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Use of Toluidine Blue-Maleic Hydrazide System in Photogalvanic Cell for Solar Energy Conversion

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Photogalvanic cell containing toluidine blue as photosensitizer and maleic hydrazide as reductant has been investigated from solar energy conversion point of view. The photopotential and photocurrent generated by this cell were 140.0 mV and 10.0 μA respectively. Effect of different parameters on the electrical output of the cell was also investigated. Current-voltage characteristics of the cell has also been studied and a mechanism for the generation of photocurrent in this photogalvanic cell has been proposed. Maximum power obtained from this cell is 0.0787 μW.

INTRODUCTION

Although photogalvanic effect was first reported by Rideal and Williams[1], but it was systematically studied by Rabinowitch[2]. Hoffman and Lichtin[3] have discussed various problems encountered in the development of this field. Theoretical conversion efficiency of photogalvanic cell is about 18%[4], but the experimentally observed conversion of photogalvanic cells are quite low as compared to the effected efficiencies. The main reasons are back-electron transfer, lower stability of dyes, aggregation of dye molecules around the electrode, etc. A detailed survey of literature reveals that different photosensitizers have been used in the photogalvanic cells like proflavin[5], thionine[6], riboflavine[7], methylene blue[8,9], brilliant cresyl blue[10] etc., but negligible attention has been paid to the use of toluidine blue in photogalvanic cell for solar energy conversion and therefore, the present work was undertaken.

EXPERIMENTAL

Toluidine blue (LC), maleic hydrazide (SDS) and sodium hydroxide (SM) were used in the present work. All the solutions were prepared in doubly distilled water. A mixture of solutions of toluidine blue—Maleic hydrazide and sodium hydroxide was taken in a H-type cell.

Platinum electrode (1 × 1 cm^2) was dipped in one limb of the cell and saturated calomel electrode (SCE) in the other. The platinum electrode was exposed to a 200 W tungsten lamp (Sylvania) and the limb containing SCE was kept in dark. A water filter was used to cut-off the thermal radiations.

The photochemical bleaching of toluidine blue by maleic hydrazide in alkaline medium was studied potentiometrically. The potential and current generated by the system TB–MH/OH^-/hν were measured by digital pH meter (Systronics Model 335) and multimeter (Systronics Model 435), respectively. The 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 Electrical Output of the Cell

It was observed that photopotential and photocurrent increases with the increase in pH value, till it reaches a maximum at a particular pH = 11.6 (Table 1). Further increase in pH resulted in the decrease in the electrical output. It was quite interesting to observe that the pH required for the optimum condition has a relation with pKa of the reductant and the desired pH is higher than its pKa value. It may be explained on the basis that the availability of reductant in its anionic form (a better-donor) will be more under these conditions.

TABLE 1

VARIATION OF pH

[Toluidine Blue] = 3.2×10^{-5} M Intensity = 10.4 mW cm^{-2}
[MH] = 4.4×10^{-3} M Temperature = 303 K

pH	Photopotential (mV)	Photocurrent (μA)
11.0	60.0	8.0
11.2	80.0	9.0
11.4	104.0	10.0
11.6	140.0	10.0
11.8	98.0	9.0
12.0	70.0	9.0
12.2	54.0	8.0

Effect of Reductant Concentration

Small output obtained for lower concentration of maleic hydrazide may be due to the less number of reductant molecules available for electron donation to excited dye molecules (Table 2). The larger concentration of maleic hydrazide alse resulted into decrease in electrical output because the large number of reductant molecules will hinder the dye molecules to reach the electrode in desired time limit.

TABLE 2

VARIATION OF REDUCTANT CONCENTRATION

[TB] = 3.2×10^{-5} M Intensity = 10.4 mW cm^{-2}
pH = 11.6 Temperature = 303 K

[MH] $\times 10^3$ M	Photopotential (mV)	Photocurrent (μA)
2.0	63.0	8.0
2.4	102.0	8.0
3.2	135.0	9.0
4.4	140.0	10.0
4.8	130.0	9.0
5.6	93.0	7.0
6.4	54.0	6.0

Effect of Variation of Dye

Similar trend has been observed in case of the effect of variation of concentration of dye on photopotential and photocurrent (Table 3). The

TABLE 3

VARIATION OF DYE CONCENTRATION

[MH] = 4.4×10^{-3} M Intensity = 10.4 mW cm^{-2}
pH = 11.6 Temperature = 303 K

[Toluidine blue] $\times 10^5$ M	Photopotential (mV)	Photocurrent (μA)
0.8	40.0	5.0
1.6	98.0	7.0
2.4	120.0	8.0
3.2	140.0	10.0
4.0	130.0	8.0
4.8	100.0	6.0
6.4	75.0	5.0

decrease in dye concentration resulted into a fall in electrical output of the cell due to less number of dye molecules available for the excitation and consecutive donation of the electrons to the platinum electrode. Larger concentration of dye also affects the output adversely as the intensity of light reaching the dye molecule near the electrode decreases sharply, because the major portion of the light is absorbed by dye molecules present in the path.

Effect of Diffusion Length

The effect of variation of diffusion length on the current parameters of the cell (i_{max}, i_{eq} and initial rate of generation of current) was investigated using H-cells of different dimensions. In first few minutes of illumination, there is a sharp increase in photocurrent to maximum (i_{max}) and then there is a gradual decrease in current to a stable value (i_{eq}) (Table 4).

TABLE 4

VARIATION OF DIFFUSION LENGTH

[TB] = 3.2×10^{-5} M Intensity = 10.4 mW cm^{-2}
[MH] = 4.4×10^{-3} M Temperature = 303 K
pH = 11.6

Diffusion length (cm)	Maximum photocurrent i_{max} (μA)	Equilibrium photocurrent i_{eq} (μA)	Rate of initial generation of current (μA min^{-1})
3.0	18.4	13.0	0.8
3.5	19.2	11.0	2.1
4.0	20.0	10.0	3.3
4.5	20.6	9.0	4.4
5.0	21.4	9.0	5.1

This kind of behaviour of photocurrent indicates an initial rapid reaction followed by a slow determining step at a later stage.

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

TABLE 5

THE PROBABLE ELECTRODE ACTIVE SPECIES

Case	Illuminated chamber	Dark chamber
I	Toluidine blue	Oxidised form of the reductant R^+
II	Leuco or semi-toluidine blue	Oxidised form of the reductant R^+
III	Leuco or semi-toluidine blue	Toluidine blue

If we consider O_XR as an electrode active species in dark chamber, then it must diffuse from the illuminated chamber to the dark chamber of the cell to accept an electron from the electrode in the dark. Under such circumstances, photocurrent should be inversely proportional to the diffusion length, but this was never observed. The initial rate of photocurrent generation and i_{max} were proportional to the diffusion length and the values of i_{eq} was found to be almost independent of the variation of diffusion length. These observations suggest that oxidised form of the reductant (O_XR) cannot be considered as the true electrode active species at the dark electrode and hence case I and II became invalid. Therefore, it may be concluded that the main electrode active species at the illuminated and dark electrodes are leuco- or semi-reduced form of the dye and the dye itself, respectively, however, the reductant and its oxidised product behave as the electron carriers in the cell.

Effect of Electrode Area and Temperature

With the increase in electrode area, the value of i_{max} increases whereas its effect on i_{eq} was negligibly small. The increase in temperature resulted into a fall in photopotential whereas photocurrent was found to increase. At higher temperature the internal resistance of the cell decreases and hence, the rise in photocurrent. The increase in photocurrent of the cell resulted 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. Due to this reason, higher temperatures should be avoided for better output from the photogalvanic cell.

Effect of Light Intensity

The effect of light intensity on the electrical output of the cell was studied by using light sources of different intensities. It was observed that photopotential increases in a logarithmic manner with the increase in the intensity of light whereas photocurrent showed a linear increasing behaviour.

The rise in photopotential and photocurrent with the increase in the light intensity is due to the increase in the number of photons per unit area (incident power) striking the dye molecules around the platinum electrode. However, increase in light intensity will also raise the temperarature of the cell, therefore, the intensity of the medium order (10.4 mW cm^{-2}) was used throughout these investigations. On a clear day, about 100 mW cm^{-2} solar insolation is falling on the earth and output from the cell should be approximately double of the output with the intensity 10.4 $mWcm^{-2}$, however, this was never achieved in the present work. 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 the light intensity.

Current-voltage (i-V) characteristics, Conversion Efficiency and Performance of the Cell

The short circuit current (i_{sc}) and the open circuit voltage (V_{oc}) of the photogalvanic cell were measured with the help of a multimeter (keeping the circuit closed) and a digital pH meter (keeping the circuit open), respectively. The potential and current 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 multimeter through which an external load was applied. It was observed that the *i*-V curve of the cell deviated from its regular rectangular shape. The power point in *i*-V curve was determined, where the product of potential and current is maximum. The V_{pp} and i_{pp} represent the value of potential and current at power point, respectively. The fill-factor and conversion efficiency of the cell were determined by using formula

$$\text{Fill-factor} = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}} \tag{1}$$

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

The performance of the cell was studied in absence of light by employing an external load necessary to have current and potential at power point. It was observed that this photogalvanic cell can be used in dark for 7.0 minutes at its power point. The fill factor and conversion efficiency of the cell were 0.20 and 0.0008% respectively. The present photogalvanic cell has an additional advantage of being used in dark.

Mechanism

On the basis of above observations, the mechanism of the photocurrent generation in the photogalvanic cell may be represented as

Illuminated chamber

$$\text{Dye} \xrightarrow{h\nu} \text{Dye}^* \tag{3}$$

$$\text{Dye}^* + \text{MH(R)} \rightarrow \text{Dye}^- + \text{MH}^+(\text{O}_x\text{R}) \tag{4}$$

$$\text{at electrode} \quad \text{Dye}^- \rightarrow \text{Dye} + e^- \tag{5}$$

Dark chamber

$$\text{at electrode} \quad \text{Dye} + e^- \rightarrow \text{Dye}^- \tag{6}$$

$$\text{Dye}^- + \text{O}_x\text{R} \rightarrow \text{R} + \text{Dye} \tag{7}$$

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