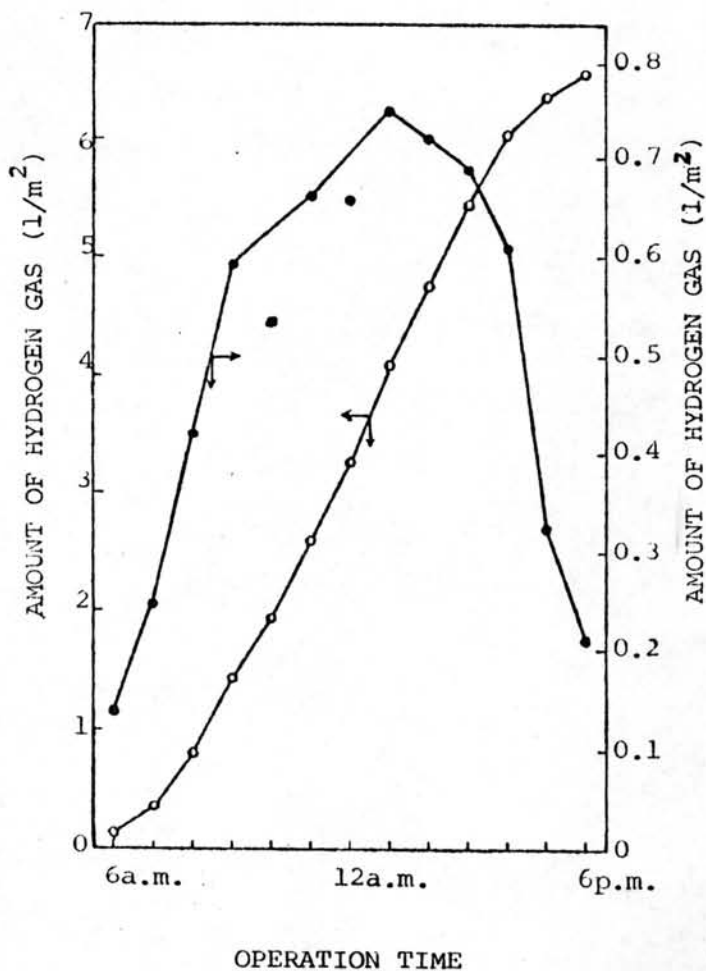


Figure 2.2.1b Hydrogen evolution by the electrochemical photocell under the sunlight. ○: Total amount of hydrogen evolution, ● hourly evolution.

In 1977, Costogue and Yasut<sup>(18)</sup> demonstrated the electrolysis of water to hydrogen using the solar energy through solar photovoltaic cells. The maximum power of the array during a sunny day varied from a minimum of 25.0 W to a maximum of 115.5 W and the hydrogen rates of this electrolysis cell with solar array are listed in Table 2.2.1

Table 2.2.1 Electrolytic H<sub>2</sub> generator/photovoltaic source operational data during a sunny day with clear sky

Hour	H <sub>2</sub> Output		Array Current Output
	ml/min	lit/hr m <sup>2*</sup>	amp.
9.00	59	2.5	8.8
11.30	110	4.7	16.4
12.00	113	4.8	17.0
12.30	116	5.0	17.3
13.00	114	4.9	17.2
14.00	107	4.6	15.9
15.00	92	3.9	13.6
16.00	72	3.1	10.5
16.30	62	2.7	9.0

\* Hydrogen production per area of the solar cells.

At noon the hydrogen rate was 113 ml/min, the combustion heat of this hydrogen is calculated to be 22 W (5.3 cal/s). From Figure 2.2.1c, the electrical power is 38.5 W, using for one electrolysis cell. Thus, the energy conversion through this system (Figure 2.2.1d) is about 57 %

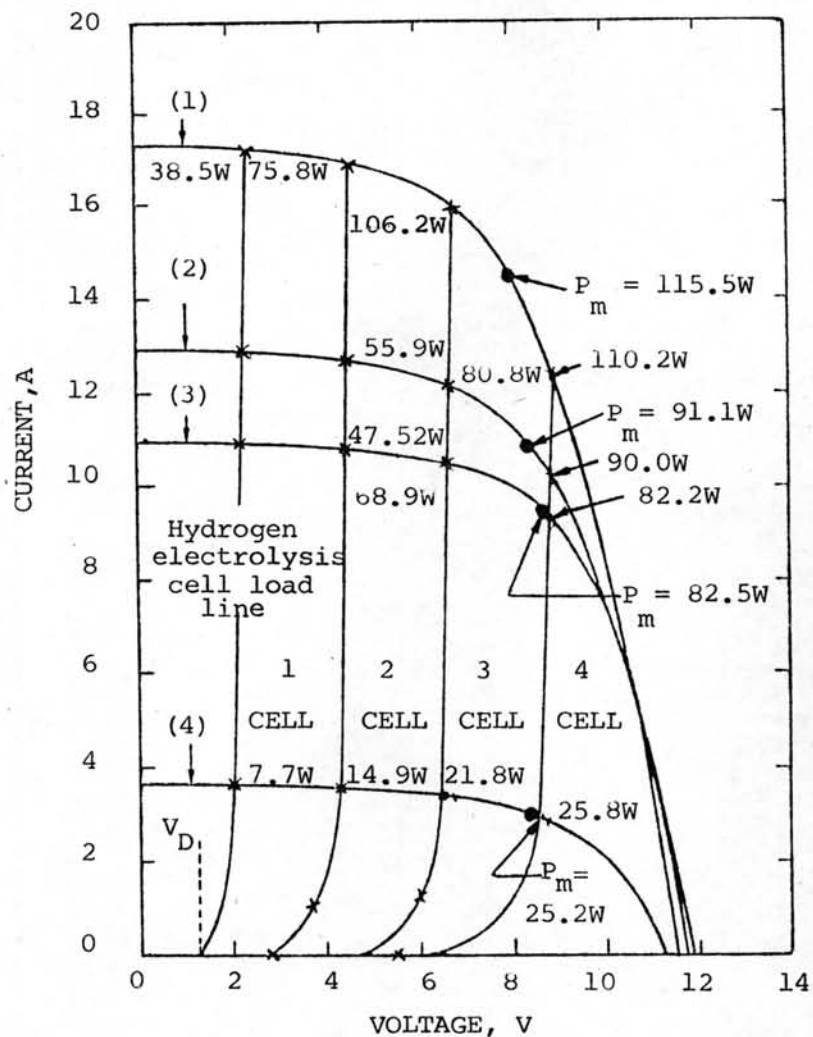


Figure 2.2.1c<sup>(18)</sup> System composite interaction of solar photovoltaic and hydrogen electrolysis cells. The solar photovoltaic source characteristics are the lines of (1) to (4), refer to the solar input of  $129 \text{ mW/cm}^2$  at 12.00 a.m. noon,  $96 \text{ mW/cm}^2$  at 10.00 a.m.,  $81 \text{ mW/cm}^2$  at 8.40 a.m. and  $27 \text{ mW/cm}^2$  at 7.30 a.m., respectively, and  $P_m$  is the maximum power point. The

dissociation voltage of water,  $V_D$ , is about 1.23 V, and the hydrogen electrolysis load lines of each cells in series show the polarization characteristics (see 3.4.1).

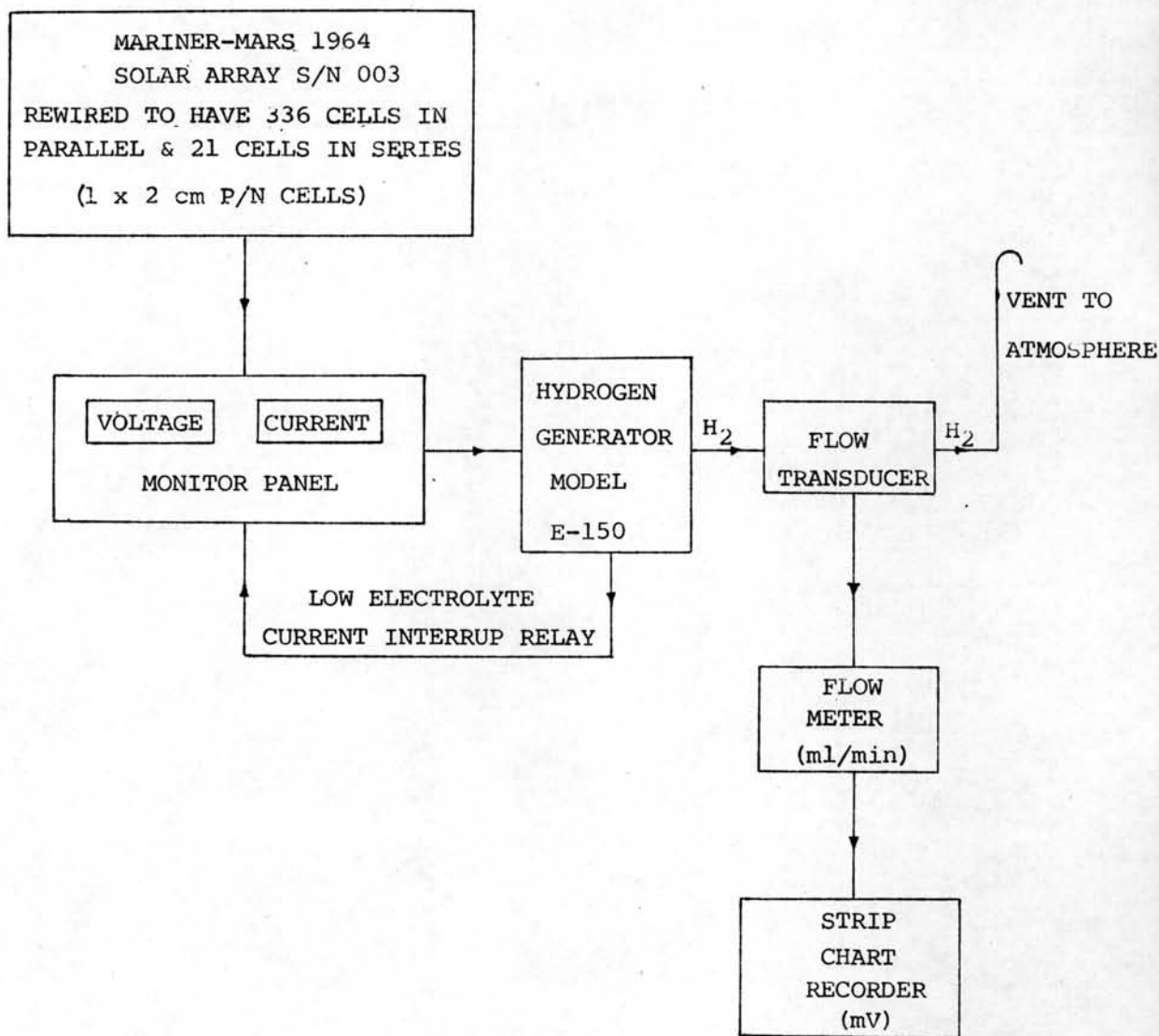


Figure 2.2.1d Block diagram of solar photovoltaic power source/hydrogen gas conversion system.



(22X100/38.5). They calculated the volumetric production rate coefficient to be about 6.5 ml/min.amp from the experimental data (in Table 2.2.1). By definition of Faraday's law (which implies that 442.5 lit at standard condition, 20°C and 1 atm, hydrogen is produced per 1000 amp-hr), the volumetric rate coefficient is about 7.5 ml/min amp, therefore the efficiency of the electrolytic cell<sup>(16)</sup> for hydrogen production is 87 % (6.5X100/7.5).

Although the high efficiency electrolysis cell(87 %) was used to connect this solar array source, some energy was used during the conversion electricity to chemical energy as hydrogen for electrolysis, and some energy was lost. They attempted to optimize this system by connecting four electrolytic cells in series in order to match operating voltage and current requirements of the cells to the maximum power point voltage and current of the array. This voltage range was 7 to 9 volt, in Figure 2.2.1c. They did not demonstrate the experiment of of four-series cells.

In this experiment, the solar array contained 7056 silicon solar cells (1X2 cm P/N cells) and the given maximum power at noon (solar intensity was 129 mW/cm<sup>2</sup>) was about 115.5 W (Figure 2.2.1c) or 8.2 mW/cm<sup>2</sup>. Solar conversion efficiency of this photovoltaic cells was also low : about 6.4 %. Therefore the total conversion efficiency of the solar energy converting to chemical energy as hydrogen by the solar photovoltaic power source/hydrogen gas conversion system (Fig.2.2.1d) may be estimated and should be about 3.6% (6.4X0.57).

A brief discussion of the major technical problems anticipated made by Costogue and Yasut. To produce hydrogen in quantity, a

large number of electrolysis cells, and large area solar arrays, was required. The electrolytic cells was a low voltage, high-current device; therefore series-parallel combinations would be required to take full advantage of the solar array capabilities. A JPL (Jet Propulsion Laboratory, California Institute of Technology) study identified a preferred current of less than 2000 A, and voltage of less than 10 kV for a terrestrail photovoltaic power plant to minimize potential environmental problems. Therefore a large scale hydrogen production via electrolysis pointed out that there were operational voltage and current limitations. Other points of interest were the land areas required to accommodate the equipment, especially the solar arrays, and the power controls and management required to efficiently and safely distribute the electrical power generated by the solar arrays. The effective power distribution and management of this magnitude of power constituted a tremendous task.

In contrast to this process for hydrogen production via electrolysis using solar energy, the direct process of photocell (by Fujishima and Honda) is a simple system not only for hydrogen production but also as a source of electrical power. The different operating paths and instruments of both methods are as follows.

1. Pathways. The indirect process is hydrogen generation via an electrolysis cell; solar energy  $\rightarrow$  solar cells  $\rightarrow$  electrolysis cell  $\rightarrow$  hydrogen product. The direct process is hydrogen generation via photocell; solar energy  $\rightarrow$  photocell  $\rightarrow$  hydrogen product

2. Efficiency. There are few previous research works comparing the efficiencies of both systems. For the indirect process the efficiency is about 3.6% by estimation from one available data, with the conversion

efficiency of the solar cell equally low. Thus this statement for the efficiency should not be considered final. It is possible that low efficiency of the system is that the more steps there are the more energy losses. For the direct process, the efficiency is low, 0.4-1.3 % for recent work published. The improved semiconductor photoelectrode in photocells have conversion efficiencies of 1.2 % and the hydrogen rate is about 0.4 ml/hr cm<sup>2</sup> or 4 lit/hr m<sup>2</sup> (c.f. the rate in Table 2.2.1). Therefore, the hydrogen production by photocells may be a efficiently and conveniently systems for solar energy storage as fuel in a chemical form.

3. Energy Requirement. The theoretical potential for splitting hydrogen and oxygen molecules in electrolysis is about 1.23 V. However in practice it is at least 2.3-2.5V because of polarization and thermodynamic characteristic of hydrogen electrolysis (Figure 2.2.1c). This one solar cell (where the maximum voltage is limited to 0.5-0.6 V of a cell) cannot give enough potential for water electrolysis. Also there are many problems for operating this process which the discussion is above. In photocells, one photoelectrode (n-type semiconductor) is used for hydrogen generation if both cathode and anode electrodes are made of some suitable materials. However, the energy required for photovoltaic cells (silicon solar cells) lies at long wavelength (visible light) ranges but photocells with photoelectrodes lie at near ultraviolet ranges,

4. Light Absorbers. The light absorbers of both processes are semiconductor materials but in solar cell semiconductors, the bandgap energies are smaller than the others. The solar cells are p-n junction cells, the construction of the junction requires a highly complicated technology therefore, the cost of cells are high. The photoelectrodes in the

photocell are n-type semiconductors which are immersed in electrolyte where they absorb light to cause the chemical reaction in solution.

Therefore, the early research (by Fujishima and Honda) of directly converting solar energy to chemical energy as hydrogen has been considered to be investigated continuously.

Fujishima and Honda's report cause the emergence of a full new branch of alternate energy research in solar energy. There are two fundamental ways for converting solar energy into chemical energy as hydrogen. One, light absorber are catalysts such as components of plants or bacteria (chlorophyll and enzymes) in biophotocatalytic processes (see 2.3.4), semiconductors and transition metal complexes (see 4.4.2). The others are photoelectrochemical cells with semiconductor electrodes or chlorophyll deposited on semiconductor electrodes. Semiconductors as catalyst and electrodes in PEC'S are more investigated than chlorophyll systems, because there are advantages and developing information of semiconductor study from solar cell technology but chlorophyll has many unknown condition of its function like it being in plants. Thus these last few years, many investigators have studied and attempted to use single crystal with doping impurity or polycrystalline of titanium dioxide and other semiconductor materials as photoelectrodes in the PEC's. Unfortunately  $\text{TiO}_2$  has the large band gap, is about 3 eV which corresponds to 415 nm wavelength of light, considering the spectrum distribution of sunlight (see Figure 2.1.1) the solar radiation lies below 415 nm is only about 10 %. Therefore semiconductors with small band gap energy such as Si (1.1 eV), GaP (2.3 eV),  $\text{Fe}_2\text{O}_3$  (2.2 eV) and  $\text{WO}_3$  (2.7 eV) etc., are

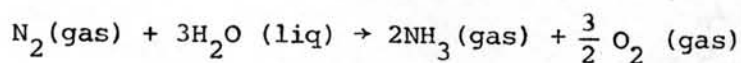
used as photoelectrodes but most semiconductors are chemically unstable in electrolytes (see 3.4.3)

Researches and development of hydrogen production by PEC'S for the last decade are described in chapter IV. To study these new devices, an understanding of the fundamental principles of electrode reactions, electrical properties of electrode solution interfaces and photochemistry at semiconductor, is required. The concept and treatments described here will be considered in Chapter III, and involve the information in Appendices.

### 2.2.2 NH<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>-production

In biological system (2.3.3) the reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> and N<sub>2</sub> to NH<sub>3</sub> occur by photosystem<sup>(13)</sup>. The NH<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> produced would need to be concentrated in order to be stored and used as fuel and/or chemicals. This research is in its infancy but is interesting because industrial processes of their production are necessary serious conditions such as NH<sub>3</sub> production, the reduction of N<sub>2</sub> in high temperature and high pressure.

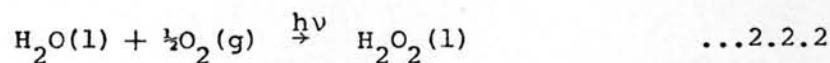
Schrauzer and Guth<sup>(87)</sup> (1977) obtained H<sub>2</sub> and O<sub>2</sub> (2:1 by volume) on UV illumination to produced TiO<sub>2</sub> in a wet atmosphere of argon. By 0.2 wt % doping with Fe<sub>2</sub>O<sub>3</sub>, this photoactivity was increased. When the argon was replaced by nitrogen, a decrease of H<sub>2</sub> production rate was observed accompanying the formation of NH<sub>3</sub> and trace amounts of N<sub>2</sub>H<sub>4</sub>, while the rate of O<sub>2</sub> evolution remained practically unaltered. The reaction of NH<sub>3</sub> formation;



$$\Delta G^{298} = 678 \text{ kJ/mole (in Table 2.1.3)}$$

Although the quantum efficiency and elementary processes for the  $N_2$  reduction have not yet been clarified, this photoelectrocatalytic pathway will be worthy of further investigation as one of the non-biological methods for nitrogen fixation.

For hydrogen peroxide ( $H_2O_2$ ) it is an important starting material for further reaction to produce more valuable compounds (aromatic compounds of Fenton reaction) for pharmaceutical industries. If water and oxygen gas are raw materials of  $H_2O_2$  synthesis under sunlight illumination by the equation



It may be an inexpensive method. The free energy change associated with Eq 2.2.2, is  $\sim 25$  kcal/mole of  $H_2O_2$  ( $\sim 1.08$  eV) and would in these terms represent an excellent match to the solar spectrum. There are photoanode materials, e.g.,  $SrTiO_3$ ,  $TiO_2$ ,  $Fe_2O_3$ , etc., that are known to be able to effect the photooxidation of  $H_2O$ . Fujihira, Satoh and Osa (1981)<sup>(35)</sup> have combined the photoelectrochemical production of  $H_2O_2$  with the Fenton reaction in succession for the heterogeneous photocatalytic oxidation of various aromatic hydrocarbons. The quantum yields is a range of 1-5 % by 500 W Xenon lamp. But the quantum yield calculation of this paper is not clear.

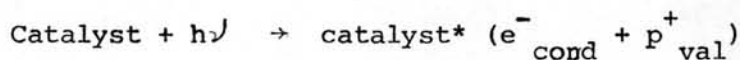
Because of the large energy gaps of  $TiO_2$  ( $E_g \sim 3$  eV) the solar efficiency for production of either  $H_2$  or  $H_2O_2$ , from  $H_2O$  is poor. Calabrese and Wrighton (1981)<sup>(15)</sup> have used p-type Si ( $E_g \sim 1.1$  eV) in PEC with nonaqueous solution for photochemical synthesis of  $H_2O_2$  under

illumination of 632 nm wavelength and 50 mW/cm<sup>2</sup>. The efficiency for a regeneration photoelectrochemical cell based on redox potential of reactant is ~ 4 % for the light conversion. The light is also converted to electricity with an efficiency of ~ 2 % (see the calculation in Chapter IV). Thus, this work is both PEC and EPC (electrochemical photovoltaic cell), but the efficiency is too low to be useful. For a chemical such as H<sub>2</sub>O<sub>2</sub> being the final product a lower efficiency might be allowable except that conventional electricity can be generated at low cost. Thus, the photoelectrochemical approach to H<sub>2</sub>O<sub>2</sub>, though being demonstrated to work, must be improved significantly regarding efficiency.

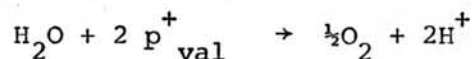
### 2.2.3 CO<sub>2</sub> reduction.

From Table 2.1.3, in aqueous phase carbon dioxide (CO<sub>2</sub>) can be converted into formic acid (HCOOH), formaldehyde (HCHO), methanol (CH<sub>3</sub>OH) and methane (CH<sub>4</sub>) by 2-, 4-, 6-, and 8- electron reduction, respectively. Since these products, especially methanol and methane are useful chemical fuels, reduction of CO<sub>2</sub> by photoelectrocatalytic processes will provide one of the most promising aspects for solar energy conversion.

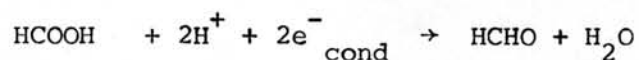
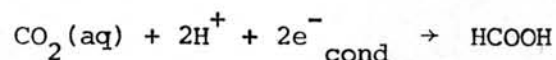
The photocatalytic reactions are considered to follow the schemes. (50)

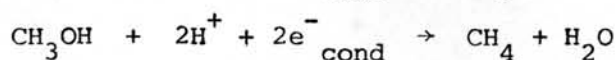
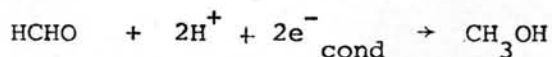


for an oxidation



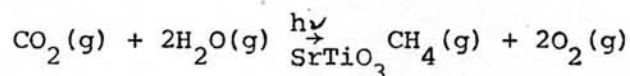
for reduction





where  $e^-_{\text{cond}}$  and  $p^+_{\text{val}}$  denote an electron in the conduction band and a positive hole in the valence band, respectively.

Hemminger et.al.<sup>(47)</sup> (1978) succeeded in producing  $\text{CH}_4$  from  $\text{CO}_2$  by a photoelectrocatalytic reaction on a single crystal of  $\text{SrTiO}_3$  placed in a gaseous atmosphere consisting of  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The overall reaction might be the following



In this case, a platinum foil was being attached to a part of the  $\text{SrTiO}_3$  surface. Without the platinum foil, the amount of  $\text{CH}_4$  produced was negligible.

Photoelectrocatalytic reduction of  $\text{CO}_2$  in aqueous solutions have been investigated by Japanese researchers<sup>(50)</sup> using a series of semiconductors as photocatalysis. It was expected that the rate of  $\text{CO}_2$  reduction would be higher with semiconductors having the conduction band edge situating at more negative potential (see Figure 2.2.3a). That was indeed the case is demonstrated by Figure 2.2.3b, which shows the quantum efficiency for the photoelectrocatalytic  $\text{CO}_2$  reduction as a function of the potential of the conduction band edge of the semiconductors used. The quantum efficiency of this energy-storing reaction reached about 1 %.

Halmann<sup>(43)</sup> (1978) have reported the photocatalytic reduction of  $\text{CO}_2$  in a homogeneous system using aromatic hydrocarbons as photocatalysts, only formic acid was detected, and an estimated quantum efficiency was about 0.3 %.



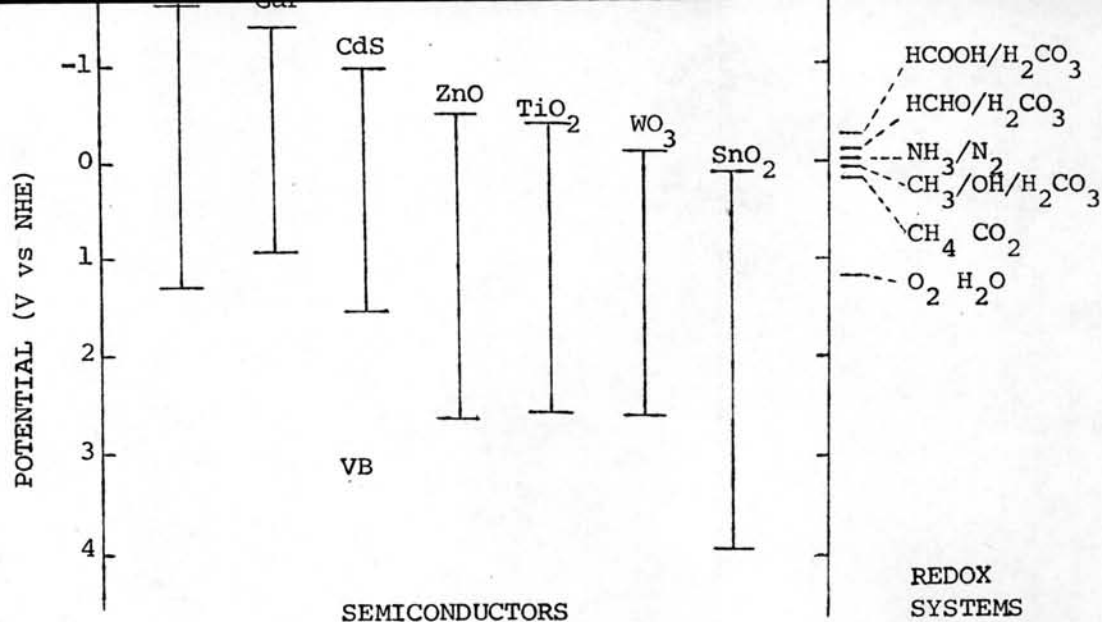


Figure 2.2.3a Correlation between the potentials of conduction band (CB)-valence band (VB) of various semiconductors and those of redox systems at pH 7.0 (See 3.4.1).

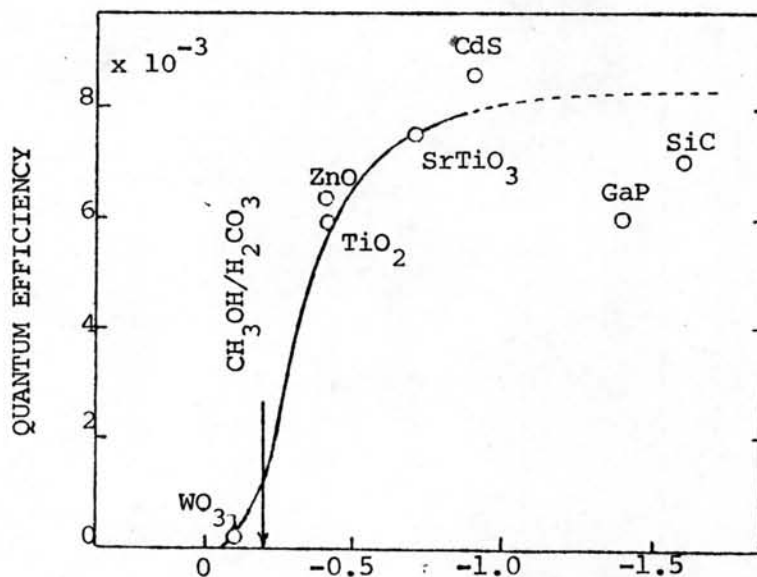


Figure 2.2.3b Relationship between the quantum efficiency for photoelectrocatalytic reduction of CO<sub>2</sub> and the potential of the conduction band (CB) edge of semiconductors (See 3.4.1).

Recent report of Aurian-Blajeni et al. (1980) <sup>(2)</sup> demonstrated the reduction of carbon dioxide and water to formic acid, formaldehyde, methane using photoassisted reactions, using semiconductor powders suspended in aqueous carbon dioxide by mercury lamp illumination and on glass-plate by sunlight illumination. Some treatments of semiconductors,  $\text{SrTiO}_3$  and  $\text{WO}_3$  have given high energy conversion of 5-7 % (by Eq.4.1.15 in Chapter IV). For  $\text{WO}_3$  the result are not like the Japanese researcher's paper. For sunlight-irradiation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the presence of  $\text{TiO}_2$  (thermal treatment : 6 hr/600<sup>o</sup>c vacuum), methanol product was 1.6  $\mu\text{mole/hr}$ , in contrast by Hg-lamp and under the same condition rate of methanol synthesis was 2.04  $\mu\text{mole/hr}$  and absorbed energy conversion ~1.2 %.

Improvement in the photosynthetic carbon dioxide reduction to organic products may be of importance in providing process for recycling some of the carbon dioxide released into the atmosphere by coal or oil-burning power stations.

### 2.3 Chemical Reactions by Photosynthesis

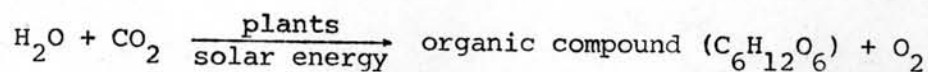
Almost all materials in the growth of plant, known as organic compounds, are derived from photosynthesis. This process is the conversion of radiant energy to chemical energy of stable organic compounds and is only carried out by plants and some bacteria. A green plant grows where there are raw material, air, water and mineral salts, and light.

For many complicated steps of whole processes of photosynthesis, some steps of the simple form of carbohydrate is explained, water splitted to oxygen and hydrogen by light activated at chlorophyll pigment and fixed

carbon dioxide to carbohydrate. Thus in high plant photosynthesis give oxygen gas molecules to the air, but in some algae and bacteria photosynthesis give hydrogen molecules.

### 2.3.1 Photosynthesis

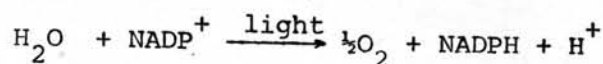
In its general form, the photosynthetic reaction may be written as:



The basic process, at the molecular level, consists of the transfer of hydrogen atoms from water molecules to carbon dioxide molecules, using energy from absorbed photons of light. The process can be divided into three stages<sup>(27)</sup>

- i. Light Collection.
- ii. Oxidation of  $\text{H}_2\text{O}$  to  $\text{O}_2$  with the formation of strong reducing molecules (NADPH) and energy-rich molecules (ATP) using the energy collected from the light.
- iii. Reduction of  $\text{CO}_2$  to  $(\text{CH}_2\text{O})_n$  and  $\text{H}_2\text{O}$ , using NADPH and ATP.

Figure 2.3.1 shows a generally accepted energetic scheme of light reaction in green plant photosynthesis through the three steps, though a number of elementary processes there remain to be clarified. Chlorophyll absorbs light strongly in two bands, near 680 nm and 700 nm in two photosystem (PS I and PS II), which connected to each other by an electron transport chain.<sup>(97)</sup> The primary processes are the oxidation of water and reduction of  $\text{NADP}^+$  (niocotinamide adenine dinucleotide phosphate), according to the following equation.



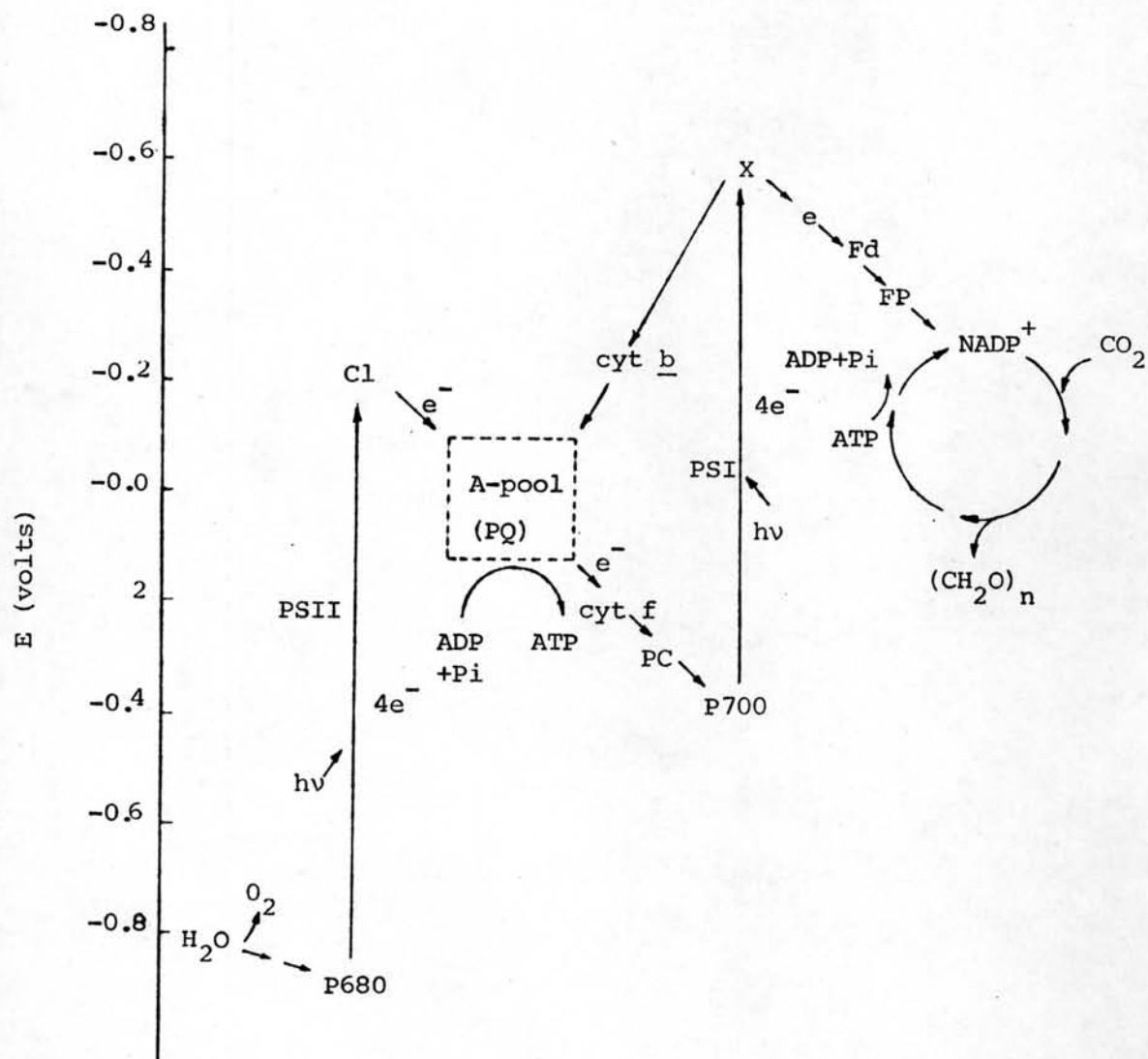


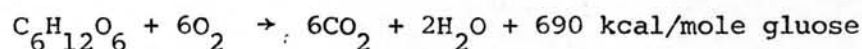
Figure 2.3.1 Electron transport systems of oxygenic photosynthetic organisms. Light absorbed by photosystem II (PSII) excites P680, the reaction center chlorophyll of PSII, and generates a strong oxidant capable of removing electrons from water. (97)

This corresponds to an energetically uphill electron transfer by 1.16V (from + 0.81V for  $H_2O/O_2$  to -0.35 V vs. NHE at pH 7.0), as shown in Figure 2.3.1. In the course of electrons flow from  $H_2O$  to  $NADP^+$ , protons are released to the interior of the thylakoid membrane, composed mainly of lipids, on which the above processes occur. A proton gradient thus created is used to produce adenosine triphosphat (ATP). The last step, by utilizing ATP (chemical energy carrier) and NADPH (reducing power),  $CO_2$  can be reduced to yield carbohydrates,  $(CH_2O)_n$ .

### 2.3.2 Efficiency of Photosynthesis

One can think of photosynthesis as a heat engine operating between the solar radiation and green plant. By the Second Law of Thermodynamic, the maximum possible efficiency is  $1 - T_P/T_R$ .  $T_P$  is the temperature of plant, about 300 K.  $T_R$  is the temperature of the solar radiation. And determining the minimum light intensity necessary for efficient photosynthesis, by calculating the temperature corresponding to the isotropic red solar radiation field, the minimum radiation temperature at which photosynthesis works well,  $T_R$  is about 1100 K. <sup>(91)</sup> Thus the maximum thermodynamic efficiency is  $1 - \frac{300 K}{1100 K}$ , 73 %

In the observation, the reversible reaction of photosynthesis is carbohydrate + Oxygen  $\rightarrow$  carbon dioxide + water + energy. Consider burning glucose, a typical carbohydrate :



and gives

$$\frac{\text{Energy}}{\text{Glucose molecule}} = \frac{690 \text{ kcal/mole} \times 4.2 \times 10^3 \text{ joule/kcal} \times 0.63 \times 10^{19} \text{ eV/joule}}{6 \times 10^{23} \text{ molecules/mole}}$$

= 30 eV/glucose molecule.

There are six carbons per one glucose molecule, so 5 eV of energy are required for each carbon atom that is fixed. The photosynthetic efficiency is maximum for near 700 nm wavelength, the energy of the photon is about 1.8 eV and from Figure 2.3.1 a minimum of eight photons of light required to transfer the four electrons from water to fix one carbon dioxide, so that the maximum efficiency for photosynthesis is  $\frac{5 \text{ eV}}{8 \times 1.8 \text{ eV}} \sim 35\%$

In comparison with the maximum possible efficiency of 73 %, the observed efficiency of 35 % is much different we must take a look at the molecular chemistry of the photosynthetic process. Thorndike<sup>(97)</sup> demonstrated the rough energy loss in the photosynthetic process for the simple carbohydrate,  $\text{CH}_2\text{O}$ , as shown in Figure 2.3.2.

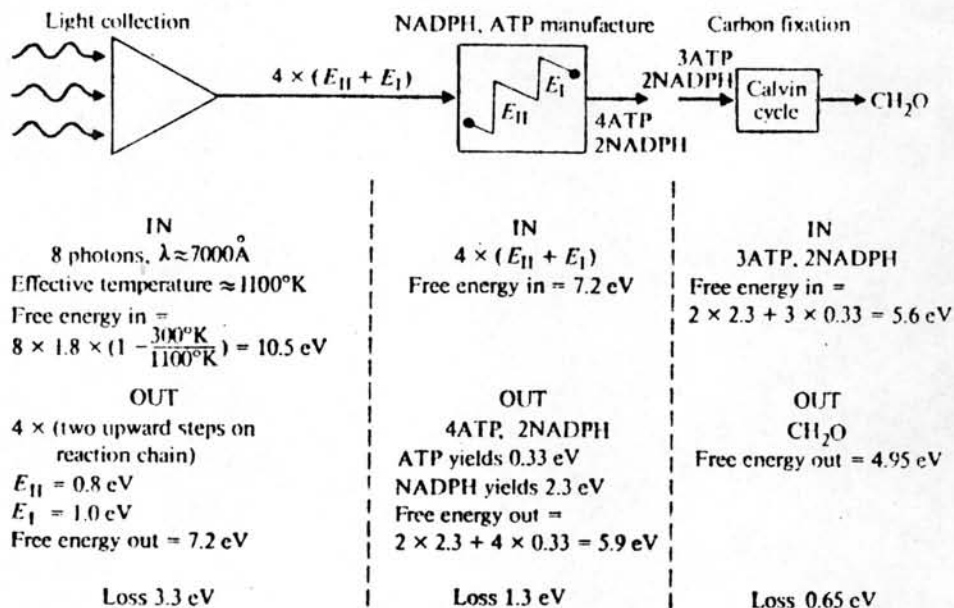


Figure 2.3.2 Three steps in photosynthesis. The energies indicated are free energies at standard concentration. (91)

For whole processes (three steps in 2.3.1), the energy loss is about 50 %.

Also he estimated the correction factor for the frequency distribution of solar radiation, by the Plank black-body distribution and numerical integrating yield is 32 %. Combining the above considerations, he expected the red light, laboratory of 35 % to be corrected by a factor of 0.32 for frequency range, a factor of 0.8 for leaf reflectivity and a factor of 0.5 for excess light intensity, to predict an efficiency for gross production under ideal field condition with solar radiation, yield was

$$0.35 \times 0.32 \times 0.8 \times 0.5 = 0.045$$

or 4-5 %. In nature, actual conditions are usually not ideal. The efficiency is less than 4.5 % because the sun's energy is not fully utilized and different surface of the earth, such as land, desert and sea surfaces. Table 2.3.2 shows average to-good yields for agriculture and photosynthetic efficiency. The annual photosynthesis conversion efficiencies in temperature area and for sub-tropical crops are 0.5-1.3 % and 0.5-2.5 % of the total radiation respectively.

Table 2.3.2 Average-to-good the yields of dry matter production<sup>(11)</sup>

	Tonnes hectare <sup>-1</sup> Yr <sup>-1</sup>	g m <sup>-2</sup> day <sup>-1</sup>	Photosynthetic efficiency(% of total radiation)
Tropical			
Napier grass	88	24	1.6
Sugar cane	66	18	1.2
Reed swamp	59	16	1.1
Annual Crops	30	-	-
Perennial crops	75-80	-	-
Rain forest	35-50	-	-
Temperate			
Perennial crops	29	8	1.0
Annual crops	22	6	0.8
Grassland	22	6	0.8
Evergreen forest	22	6	0.8
Deciduous forest	15	4	0.6
Savanna	11	3	-
Desert	1	0.3	0.02





2.3.3. Photobiological Production of Hydrogen

In bacteria and some algae, the enzyme hydrogenase which catalyzes the reaction  $2H^+ + 2e^- \rightarrow H_2$  is found and its activity could be coupled to ferredoxin for the metabolism of hydrogen in most of these organisms. For the photosynthetic bacteria used to purify organic industrial waste because they need organic substrates in hydrogen evolution and useful in biomass area.

The possibility of hydrogen evolution by micro-organism is shown as follows: (86)

Bacteria	Organic substrates	---->E	----> H <sub>2</sub>	Dark	
Purple bacteria	Organic substrates, thiosulphate	---->Photosynthetic system	---->E	---->H <sub>2</sub>	
	CO <sub>2</sub> , H <sub>2</sub> O	---->Photosynthetic system	---->Organic Substrates	---->E	---->H <sub>2</sub>
Algae		H <sub>2</sub> O	---->Photosynthetic system	---->E	---->H <sub>2</sub>

where E is an enzyme hydrogenase. If then, an active hydrogenase preparation is added to an illuminated chloroplast system, the photon generated by the photolysis of water could be combined with the electrons donated from reduced ferredoxin to produce hydrogen. The early report of production of H<sub>2</sub> gas by light-activated water splitting using components from plants (Chloroplast-membranes and ferredoxin) and bacteria was in 1973 (Figure 2.3.3). The rate of H<sub>2</sub> evolution were low and the system only ran for 15 min.

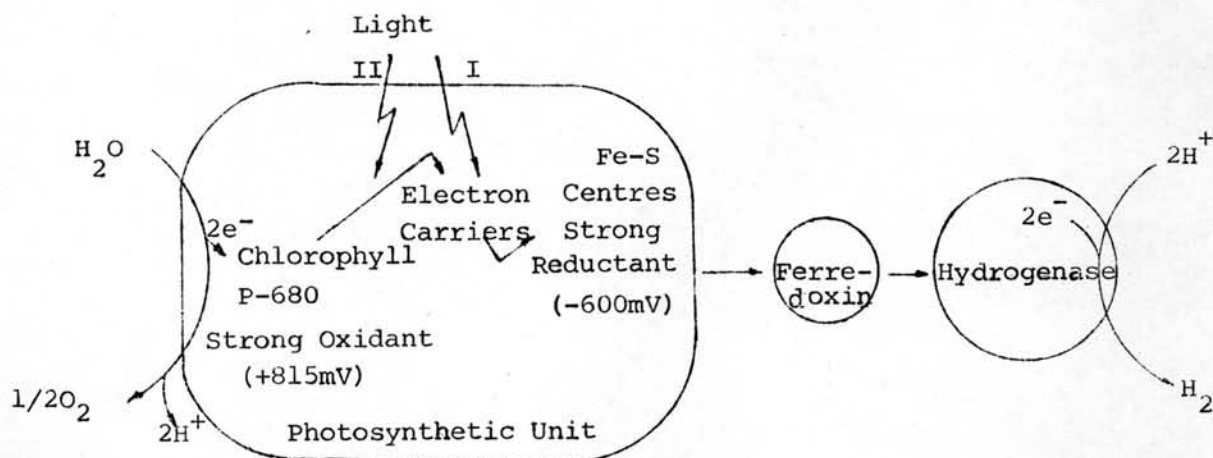


Figure 2.3.3a Coupling of solar energy to  $H_2$  production as a result of  $H_2O$  splitting by chloroplast membranes in the presence of the Fe-S enzyme ferredoxin and hydrogenase

The researches and developments of this photobiological production of hydrogen were surveyed from literature by Weaver.<sup>(97)</sup> The economic of this is a mid-to-long-term good in the future. Two major considerations are, firstly, technology and, secondly economic. Although much is known about biological hydrogen production, a great deal more basic and applied research is necessary before it will be possible to select proper system application on any practical scale.

Instead of producing  $H_2$  gas, using a system consisting of the suitable substrates, it is possible to produce  $H_2O_2$  or  $NH_3$  etc. Fig.2.3.3b shows diagrammatically this ability of plant membranes to produce low potentials and the reactions which can be catalysed once the low potential has been produced across the membrane. During normal photosynthesis the photons

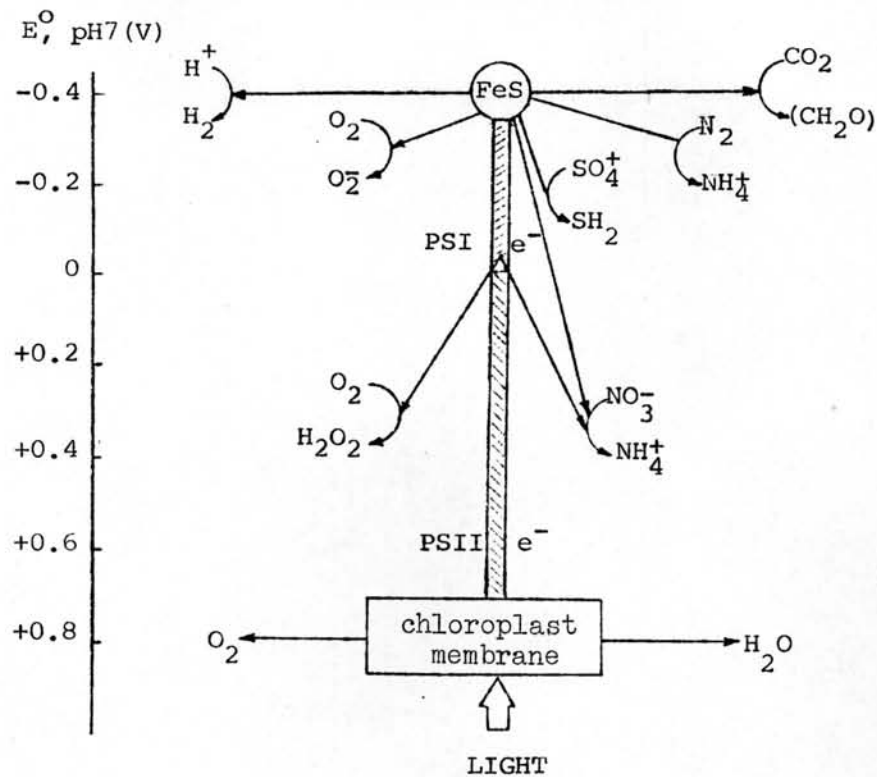


Figure 2.3.3b Schematic representation of the ability of plant membranes to produce low (reducing) potentials and the reactions catalyzed by the reduced Fe-S enzyme catalysts

captured by PS II and PS I of the chloroplast membrane are used to liberate oxygen and to generate ATP and  $NADH_2$  (Figure 2.3.1). The precursor of  $NADPH_2$  in photosynthetic electron transport pathway is reduced ferredoxin which plays an active catalytic role in a number of other biological reaction like nitrite and sulphite reduction, etc. (Fig.2.3.3b). In this system only one of the photosystem of the chloroplast membrane, is sufficient to reduce  $O_2$  to  $H_2O_2$  (redox potential +0.3V). The overall efficiency would be twice the  $H_2$  production since only one, and not two, photosystems would be operating. It is premature to speculate on efficiencies of either the  $H_2$ - or  $H_2O_2$ - producing system until we can produce these compounds on a continuous long-term basis.

#### 2.3.4 Light Energy Conversion with Chlorophyll Electrodes

As chlorophyll is the best available solar absorber, many investigators attempted to use it in photoelectrochemical cell for chemical production, expected to duplicate photosynthesis in plants. The early researches, chlorophyll was deposited on a metal substrate as photoelectrode, immersed in an electrolyte solution, driven a redox reaction under illumination, giving rise to a photocurrent through the external circuit. The energy conversion efficiency and the quantum efficiency (under a bias of 2V) were ca. 0.1 % and 3 %, respectively and the peak of photocurrents was observed at around 745 nm.

In contrast to the photoelectrochemical cell, the electron-transport chain in photosynthesis (Figure 2.3.1) as a conducting wire, PS I and PS II (composed mainly of Chl a) can be simulated as a photocathode and a photoanode, respectively (Figure 2.3.4). Based on this idea, several research groups have recently attempted to construct photoelectrochemical cells using Chl electrodes.

Miyasaka and Watanabe (1978)<sup>(68,69)</sup> have coated the chlorophyll monolayer on  $\text{SnO}_2$  as photoelectrode. On illumination the chlorophyll electrodes, photocurrents were observed at around blue and red peak of halogen lamp light, in accordance with an electron injection from excited chlorophyll molecules to the conduction band of  $\text{SnO}_2$  (Figure 2.3.5). From biological observations, it has been proposed that chlorophyll molecules on thylakoid membranes assume a highly ordered structure<sup>(27)</sup>, through hydrophobic interaction between phytol chains and lipid or proteins. A monomolecular layer of chlorophyll prepared on a suitable substrate by

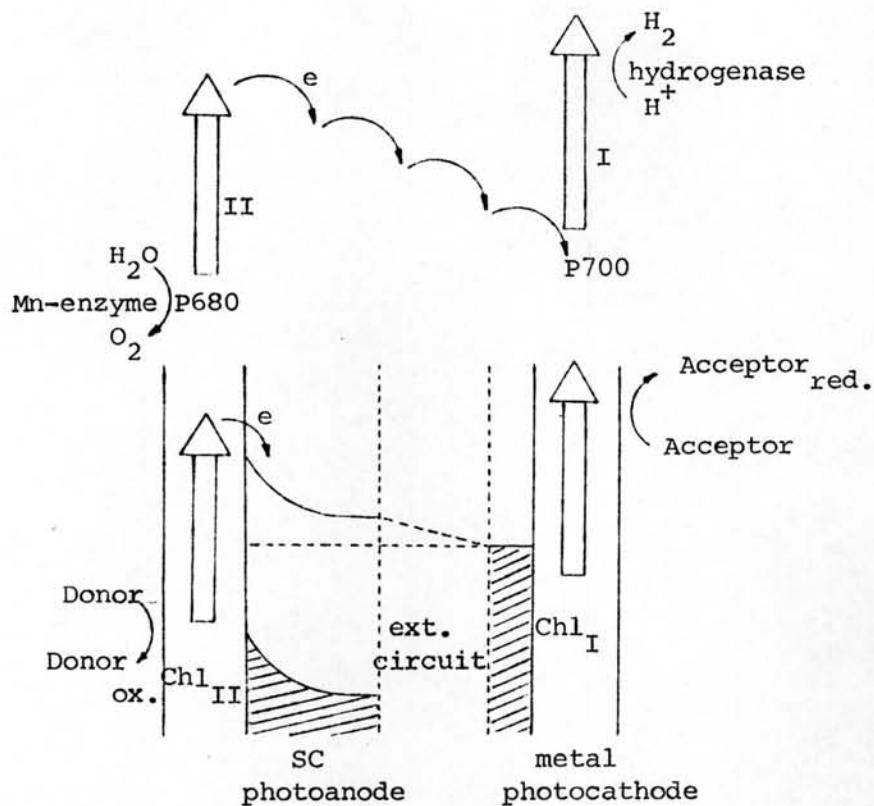


Figure 2.3.4 Schematic for the photoelectrochemical simulation of the photosynthetic electron-pumping processes (upper sketch) by means of a Chl-semiconductor photoanode and a Chl-metal photocathode.

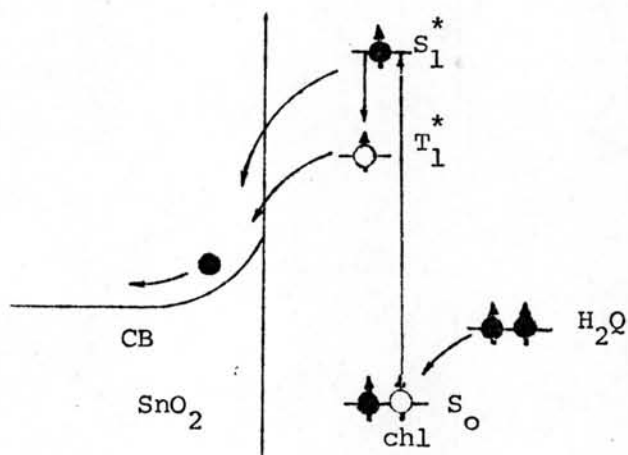


Figure 2.3.5 Scheme for the electron transfer in dye sensitization process at the interfacial layer of Chl on  $\text{SnO}_2$  electrode<sup>(75)</sup>

means of the Langeneir-Blodgett technique<sup>(70)</sup>, was close to the biological system. In order to control the surface concentration of chlorophyll, they mixed monolayers of chlorophyll and stearic acid ( $C_{18}$ ) and deposited on  $SnO_2$  electrode, used in photoelectrochemical cells, as electrical sources. The quantum efficiency for photocurrent generation of cell, the highest value was about 12-16 % (its calculation is from Eq.4.1.3c) In 1980, they have demonstrated the chlorophyll electrode by coating chlorophyll on platinum substrate and  $SnO_2$  again, but mixed chlorophyll with lecithin in order to increase the efficiency.<sup>(69)</sup>

For investigations cited above, only light energy is converted to electrical energy, no chemical energy observation. Fong and his co-workers<sup>(26)</sup> (1978) attempted to prepared two different Chl a- $H_2O$  adducts,  $(Chl\ a-H_2O)_2$  and  $(Chl\ a-H_2O)_{n \geq 2}$ , and examined their photoelectrochemical properties using Pt as a substrate. Photocurrents were observed at around 740 nm due to aggregation, and the quantum efficiency was on the order of 1 %. They found the occurrence of water splitting into  $H_2$  and  $O_2$  at an illuminated  $(Chl\ a-H_2O)_n$  electrode by mass spectrometric analysis. The yield of water decomposition was still limited to a very low level. In 1979, Fruge & Fong<sup>(29)</sup> demonstrated evidence for photoreduction of  $CO_2$  by  $H_2O$  to formic acid by platinized  $(Chl\ a-2H_2O)_n$ . The reduction was shown to be photocatalyzed by chlorophyll and may additionally produce formaldehyde. This was verified by mass spectrometric analyses.

Although chlorophyll isolated from living organisms, is unstable under ambient condition, the usefulness of chlorophyll as a photoreceptor in artificial systems (photoelectrochemical cells) studies

is important for the following reasons; <sup>(75)</sup>

- (a) its capability of utilizing incident red light,
- (b) strong redox reactivities in its excited states,
- (c) the occurrence of highly efficient energy migration among excited molecules,
- (d) the ability to form a wide variety of photoactive derivatives absorbing in far red region, such as Chl-nucleophile aggregates, and
- (e) the availability of its surfactant structure which enables an ideal incorporation of the molecule into membrane structures.

Based on these characteristics, a number of investigations of the photoelectrochemical as well as the photovoltaic effects of artificial system chlorophyll have appeared up to day.

The problems of chlorophyll in artificial systems are

- (a) the stability of chlorophyll electrode,
- (b) low energy conversion efficiency,
- (c) condition for the suitable system, e.g. electrode substrate and electrolyte, etc.