USE OF EOSIN–EDTA SYSTEM IN A PHOTOGALVANIC CELL FOR SOLAR ENERGY CONVERSION

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ABSTRACT

A photogalvanic cell containing eosin as photosensitizer and EDTA as a reductnat was investigated for solar energy conversion. Maximum photocurrent and photopotential generated by this cell were 16 μA and 560 mV, respectively. The effect of various parameters on the power output of the cell was studied. Current voltage (i–V) characteristics of the cell was also examined and a tentative mechanism for the generation of photocurrent in the photogalvanic cell has been proposed.

Key words: Photogalvanic cell, Solar energy cenersion, Photogeneration.

INTRODUCTION

Photogalvanic effect (PGE) was first discovered by Rideal and Williams[1], but was systematically investigated by Rabinowitch[2]. Thereafter, this kind of work was pursued by various workers throughout the world[3–15]. Hoffman and Lichtin[16] discussed the various difficulties encountered in the development of this field. Theoretical conversion efficiency of photogalvanic cells is about 18%, but unfortunately the observed conversion efficiencies are quite low (0.03–0.1%). Back–electron transfer, lower stability of dyes, and aggregation of dye molecules around the electrode, etc., are the main reasons for the low values.

A detailed survey of literature reveals that no attention has been paid to eosin–EDTA system in a photogalvanic cell for solar energy conversion and, therefore, the present work was undertaken.

EXPERIMENTAL

Eosin (Chroma), EDTA (Ranbaxy) and sodium hydroxide (IDPL) were used. All the solutions were prepared in doubly distilled water. A mixtue of solutions of dye, EDTA and NaOH was taken in a H–shaped glass cell, Platinum electrode (1 x 1 cm^2) was dipped in one limb of the cell and saturated calomel electrode (SCE) in the other. The platinum electrode was

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exposed to a 200 tungsten lamp (Sylvania) and the limb containing SCE was kept in the dark. A water filter was used to avoid thermal effects.

The photopotential and photocurrent generated by the system Eosin/EDTA/OH$^-$/hv were measured by a digital pH meter (Systronics–Model 335) and a multimeter (Systronics Model 435), respectively. The current voltage (i–V) characteristics of the cell was studied by using an external load (log 500 K) in the circuit.

RESULTS AND DISCUSSION

Effect of pH on the Electrical Output of the Cell

The effect of the variation of pH on the electrical output of the cell was observed and the results are reported in Table 1.

Table 1. Variation of pH

[Eosin]   = 2.50 x 10^{-5} M   Temperature = 303 K

[EDTA]   = 37.5 x 10^{-4} M   Intensity   = 10.4 mWcm^{-2}

pH	Photopotential (mV)	Photocurrent (μA)
9.6	380.0	12.0
9.8	399.0	12.5
10.0	425.0	13.0
10.2	552.0	15.6
10.4	745.0	20.0
10.6	805.0	22.0
10.8	707.0	20.2
11.0	647.0	18.0
11.3	561.0	17.2
11.5	530.0	16.0

It is clear from the data in Table 1. that with the increase in pH value, there is an increase in the photopotential and photocurrent, till it reaches a maximum at a particular pH. A further increase in pH resulted in the decrease in the electrical output. It was quite interesting to observe that the pH for the optimum condition had a relationship with the pKa of the reductant and the desired pH was higher than its pKa value (pH > pKa). This may be due to the availability of the reductant in its anionic form, which is its better donor form.

Effect of Dye and Reductant Concentration

Dependence of photopotential and photocurrent on the concentrations of dye and reductant was studied and the results are summarised in Table 2 and 3, respectively.

Table 2. Variation of Dye Concentration

[EDTA] = 3.75×10^{-4} M   Temperature = 303 K

pH = 10.6   Intensity = 10.4 mWcm^{-2}

[Eosin] x 10^5 M	Photopotential (mV)	Photocurrent (μA)
1.25	506.0	11.0
1.60	568.0	17.0
2.00	670.0	17.2
2.25	739.0	19.2
2.50	805.0	22.0
3.00	750.0	20.0
3.40	692.0	16.9
3.75	627.0	14.0
4.10	577.0	12.5
4.50	526.0	11.1
5.00	475.0	10.0

Table 3. Variation of EDTA concentration

[Eosin] = 2.50×10^{-5} M   Temperature = 303 K

pH = 10.6   Intensity = 10.4 mWcm^{-2}

[EDTA] x 10^4 M	Photopotential (mV)	Photocurrent (μA)
2.50	700.0	17.0
2.75	723.0	18.0
3.00	750.0	19.0
3.25	774.0	20.1
3.50	792.0	21.0
3.75	805.0	22.0
4.00	796.0	21.3
4.25	778.0	20.2
4.50	764.0	20.0
4.75	755.0	18.8
5.00	740.0	18.0
5.50	727.0	16.9
6.00	710.0	15.3
6.25	705.0	15.0
6.50	662.0	15.0

A small output was obtained for a lower concentration of eosin because a small number of dye moleculed were available for excitation and consecutive donation of the electrons to the platinum electrode. Large concentrations of dye again resulted in a decrease in photopotential as the intensity of light reaching the dye molecule (near the electrode) decreases after the absorption of the major portion of the light by the dye molecules available in the path.

A similar trend was observed for the variation of the concentration of reductant. The decrease in the concentration of EDTA resulted into a fall in power output due to the lower number of reductant molecules available for electron donation to dye molecules, whereas a large concentration of reductant hinders the movement of dye molecules reaching the electrode in the desired time limit.

Effect of Diffusion Length

H–cells of different dimensions were used to study the effect of the variation of diffusion length on the current parameters of the cell (i_{max}, i_{eq} and initial rate of generation of current). The results are reported in Table 4.

It was observed that there is a sharp increase in photocurrent (i_{max}) and then there is a gradual decrease to a stable value of photocurrent. This photocurrent at equilibrium is represented as i_{eq}. This behaviour of the photocurrent indicates an initial rapid reaction, followed by a slow rate determining step at a later stage.

Three probable cases can be considered to understand more about the nature of electrode active species. These are given in Table 5.

Table 4 . Variation of Diffusion Length

[Eosin]	=	2.50×10^{-5} M	pH = 10.6
[EDTA]	=	3.75×10^{-4} M	Temperature = 303 K
Intensity	=	10.4 mWcm^{-2}	

Diffusion length (mm)	Maximum photocurrent i_{max} (µA)	Equilibrium photocurrent i_{eq} (µA)	Rate of initial generation of current (µA min^{-1})
30.0	97.0	21.0	9.9
35.0	110.0	22.0	10.8
40.0	118.0	22.0	11.8
45.0	130.0	22.0	12.7
50.0	141.0	21.0	13.9

Table 5. The Probable Electrode Active Species

Case	Illuminated chamber	Dark Chamber
(a)	Eosin	Oxidized form of the reductant (OxR)
(b)	Leuco–or semi–eosin	Oxidized form of the reductant (OxR)
(c)	Leuco–or semi–eosin	Eosin

If an oxidized form of the reductant (OxR) is considered as the electrode active species, it must then diffuse from the illuminated chamber to the dark chamber of the cell to accept an electron from the electrode in the dark. If this is the case, then the photocurrent should be inversely proportional to the diffusion length, but it was observed that i_{max} and initial rate of photocurrent generation were proportional to the variation of diffusion length (distance between the electrodes). These observations suggest that the oxidized form of the reductant cannot be considered as the true electrode active species at the dark electrode and hence case (a) and (b) (cf. Table 4) become invalid. Therefore, it may be concluded that the leuco–reduced or semi–reduced form of the dye and the dye itself are the main electrode active species at the illuminated and dark electrodes, respectively. However, the reductants and its oxidized products behave as the electron carriers in the cell diffusing through the path.

Effect of Electrode Area and Temperature

The effect of the variation of the electrode area and temperature on the electrical output of the cell is given in Table 6 and 7, respectively.

Table 6. Effect of Surface Area of the Electrode

[Eosin] = 2.50×10^{-5} M   [EDTA] = 3.75×10^{-4} M

Intensity = 10.4 mWcm^{-2} pH = 10.6

Temperature = 303 K

Surface area (cm^2)	Maximum photocurrent i_{max} (μA)	Equilibrium photocurrent i_{eq} (μA)
0.16	94.0	23.0
0.36	103.0	22.0
0.46	110.0	22.0
1.00	118.0	22.0
1.44	130.0	20.0

Table 7. Effect of Temperature

[Eosin] $= 2.50 \times 10^{-5}$ M   [EDTA] $= 3.75 \times 10^{-4}$ M

Intensity $= 10.4$ m Wcm^{-2} pH $= 10.6$

Temperature (K)	Photopotential (mV)	Photocurrent (μA)
295.0	830.0	20.0
303.0	805.0	22.0
310.0	785.0	24.0
315.0	752.0	25.0

With the increase of electrode area, the value of i_{max} increase, but the effect on i_{eq} was negligibly small. With the rise in temperature, the photopotential showed a rapid fall, whereas the photocurrent was found to increase with the increase in temperature of the system. The increasing behaviour of photocurrent with the rise in temperature may be due to the corresponding decrease in the internal resistance of the cell at higher temperatures. The decrease in internal resistance of the cell and resultant rise in photocurrent will result in a corresponding fall in photopotential, however, the rapid fall of potential cannot be compensated by the corresponding rise in photocurrent as far as the power of the cell is concerned. Because of this, higher temperatures should be avoided for better output from the cell.

Effect of Light Intensity

Light sources of different intensities (different watts) were used to study the effect of light intensity on the electrical output of the cell. The results are given in Table 8.

Table 8. Effect of Light Intensity

[Eosin] $=$ 2.50×10^{-5} M   [EDTA] $= 3.75 \times 10^{-4}$ M

Temperature $=$ 303 K   pH $= 10.6$

Light intensity I (mWcm^{-2})	Photopotential (V) (mV)	Log V	Photocurrent (μA)
3.1	750.0	2.8751	18.0
5.2	775.0	2.8893	19.0
10.4	805.0	2.9058	22.0
15.6	840.0	2.9243	24.0
26.4	1584.0	3.1997	28.0

It was observed that the photocurrent showed a linear increasing behaviour with an increase in the intensity of light, whereas the photopotential increases in a lograthmic manner.

The number of photons per unit area, (indicent power), striking the dye molecules around the platinum electrode, increase with the increase in the light intensity and there is a rise in photopotential and photocurrent. However, an increase in light intensity will also raise the temperature of the cell. Therefore, intensity of medium order (10.4 mWcm^{-2}) was used for all investigations. About 100 mWcm^{-2} solar insolation falls on the earth on a clear day and the output from the cell should be approximately double the output with intensity 10.4 mWcm^{-2} (because $\log_{10} 100 = 2.0$), however, this was never achieved in the present investigation. This may be due to the lower intensity of sunlight or the presence of a saturation point above which the photopotential is not affected by the increase in light intensity.

Current Voltage (i–V) Characteristics, Conversion Efficiency and Performance of the Cell

The open circuit voltage (V_{oc}) and short circuit current (i_{sc}) of the photogalvanic cell were measured from a digital pH meter (keeping the circuit open) and from a multimeter (keeping the circuit closed), respectively. The current and potential values in between these two extreme values (V_{oc} and i_{sc}) were recorded with the help of a carbon pot (log 500 K) connected in the circuit of the multimeter, through which an external load was applied. The data are reported in Table 9.

It was observed that the *i–V* curve of the cell deviated from its ideal regular rectangular shape. A point in the *i–V* curve, called the power point (pp) was determined, where the product of potential and current is maximum. The values of potential and current at power point is represented as V_{PP} and i_{PP}, respectively. With the help of the (*i–V*) curve, the fill–factor and conversion efficiency of the cell were determined as 0.46 and 0.3461%, respectively, using the formula:

Table 9. Current –Voltage Characteristics of the cell

[Eosin]   = 2.50×10^{-5} M   [EDTA] = 3.75×10^{-4} M

Intensity   =   10.4 mWcm^{-2} pH = 10.6

                                                                             Temperature = 303 K

Potential* (mV)	Photocurrent (µA)	Fill factor
0.0	22.0	
52.0	21.0	
137.0	20.0	
224.0	19.5	
351.0	18.7	0.42
480.0	18.0	

Continued...

Table 9. Continued...

Potential* (mV)	Photocurrent (µA)	Fill factor
560.0	16.0	
600.0	14.0	
675.0	10.0	
700.0	8.0	
750.0	6.0	
800.0	5.0	
825.0	4.0	
960.0	0.0	

*Absolute values of the potential.

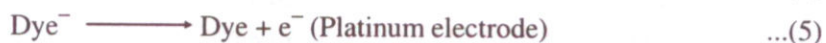$$\text{Fill factor} = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}} \qquad ...(1)$$

$$\text{Conversion efficiency} = \frac{V_{pp} \times i_{pp}}{10.4 \text{ mWcm}^{-2}} \times 100 \% \qquad ...(2)$$

The performance of the cell was studied by applying the external load necessary to have current and potential at power point after removing the source of light. It was observed that the cell can be used in the dark at its power point for three minutes. The photovoltaic cell cannot be used in the dark even for a second, whereas, the photogalvanic system has an additional advantage of being used in the dark, of course, with lower conversion efficiency. (in this case 0.086%).

MECHANISM

On the basis of the information gained above, the mechanism of photocurrent generation in the photogalvanic cell can be represented as:
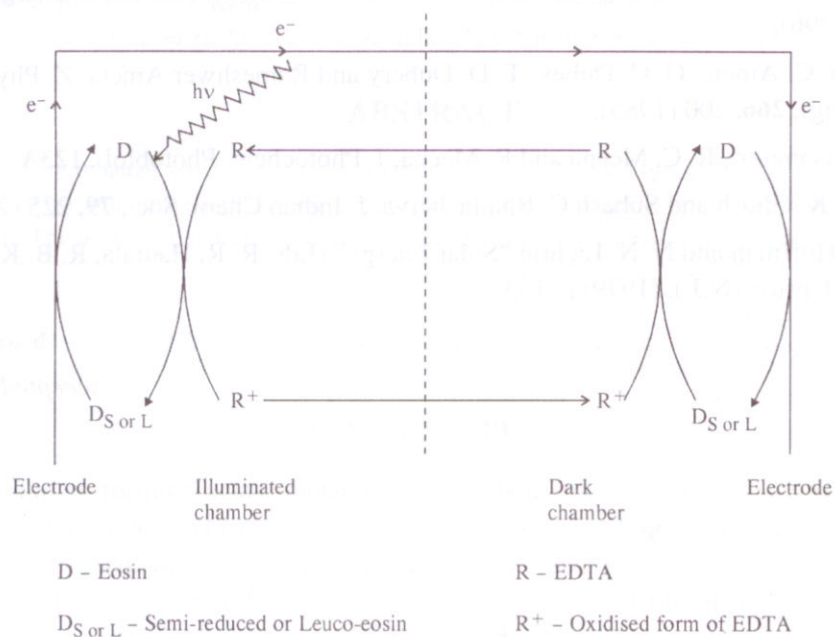
Illuminated Chamber

$$\text{Dye} \xrightarrow{h\nu} \text{Dye*} \qquad ...(3)$$

$$\text{EDTA (R)} + \text{Dye*} \longrightarrow \text{Dye}^- + \text{R}^+ \qquad ...(4)$$

$$\text{Dye}^- \longrightarrow \text{Dye} + e^- \text{ (Platinum electrode)} \qquad ...(5)$$

Dark Chamber

$$Dye + e^- \longrightarrow Dye^- \qquad ...(6)$$

$$Dye^- + R^+ \longrightarrow Dye + R \text{ (SCE–electrode)} \qquad ...(7)$$

Where R, R^+, Dye and Dye– are the reductant EDTA, its oxidised form, eosin and its leuco–form, respectively.

The photogeneration of current in photogalvanic cell may be presented as :

Electrode   Illuminated   Dark   Electrode
                   chamber   chamber

D – Eosin   R – EDTA

$D_{S \text{ or } L}$ – Semi-reduced or Leuco-eosin R^+ – Oxidised form of EDTA

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