

Use of Mixed Dyes in Photogalvanic Cell for Solar Energy Conversion and Storage: EDTA-Toluidine Blue and Azur-B System

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Photogalvanic effect was studied in photogalvanic cell containing EDTA as reductant, Toluidine blue and Azur-B as photosensitizer. The photopotential and photocurrent generated by this system were 802.0 mV and 40.0 μ A, respectively. The observed conversion efficiency was 0.0708 % and the maximum output of cell was 32.08 μ W. The photogalvanic cell can be used for 2 h in dark. The effects of different parameters on electrical output of the cell were observed and a mechanism has also been proposed for the generation of photocurrent in photogalvanic cell.

Key Words: Toluidine blue, Azur-B, Fill factor, Power point, Conversion efficiency.

INTRODUCTION

Becquerel^{1,2} first observed in 1839 the flow of current between two unsymmetrical illuminated metal electrodes in sunlight. The photogalvanic effect was first of all reported by Rideal and Williams³ but it was systematically investigated by Rabinowitch^{4,5} Later on, Kaneko and Yamada⁶, Murthy *et al.*⁷, Rohatgi Mukherjee *et al.*⁸, Ameta *et al.*^{9,10} and Gangotri *et al.*^{11,12} have reported some interesting photogalvanic systems. Theoretical conversion efficiency of photogalvanic cell is about 18 % but the observed conversion efficiencies are quite low due to lower stability of dyes, back electron transfer, aggregation of dye molecules around electrode, *etc.* Hoffman and Lichtin¹³ have discussed various problems encountered in the development of this field.

A detailed literature survey¹⁴⁻²⁸ reveals that different photosensitizers and reductants have been used in photogalvanic cells, but no attention has been paid to use of the EDTA-Toluidine blue (TB) + Azur-B (AB) systems in the photogalvanic cells for energy conversion and storage. Therefore, the present work was undertaken.

EXPERIMENTAL

EDTA (Sisco), Toluidine blue (Loba), Azur-B (S.D. Fine) and sodium hydroxide (Ranbaxy) were used in present work. All the solutions were prepared in doubly distilled water and were kept in amber coloured containers to protect them from sunlight. A mixture of EDTA, toluidine blue, Azur-B and sodium hydroxide was taken in an H-type glass tube. A platinum electrode ($1.0 \times 1.0 \text{ cm}^2$) was immersed in one arm of the H-tube and saturated calomel electrode (SCE) was kept in the other arm. The whole system was first placed in dark till a stable potential was obtained, then the arm containing the SCE was kept in dark, and the platinum electrode was exposed to a 200 W tungsten lamp (ECE). A water filter was used to cut off infra-red radiations. The photochemical bleaching of toluidine blue and Azur-B was studied potentiometrically. A digital pH meter (Agronic Model 511) and a microammeter (OSAW, India) were used to measure the potential and current generated by the system, respectively.

RESULTS AND DISCUSSION

Effect of Variation of pH: The electrical output of the cell was affected by the variation in pH of the system. It can be observed from Table-1 that there is an increase in electrical output of the cell with the increase in pH, values. At pH 12.8 a maxima was obtained. On further increase in pH, there was a decrease in photopotential and photocurrent. Thus, photogalvanic cells containing the EDTA-toluidine blue + Azur-B system were found to be quite sensitive to the pH of the solutions.

TABLE-1
EFFECT OF VARIATION OF pH
[TB] = 1.0×10^{-5} M; [EDTA] = 2.24×10^{-3} M; [AB] = 3.6×10^{-5} M
Light intensity = 10.4 m W cm^{-2} ; Temp. = 303 K

	pH				
	12.4	12.6	12.8	13.0	13.2
Photopotential (mV)	652.0	729.0	802.0	667.0	604.0
Photocurrent (μA)	27.0	33.0	40.0	25.0	19.0
Power (μW)	17.60	24.05	32.08	16.67	11.47

It was observed that the pH for the optimum condition has a relation with pKa of the reductant and the desired pH is higher than its pKa value ($\text{pH} > \text{pKa}$). The reason may be the availability of reductant in its anionic form, which is a better donor form.

Effect of variation of [EDTA] concentrations: The electrical output of the cell was affected by the variation of reducing agent concentration [EDTA] in the system; the results are summarized in Table-2.

TABLE-2
EFFECT OF VARIATION OF [EDTA] CONCENTRATIONS
[TB] = 1.08×10^{-5} M; [AB] = 3.6×10^{-5} M
Light intensity = 10.4 mW cm^{-2} ; Temp. = 303 K; pH = 12.8

	[EDTA] $\times 10^3$ M				
	1.8	2.0	2.2	2.4	2.6
Photopotential (mV)	652.00	725.00	802.00	705.00	660.00
Photocurrent (μA)	24.00	31.00	40.00	28.00	25.00
Power (μW)	15.67	27.47	32.08	19.74	16.50

Lower concentrations of reducing agents resulted into a fall in electrical output because fewer reducing agent molecules available for electron donation to dyes molecules.

Large concentration of reducing agent again resulted into a decrease in electrical output, because the large number of reducing agent molecules hinder the dyes molecules reaching the electrode in the desired time limit.

Effect of variation of mixed dyes [TB + AB] concentrations:
Dependence of photopotential and photocurrent on the concentration of dyes was studied and the results are summarized in Table-3a and b.

TABLE-3(a)
EFFECT OF VARIATION OF [TB] CONCENTRATIONS
[AB] = 3.6×10^{-5} M; [EDTA] = 2.24×10^{-3} M
Light intensity = 10.4 mW cm^{-2} ; Temp. = 303 K; pH = 12.8

	[TB] $\times 10^5$ M				
	1.00	1.04	1.08	1.12	1.16
Photopotential (mV)	635.00	715.00	802.00	740.00	676.00
Photocurrent (μA)	25.00	31.00	40.00	36.00	27.00
Power (μW)	15.87	22.16	32.08	26.64	18.25

TABLE-3(b)
EFFECT OF VARIATION OF [AB] CONCENTRATIONS
[TB] = 1.08×10^{-5} M; [EDTA] = 2.24×10^{-3} M
Light intensity = 10.4 mW cm^{-2} ; Temp. = 303 K; pH = 12.8

	[AB] $\times 10^5$ M				
	2.8	3.2	3.6	4.0	4.4
Photopotential (mV)	596.00	707.00	802.00	732.00	629.00
Photocurrent (μA)	23.00	30.00	40.00	35.00	26.00
Power (μW)	13.70	21.21	32.08	25.62	16.35

Lower concentration of dyes resulted into a fall in photopotential and photocurrent because fewer dyes molecules are available for the excitation and consecutive donation of the electrons to the platinum electrode. The greater concentration of dyes again resulted in a decrease in electrical output as the intensity of light reaching the dyes molecule near the electrode

decreases due to absorption of the major portion of the light by dyes molecules present in path.

Effect of diffusion length: The effect of variation of diffusion length (distance between the two electrodes) on the current parameters of the cell was studied using H-cells of different dimension. The results are reported in Table-4.

TABLE-4
EFFECT OF DIFFUSION LENGTH
[TB] = 1.08×10^{-5} M; [EDTA] = 2.24×10^{-3} M; [AB] = 3.6×10^{-5} M
Light intensity = 10.4 mW cm^{-2} ; Temp. = 303 K

Diffusion path length D_L (mm)	Maximum photocurrent i_{\max} (μA)	Equilibrium photocurrent I_{eq} (μA)	Rate of initial generation of current ($\mu\text{A min}^{-1}$)
35.0	120.0	41.0	5.5
40.0	122.0	41.0	6.7
45.0	125.0	40.0	7.8
50.0	127.0	38.0	8.9
55.0	130.0	38.0	10.0

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

On the basis of the effect of diffusion path length on the current parameters, as investigated by Kaneko and Yamada⁶, it may be concluded that the leuco or semi reduced form of dyes, and the dyes itself are the main electroactive species at the illuminated and the dark electrodes, respectively. However, the reducing agent and its oxidized product behave as the electron carriers in the cell diffusing through the path.

Current voltage (i-V) characteristics of the cell: It was observed that i-V curve deviated from its ideal regular rectangular shape as given in the Fig. 1.

A Point in i-V curve, called power point (pp) was determined where the product of potential and current was maximum: V_{pp} and i_{pp} , respectively. With the help of i-V curve, the fill factor and the conversion efficiency of cell were determined as 0.19 and 0.0708 %, respectively using the following formula:

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

$$\text{Conversion efficiency} = \frac{V_{\text{pp}} \times i_{\text{pp}}}{10.4(\text{mW}/\text{cm}^2)} \times 100\%$$

where V_{pp} , i_{pp} , V_{oc} , i_{sc} are the potential at power point, current at power point, open circuit voltage and short circuit current, respectively. The system (at its optimum condition) was exposed to sunlight. The conversion data for the photogalvanic cell is reported in Table-5.

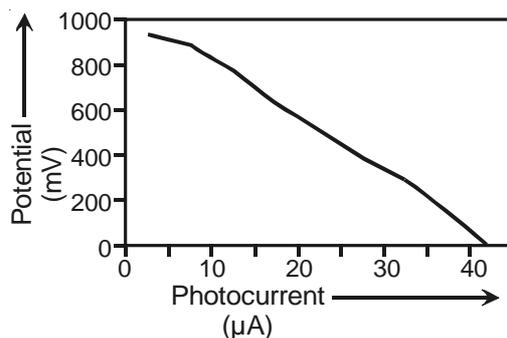


Fig. 1. Current voltage (i-V) curve of the cell

TABLE-5
 CONVERSION EFFICIENCY AND SUNLIGHT CONVERSION DATA
 $[TB] = 1.08 \times 10^{-5} \text{ M}$; $[EDTA] = 2.24 \times 10^{-3} \text{ M}$; $[AB] = 3.6 \times 10^{-5} \text{ M}$
 Light intensity = 10.4 mW cm^{-2} ; Temp. = 303 K; pH = 12.8

	Conversion efficiency (%)	Sunlight conversion data	
		Photopotential (mV)	Photocurrent (μV)
EDTA-TB +AB System	0.0708	1380.0	95.0

Cell performance: The performance of the cell was studied by applying the external load necessary to have the current and potential at the power point after removing the source of light until the output (power) to its half value at the power point in the dark. It was observed that the cell can be used in the dark at its power point for 2 h.

Electroactive species: Various probable processes may be considered for the photocurrent generation in photogalvanic cells. The results of the effect of diffusion length on current parameters were utilized to know more about the electroactive species. The possible combinations for electroactive species in photogalvanic cell are given in Table-6.

TABLE-6
 POSSIBLE COMBINATIONS FOR ELECTROACTIVE SPECIES

In illuminated chamber	In dark chamber
TB + AB	Oxidized from of reductant (R^+)
Leuco or Semi- $TB^- + AB^-$	Oxidized from of reductant (R^+)
Leuco or Semi- $TB^- + AB^-$	TB + AB

The oxidized form of the reductant is formed only in the illuminated chamber and if it is considered to be the electroactive species in the dark chamber, then it must diffuse from the illuminated chamber to the dark chamber to accept an electron from the electrode. As a consequence, the maximum photocurrent (i_{\max}) and rate of increase in photocurrent should decrease with an increase in diffusion length, but this was not observed experimentally. The value (i_{eq}) was also observed to be independent with respect to change in diffusion length (rather, it decreases slightly). Therefore, it may be concluded that the main electroactive species are the leuco or semi- $\text{TB}^- + \text{AB}^-$ and the dyes ($\text{TB} + \text{AB}$) in illuminated chamber and dark chamber, respectively. However, the reductant and its oxidized products act only as electron carriers in the path.

Mechanism: On the basis of the above investigations, the mechanism of photocurrent generation in the photogalvanic cell can be proposed as follows:

Illuminated chamber

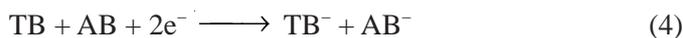


At electrode



Dark chamber

At electrode



where $\text{TB} + \text{AB}$, $\text{TB}^* + \text{AB}^*$, $\text{TB}^- + \text{AB}^-$, R and R^+ are the toluidine blue + Azur-B, their excited forms, leuco or semi leuco forms, reductant and its oxidized form, respectively.

Conclusion

Scientists have developed the photogalvanic cells containing a reductant and a photosensitizer with reasonable electrical output, but by combining two different photosensitizers (mixed dyes) the electrical output has increased 1.5-2.0 times, as the observations show.

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