CHAPTER I

INTRODUCTION

1.1 General

The world is well aware that oil and gas reserves used as a fuel and a source of chemicals are being depleted rapidly and sometimes within the next 20 years or so, serious shortages may occur.

Alternative energy sources exist such as nuclear energy, coal, oil shales, and a host of renewable energy systems such as solar, wind, geothermal biomass and other systems. Nuclear fission is an important source of electricity in most developed countries; well known problems of operating safety and waste disposal remain and most developing countries would choose not to go nuclear for these reasons. Energy from nuclear fusion will probably be developped within the next century and will probably be the long term answer to modern man's energy requirements. Coal and oil shales reserve are quite extensive, the first source has been used extensively in the past and is being used now and will continue to be used in the future, the second source has great potentials but is uneconomic to use as an energy source in the present world energy picture. Both create environmental problems: mining operations related air pollution related, and the danger of releasing vast amounts of carbon dioxide which may adversely affect earth's ecology. The renewable

energy options are much cleaner sources of energy but occur in a decentralized fashion and unconcentrated form.

Some of such renewable energy systems are economically viable but many of them are not. Among the most economically attractive systems are solar photovoltaics for electricity, solar thermal systems for heat energy, geothermal sources for electricity and heat energy, all forms of biomass used as solid, liquid or gaseous fuels for varied applications. Research and development is being undertaken by many groups of researchers in all these areas in order to offer a combination of optimal solution to man's energy requirements.

The use of direct solar energy as a renewable energy source has received continuous attention from research groups. There are two fundamental approaches for converting solar energy into useful forms, the first being thermal conversion, the second approach being quantum conversion, in which solar radiation is used to cause a photochemical or a photoelectric phenomena in the solar radiation absorbing system.

Using the latter approach the well-known example is a solar cell converting solar energy into electricity by a photoelectric process operating through the seperation of charges generated by excitation from solar radiation through p-n junction semiconductors. In view of solar cells developments, when the cost of silicon solar cells is a major problem, many investigators have recently paid attention to the development of new materials for solid state solar cells at

lower costs. The quantum conversion approach has a second potentially very interesting process namely the photochemical conversion of solar energy into chemical energy which is well-known as photosynthesis.

Each year plant photosynthesis fixes $2X10^{11}$ tons of carbon with an energy content of $3X10^{21}$ joules, even though the process is operating at only 0.1% efficiency (total incoming radiation on the earth's surface is about $3X10^{24}$ joules per year). Despite nature's wide-spread use of this process on earth man is only beginning to study and duplicate photosynthesis in the laboratory. The primary process of photosynthesis, the splitting of water molecules by visible light to produce oxygen and hydrogen ions can be used as the basis for other modified photosynthesis processes.

Nature's photosynthesis processes can be duplicated in the laboratory and controlled to produce other products such as hydrogen, reduced carbon compounds (methanol, etc.), ammonia, the process can of course be also used to produce electricity. Hydrogen has been a prominent candidate product for study in the last decade. It is a promising fuel for a number of energy-generating devices. As a chemical, hydrogen is used in the production of plastics, pesticides, and chemical intermediates. Larger volumes of hydrogen are used in the production of aniline. It is used in many industries such as the treating and refining of metals, the hydrogenation of fats and oils in the pharmaceutical and food industries. As for the future, much talk has been heard in recent years about a so called hydrogen eco-

nomy in the future as a real possibility. At present hydrogen is produced by steam reforming of natural gas and the volume of by-produce hydrogen purchased from petroleum refineries in the United States stands at $3X10^{12}$ standard cubic feet per year obtained mostly from fossil fuels.

If hydrogen is to become a widely used energy carrier, it must be produced economically and efficiently on a large-scale basis. A commercially available process for producing hydrogen is electrolysis of water. This process utilizes direct electric current to force the chemical seperation of hydrogen and oxygen. Large-scale hydrogen production via electrolysis using solar energy requires answers to a number of technical problems, such as the requirement to generate many kilowatts of dc electricity, the need to process the electrical power (through photovoltaic solar cells) for the electrolysis cells, the impact on the environment, and others. Cost is also a major consideration since it may be a major drawback to the electrolysis approach.

In 1975, Japanese researchers demonstrated a direct method of hydrogen production by electrochemical photocells under illumination with sunlight. The photoelectrochemical device used was a semiconductor-liquid interface which was easily created by immersing a semiconductor electrode into a solution which plays a similar role of charge seperation as the solid state Schottky junction of the solar cell. Their results were followed by a series of related research papers from several other research groups throughout the

world indicating the widespread interest of this new approach. Using solar radiation, water decomposition to hydrogen and oxygen is one important chemical reaction that can serve to store solar energy. Other chemical conversions of solar energy such as the reduction of carbon dioxide to organic compounds, formic acid, formaldehyde, methanol and methane have been studied in photoelectrochemical cells (PEC's) in the past few years. Such products particularly methanol may become an accepted liquid fuel in the near future as gasoline additive for automotive fuel. Physical properties of some gaseous and liquid fuels are compared in Table 1.1 for reference. It is believed that PEC's are solar conversion devices that will be improved and may attain economic feasibility sometimes in the future.

TABLE 1.1: PROPERTIES OF HYDROGEN AND OTHER COMMON FUELS RELEVANT TO SAFETY

Property	Hydrogen (H_2)	Methane (CH_4)	Methanol (CH_3OH)	Gasoline	Jet Fuel (JP-4)
Temperature of liquid at normal boiling point	20.3 K	112 K	338 K	*	*
Heat of vaporization	0.45 MJ/kg	0.51 MJ/kg	1.1 MJ/kg		
Density of hydrogen gas (at normal boiling point) relative to the density of air (at STP)	1.03	1.38			
Density of gas relative to the density of air (at STP)	0.070	0.55			
Diffusion coefficient	0.63 cm^2/sec	0.2 cm^2/sec		0.08 cm^2/sec	
Flammability limits in air (by volume)	(4.1-74)%	(5.3-15)%	(6.0-37)%	(1.5-7.6)%	(0.8-5.6)%
Detonatability limits in air (by volume)	(18-59)%	(6.3-14)%			
Ignition temperature	850 K	807 K	700 K	530 K	522 K
Ignition energy	20 J	300 J		250 J	
Flame temperature	2400 K	2190 K			
Flame velocity	2.75 m/sec	0.37 m/sec	0.41 m/sec	0.3 m/sec	
Quenching distance	0.06 cm	0.23 cm		0.25 cm	
Emissivity of flame	0.10	1.0			
Heat of combustion	120 MJ/kg	50 MJ/kg	20 MJ/kg	44 MJ/kg	43 MJ/kg
	8.5 GJ/m^3	21 GJ/m^3	16 GJ/m^3	31 GJ/m^3	34 GJ/m^3

* Not applicable; these fuels are not single molecular species and their components exhibit a wide range of boiling points.

1.2 Solar Energy Storage in Photoelectrochemical Cells

PEC's are devices that combine both photochemical and photovoltaic processes. The concepts and theories on which PEC's rest are new and have yet to be fully understood in particular with respect to well known photoelectric cells, and with respect to less well known naturally occuring photochemical processes. PEC's are generally classified into two types: those in which the light is absorbed by components in the electrolyte solution; the products of the photochemistry then migrate to electrodes (these are usually called photogalvanic cells); and secondly those in which the light is absorbed near the electrode surface (almost always the electrode is a semiconductor). In the latter case, the potential generated by the light can drive an endergonic chemical reaction or produce electrical power.

1.2.1 Photogalvanic Cells

A photogalvanic device is taken to be a battery in which the entire solution absorbs light directly to generate photochemical species which, upon back reaction through an external circuit with the aid of suitable electrodes(invariably made of platinum metal), produce electrical power: Figure 1.2.1 shows the first investigation of the photogalvanic effect for solar energy conversion in the iron-thionine cell, as a light-to-electricity convertor. By estimation, the power conversion efficiency of such a cell could be as high as 18%, but a more realistic estimate would be between 5 and 9%[13]. Unfortunately, efficiencies obtained in experiments to date have not been too promising. The principal difficulty appears to be how to prevent

the back reactions before the products of the photochemical reactions have a chance to migrate to the electrodes.

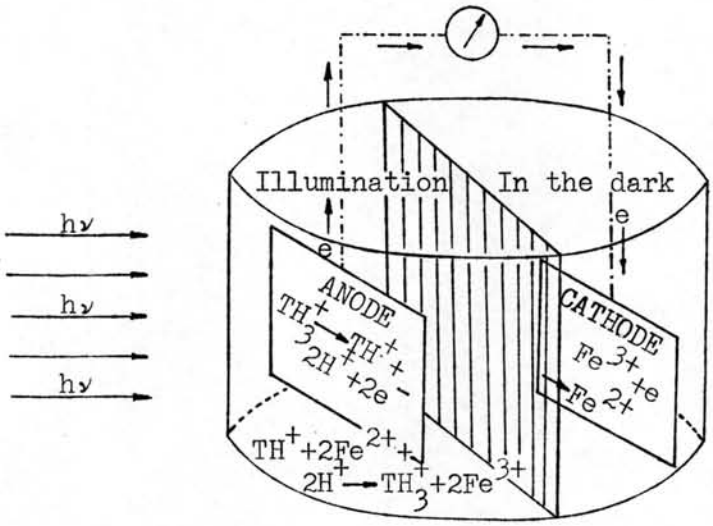
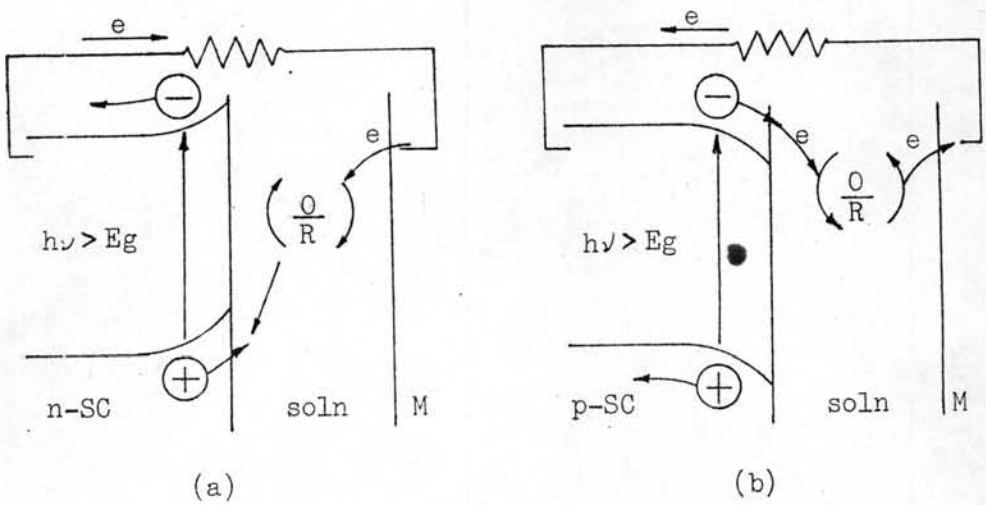


Figure 1.2.1 Primitive iron-thionine photogalvanic cell.[11]

1.2.2 Photoelectrochemical Cells (PEC's) with Semiconductor Electrodes

These PEC's can be divided into three types: electrochemical photovoltaic cells or semiconductor liquid-junction solar cells, photoelectrosynthetic cells (also called photoelectrolysis cells or PEC's) and photocatalytic cells. The schematic representation of these different types of PEC's and examples of these are showed in Figure 1.2.2. As noted above, in this type of cell the light is absorbed near the surface of one or both electrodes. Due to the electric field built up at the phase barrier between the semiconductor and the electrolyte, the electron and hole created by the absorption of a photon can be seperated before recombination. If

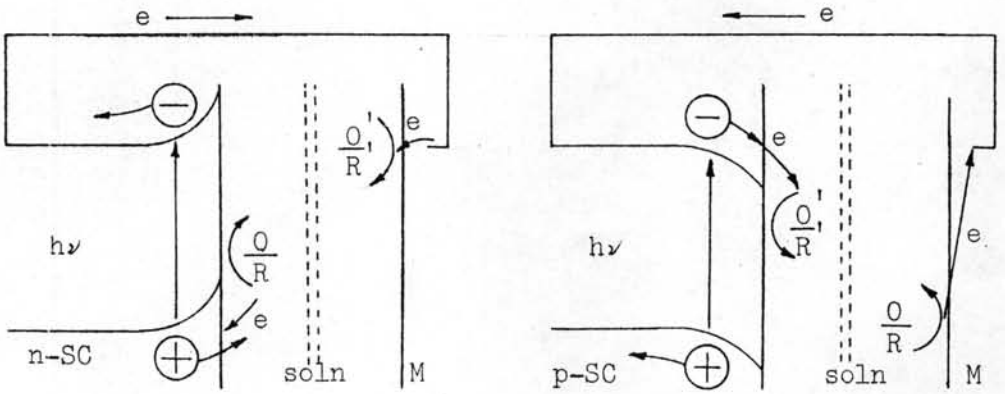
Figure 1.2.2 Schematic representation of different types of PEC's[6] and the examples



Photovoltaic cells: (a) n-type; n-CdSe/Se^{2-}, Se_2^{2-}/Pt[81] or

n-GaAs/Se^{2-}, Se_2^{2-}/C[65]

(b) p-type; p-MoS_2/I^-, I_2/Pt[20]



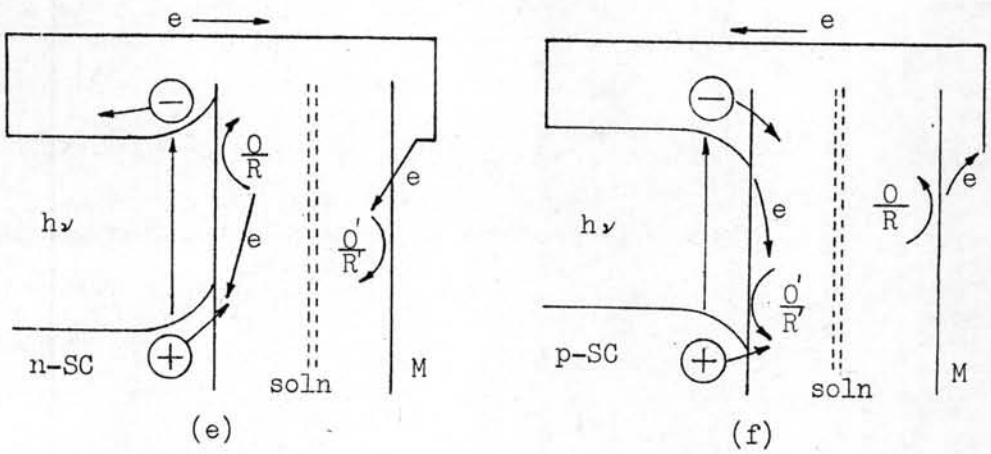
$$R + O' \xrightarrow{h\nu} O + R' \quad \Delta G_{dark} > 0$$

Photoelectrosynthesis cells: (c) n-type; $n\text{-}SrTiO_3/H_2O/Pt$ [95]

$(H_2O \longrightarrow H_2 + \tfrac{1}{2}O_2)$

(d) p-type; $p\text{-}GaP/CO_2, H_2O/C$ [42]

(reduction of CO_2)



Photocatalytic cells: (e) n-type; $n\text{-}TiO_2/CH_3COOH/Pt$ [16]

$(CH_3COOH \longrightarrow \tfrac{1}{2}C_2H_6 + CO_2 + H_2)$

(f) p-type; $p\text{-}GaP/DME, AlCl_3, N_2/Al$ [6]

(reduction of N_2 by Al)

the surface becomes electron-rich in the light (this happens in an n-type semiconductor) the components in the solution may be reduced if the redox potential is appropriate. Conversely, if the electrode surface becomes electron-deficient in the light (this happens in an p-type semiconductor), components in the solution may become oxidized again if the redox potential is appropriate.

If the electrode reactions are reversible, and lead only to products that essentially carry charge from one electrode to the other, the only product is electrical power. This occurs in the photovoltaic cell. A problem with the cell is the decomposition of electrodes in the solution. Many investigators have attemped to improve the cell with power conversion efficiencies between 10-19%. Thus these cells may well become competitive one day with solid state solar cells.

In other cases the electrode reactions may be irreversible, thus leading to a stable chemical product, it occurs in the latter two types of PEC's. In electrosynthetic cells, the reaction at the counter electrode is different than that at the semiconductor (so that a seperator might be necessary in the all to keep the products a part). In this case, the net cell reaction is driven by light in the nonspontaneous direction ($\Delta G > 0$), so that radiant energy is stored as chemical energy. If this condition does not exist, it is still possible to drive the reaction in the desired direction by applying an external bias to the cell. Photocatalytic cells are similar to these, except that the relative locations of the potentials

of the O/R and O'/R' couples are changed. In this case the reaction is driven in the spontaneous direction (which is presumably very slow in the dark with $\Delta G < 0$), with the light energy used to overcome the energy of activation of the process.

For photodecomposition of water into hydrogen, the suitable semiconductor electrodes are TiO_2 and $SrTiO_3$ electrodes. They are stable in aqueous solution, but their large bandgap ($\sim$ 3eV) brings about only small efficiencies when using the solar spectra.

The possible ways for increasing sunlight conversion efficiency of PEC's with improved semiconductor electrodes are as follows:

1. New small band gap semiconductors: Because most of the solar radiation lies at the long wavelengths range, this will be important when selective absorbers are considered for suitble bandgap energy corresponding to the spectra energy. The common n-type semiconductors with small bandgap energy such as CdS, Si, GaAs etc. have been prepared and tested for use in PEC's in various laboratories. The major problem of small bandgap materials is their unstable nature over a long time for PEC's. Some present reviews show that they may be stable in suitable solution (electrolytes).

2. Dye sensitization: A large number of dyes (e.g. chlorophyll, a variety of cyanine dyes etc.) are capable of absorbing incident visible light and transfering the excited state to the substrate material (semiconductor with large bandgap) in Figure 1.2.2 g.

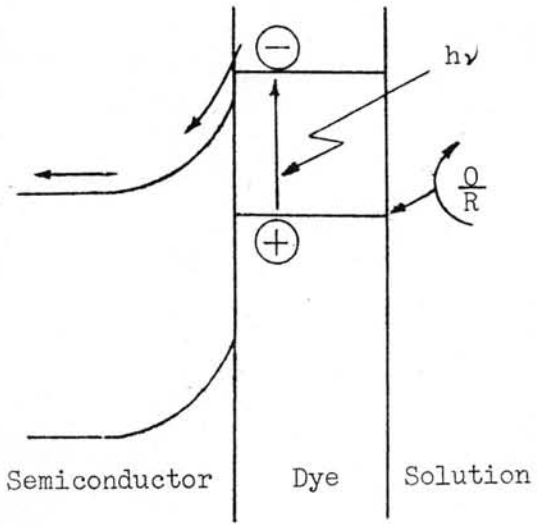


Figure 1.2.2g. Dye sensitization of photoprocess at semiconductor electrode.

The major problem with the dyes studied is the rapid degradation of respone in PEC's with the dye-coated electrodes. Recently, many review papers[69,75] of PEC's with semiconductor (or metal) coated with chlorophyll have given a satisfactory response for electricity conversion, but poor response for chemical conversion. However, the permanent coating of dye material on semiconductors and their performance have been avoided for a long time in PEC's work.

3. Impurity sensitization: An interesting approach for extending the response of a large band gap semiconductor to visible light is impurity doping. The excitation of the impurity into the semiconductor band can result in free electron and hole formation. There are many reports of water photoelectrolysis by TiO_2 electrodes with doping transition impurities (such as Fe, Al, Cr, Mn, V, Ni). Further work is in progress to find other dopants and new techniques which can give stronger absorptions.

4. Heterostructure formation: This method of sensitiza-

tion is an attempt to combine the corrosion resistance of several large band gap semiconductors with the good sunlight absorbing characteristics of smaller band gap materials. This type of heterostructure device is used with the stable large band gap semiconductor, which is transparent to most of the incident solar spectrum, in contact with the solution. The optical generation of hole-electron pairs in then expected to occur in the shielded small band gap material, so that subsequent carrier transport through the large band gap material is essential for the device to operate. There have been attempts to form heterostructure devices by depositing TiO_2 on GaAs, GaP, CdS, CdSe and Si. Studies have also been made on structures where a thin metal film, such as gold, was used to protect small band gap semiconductors from corrosion. Of course, a film of metal sharply reduces the light transmission to the substrate. However, there remains the question of long term stability of these devices, and this problem will require further studies.

1.2.3 Photoelectrocatalytic Cells

Photoelectrocatalytic Cells are similar to PEC's but the semiconductor acts as a photocatalyst for chemical synthesis (e.g., H_2, NH_3 and CO_2 reduction products). The photogenerated electrons and holes (in Figure 1.2.3) can be effectively separated in the interfacial region, and cause various redox reactions on the surface of semiconductor particles suspended in aqueons or ther solutions.

The overall reaction: $R + O' \xrightarrow[\text{semiconductor}]{h\nu} R' + O$

These cell systems are still unconvenient to use with sunlight

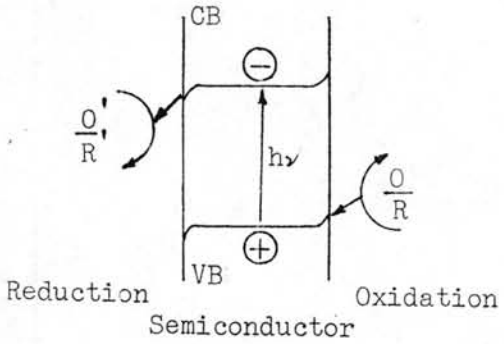


Figure 1.2.3 Schematic presentation of photoelectrocatalytic redox reaction on semiconductor.

illumination and the conversion efficiencies should be improved.

1.2.4 Previous Work on Electrochemical Photocell Hydrogen Production

Electrochemical Photocell (EPC) is a kind of PEC's for hydrogen synthesis. The photoelectrode always is TiO_2 semiconductor in crystal form, it is robust, long lived and suited to direct hydrogen production. Therefore it is of possible economic interest if prepared in sufficiently low cost, large surface area form. There are many methods of electrode preparation, as against crystal preparation.

Earlier, Fujishima and Honda[33] have discussed the methods of forming oxide films on Ti-metal, three methods were studied the thermal formation of oxide film by simple heating was found to be the best. Fleischauer and Allen[25] prepared TiO_2-thin-film electrodes by the radio-frequency sputtering of TiO_2 on conductive substrates. For the TiO_2 thin film combined with dye sensitizers, an applied bias voltage is necessary for visual observation of sensitized hydrogen formation. Haneman and Holmes[43] prepared TiO_2 thin-film by sputtering, but only on Ti-metal targets. They studied

stability and photoresponse on light intensity only. Ahlgren[1] studied the current-voltage characteristics of photoelectrolysis cells for optimizating bias voltages to apply to the alls, where the photoelectrodes were made of TiO_2 thin film by simple heating.

1.3 Purpose of the study

PEC's offers a new dimension of research in the general direction of the well-known photocell with two possible variants one being a competitor to the photocell for electricity and secondly as a novel process to copy the photosynthesis process with man-made materials and to produce a host of chemicals directly from solar energy. PEC's offers this possibility which will have to be investigated further. For Thailand this topic offers challenging perspectives to start on this interesting topic by being within sight from the forefront of knowledge in this area. The basic approach of this study is to read the literature, keep up with the latest efforts, duplicate experiment, study untested parameters and particularly engineering parameters, and generally visualize the study as an important springboard for future work in this area. Fujishima and Honda's EPC for hydrogen production without any external supply is chosen to confirm the device's reliability and study some parameters in the system.