

**STUDIES IN THE USE OF  
TOLUIDINE BLUE–GLUCOSE SYSTEM  
IN A PHOTOGALVANIC CELL**

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الخلاصة :

استخدم التوليد الأزرق (TB) كمادة ضوئية حاسة في خلية جلفانو ضوئية مع الجلوكوز . ووجد أن فرق الجهد والتيار المتولد بهذه الطريقة هو ٩٣٠ ملليشولت و ٤٥ ميكروامبير على التوالي . وقد درس تأثير المتغيرات المختلفة على التيار المتولد كما لوحظت خصائص جهد ( $i - V$ ) الخلية وقد اقترحت ميكانيكية لتوليد التيار الضوئي في الخلية الجلفانو ضوئية . كذلك قيّم أداء الخلية في الظلام أثناء عمل الخلية .

**ABSTRACT**

Toluidine blue (TB) as photosensitizer and glucose as reductant have been used in a photogalvanic cell. The photopotential and photocurrent generated by this cell were 930 mV and 45  $\mu$ A, respectively. Effect of various parameters on the electrical output of the cell has been studied. Current voltage ( $i - V$ ) characteristics of the cell has been also observed and a tentative mechanism for the generation of photocurrent in the photogalvanic cell has been proposed. Performance of the cell was determined in the dark at its power point.

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## STUDIES IN THE USE OF TOLUIDINE BLUE–GLUCOSE SYSTEM IN A PHOTOGALVANIC CELL

### INTRODUCTION

The photogalvanic effect was first discovered in 1925 by Rideal and Williams [1], but it was systematically investigated by Rabinowitch [2]. Later on, this kind of work was followed up by various workers throughout the world [3–18]. Various problems encountered in the development of this field have been discussed by Hoffman and Lichtin [16]. The theoretical conversion efficiency of an ideal photogalvanic cell is about 18% [17], but the observed conversion efficiencies are quite low. Back-electron transfer, lower stability of dyes, aggregation of dye molecules around the electrode, *etc.* are the main reasons for the low values.

A detailed survey of the literature reveals that no attention has been paid to the use of the toluidine blue–glucose system in photogalvanic cells for solar energy conversion and, therefore, the present work was undertaken.

### EXPERIMENTAL

Toluidine blue (Loba), sodium hydroxide (SM) and glucose (E. Merck) were used in the present work. All the solutions were prepared in double distilled water. A mixture of solutions of dye, glucose, and sodium hydroxide was taken in a H-type cell. A platinum electrode ( $1 \times 1 \text{ cm}^2$ ) was dipped in one limb of the cell and a saturated calomel electrode (SCE) in the other. The platinum electrode was exposed to a 200 W tungsten lamp (Sylvania) and the limb containing the SCE was kept in the dark. A water filter was used to cut off the thermal radiations.

The photochemical bleaching of toluidine blue was studied potentiometrically. The photopotential and photocurrent generated by the system TB/glucose/ $\text{OH}^-/h\nu$  were measured by a digital pH meter (Systronics-Model 335) and multimeter (Systronics Model 435), respectively. The  $i-V$  characteristics of the cell were studied by using an external load (log 500 K) in the circuit. The intensity of the light source was measured by a Solarimeter (Model CEL SM 203).

### RESULTS AND DISCUSSION

#### Effect of pH on Electrical Output of the Cell

The effect of variation in pH on the electrical output of the cell was observed and the results are reported in Table 1.

Table 1. Variation with pH

| pH   | [TB] = $3.2 \times 10^{-5} \text{ M}$<br>Temperature = 303 K |                                | [Glucose] = $2.0 \times 10^{-3} \text{ M}$<br>Intensity = $10.4 \text{ mW cm}^{-2}$ |                                |
|------|--|--------------------------------|---|--------------------------------|
|      | Photopotential (mV)  | Photocurrent ( $\mu\text{A}$ ) | Photopotential (mV)   | Photocurrent ( $\mu\text{A}$ ) |
| 11.9 | 435.0  | 27.0                           |   |                                |
| 12.0 | 520.0  | 33.0                           |   |                                |
| 12.1 | 610.0  | 38.0                           |   |                                |
| 12.3 | 930.0  | 45.0                           |   |                                |
| 12.4 | 800.0  | 40.0                           |   |                                |
| 12.6 | 715.0  | 34.0                           |   |                                |
| 12.8 | 575.0  | 29.0                           |   |                                |

From the above table it is clear that with the increase in pH value, the electrical output of the cell also increases reaching a maximum at a particular pH. Further increase in pH resulted in the decrease in the electrical output. It was quite interesting to observe that the pH for the optimum condition has a relation with  $pK_a$  of the reductant and the desired pH is higher than its  $pK_a$  value ( $\text{pH} > pK_a$ ). It may be due to the availability of reductant in its anionic form which is its better donor form.

#### Effect of Dye and Reductant Conversion

Dependence of photopotential and photocurrent on the concentrations of dye and reductant was studied and results are summarized in Table 2.

Table 2. Variation of Dye and Reductant Concentration

| pH = 12.3<br>Temperature = 303 K |                                   | Intensity = $10.4 \text{ mW cm}^{-2}$ |                                |
|----------------------------------|-----------------------------------|---------------------------------------|--------------------------------|
| [TB] $\times 10^5 \text{ M}$     | [Glucose] $\times 10^3 \text{ M}$ | Photopotential (mV)                   | Photocurrent ( $\mu\text{A}$ ) |
| 3.2                              | 1.2                               | 605.0                                 | 36.0                           |
| 3.2                              | 1.6                               | 725.0                                 | 41.0                           |
| 3.2                              | 2.0                               | 930.0                                 | 45.0                           |
| 3.2                              | 2.4                               | 790.0                                 | 40.0                           |
| 3.2                              | 2.8                               | 586.0                                 | 34.0                           |
| 3.2                              | 3.2                               | 375.0                                 | 28.0                           |
| 1.6                              | 2.0                               | 577.0                                 | 33.0                           |
| 2.4                              | 2.0                               | 779.0                                 | 39.0                           |
| 3.2                              | 2.0                               | 930.0                                 | 45.0                           |
| 4.0                              | 2.0                               | 777.0                                 | 40.0                           |
| 4.8                              | 2.0                               | 585.0                                 | 36.0                           |
| 5.6                              | 2.0                               | 395.0                                 | 31.0                           |

A small output was obtained for lower concentrations of toluidine blue because a small number of dye molecules were available for excitation and subsequent donation of the electron to the platinum electrode. Larger concentrations of dye again resulted in a decrease in photopotential as the intensity of light reaching the dye molecule near the electrode will decrease after the absorption of the major portion of the light by the dye molecules available in the path.

A similar trend has been observed for the variation of the concentration of reductant (glucose). The decrease in the concentration of glucose resulted in a fall in power output due to the lower number of reductant molecules available for electron donation to dye molecules whereas a larger concentration of reductant will hinder the movement of dye molecules to reach the electrode in the desired time limit.

#### Effect of Diffusion length

H-cells of different dimensions were used to study 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). The results are reported in Table 3.

**Table 3. Variation of Diffusion Length**

| [TB] = $3.2 \times 10^{-5}$ M |  | [Glucose] = $2.0 \times 10^{-3}$ M              |  |
|-------------------------------|--|---|--|
| Temperature = 303 K           |  | Intensity = $10.4 \text{ mW cm}^{-2}$           |  |
| pH = 12.3                     |  |   |  |
| Diffusion Length (mm)         | Maximum photocurrent $i_{max} (\mu\text{A})$ | Equilibrium photocurrent $i_{eq} (\mu\text{A})$ | Rate of initial generation of current $(\mu\text{A min}^{-1})$ |
| 30.0                          | 57.0   | 46.0  | 1.1  |
| 35.0                          | 67.0   | 47.0  | 2.4  |
| 40.0                          | 79.0   | 45.0  | 3.9  |
| 45.0                          | 93.0   | 46.0  | 5.4  |
| 50.0                          | 103.0  | 44.0  | 6.7  |

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

On the basis of the effect of diffusion length (distance between the electrodes) on the current

parameters [7], it may be concluded that the leuco- or semi-reduced form of the dye and the dye itself are the main electrode-active species at the illuminated and dark electrodes, respectively. However, the reductants and its oxidized products behave as the electron carriers in the cell diffusing through the path.

#### Effect of Light Intensity

The effect of light intensity on the electrical output of the cell was studied using light sources of different intensities (different wattage). The results are reported in Table 4. It was observed that the photocurrent showed a linear increasing behavior with the increase in the intensity of the light, whereas the photopotential increases with increasing light intensity in a logarithmic manner (*cf.* Table 4) *i.e.* a plot of  $\log V$  versus  $I$  was linear.

**Table 4.**

| [TB] = $3.2 \times 10^{-5}$ M               |                         | [Glucose] = $2.0 \times 10^{-3}$ M |                                |
|---|-------------------------|------------------------------------|--------------------------------|
| Temperature = 303 K                         |                         | pH = 12.3                          |                                |
| Light Intensity $I$ ( $\text{mW cm}^{-2}$ ) | Photopotential $V$ (mV) | Log $V$                            | Photocurrent ( $\mu\text{A}$ ) |
| 3.1   | 889.0                   | 2.9489                             | 43.8                           |
| 5.2   | 899.7                   | 2.9541                             | 44.1                           |
| 10.4  | 930.0                   | 2.9685                             | 45.0                           |
| 15.6  | 960.0                   | 2.9798                             | 46.5                           |
| 26.0  | 1032.0                  | 3.0137                             | 48.3                           |

As the intensity of light increases, the number of photons per unit area (incident power) striking the dye molecules around platinum electrode also increases and therefore, there is a corresponding increase in the electrical output of the cell. However, an increase in light intensity will also raise the temperature of the cell and therefore a intensity of medium order ( $10.4 \text{ mW cm}^{-2}$ ) was used in all experiments. The solar insolation falling on the earth is about  $100 \text{ mW cm}^{-2}$  on a clear day and the output (when placed in sunlight) from the cell should be approximately double the output with the intensity at  $10.4 \text{ mW cm}^{-2}$  (because  $\log_{10} 100 = 2.0$ ), however, this was never obtained. The photopotential and photocurrent generated by the cell in sunlight were 1156 mV and  $55 \mu\text{A}$ , respectively. 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 intensity of the light.

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

The open circuit voltage ( $V_{oc}$ ) and short circuit current ( $i_{sc}$ ) of the photogalvanic cell were measured by a digital pH meter (keeping the circuit open) and by a multimeter (keeping the circuit closed), respectively. The current and potential values in between these two value ( $V_{oc}$  and  $i_{sc}$ ) were recorded with the help of a carbon pot (log 500 K) connected in the circuit with the multimeter through which an external load was applied. The results are graphically represented in Figure 1.

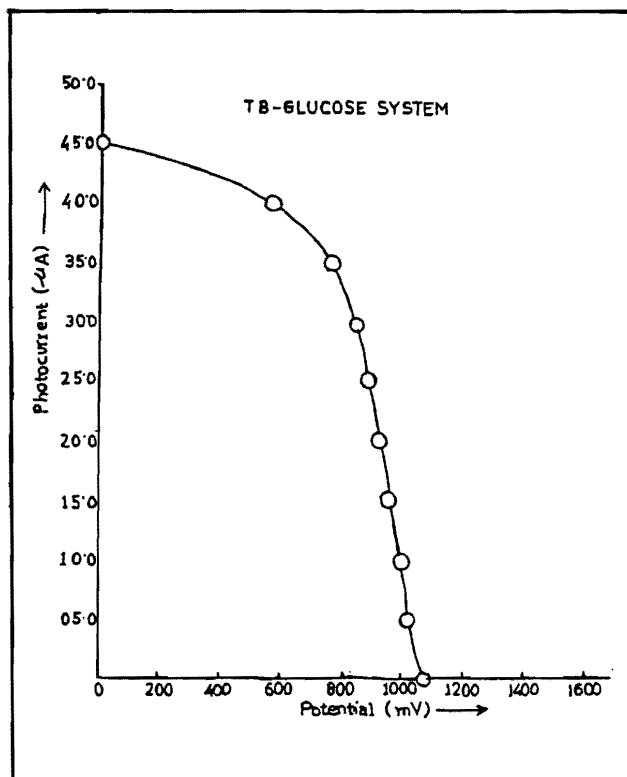


Figure 1.

It was observed that the *i*-*V* curve of the cell deviated from its ideal regular rectangular shape. A point in *i*-*V* curve called power point (pp) is determined where the product of potential and current is maximum. The values of potential and current obtained at power point were 820.0 ( $V_{pp}$ ) and 32.5 ( $i_{pp}$ ), respectively. With the help of (*i*-*V*) curve, the fill-factor and conversion efficiency of the cell were determined as 0.55 and 0.2563%, respectively, using formula (1).

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

Where,  $V_{oc} = 1080 \text{ mV}$ , and  $i_{sc} = 45.0 \mu\text{A}$  (cf. Figure 1).

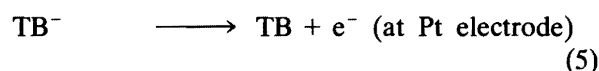
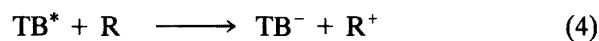
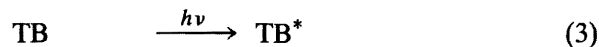
$$\text{Conversion Efficiency} = \frac{V_{pp} \times i_{pp}}{10.4 \text{ mW cm}^{-2}} \times 100\% \quad (2)$$

The performance of the cell was studied by applying the external load necessary to have a current and potential at power point after removing the source of light. It was observed that the cell can be used in the dark at its power point for thirty minutes. The photovoltaic cell cannot be used in dark even for a second whereas the photogalvanic system (TB-glucose) has the additional advantage of being usable in the dark, of course with lower conversion efficiency.

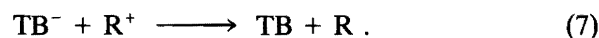
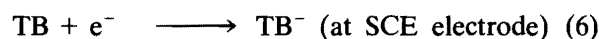
**MECHANISM**

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

*Illuminated chamber*



*Dark chamber*



Where TB,  $\text{TB}^-$ , R, and  $\text{R}^+$  represent toluidine blue, its leuco-form, reductant glucose, and its oxidized form, respectively.

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