1. INTRODUCTION

The search for renewable sources of energy has led to an increasing interest in photoelectrochemical cells because of their potential applicability in directly converting light into electrical energy. Photoelectrochemical devices can be divided into three main categories (1) : (a) those in which absorption of ultrabandgap light by a semiconducting electrode or particle results in minority carrier injection into solution thereby driving a desirable Faradic process at a thermodynamic underpotential (semiconductor liquid junction solar cells) (2,3); (b) those in which light absorption in a pigmented micelle, membrane or coating yields charge separation in or across an insulating support medium (model systems for photosynthesis) (4); (c) those in which a homogeneous photochemical reaction, nearly always an electron transfer, yields electroactive products which can diffuse to, and react at conventional electrodes (homogeneous photogalvanic cells). The third category of devices are the subject of this research.

The term 'photogalvanic effect' (5a) is used to denote a special case of the so-called Bequerel effect (6), in which the influence of light on the electrode potential is due to a photochemical process in the body of the electrolyte (as distinct from photochemical or photoelectric processes in the surface layer of the

electrode, which are the basis of the original Becquerel effect).

Albery (7) has divided photogolvanic cells into two types illustrated in Figure 1. In the semiconductor

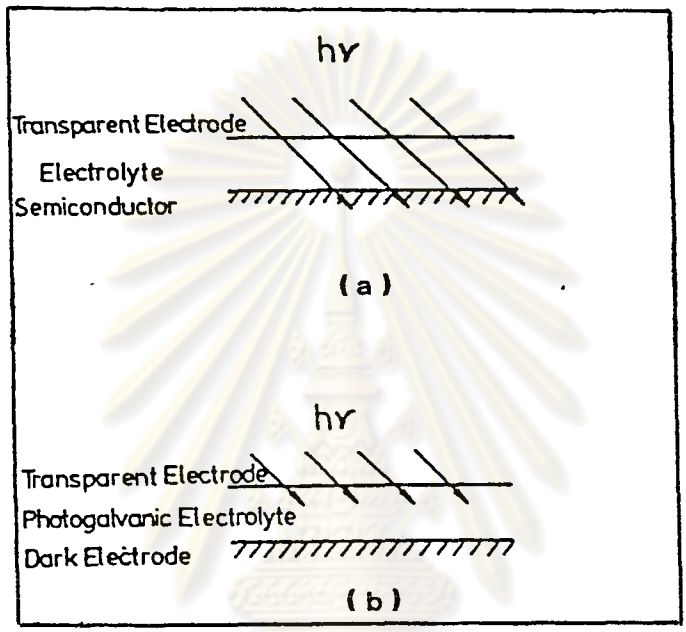


Figure 1. Two types of photogalvanic cells: (a) semiconductor device (b) homogeneous photogalvanic device

device (semiconductor-liquid junction cell as the first category stated by Archer and Ferreira) (1) solar energy is absorbed in a semiconductor electrode. As shown in Figure 2, the field in the space-charge layer helps to separate the promoted electron from the hole it left behind. For an n-type semiconductor the holes accumulate at the electrode surface and carry out the oxidation of the reduced species in the electrolyte. At the other electrode, the reverse reaction takes place. In this

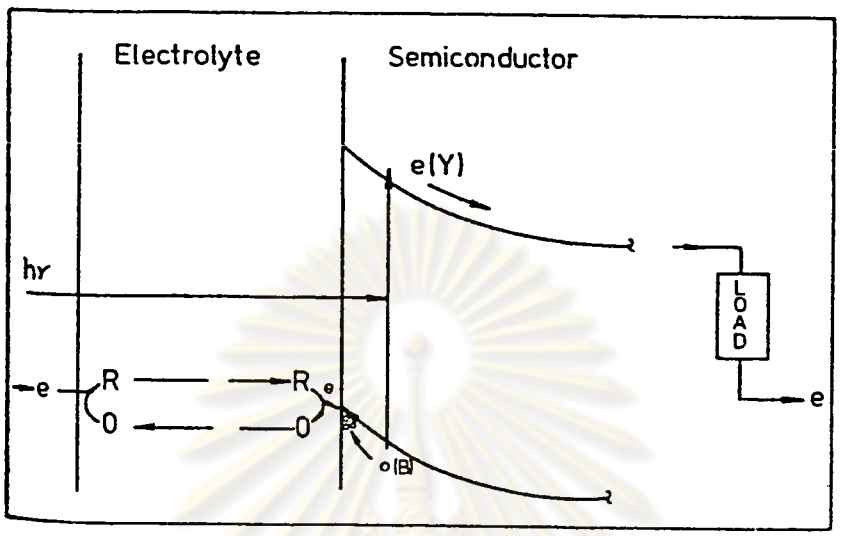


Figure 2. Schematic operation of an n-type semiconductor photogalvanic cell.

device electrochemical reactions in the electrolyte serve to carry the current. The concentration of holes may be more than a million times that in the bulk of the semiconductor (8,9) in order to drive the necessary current through the interface. This accumulation means instead of carrying out the desired oxidation, the holes oxidize the semiconductor material itself. This is the main disadvantage of this type of cell. The second disadvantage is that the high efficiencies are achieved only with single crystals. Indeed Parkinson, Heller, and Miller (10) have shown that a cell consisting of n-type GaAs with a selenide-polyselenide redox system achieves power conversion efficiencies of 12%. That is, 12% of the energy of the incoming solar radiation (including all

wavelengths) is converted into electrical energy. While cells using powders give efficiencies of about 8%, they can still suffer from problems of corrosion. Unfortunately, even a little corrosion is a serious problem.

The corrosion problem is not nearly so serious for the second type of photogalvanic cell illustrated in Figure 2 (b). Here the solar radiation is absorbed by a dye in the electrolyte, and it is in this phase (so called homogeneous photogalvanic cell) that the energetic species are made and separated. While photochemical degradation of the dye will take place, it is much easier to replace the electrolyte than the corroded electrodes in the first type.

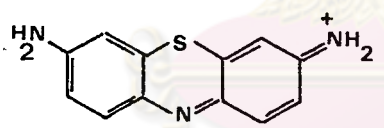
A number of photogalvanic cells have been proposed and studied with the aim of obtaining higher photoinduced potential (photopotential) and photocurrent. A few among them with their maximum photopotentials are aqueous systems of thionine-ferrous (250 mV) (5), proflavin-EDTA (476 mV) (11) phenosafranine-EDTA (615 mV) (12), riboflavin-EDTA (654 mV) (13) and tolusafranine (SAF)-EDTA* (844 mV) (14).

* This photogalvanic system has been found to exhibit a photoinduced potential of 926 mV under the optimum conditions (15).

Rabinowitch (5a) found the photogalvanic effect in thionine-ferrous system. He first studied the photochemistry of this system and its photogalvanic properties (5b) including a general kinetic theory of this effect (5c). The system consists of a reversibly reducible organic dyestuff, thionine, together with an inorganic oxidation-reduction pair, Fe^{3+}/Fe^{2+}. The reaction is given as,

$$\text{Thionine} + 2Fe^{2+} \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} \text{leucothionine} + 2Fe^{3+} \quad (1)$$

Thionine is a purple dye of the thiazine class whose structure is shown below:



Thionine

The absorption maximum (λ_{max}) lies at 597 nm (5a). When an aqueous solution of thionine and ferrous ion is illuminated by light the ferrous ion reduces the purple-colored dye thionine (i.e. transfers an electron to it) to give colorless leucothionine and ferric ion. When the light is removed the reaction reverses over a period of several minutes and the purple color of the dye returns. The operation can be repeated through an indefinite

number of cycles. If two electrodes are placed in the solution which is then illuminated, it is possible to obtain a voltage between the electrodes up to 0.25 volt, because of the difference in concentration of the oxidized and reduced materials. When the electrodes are connected by a wire, the electrons pass from the leucothionine to the Fe^{3+} ion through the connecting wire, and the thionine with its purple color is restored. In this way some of light energy is stored for a while and then made available as electrical energy. Figure 3 illustrates the response of a thionine-ferrous solution to light as a function of time. The curve represents the changes in the potential of an electrode (eg. Pt electrode) placed in the solution-the "Photogalvanic effect."

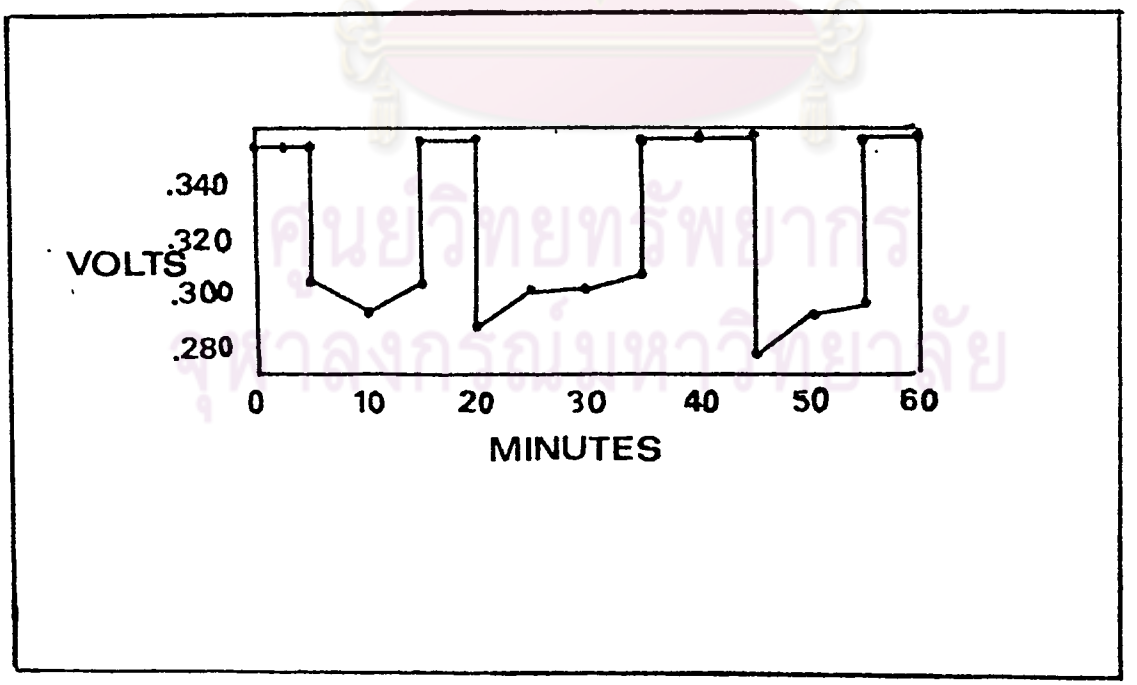


Figure 3. Response of a thionine ferrous solution to light as a function of time.

The absolute value of the effect depends (5b) on the concentrations of thionine and ferrous ion, pH, and light intensity.

Shifts in oxidation-reduction equilibria are probably the cause of most photogalvanic effects. This photogalvanic cell, thionine-ferrous system, is probably the most highly light-sensitive oxidation-reduction equilibrium known. Up to now it is expected to be the most successful homogeneous photogalvanic cell (16). Photochemically, it is similar to the well-known inorganic, iodine-iron, system. The later is, however, about 100 times slower in attaining both its steady state in light and its stable state in the dark. The reaction is shown as,

$$I_2 + 2Fe^{2+} \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} 2I^- + 2Fe^{3+} \qquad (2)$$

The iodine-iron system also shows photogalvanic effect (17). But apart from being more sluggish than the thionine-iron system, it is also considerably less sensitive, probably first because the difference between the normal potentials of iodine and iron (0.14 volt) is much smaller than those of thionine and iron (0.41 volt at pH 2) (5a). Secondly because the maximum extinction coefficient of iodine ($\varepsilon_{max} = 8 \times 10^2$) is much lower than that of thionine (18) (ε_{max} 5×10^4).

Although the performance of thionine-iron redox system in photogalvanic cells has been investigated, developed, and improved by many workers (16, 19-24) to be the most successful photogalvanic cell, the power conversion efficiencies of those cells have been found to be very low (< 0.1%) (24). However, theoretical considerations indicate that efficiencies as high as 18% could be obtained (25). Two reasons (24) for the poor performance of the cells are first the low solubility of thionine, which means that the incident solar radiation is absorbed too far from the illuminated electrode, and secondly the formation of dimers which do not undergo the desired photoredox reaction.

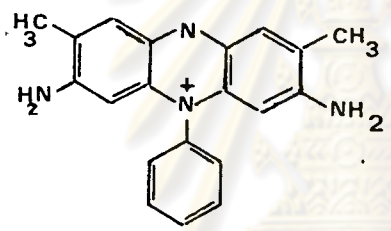
Other three photogalvanic systems which give the highest photopotentials 476, 615, and 654 mV are proflavin-EDTA, phenosafranine-EDTA, and riboflavin-EDTA aqueous systems, respectively. These values are higher than that of thionine-iron system, but are much lower than the potential difference of ca. 800 mV induced by photosystem I or II involved in the photosynthesis unit in green plants.

In 1977, Kaneko and Yamada (17) reported the production of a simple system, synthetic dyestuff (tolusafranine (SAF))-EDTA, which exhibited a remarkably high photopotential of over 800 mV. This is considerably greater than the 250 mV photopotentials recorded for the

well characterized thionine-iron system and equals the approximately 800 mV potential difference induced in photosystem I or II in green plant photosynthesis. The reaction in the safranine-EDTA system is believed to be:

$$\text{SAP} + \text{EDTA} \xrightarrow{\text{light}} \text{leuco-SAF} + \text{oxidized-EDTA} \quad (3)$$

Tolusafranine (safranine T; SAF) is a dye of the phenazine class. The structure is shown below:



SAF

The usefulness of this system for photochemical energy storage is, however, limited by the irreversible nature of EDTA photochemical reactions. The similar anaerobic photoreduction of either methylene blue or thionine by EDTA results in photobleaching of the dye and irreversible oxidation of EDTA. The leucodye formed in the photoreaction can be reoxidized by oxygen, with EDTA remaining permanently oxidized. The SAF-EDTA system exhibits an identical behavior.

The principal purpose of this work is to search for new aqueous systems of photogalvanic cells which can give reasonably high photopotentials (> 400 mV) and to

study of the photogalvanic properties of these new systems. The effects of variables such as the concentration of the components, pH, temperature, organic solvents, oxygen gas, and diffusion lengths, on the photopotential and photocurrent are also investigated. The optimum condition for each photogalvanic system is reported and the behavior of the photocurrent is discussed.

The new photogalvanic systems are found by selecting many types of synthetic organic dyes as the light absorbers, and redox couples which can donate or accept an electron to or from the active species of the dyes.

Besides finding new systems, the well-known and interesting photogalvanic systems such as thionine-ferrous and SAF-EDTA are also studied for comparison.

Cell efficiency, for solar energy conversion, is expressed as the ratio of power output at the maximum power point to incident radiant power (1). As stated before, the power conversion efficiencies of photogalvanic cells have been found to be very low, while the maximum efficiencies of semiconductor liquid junction cells ($\sim$ 12%) (16) and of solid-state solar cells ($\sim$ 1%) (16) are much greater. In the present investigation the power conversion efficiencies of the new photogalvanic cells are calculated and reported.