



Enhancement of Photogalvanic Effect of Toluidine Blue Dye using Sodium Lauryl Sulphate as an Efficient Additive for Solar Energy Conversion and Storage

SAMARVEER SINGH, DEEP SHIKHA, VIKKY SINGH and SUSHMITA GUPTA^{*ID}

Department of Applied Chemistry, Mahatma Jyotiba Phule Rohilkhand University, Bareilly-243006, India

*Corresponding author: E-mail: drsushmitagupta12@gmail.com

Received: 15 July 2020;

Accepted: 23 December 2020;

Published online: 16 February 2021;

AJC-20244

In photogalvanic cells, electron transfer reactions can lead to the inexpensive production of solar power with an inherent storage capacity because in solution, the ions involved act as mobile charges through diffusion. This study improved the storage capacity and solar power of photogalvanic cells comprising ethylenediamine acetic acid (EDTA), toluidine blue and sodium lauryl sulphate (NaLS) as a reductant, photosensitizer and surfactant, respectively. The observed maximum photocurrent, photopotential, and open circuit voltage, of the photogalvanic cell were 150 A, 743 mV and 1065 mV, respectively. The efficiency of conversion cells was approximately 0.2630%. In the dark, the storage capacity ($t_{0.5}$) was 124 min for the photogalvanic cell. The optimization of the influence of different parameters such as variation in photosensitizer concentration, surfactant, reductant, pH, and temperature as well as the electrical output was performed. A mechanism was proposed for photocurrent generation in the photogalvanic cell.

Keywords: Photopotential, Photocurrent, Conversion efficiency, Storage capacity, Fill factor, Solar energy, Surfactant.

INTRODUCTION

Energy is an important component related to the environmental, social and economic development of a country. With an increase in industrial and agriculture activities, energy demands increase. In greenhouse gas emission, energy conversion results in environmental problem development. The resources of renewable energy are a highly effective and efficient solution for environmental problems [1]. A new approach to the renewable energy sources has resulted in an increase in the interest in the photogalvanic cell due to their storage capacity and reliable solar energy conversion [2].

A photogalvanic cell comprises cathodic and anodic electrodes placed in a mixture of reductants, photosensitizer and acid/alkali. A surfactant is added into this mixture for increasing the electric output. To enhance the electrical performance of photogalvanic cells, numerous researchers [3-7] have investigated different organic reductants, dye sensitizers and micelles. In an alkaline medium, the sensitiser-reductant-surfactant chemical combination can be termed as photogalvanic chemical systems. For their practical applicability and in terms of the requirement of increasing their storage capacity and conversion

efficiency, the studies in the photogalvanic cell field are currently in the initial stage. The utilization of novel dyes with organic reductants has considerably enhanced cell performance.

The photogalvanic cell is a diffusion-controlled cell that depends on ion diffusion in the bulk electrolytic solution. Thus, the sensitivity and diffusion of electrodes are principal determinants of the efficiency of photogalvanic cells. Hence, to ensure high sensitivity and diffusion, a small platinum electrode (that causes less hindrance to ion mobility) with a highly sensitive electrode (only saturated calomel electrode, SCE, terminal employed) has been investigated by researchers for successfully enhancing the performance of photogalvanic cells [8].

For enhanced photogalvanic cells, a photogalvanic chemical system, which is based on an organic reductant (ethylene glycol) a mixed-dye photosensitizer (toluidine blue + brilliant cresyl blue), and an anionic surfactant (NaLS), was used [9]. Similarly, Gangotri & Lal [10] employed methylene blue and thionine as photosensitizers and EDTA as a reductant in a photogalvanic cell for the storage and conversion of solar energy. Genwa *et al.* [11] investigated the photogalvanic effect with an arabinose-NaLS system by employing malachite green and toluidine blue as photosensitizers. However, for photogalvanic cells, mixed

dyes did not lead to high performance. The surfactant plays a crucial role in their high performance. This performance can be caused by the catalytic effect induced by carefully selected surfactants on a chemical reaction and the surfactant's capacity to dissolve specific molecules (photosensitising dyes) [12]. In literature, EDTA-toluidine blue-NaLS systems for photogalvanic cells have received no attention; thus, this study was conducted. Toluidine blue is a stable, inexpensive and basic thiazine metachromatic dye having a high affinity to tissue components. Hence, with the anionic surfactant, toluidine blue dye was selected. This study investigated the surfactant for the storage and conversion of solar energy by using the EDTA-toluidine blue-NaLS system and optimized the influence of various parameters on electrical outputs of photogalvanic cells.

EXPERIMENTAL

Highest-purity sodium lauryl sulphate (NaLS), toluidine blue, EDTA (S.D. fine chemicals, India) and sodium hydroxide (Merck, India) were used. Double distilled water was used to prepare all the employed solutions. These solutions were stored in Amber-coloured containers for protecting them from light. An H-shaped glass cell containing a known quantity of reductant EDTA, photosensitizer toluidine blue and surfactants NaOH and NaLS was employed. The total volume (25 mL) of mixture solution was constant. SCE was placed in a limb of an H-shaped tube. In a limb of the cell with a window, the platinum electrode (1 cm × 1 cm) was dipped. To a digital pH meter, the electrode terminal was connected. Initially, the entire system was placed in dark, and the potential was measured till a stable potential observed. Subsequently, the limb-containing platinum electrode was subjected to a light source of the tungsten lamp of 200 W. The limb-containing SCE was placed in dark. Between the light source and exposed limb, a water filter was kept to eliminate the infrared radiation.

Toluidine blue photochemical bleaching was potentiometrically investigated. The current and potential produced using the system were estimated by employing the microammeter (OSAW) digital and pH meter (Systronics Modal 335), respectively. The current-voltage properties of cells were explored using external loads by employing a carbon pot (log 470 k) connected in a circuit with a key to acquire an open-circuit and a closed-circuit device.

RESULTS AND DISCUSSION

Effect of EDTA concentration: With an increase in the reductant EDTA concentration, the photopotential increased until it attained the maximum value. With a further increase in the EDTA concentration, the cell's electrical output decreased. At the optimal concentration of 2.40×10^3 M, the maximum photocurrent (70 μ A) and photopotential (743 mV) were obtained. With a decrease in the reductant concentration, the number of molecules available for electron donation in the dye decreased. By contrast, the high reductant concentration may hinder the dye molecule movement for reaching the electrode in the required time limit, which may lead to a decrease in the electric output.

Table-1 presents the influence of variations in the EDTA concentration on the power output, photocurrent and photopotential of the investigated system.

TABLE-1
EFFECT OF VARIATION OF EDTA,
TOLUIDINE BLUE, NaLS AND pH

Parameters	Photopotential (mV)	Photocurrent (μ A)	Power (μ W)
[EDTA] $\times 10^3$ M			
1.0	505.0	40.0	20.20
1.6	600.0	60.0	36.00
2.4	743.0	70.0	52.01
3.2	635.0	64.0	40.64
4.0	532.0	43.0	22.87
[Toluidine blue] $\times 10^5$ M			
3.0	534.0	45.0	24.03
3.5	635.0	65.0	41.27
4.0	743.0	70.0	52.01
4.5	680.0	63.0	42.84
5.0	520.0	48.0	24.96
[NaLS] $\times 10^3$ M			
4.6	492.0	40.0	19.68
5.2	645.0	53.0	34.18
6.0	743.0	70.0	52.01
6.8	680.0	61.0	41.48
7.6	540.0	43.0	23.22
pH			
11.5	438.0	43.0	18.83
12.0	592.0	59.0	34.92
12.6	743.0	70.0	52.01
13.0	620.0	61.0	37.82
13.5	513.0	42.0	21.54
[Toluidine blue] = 4.00×10^{-5} M, [EDTA] = 2.40×10^{-3} M, [NaLS] = 6.00×10^{-3} M, Light intensity = 10.4 mW cm ⁻² , pH = 12.64, Temp. 303 K.			

Effect of photosensitizer (toluidine blue) concentration:

To a certain extent, the photopotential power and photocurrent increased with an increase in the photosensitizer concentration. With further increase in this concentration, the cell's electrical output decreased. The maximum photocurrent (70 A) and photopotential (743 mV) were observed at a concentration of 4×10^5 M. At the lower concentration, fewer dye molecules were available for absorbing the major light portion in the path and fewer electrons reached the platinum electrode. Thus, the electrical output of the cell decreased. When the dye concentration increased, near platinum electrode, the number of excited dye molecules increase. Consequently, electron transfer led to an increase in the photocurrent, photopotential and power output. With the further increase in the dye concentration, the light intensity decreased because many dye molecules present absorbed the major light portion and the transfer of electrons from the dye molecules to electrode decreased, leading to a low electric output. Table-1 presents the influence of variations in the concentration of toluidine blue on the photocurrent, photopotential, and power output of the system.

Effect of sodium lauryl sulphate (NaLS) concentration:

The electrical output of the cell increased with an increase in the NaLS concentration. At the optimum concentration of $6 \times$

10^3 M, the maximum electrical output was obtained. With the further increase in the concentration, the photocurrent and photopotential of the photogalvanic cell decreased. The dye molecule was solubilized to the maximum extent by using the surfactant. Thus, the CMC value changed in the electric output. The highest electric output of the cell is dependent of surfactant CMC [5]. Table-1 presents the results of variations in surfactant concentrations on the photocurrent and photopotential of the system under study.

Effect of pH: The photogalvanic cell comprising the EDTA-toluidine blue-NaLS system is highly sensitive towards the pH of solutions. In alkaline range, the photopotential increased with an increase in pH. At the pH of 12.64, the highest photocurrent and photopotential were observed. With a further increase in pH, photocurrent and photopotential decreased (Table-1). Desired pH must be greater than the pK_a ($pH > pK_a$) values of the reductant. The electronic output increased because of the availability of reductant in the anionic form. The anionic form of the reductant is better electron donor than the unionised form of the reductant.

Effect of diffusion length: The influence of diffusion length variations on the initial rate of photocurrent generation and current parameters of the cell (I_{max} and $I_{i.e.}$) was explored using the H-shaped cells having different dimensions. With an increase in the diffusion length, the initial rate of current generation and maximum photocurrent increased because the path for the photochemical reaction increased. However, this phenomenon was not experimentally observed. With an increase in the diffusion length, the equilibrium photocurrent (i_{eq}) exhibited a negligible decreasing behaviour. Thus, the semi-form or leuco of the dye are the main electroactive species in the dark and illuminated chamber, respectively. In the path, the and the oxidized products of the reductant behave only as electron carriers. The results are summarized in Table-2.

Diffusion length D_L (mm)	Maximum photocurrent (i_{max})	Equilibrium photocurrent (i_{eq})	Rate of initial generation of current ($\mu A \text{ min}^{-1}$)
35	143.0	76.0	15.0
40	146.0	73.0	15.8
45	150.0	70.0	16.6
50	154.0	67.0	17.4
55	158.0	64.0	18.2

[TB] = 4.00×10^{-5} M, [EDTA] = 2.40×10^{-3} M, [NaLS] = 6.00×10^{-3} M, Light intensity = 10.4 mW cm^{-2} , pH = 12.64, Temp. 303 K.

Effect of light intensity: The influence of light intensity on the electrical output was explored by employing the different intensity (watts) light sources. The photocurrent exhibited a linear increasing behaviour when the light intensity increased. The photopotential increased in the logarithmic manner. An increase in the number of photons with an increase in the light intensity led to this increasing trend of the electrical output. Table-3 presents the effect of light intensity variations on the photocurrent and photopotential.

Light intensity (mW cm^{-2})	Photopotential (mV)	Photocurrent (μA)	log V
3.1	672.0	64.0	2.82
5.2	680.0	66.0	2.83
10.4	743.0	70.0	2.87
15.6	800.0	74.0	2.90
26.0	950.0	82.0	2.97

[TB] = 4.00×10^{-5} M, [EDTA] = 2.40×10^{-3} M, [NaLS] = 6.00×10^{-3} M, pH = 12.64, Temp. 303 K.

i-V Characteristics of the cell: The open-circuit voltage (V_{oc}) and short-circuit current (i_{sc}) of photogalvanic cells were determined. The potential and current acquired between these two extreme values (V_{oc} and i_{sc}) were measured using the carbon pot (log 470 K) connected in a circuit of multimeter. Through the multimeter, external loads were applied. Fig. 1 illustrates the i-V characteristics of the photogalvanic cell comprising EDTA-toluidine blue-NaLS. Deviations in the i-V curve from its regular rectangular shape were observed. Power points (where the product of potential and current is the highest) were estimated. The fill factor was computed using eqn. 1:

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

where V_{pp} and i_{pp} represent the value of potential and current at power point, respectively; V_{oc} and i_{sc} represent open circuit voltage and short circuit current, respectively.

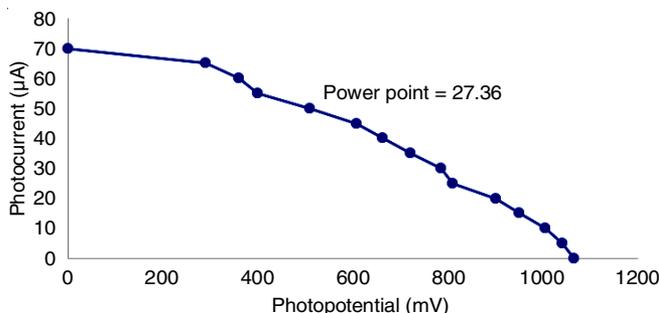


Fig. 1. Current voltage (i-V) curve for EDTA-toluidine blue-NaLS system

Performance of the cell: Immediately after illumination termination when the potential became constant, photogalvanic cell performance was studied by applying the external load (to obtain the current at power points). Performance was determined in $t_{0.5}$, i.e., the time required for output (power) to decrease to its half at the power point in dark. The cell comprising EDTA-toluidine blue-NaLS can be utilized in dark for 124 min (Fig. 2).

Conversion efficiency of the cell: With the aid of the incident power of radiations and potential and current at the power point (pp), the cell conversion efficiency was calculated to be 0.263% in the presence of the EDTA-toluidine blue-NaLS system by using eqn. 2:

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

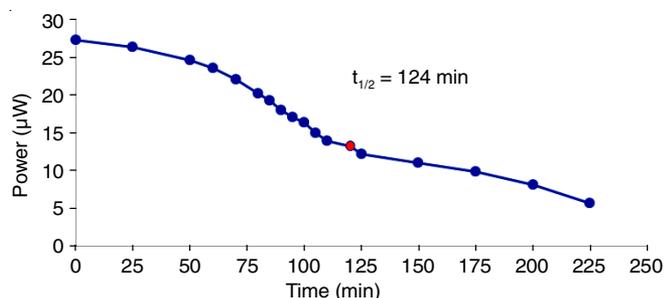
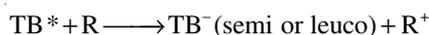
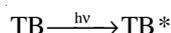


Fig. 2. Performance of the cell (EDTA-toluidine blue-NaLS)

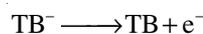
Mechanism

On the basis of these observations, a mechanism is suggested for the generation of photocurrent in the photogalvanic cell as follows:

Illuminated chamber:



At platinum electrode



Dark chamber



where TB, TB*, TB⁻, R and R⁺ are the toluidine blue, excited toluidine blue, semi- or leuco-toluidine blue, reductant and oxidized form of the reductant, respectively.

Conclusion

According to the results, the EDTA-toluidine blue-NaLS system can efficiently increase the storage and conversion capacity of cells. The storage capacity and conversion

efficiency of the fabricated photogalvanic cell were 124 min and 0.263%, respectively. Because inexpensive reductants, photosensitizers and surfactants are used in the cells, the photogalvanic cells are economical. Further efforts are required to improve the storage capacity and electric output and to decrease the cost of photogalvanic cells by selecting suitable reductants and redox couples.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. P.A. Owusu and S. Asumadu-Sarkodie, *Cogent Eng.*, **3**, 116790 (2016); <https://doi.org/10.1080/23311916.2016.1167990>
2. A. Malviya and P.P. Solanki, *Renew. Sustain. Energy Rev.*, **59**, 662 (2016); <https://doi.org/10.1016/j.rser.2015.12.295>
3. P. Tanwar, *Energy Source Part A*, **37**, 1318 (2015); <https://doi.org/10.1080/15567036.2011.603022>
4. P. Koli, Y. Dayma, R.K. Pareek and M. Jonwal, *Sci. Rep.*, **10**, 19264 (2020); <https://doi.org/10.1038/s41598-020-76388-5>
5. S. Tiwari, C. Mall, P.P. Solanki, *Surf. Interface*, **18**, 100427 (2020); <https://doi.org/10.1016/j.surfin.2019.100427>
6. P. Koli, U. Sharma and K.M. Gangotri, *Renew. Energy*, **37**, 250 (2012); <https://doi.org/10.1016/j.renene.2011.06.022>
7. A. Sonel and P. Chouhan, *AIP Conf. Proc.*, **2220**, 070010 (2020); <https://doi.org/10.1063/5.0002206>
8. P. Koli, *Wires, Energy Environ.*, **7**, e274 (2018); <https://doi.org/10.1002/wene.274>
9. K.M. Gangotri and A.K. Mahawar, *Environ. Prog. Sustain. Energy*, **31**, 474 (2012); <https://doi.org/10.1002/ep.10579>
10. K.M. Gangotri and C. Lal, *Proc. Inst. Mech. Eng., Part A*, **219**, 315 (2005); <https://doi.org/10.1243/095765005X28599>
11. K.R. Genwa, A. Kumar and A. Sonel, *Appl. Energy*, **86**, 1431 (2009); <https://doi.org/10.1016/j.apenergy.2008.11.026>
12. R. Vittal, H. Gomathi and K.-J. Kim, *Adv. Colloid Interface Sci.*, **119**, 55 (2006); <https://doi.org/10.1016/j.cis.2005.09.004>