Short communication

Use of mixed dyes in a photogalvanic cell for solar energy conversion and storage: EDTA–thionine–azur-B system

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Abstract

The photogalvanic effect was studied in a photogalvanic cell containing ethylene diamine tetraacetic acid [EDTA] as reductant and thionine and azur-B as photosensitizers. The photopotential and photocurrent generated were 745.0 mV and 76.0 μA, respectively. The observed conversion efficiency was 0.18% and the maximum output (power) of the cell was 56.62 μW. The photogalvanic cell can be used at this power level for 59.0 min in the dark due to the storage capacity of the cell. The effects of various parameters on the electrical output of the cell were observed. The mechanism of generation of the photocurrent in these photogalvanic cells has also been proposed.
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Keywords: Photogalvanic cell; Thionine; Azur-B; Fill factor; Conversion efficiency; Power point

1. Introduction

Energy consumption is directly proportional to economic development. Energy is only one vital requirement for humanity and life on the earth. Solar energy is a source of life on earth. In the absence of the sun, life on earth would come to a grinding halt. The sun provides warmth, light and is a primary source of energy available on earth. A small amount of solar energy (0.023%) is utilized by nature in the process of photosynthesis. A small fraction of this solar input can fulfill the energy demands of the whole world. Photosynthesis is a natural photochemical process which is a challenge to mimic in the laboratory.

The photogalvanic effect was reported by Rideal and Williams [1], and was systematically investigated by Rabinowitch [2,3]. Some interesting photogalvanic systems have been studied [4–8]. Hoffman and Lichtin [9] have discussed various problems encountered in the development of this field.

A search of literature reveals that different photosensitizers and reductants have been used in photogalvanic cells [10–14]. Recently, photogalvanic effects were observed in photogalvanic cells containing dyes and reductants [15–18]. We have studied the use of EDTA–thionine + azur-B system in the photogalvanic cell for solar energy conversion and storage.

2. Experimental

An H-shaped glass cell was fabricated and blackened keeping a window in one arm of this cell. The solutions of EDTA-disodium salt (SISCO), thionine (Loba), azur-B (s.d. fine) and sodium hydroxide (Ranbaxy) were prepared with doubly distilled water and kept in dark coloured containers. A mixture of a solution of EDTA, thionine + azur-B and sodium hydroxide was taken in the H-shaped glass cell. A platinum electrode (1.0 cm × 1.0 cm) was immersed in one arm of the H-cell and a saturated calomel electrode (SCE) was kept in the other arm. The terminals of the electrodes were connected to a pH meter (Systronics-335) and a microammeter (INCO-65). The whole system was first placed in the dark till a stable potential was obtained. Then, the H-shaped cell was divided into two chambers, one a dark chamber (the arm having SCE) and the other an illuminated chamber (the arm having platinum electrode just before the window). The platinum electrode was exposed to a 200 W tungsten lamp (from Philips), which was used as a light source. A water filter was used to obstruct infrared radiation.

On illumination, the photochemical bleaching of thionine + azur-B was studied potentiometrically. The potential and

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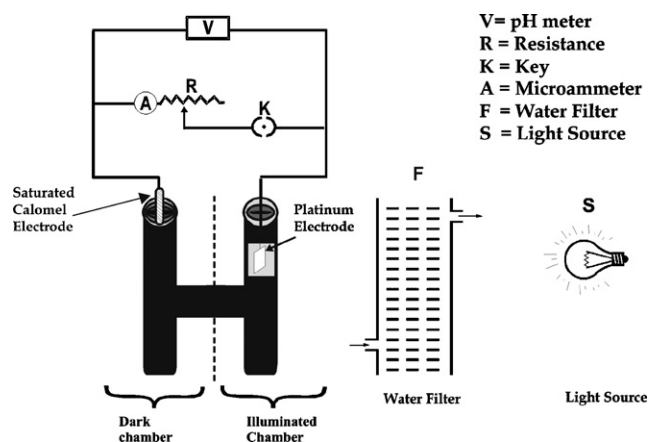 *E-mail address:* c_lal12@rediffmail.com.

Fig. 1. Experimental set-up of photogalvanic cell.

current generated by the system were measured with the digital pH meter and the microammeter, using the key to close one circuit and open the other circuit. The current–potential (i–V) characteristics of the cell were studied by applying an external load with a variable resistor and the i–V curve plotted. The experimental set-up of photogalvanic cell is shown in Fig. 1.

3. Results

3.1. Effect of variation of pH

The electrical output of the cell was affected by variation in the pH. The electrical output of the cell increases with increase in pH (Table 1). The maximum photopotential and photocurrent were obtained at pH 12.8, however, further increase in pH resulted in a decrease in the electrical output of the cell. Thus, photogalvanic cells containing EDTA–thionine + azur-B systems were found to be sensitive to the pH of the solutions.

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

3.2. Effect of variation of [EDTA] concentration

The electrical output of the cell was also affected by the variation in the reducing agent [EDTA] concentration of the system—the results are shown in Table 2.

Table 1
Effect of variation of pH

pH	Photopotential (mV)	Photocurrent (μA)	Power (μW)
12.4	596.0	50.0	29.80
12.6	672.0	62.0	41.66
12.8	745.0	76.0	56.62
13.0	667.0	48.0	32.01
13.2	604.0	38.0	22.95

[TH] = 1.60×10^{-5} M; [AB] = 2.40×10^{-5} M; [EDTA] = 2.2×10^{-3} M; light intensity = 10.4 mW cm^{-2}; temperature = 303 K.

Table 2
Effect of variation of [EDTA] concentration

[EDTA] $\times 10^3$ M	Photopotential (mV)	Photocurrent (μA)	Power (μW)
1.8	598.0	45.0	26.91
2.0	731.0	59.0	43.12
2.2	745.0	76.0	56.62
2.4	692.0	55.0	38.06
2.6	612.0	42.0	25.70

[TH] = 1.60×10^{-5} M; [AB] = 2.40×10^{-5} M; pH = 12.8; light intensity = 10.4 mW cm^{-2}; temperature = 303 K.

Table 3a
Effect of variation of [thionine] concentration

[TH] $\times 10^5$ M	Photopotential (mV)	Photocurrent (μA)	Power (μW)
1.20	602.0	48.0	28.89
1.40	705.0	55.0	38.77
1.60	745.0	76.0	56.62
1.80	695.0	52.0	36.14
2.00	610.0	51.0	31.11

[AB] = 2.40×10^{-5} M; pH = 12.8; [EDTA] = 2.2×10^{-3} M; light intensity = 10.4 mW cm^{-2}; temperature = 303 K.

Lower concentrations of reducing agent resulted in a decrease in the electrical output, because fewer reducing agent molecules were available for electron donation to the dye molecules.

Large concentrations of the reducing agent again resulted a decrease in electrical output, because the large number of reducing agent molecules hindered the dye molecules from reaching the electrode.

3.3. Effect of variation of the mixed dyes (thionine + azur-B) concentration

The dependence of the photopotential and photocurrent on the concentration of the dyes was studied and the results are summarized in Tables 3a and 3b.

A lower concentration of dyes ([TH] < 1.60×10^{-5} M, [AB] < 2.40×10^{-5} M) resulted in a decrease in photopotential and photocurrent because fewer dye molecules were available for the excitation and consecutive donation of the electrons to the platinum electrode. A greater concentration ([TH] > 1.60×10^{-5} M, [AB] > 2.40×10^{-5} M) of dyes again resulted in a decrease in the electrical output as the intensity of light, reaching the dyes molecules near the electrode decreased due to the absorption of the major portion of the light by the dyes molecules.

Table 3b
Effect of variation of [azur-B] concentration

[AB] $\times 10^5$ M	Photopotential (mV)	Photocurrent (μA)	Power (μW)
1.60	590.0	52.0	30.68
2.00	695.0	59.0	41.00
2.40	745.0	76.0	56.62
2.80	675.0	55.0	37.12
3.20	626.0	57.0	35.68

[TH] = 1.60×10^{-5} M; pH = 12.8; [EDTA] = 2.2×10^{-3} M; light intensity = 10.4 mW cm^{-2}; temperature = 303 K.
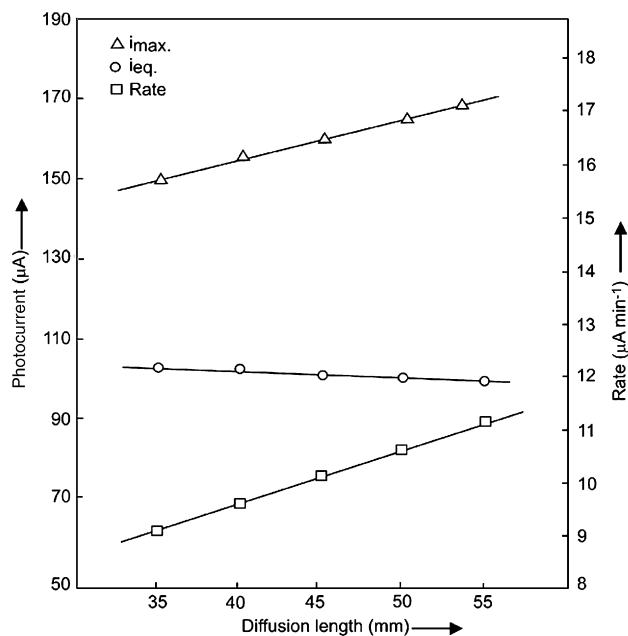
Fig. 2. Effect of variation of diffusion length.

Table 4
Effect of electrode area

Electrode area (cm^2)	Maximum photocurrent i_{max} (μA)	Equilibrium photocurrent i_{eq} (μA)
0.36	135.0	80.0
0.64	149.0	78.0
1.00	159.0	76.0
1.44	169.0	75.0
1.69	181.0	74.0

[TH] = 1.60×10^{-5} M; [AB] = 2.40×10^{-5} M; pH = 12.8; [EDTA] = 2.2×10^{-3} M; light intensity = 10.4 mW cm^{-2}; temperature = 303 K.

3.4. Effect of diffusion length

The effect of variation of the diffusion length (distance between the two electrodes) on the current parameters (i_{max}, i_{eq} and rate of initial generation of current) of the cell was studied using H-cells of different dimensions. The results are graphically shown in Fig. 2.

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 in photocurrent to a stable value. This photocurrent at equilibrium is represented as (i_{eq}). The spontaneous increase in photocurrent on illumination shows an initial rapid reaction followed by a slow rate-determining step at a later stage.

The results of the effect of diffusion length on current parameters were utilized to know more about the electroactive species.

3.5. Effect of electrode area

The effect of electrode area on the current parameters of the cell has also been studied and it was observed that with an increase in the electrode area, the value of maximum photocurrent (i_{max}) was found to increase, whereas photocurrent at equilibrium (i_{eq}) was found to be almost independent with respect to change in electrode area (rather it is affected in reverse manner). The effect of variation of electrode area on i_{max} and i_{eq} are reported in Table 4.

3.6. Current–potential (i–V) characteristics of the cell

The short circuit current (i_{sc}, 76 μA), and open circuit voltage (V_{oc}, 975 mV) of the cell were measured with the help of a microammeter (keeping the circuit closed) and a digital pH meter (keeping the other circuit open), respectively. The current

and potential values in between these two extreme values were recorded with the help of a resistor (carbon pot log 500 K) connected in the circuit of microammeter, through which an external load was applied.

A point in the i–V curve, called the "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 was determined as 0.25 and conversion efficiency as 0.18% using the formula:

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

$$\text{Coversion effciency} = \frac{V_{pp}i_{pp}}{10.4 \text{ mW cm}^{-2}} \times 100\% \tag{2}$$

where V_{pp}, i_{pp}, V_{oc} and i_{sc} are the potential at power point, the current at the power point, the open circuit voltage and the short circuit current, respectively. The conversion efficiency of the photogalvanic system was calculated using the output at the power point and the power of the incident radiation. The system at its optimum condition was exposed to sunlight. It was observed that i–V curve deviated from its ideal regular rectangular shape as shown in Fig. 3.
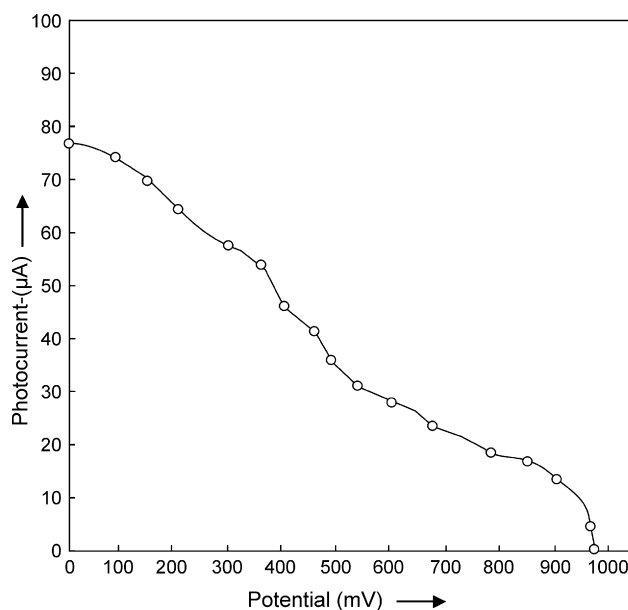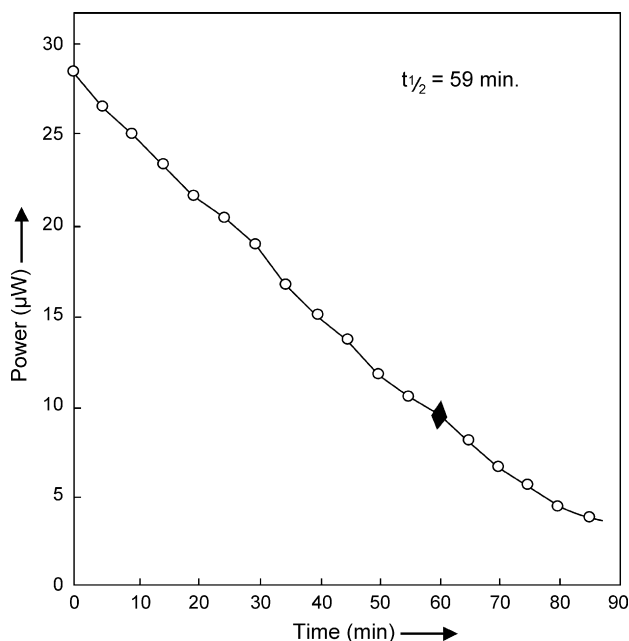

Fig. 3. Current–potential (i–V) curve of the cell.

Fig. 4. Performance of the cell.

3.7. Performance of the cell

The performance of the photogalvanic cell containing EDTA-mixed dyes system was studied by applying the desired external load necessary to have the potential and the current corresponding to the power point, after removing the source of illumination till the output (power) was reduced to half its value at the power point in the dark. The performance of the cell was determined in terms of $t_{1/2}$, i.e. time required for the fall of the output (power) to half its 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 59.0 min. The performance of the cell is graphically represented in Fig. 4.

4. Discussion

4.1. Electroactive species

Various probable processes may be considered for the photocurrent generation in photogalvanic cells. The possible combinations for electroactive species in photogalvanic cell are as follows:

Probable electroactive species	
In the illuminated chamber	In the dark chamber
TH + AB	Oxidized form of reductant (R^+)
Leuco or semi-$TH^- + AB^-$	Oxidized form of reductant (R^+)
Leuco or semi-$TH^- + AB^-$	TH + 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 generation of photocurrent should decrease with an

increase in the diffusion length, but this was not observed experimentally. The value of the photocurrent at equilibrium (i_{eq}) was also observed to be independent with respect to change in diffusion length (rather, it decreases slightly). Therefore, on the basis of effect of diffusion length on current parameters as reported [7], it may be concluded that the main electroactive species are the leuco or semi-$TH^- + AB^-$ and the dyes TH + AB in the illuminated chamber and the dark chamber, respectively. However, the reductant and its oxidized product act only as electron carriers in the path.

The observed conversion efficiency (0.18%) was determined with a tungsten lamp of 200 W (as light source), which has a light intensity around 15 times less than direct sunlight. Therefore, the conversion efficiency has experimentally been observed as 2.7%. The observed low conversion efficiency in comparison to the theoretical conversion efficiency of the photogalvanic cells (18%) seems due to the lower stability of the dyes, back-electron transfer, aggregation of dye molecules around the electrode, etc.

We believe that the investigated electrochemical device is advantageous with respect to lower charging time (2 h), storage capacity (59.0 min) and better electrical output than devices reported so far.

4.2. Mechanism

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

4.3. Illuminated chamber

On irradiation, dyes molecules get excited:

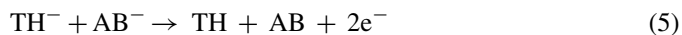$$TH + AB \xrightarrow{h\nu} TH^* + AB^* \qquad (3)$$

The excited dye molecules accept electrons from reductant and are converted into the semi or leuco form of the dyes and the reductant into its oxidized form:

$$TH^- + AB^- + 2R \rightarrow TH + AB + 2R^+ \qquad (4)$$

4.3.1. At platinum electrode

The semi or leuco form of dyes lose electrons and are converted into the original dye molecules:

$$TH^- + AB^- \rightarrow TH + AB + 2e^- \qquad (5)$$

4.4. Dark chamber

4.4.1. At the counter electrode (SCE)

Dye molecules accept electrons from the electrode and are converted into semi or leuco forms:

$$TH + AB + 2e^- \rightarrow TH^- + AB^- \qquad (6)$$

Finally, the leuco/semi form of dyes and oxidized forms of the reductant combine to regenerate the original dyes and reductant

molecules:

$$TH + AB + 2R^+ \rightarrow TH^- + AB^- + 2R \qquad (7)$$

where $TH + AB$, $TH^* + AB^*$, $TH^- + AB^-$, R and R^+ are the thionine + azur-B, their excited forms and its leuco or semi leuco forms, reductant and its oxidized form, respectively.

5. Conclusions

Previous workers [19,20] have developed photogalvanic cells containing a reductant and a photosensitizer with considerable electrical output, but our observations show that the electrical output can be been increased by 1.5–2.0 times by combining two different photosensitizers (mixed dyes) as shown in the present investigations.

However, further studies are still required to increase the conversion efficiency and storage capacity by selecting suitable substances for commercial viability of the photogalvanic cells.

Acknowledgement

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