

Short communication

## Use of Bromophenol Red–EDTA system for generation of electricity in a photogalvanic cell

Suresh C. Ameta, Pinki B. Punjabi, Jitendra Vardia\*, Soniya Madhwani, Sweta Chaudhary

*Solar Energy Laboratory, Department of Chemistry, University College of Science, M. L. Sukhadia University, Udaipur 313002, Rajasthan, India*

Received 15 July 2005; accepted 4 November 2005  
Available online 20 December 2005

### Abstract

Bromophenol Red is used as a photosensitizer in a photogalvanic cell for solar energy conversion. EDTA was used as an electron donor. The photopotential and photocurrent generated by the cell are 581.0 mV and 45.0  $\mu$ A, respectively. The effects of various operating parameters, e.g. pH, light intensity, diffusion length, reductant concentration, dye concentration, on the electrical output of the cell is examined. The current–voltage (*i*–*V*) characteristics of the cell are also observed and a tentative mechanism for the generation of the photocurrent is proposed. The performance of the cell is determined in the dark at its power point.

© 2005 Elsevier B.V. All rights reserved.

**Keywords:** Photogalvanic cell; Bromophenol Red; EDTA; Photopotential; Photocurrent; Photosensitizer

### 1. Introduction

Today, global warming and the rapid decrease in energy resources caused by the large-scale consumption of fossil fuels have become serious. Accordingly renewable energy resources are attracting a great deal of attention, and solar energy is one of the most promising future energy resources. The photochemical production of electricity has attracted the attention of many scientists as a viable media for solar energy conversion. The photogalvanic effect was first discovered in 1925 by Rideal and Williams [1] but was systematically investigated later by Rabinowitch [2]. The photoelectrochemical behaviour of TiO<sub>2</sub> modified by Prussian blue and rhodamine-B sensitized SnO<sub>2</sub> electrodes was observed by De Berry and Viehbeck [3] and Itoh et al. [4], respectively. Jana and Bhowmik [5] reported enhancement in the power output of a solar cell consisting of mixed dyes. Cahen et al. [6] observed the nature of photovoltaic action in a dye-sensitized solar cell. Garica et al. [7] used a fruit extract and ruthenium polypyridine dyes to sensitize TiO<sub>2</sub> in photoelectrochemical solar cell. Nusbaumer et al. [8] reported

dye-sensitized photovoltaic cells. Ferber and Luther [9] undertook the modelling of the photovoltage and the photocurrent of a dye-sensitized TiO<sub>2</sub> solar cell as Ameta et al. [10–12] examined some interesting photogalvanic systems for solar energy conversion. A solar cell with sensitized rutile and anatase-based TiO<sub>2</sub> was evaluated by Park and Vande Lagemaat [13]. Tennakone et al. [14] used dye-sensitized photoelectrochemical and solid solar cells for charge separation, transport and recombination. The use of micelles in the photochemical conversion of solar energy has been investigated by Ameta et al. [15,16]. Schwarzburg and Willig [17] explored the origin of photovoltage and photocurrent in nanoporous, dye-sensitized, photoelectrochemical solar cell. The sensitization of nanoporous films of TiO<sub>2</sub> with santaline (red sandal wood pigment) and the construction of a dye-sensitized solid-state photovoltaic cell was attempted by Tennakone and Kumara [18]. Recently, Madhwani et al. [19] reported use of a fluorescein-EDTA system in photogalvanic cells.

The research in the field of photogalvanic cells is still in its infancy with respect to its viability and practical applicability and, therefore, requires thorough exploration to increase the conversion efficiency and storage capacity by selecting a suitable redox couple and photosensitizers. A detailed survey of literature reveals that no attention has been paid to the Bromophenol Red–EDTA system in a photogalvanic cell for solar energy conversion and, therefore, the present work has been undertaken.

\* Corresponding author. Tel.: +91 294 2413955; fax: +91 294 2526160.

*E-mail addresses:* [ameta\\_sc@yahoo.com](mailto:ameta_sc@yahoo.com) (S.C. Ameta), [jjitendravardia@yahoo.com](mailto:jjitendravardia@yahoo.com) (J. Vardia).

## 2. Materials and methods

Bromophenol Red (S.D. Fine), EDTA (Ranbaxy) and sodium hydroxide (Ranbaxy) were used. All the solutions were prepared in doubly-distilled water and stored in amber-coloured containers to protect them from light. A mixture of the solution of the dye, EDTA, NaOH and water was filled into an H-shaped glass cell. A platinum electrode (1.0 cm × 1.0 cm) was placed in one compartment of the cell and a saturated calomel reference electrode (SCE) in the other. The platinum electrode was exposed to a 200 W tungsten lamp (Philips) while the SCE was kept in the dark. A direct-reading, solar intensity meter (SM CEL 501) was used to measure the light intensity. A water filter was used to avoid thermal effects. A digital pH meter (Systronics model 324) measured the pH of the solution, which was adjusted by the addition of a previously standardized sodium hydroxide solution. The temperature of the system was maintained at 303 K ( $\pm 0.1$  K).

The photopotential and photocurrent generated by the system Bromophenol Red|EDTA|OH<sup>-</sup>|h $\nu$  were measured by a digital multimeter (CIE 5605) and microammeter (Kew), respectively. The current–voltage (*i*–*V*) characteristics of the cell were studied by using an external load (linear 470 K) in the circuit.

## 3. Results and discussion

### 3.1. Variation of potential and current with time

The potential of the photogalvanic cell was first stabilized in then dark and then the platinum electrode was exposed to light. The potential is observed to fall with the duration of illumination. It then becomes stable and changes in direction (to small extent only) on removing the source of illumination.

A photogalvanic cell containing Bromophenol Red and a EDTA reductant exhibits a rapid change in potential on illumination (6.09 mV min<sup>-1</sup>). On the other hand, the fall in potential on removing the source of illumination is quite low in the presence of dye. Therefore, Bromophenol Red can be used successfully in a photogalvanic cell as a photosensitizer.

The current increases rapidly in the first few minutes of illumination to reach a maximum value (*i*<sub>max</sub>). It then decreases slowly to attain a stable value at equilibrium (*i*<sub>eq</sub>). A fall in the current is observed on removing the source of irradiation. The rate of current fall for the cell containing Bromophenol Red is 0.24  $\mu$ A min<sup>-1</sup>.

### 3.2. Effect of pH

The effect of variation in pH on the electrical output of the cell is shown in Table 1. With increase in pH, there is an increase in photopotential and photocurrent until pH = 10.6. Further increase in pH results in a decrease in the electrical output of the cell. It is interesting to observe that the pH for the reductant is related to its p*K*<sub>a</sub> value, i.e. the desired pH is slightly higher than its p*K*<sub>a</sub> value (pH > p*K*<sub>a</sub>). This may be due to the availability of the reductant in an anionic form, which is a better electron donor than its unionized form.

Table 1  
Effect of pH

pH	Photopotential (mV)	Photocurrent ( $\mu$ A)
10.3	322.0	37.0
10.4	393.0	39.0
10.5	452.0	42.0
10.6	581.0	45.0
10.7	426.0	41.0
10.8	361.0	38.0
10.9	290.0	36.0

[Bromophenol Red] =  $4.00 \times 10^{-5}$  M; [EDTA] =  $5.33 \times 10^{-3}$  M; intensity = 25.0 mW cm<sup>-2</sup>; temperature = 303 K.

Table 2  
Effect of Bromophenol Red concentration

[Bromophenol Red] × 10 <sup>5</sup> M	Photopotential (mV)	Photocurrent ( $\mu$ A)
2.00	355.0	38.0
2.66	438.0	41.0
3.33	493.0	43.0
4.00	581.0	45.0
4.66	476.0	42.0
5.33	394.0	39.0
6.00	341.0	34.0

[EDTA] =  $5.33 \times 10^{-3}$  M; pH = 10.6; intensity = 25.0 mW cm<sup>-2</sup>; temperature = 303 K.

### 3.3. Effect of dye and reductant concentration

The dependence of photopotential and photocurrent on the concentration of the dye and the reductant was studied and the results are summarized in Tables 2 and 3, respectively. On increasing the concentration of Bromophenol Red, both the photopotential and the photocurrent increases till a maximum is achieved at  $4.00 \times 10^{-5}$  M, after which both characteristics decreases. A small output is obtained at a low concentration of Bromophenol Red because a smaller number of dye molecules are available for excitation and consecutive donation of electrons to the platinum electrode. A large concentration of dye results in a decrease in photopotential because the intensity of light reaching the dye molecules (near the electrode) decreases due to the major portion of the light being absorbed by the dyes molecule available in its path.

A similar trend is observed with variation of the concentration of reductant (EDTA) and both the photopotential and

Table 3  
Effect of EDTA concentration

[EDTA] × 10 <sup>3</sup> M	Photopotential (mV)	Photocurrent ( $\mu$ A)
4.53	418.0	40.0
4.80	466.0	41.0
5.06	532.0	43.0
5.33	581.0	45.0
5.60	521.0	43.0
5.87	453.0	40.0
6.13	385.0	39.0

[Bromophenol Red] =  $4.00 \times 10^{-5}$  M; pH = 10.6; intensity = 25.0 mW cm<sup>-2</sup>; temperature = 303 K.

Table 4  
Effect of light intensity

Intensity, $I$ ( $\text{mW cm}^{-2}$ )	Photocurrent ( $\mu\text{A}$ )	Photopotential, $V$ (mV)	$\log V$
7.0	495.0	2.6946	32.0
12.0	521.0	2.7168	36.0
16.0	537.0	2.7299	39.0
20.0	553.0	2.7427	42.0
25.0	581.0	2.7641	45.0

[Bromophenol Red] =  $4.00 \times 10^{-5}$  M; [EDTA] =  $5.33 \times 10^{-3}$  M; pH = 10.6; temperature = 303 K.

the photocurrent achieve maximum values at a concentration of  $5.33 \times 10^{-3}$  M. At low concentrations, the power output is small due to the fewer number of reductant molecules available for electron donation to the dye molecules, whereas a large concentration of reductant hinders the movement of dye molecules reaching the electrode in the desired time limit.

### 3.4. Effect of light intensity

The photocurrent shows a linear increasing behaviour with increase in the intensity of the light, whereas the photopotential increases in a logarithmic manner. The variation of these electric parameters with light intensity is shown in Table 4.

The number of photons per unit area (incident power) that strike the dye molecules around the platinum electrode increases with the increase in the light intensity. Hence, the photocurrent and the photopotential of the photogalvanic cell are affected favourably (increases). On the other hand, increase in light intensity also raises the temperature of the cell. Therefore, an intensity of medium order ( $25.0 \text{ mW cm}^{-2}$ ) was used for all investigations.

### 3.5. 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 ( $i_{\text{max}}$ ,  $i_{\text{eq}}$ , initial rate of current generation). The results are reported in Table 5. There is a sharp increase in photocurrent ( $i_{\text{max}}$ ) and then there is a gradual decrease to a stable value. The photocurrent at equilibrium is represented as  $i_{\text{eq}}$ . This behaviour indicates an initial rapid reaction, followed by a slow

Table 5  
Effect of diffusion length on current parameters

Diffusion length (cm)	Maximum photocurrent, $i_{\text{max}}$ ( $\mu\text{A}$ )	Equilibrium photocurrent, $i_{\text{eq}}$ ( $\mu\text{A}$ )
2.0	41.0	35.0
2.5	43.0	34.0
3.0	44.0	34.0
3.5	45.0	32.0
4.0	47.0	31.0

[Bromophenol Red] =  $4.00 \times 10^{-5}$  M; [EDTA] =  $5.33 \times 10^{-3}$  M; pH = 10.6; intensity =  $25.0 \text{ mW cm}^{-2}$ ; temperature = 303 K.

Table 6  
The probable electrode active species

Case	Illuminated chamber	Dark chamber
(a)	Bromophenol Red	Oxidized form of reductant (OxR)
(b)	Leuco- or semi-Bromophenol Red	Oxidized form of reductant (OxR)
(c)	Leuco- or semi-Bromophenol Red	Bromophenol Red

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 listed in Table 6.

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. It is observed, however, that  $i_{\text{max}}$  and the initial rate of photocurrent generation are 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 cases (a) and (b) (cf. Table 6) 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. Nevertheless, the reductant and its oxidized products behave as the electron carriers in the cell and diffuse through the path.

### 3.6. Current–voltage ( $i$ – $V$ ) characteristics, conversion efficiency and performance of the cell

The open-circuit voltage ( $V_{\text{oc}}$ ) and short-circuit current ( $i_{\text{sc}}$ ) of the photogalvanic cell were measured by means of a digital multimeter (keeping the circuit open) and a micro-ammeter (keeping the circuit closed), respectively. The current and potential between two extreme values ( $V_{\text{oc}}$  and  $i_{\text{sc}}$ ) were recorded with the assistance of a carbon pot (linear 470 K) that was connected in the circuit of the multimeter and through which an external load was applied.

The  $i$ – $V$  characteristics of the cell containing a Bromophenol Red–EDTA system are shown graphically in Fig. 1. The curve for the cell deviates from its ideal regular rectangular shape. A point in the  $i$ – $V$  curve, called the power point (pp), was determined where the product of photocurrent and photopotential is maximum. The potential and the current at the power point are represented by  $V_{\text{pp}}$  and  $i_{\text{pp}}$ , respectively. With the help of the ( $i$ – $V$ ) curve, the fill factor and conversion efficiency of the cell are found to be 0.27 and 0.0360%, respectively, using the formulae:

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

$$\text{conversion efficiency} = \frac{V_{\text{pp}} \times i_{\text{pp}}}{25.0 \text{ mW cm}^{-2}} \times 100\% \quad (2)$$

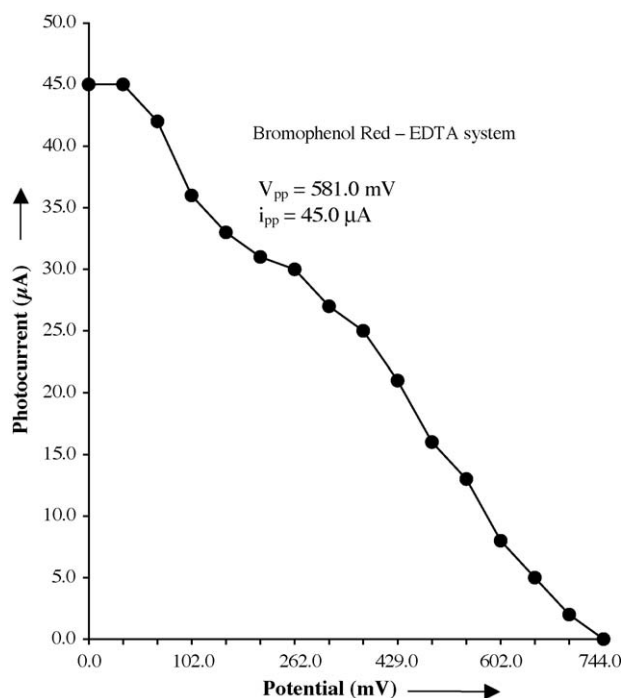
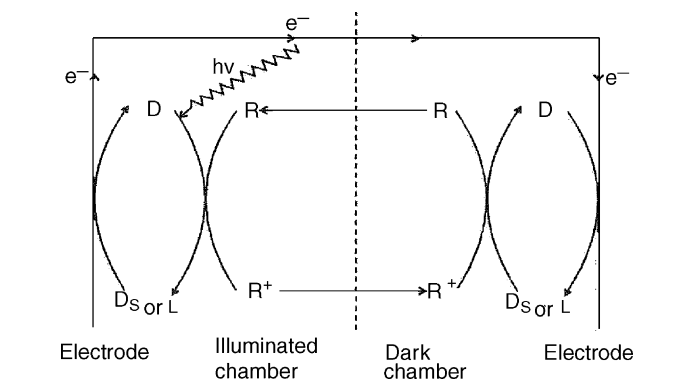


Fig. 1. Current-voltage ( $i$ - $V$ ) curve of photogalvanic cell.

The performance of the cell was studied by applying the external load that was necessary to have the current and the potential at the power point after removing the source of light. The cell can be used in the dark at its power point for 35 min. Thus, whereas photovoltaic cell cannot be used in the dark even for a second, a photogalvanic system has the advantage of being used in the dark, but at a lower conversion efficiency. Other dyes like Bromocresol purple, Pyronine-B and Fast green have also been used as sensitizers. It is found that the cell can be used in dark at its power point for 32.0, 26.0 and 20.0 min with Bromocresol purple, Pyronine-B and Fast green, respectively. This shows that Bromophenol Red provides the best performance.

### 3.7. Mechanism

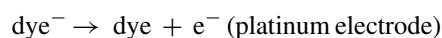
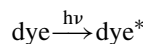
As no reaction is observed between the dye and EDTA in the dark, it may be concluded that the redox potential of EDTA is much higher than that of Bromophenol Red. A rapid fall in potential is observed when the platinum electrode is illuminated. The potential reaches a steady value after certain period of exposure. Although the direction of the change of potential is reversed on removing the source of light, the potential does not return to its initial value. This means that the main reversible photochemical reaction is also accompanied by some side irreversible reactions. The electroactive species in this photogalvanic system is thus different from that of the well-studied thionine-iron(II) system. In the present case, the leuco- or semi-reduced dye is considered to be the electrode active species in the illuminated chamber, and the dye itself in dark chamber. On the basis of the information gained above, the mechanism of photocurrent generation in the photogalvanic cell can be represented as:



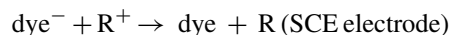
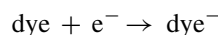
D: Bromophenol Red; R: EDTA;

$D_s$  or  $L$ : semi-reduced or leuco-Bromophenol Red,  $R^+$ : oxidized form of EDTA.

Illuminated chamber



Dark chamber



where R,  $R^+$ , dye,  $\text{dye}^-$  are the reductant EDTA, its oxidized form, Bromophenol Red and its leuco form, respectively.

## 4. Conclusions

On the basis of above results, it is concluded that Bromophenol Red can be used successfully as a photosensitizer in a photogalvanic cell. The conversion efficiency of the cell is 0.036% and the cell can be used in dark at its power point for 35 min. Other photosensitizers such as Bromocresol purple, Pyronine-B and Fast green have also been investigated, but the best performance of the photogalvanic cell is obtained when using Bromophenol Red. Photovoltaic cells have better conversion efficiency than photogalvanic cells, but they lack storage capacity. Photogalvanic cells have the added advantage of having in-built storage capacity. The time is not far off when the conversion efficiency of these cells will be comparable with that of existing solar cells. Thus, photogalvanic cells show good prospects of becoming commercially viable.

## References

- [1] E.K. Rideal, D.C. Williams, J. Chem. Soc. (1925) 258.
- [2] E. Rabinowitch, J. Phys. Chem. 8 (1940) 551.
- [3] B.W. De Berry, A. Viehbeck, J. Electroanal. Soc. 130 (1983) 249.
- [4] K. Itoh, M. Nakao, K. Honda, J. Electroanal. Soc. 178 (1984) 329.
- [5] A.K. Jana, B.B. Bhowmik, J. Photochem. Photobiol. 122A (1999) 53.
- [6] D. Cahen, G. Hotes, M. Gratzel, J.F. Guillemoles, I. Riess, J. Phys. Chem. 104B (2000) 2053.

- [7] C.G. Garica, A.S. Polo, N.Y.M. Iha, J. Photochem. Photobiol. 160A (2003) 87.
- [8] H. Nasbaumer, J.E. Moser, S.M. Zakeeruddin, M.K. Nazeeruddin, M. Gratzel, J. Phys. Chem. 105B (2001) 10461.
- [9] J. Ferber, J. Luther, J. Phys. Chem. 105B (2001) 4895.
- [10] S.C. Ameta, T.D. Dubey, G.C. Dubey, R.C. Ameta, Z. Phys. Chem. Leipzig 265 (1984) 838.
- [11] S.C. Ameta, R. Ameta, S. Seth, T.D. Dubey, Afinidad XIV (1988) 362.
- [12] S.C. Ameta, R. Ameta, M. Bala, S. Khamesara, Int. J. Energy Res. 14 (1990) 163.
- [13] N.G. Park, J. Vande Lagemaat, A.J. Frank, J. Phys. Chem. 104B (2000) 8989.
- [14] K. Tennakone, P.V.V. Jayaweera, P.K.M. Bandarana Yake, J. Photochem. Photobiol. 158A (2003) 125.
- [15] S.C. Ameta, S. Khamesra, R. Ameta, A.K. Chittora, Z. Phys. Chem. Leipzig 271 (1990) 427.
- [16] S.C. Ameta, S.L. Sharma, A. Lodha, S. Dube, Int. J. Energy Res. 17 (1993) 359.
- [17] K. Schwarzburg, F. Willig, J. Phys. Chem. 103B (1999) 5743.
- [18] K. Tennakone, GRR.A. Kumara, J. Photochem. Photobiol. 117A (1998) 137.
- [19] S. Madhwani, R. Ameta, J. Vardia, P.B. Punjabi, V.K. Sharma, Energy Sources (2005), accepted for publication.