

Photogalvanic Cell for Solar Energy Conversion: Eosin-Glucose System

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A photogalvanic cell containing eosin as the photosensitizer and glucose as the reductant has been used for solar energy conversion. The photopotential and photocurrent generated by this cell were 412 mV and 16.0 μ A respectively. The effects of various parameters like pH, reductant and dye concentration, light intensity, temperature etc. on the electrical output of the cell have been studied. The current-voltage (*i*-*V*) characteristics of the cell have also been observed. A tentative mechanism for the generation of the photocurrent in this photogalvanic cell has been proposed.

Key Words: Photogalvanic cell, Solar energy, Eosin, Glucose.

INTRODUCTION

Robinowitch¹ first studied the photogalvanic effect in an iron-thionine system. Later this kind of work was carried out by various workers^{2–13} throughout the world. Hoffmann and Lichtin¹⁴ discussed the various difficulties encountered in the development of this field. Although, theoretical conversion efficiency of photogalvanic cell is about 18%, but unfortunately the observed conversion efficiencies are quite low (0.03–0.1%). Back-electron transfer, lower stability of dyes, aggregation of dye molecules around the electrodes etc. are the main reasons for the low values. The present work describes the use of eosin-glucose system in a photogalvanic cell for solar energy conversion.

EXPERIMENTAL

Eosin, sodium hydroxide and glucose were used in the present work. All the solutions were prepared in doubly distilled water. A mixture of solution of dye (eosin), glucose and sodium hydroxide was contained in an H-type cell. A platinum electrode ($0.01 \times 0.01 \text{ m}^2$) was dipped into one limb of the cell and a saturated calomel electrode (SCE) in the other. The platinum electrode was exposed to a 200 W tungsten lamp and the limb containing SCE was kept in dark. A water filter was used to cut off thermal radiations. The photocurrent and photopotential generated in this system were measured by a multimeter (Systronics model 435) and digital pH-meter (Systronics model 335), respectively. The light intensity was

measured with the help of a solarimeter (CEL 201). The current-voltage characteristic of the cell was studied using an external load (log 500 k Ω) in the circuit.

RESULTS AND DISCUSSION

Photogalvanic cell was first placed in dark to attain a stable potential and then the platinum electrode was exposed to light. It was observed that the potential changes on illumination and it reaches a constant value after a certain period. When the light source was removed, the direction of change in potential was reversed and again after some time a stable potential was obtained. The rate of fall of potential in the presence of light and the rise in potential in dark were found to be 5.8 mV min⁻¹ and 2.5 mV min⁻¹ respectively. Similarly it was observed that there is a rapid rise in the current of eosin-glucose system on illumination and it reaches a maximum value (i_{\max}) within a few minutes. The current was then found to decrease gradually with further increase in the period of illumination and finally reaching a constant value (i_{eq}). The current was also found to decrease on removing the source of illumination. The rate of fall of current in light from i_{\max} to i_{eq} and dark are 0.72 $\mu\text{A min}^{-1}$ and 0.12 $\mu\text{A min}^{-1}$, respectively.

Effect of Variation of pH

Photogalvanic cell containing eosin-glucose system was found to be quite sensitive to the pH of the solution. It was observed that there is an increase in the photopotential of this system with the increase in pH value (in the alkaline range). At pH = 10.6, a maximum was obtained. On further increase in pH, a decrease in photopotential was observed. This behaviour was shown in Table-1.

It has been observed that the pH for optimum condition for this system has a relation with the pK_a value of the reductant used and the desired pH is towards strong alkaline nature (pH \approx pK_a + 1 to 2). This may be due to availability of reductant in a better donor form (in anionic form).

TABLE-1
EFFECT OF pH VARIATION

[Eosin] = 2.5×10^{-5} M; [Glucose] = 3.75×10^{-4} M; Intensity = 10.4 mW cm⁻²;
Temperature = 303 K

pH	Photopotential (mV)	Photocurrent (μA)
9.50	420	12.0
9.75	500	14.0
10.05	582	16.0
10.25	625	18.0
10.60	700	20.0
10.70	635	18.0
11.00	554	15.0
11.25	498	16.0
11.50	430	12.0

Effect of Variation of Glucose Concentration

The effect of variation of the glucose concentration on the photopotential and photocurrent of this system is given in Table-2.

TABLE-2
EFFECT OF GLUCOSE CONCENTRATION

[Eosin] = 2.5×10^{-5} M; pH = 10.6; Intensity = 10.4 mW cm^{-2} ; Temperature = 303 K

[Glucose] $\times 10^4$ M	Photopotential (mV)	Photocurrent (μA)
2.50	514	14.0
2.75	550	15.0
3.25	619	17.5
3.50	652	19.0
3.75	700	20.0
4.50	663	18.4
5.00	638	17.5
6.00	575	15.5
7.00	568	13.7

It was observed that the increase in the concentration of reductant was associated with a corresponding increase in the photopotential till it reaches a maximum and then there is a decrease in photopotential on further increase in the concentration of reductant. This behaviour is similar to that of pH dependence. The lowering in concentration of reductant resulted into a fall in power output due to less number of molecules available for electron donation to Dye* (excited state of the dye) whereas the larger concentrations of reductant will hinder the movement of dye molecules to reach the electrode in the desired time limit.

Effect of variation of Eosin Concentration

It was observed that the photopotential and photocurrent were increased with the increase in the concentration of eosin. A maximum was obtained for a particular value of eosin concentration, above which a decrease in the electrical output was obtained. The effect of variation of eosin concentration on photopotential and photocurrent is reported in Table-3.

It was observed that the concentration of eosin necessary for efficient conversion of light into electrical energy in this photogalvanic cell was *ca.* 10^{-5} M. The lower concentration of eosin gives less photopotential because of the small number of dye molecules available in the system for excitation and the donation of the electrons to the platinum electrode whereas larger concentrations of eosin again resulted into lower photopotential because of the lowering of intensity of light reaching the dye molecules near the electrode as the major part of light may be absorbed by the dye molecules available in the path. In other words, the dye itself may act as a filter.

TABLE-3
EFFECT OF EOSIN CONCENTRATION

[Glucose] = 3.75×10^{-4} M; pH = 10.6; Intensity = 10.4 mW cm^{-2} ; Temperature = 303 K

[Eosin] $\times 10^5$ M	Photopotential (mV)	Photocurrent (μA)
1.25	576	16.0
1.60	610	17.2
2.00	652	18.0
2.50	700	20.0
3.00	672	18.6
3.75	643	18.0
5.00	548	16.0
6.00	515	13.5
7.00	470	12.0

i-V Characteristics of the Cell

The short circuit current (i_{sc}) and open circuit voltage (V_{oc}) of the photogalvanic cell were measured by multimeter (keeping the circuit closed) and from digital pH-meter (keeping the other circuit open), respectively. The current and potential values in between these two extremes were recorded with the help of a carbon pot (log 500 k Ω) connected in the circuit of multimeter through which the external load was applied. The i-V characteristics of photogalvanic cell containing eosin-glucose system are graphically represented in Fig. 1.

It was observed that i-V curve deviated from its regular rectangular shape. A

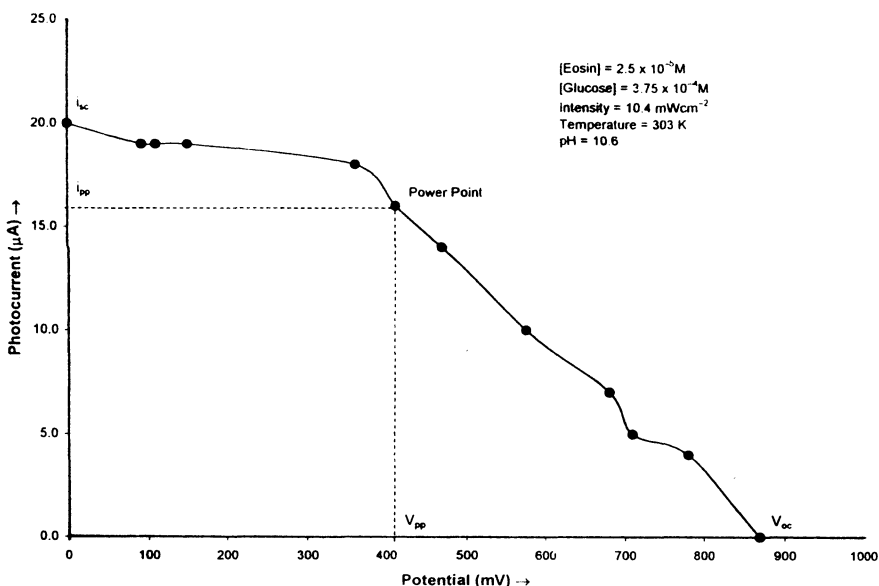


Fig. 1. Current-potential (i-V) curve of the cell

point in *i*-*V* curve, called power point (pp) was determined where the product of current and potential is maximum and the fill-factor was calculated using the formula

$$n = \text{fill factor} = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}} \quad (1)$$

where V_{pp} and i_{pp} represent the values of potential and current at power point, respectively. The value of fill-factor for this system was 0.38. It indicates that the system is 38% effective as compared to its expected theoretical efficiency.

Effect of Diffusion Length

The effect of variation of diffusion length (distance between electrodes) on the current parameters of the cell (i_{max} , i_{eq} and initial rate of generation of photocurrent) was studied using H-cells of different dimensions. It was observed that with the increase in diffusion length, i_{max} and rate ($\mu\text{A min}^{-1}$) increased but the i_{eq} showed a negligibly small decreasing behaviour with the increase in diffusion length. So virtually, it may be considered as unaffected by the change in diffusion length. The results are summarized in Table-4.

TABLE-4
EFFECT OF DIFFUSION LENGTH

[Eosin] = 2.5×10^{-5} M; [Glucose] = 3.75×10^{-4} M; pH = 10.6; Intensity = 10.4 mW cm^{-2} ; Temperature = 303 K

Diffusion length D_L (cm)	Maximum current i_{max} (μA)	Equilibrium current i_{eq} (μA)	Rate of initial generation of current
3.0	80.0	21.0	6.6
3.5	88.0	20.0	8.3
4.0	100.0	20.0	10.0
4.5	107.0	20.0	12.6
5.0	114.0	20.0	13.2

It was observed that there is a sharp increase in photocurrent in first few minutes of illumination (i_{max}) and then there is a gradual decrease to a stable value of photocurrent (i_{eq}). This type of behaviour of photocurrent indicates an initial rapid reaction followed by slow rate determining step at a later stage. Three probable cases may be considered to give a better understanding of the nature of the active electrodes species (Table-5).

TABLE-5
PROBABLE ELECTRODE ACTIVE SPECIES

Case	Illuminated chamber	Dark chamber
I	Eosin	Oxidized form of the reductant (O_xR)
II	Leuco- or semireduced eosin	Oxidized form of the reductant (O_xR)
III	Leuco- or semireduced eosin	Eosin

If the oxidized form of the reductant (O_xR) is considered as the electrode active species, then it must diffuse from the illuminated chamber to the dark chamber to accept an electron from the dark electrode and correspondingly the rate of increase of the photocurrent i_{max} should be inversely proportional to the diffusion length, but this is not in agreement with the experimental data. It was observed that the value of i_{max} and the initial rate of photocurrent generation were proportional to the diffusion length; however, the value of i_{eq} was found to be independent of this variation (rather it showed negligibly small decreasing behaviour). On the basis of these observations, the oxidized form of the reductant cannot be considered as the true electrode active species at the dark electrode and the cases (I) and (II) given above become out of consideration. It may, therefore, be concluded that main electrode active species at the illuminated and dark electrodes are leuco or semireduced eosin and the dye eosin itself, respectively. The reductant and its oxidized product behave only as the electron carriers through the path.

Effect of Electrode Area, Temperature and Light Intensity

The effect of electrode area on the current parameters of the cell was also studied. It was found that with the increase in the electrode area, the value of maximum photocurrent (i_{max}) was found to increase, whereas i_{eq} was found almost independent of this variation (rather it is affected in reverse manner).

With the increase in temperature, the photocurrent of photogalvanic cell was found to increase with a corresponding rapid fall in potential. Further, it was observed that photocurrent and photopotential both showed direct linear relationship with change in temperature. This increase in photocurrent with the rise in temperature can be explained on the fact that internal resistance of the cell decreases at higher temperatures. The decrease in internal resistance of the cell and resultant increase in photocurrent will result into a corresponding fall in photopotential; however, the rapid fall of potential cannot be compensated with the corresponding rise in photocurrent as far as the power of the cell is concerned. It is, therefore, necessary to avoid higher temperatures for better output from photogalvanic cells.

It was found that photocurrent showed a linear increasing behaviour with the increase in light intensity whereas photopotential increases in logarithmic manner. The increase in light intensity increases the number of photons per unit area (incident power) striking the dye molecules around platinum electrode and there is a corresponding increase in the photopotential and photocurrent of the photogalvanic cell. However, increase in light intensity will also raise the temperature of the cell, unless an IR filter is used. In the present investigations a water filter was used to cut thermal radiations and the light intensity of the medium order (10.4 mW cm^{-2}) was used for all variations.

Conversion Efficiency and Performance of the Cell

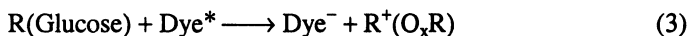
The performance of the photogalvanic cell was studied by applying the external load necessary to bring the current and potential to the power point after removing the source of light. It was observed that the cell could be used in

darkness for 3 min. The photovoltaic cell cannot be used in dark even for a second, whereas this photogalvanic system (eosin-glucose) has an additional advantage of being usable in the dark. Of course the conversion efficiency is low (0.06% in this case).

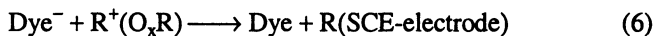
Mechanism

On the basis of the above observation a mechanism of photocurrent generation in the photogalvanic cell is represented as:

Illuminated chamber:



Dark chamber:



R, R⁺, Dye, Dye⁻ are the reductant glucose, its oxidized form, eosin and its leuco form respectively.

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