Role of Heterocyclic Dye (Azur B) with Reductant and Surfactant in Photogalvanic Cell for Solar Energy Conversion and Storage

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Abstract

Studies of heterocyclic dye (Azur B) with reductant and surfactant in photogalvanic cell containing Azur B-EDTA- CTAB cell for solar energy conversion and storage. The photopotential and photocurrent of the cell is observed 795.0 mV and 395.0 μA respectively. The conversion efficiency and fill factor of the cell are determined 1.004 % and 0.2556 respectively. The storage capacity (performance) of the cell is observed 140.0 minutes in dark. The effects of different parameters on the electrical output of the cell are observed and current-voltage (i-V) characteristics of the cell are also studied. The proposed mechanism for the generation of photocurrent in photogalvanic cell is also explained here.

Keywords: conversion efficiency, fill factor, storage capacity.

1. Introduction

Achieving a secure, efficient and clean energy supply is one of the major issues facing the world community. Since, there is an urgent need to focus the higher attention on development of new energy sources. The solar energy is easily available, cheap and eco-friendly source of energy has edge over the other renewable sources of energy with special reference to abundantly available and its promising nature. The new approach for renewable energy sources has led to an increasing interest in photogalvanic cells because of their reliable solar energy conversion and storage capacity. The photogalvanic cells are a photoelectrochemical device in which solar energy convert into electrical energy via formation of an energy rich species that exhibit the photogalvanic effect. The photogalvanic effect was first of all recognised by Rideal and Williams (1925) and it was systematically studied by Rabinowitch (1940), and then by other workers (1959, 1960, 1983, 2007, 1982 and 1985). Some researchers (2003 and 1977) have studied on how to enhance the performance and optimum efficiency of dye sensitized solar cell for solar energy conversion. Later on studies on photogalvanic cell consisting of various photosensitizers with reductant, mixed sensitizers with reductant and sensitizer with reductant and surfactant for solar energy conversion and storage reported time to time (1989, 1997, 2003, 2007, 1999, 2001, 2007, 2006, 2009, 2010, 2010, 2011, 2011, 2011 and 2012). Recently some photogalvanic cells are developed by Meena and his co-workers (2010, 2011 and 2012) and Meena (2013) for generation of electrical energy from various photosensitiser with reductant and photosensitizer with reductant in micelles media. Present work is the effort to observe the role of heterocyclic dye (Azur B) with reductant and surfactant in photogalvanic cell for solar energy conversion and storage.

2. Experimental Methods

Azur B (MERCK), CTAB (MERCK), EDTA (MERCK) and NaOH (MERCK) are used in the present research work. All the solutions are prepared in doubly distilled water and the stock solutions of all chemicals are prepared by direct weighing and are kept in coloured container to protect them from the light. The entire cell is set systematically for photogalvanic studies, which consists of thin foil of electrochemically treated platinum as electrode and saturated calomel electrodes as a reference electrode. The distance between the illuminated and dark electrode is 45 mm. An ordinary tungsten lamp of 200 W is used as light source. Water filter is used to cut-off IR radiations. The photopotential is obtained as the difference between the initial potential of the cell in dark and the equilibrium potential attained by the cell under constant illumination. The potential is first measured in dark and the change in potential on illumination is measured as a function of time. The solution is bubbled with prepurified nitrogen gas for nearly twenty minutes to remove dissolved oxygen. Solutions of dye, reductant, surfactant and sodium hydroxide are taken in an H-type glass tube. A platinum electrode (1.0 x 1.0 cm2) is immersed into one arm of H-tube and a saturated calomel electrode (SCE) is kept in the other. The whole cell is first placed in dark till a stable
potential is obtained and then, the arm containing the SCE is kept in the dark and the platinum electrode is exposed to a 200 W tungsten lamp. A water-filter is used to cut off infrared radiations. The photochemical bleaching of Azur B is studied potentiometrically. A digital pH meter (Systrons Model-335) and a microammeter (Ruttonsha Simpson) are used to measure the potential and current generated by the cell, respectively. The current–voltage characteristics of photosgalvanic cell have been studied by applying an external load with the help of a carbon pot (log 470 K) connected in the circuit through a key to have close circuit and open circuit device. The experimental set-up of photosgalvanic cell is given in Figure 1. The effect of variation of different parameters has also been observed. The rate of change in potential after removing the source of illumination is 0.90mV min⁻¹ in Azur B-EDTA-CTAB cell.

![Figure 1 Experimental set-up of photosgalvanic cell](image)

3. Results and Discussion

3.1. Effect of variation in photosensitizer, reductant and surfactant concentration on the cell:

The effect of variation in photosensitizer, reductant and surfactant concentration on photoelectric parameters is studied. It is observed that the photopotential and photocurrent are increasing with respect to the concentration of the photosensitizer, reductant and surfactant. A maximum is obtained for a particular value of photosensitizer (Azur B) concentration, reductant (EDTA) concentration and surfactant (CTAB) concentration. On further increase in concentration of photosensitizer (Azur B), reductant (EDTA) and surfactant (CTAB), a decrease in the electrical output of the cell is obtained.

The reason of the change in electrical output is that lower concentration of photosensitizer resulted into a fall in electrical output because fewer photosensitizer (Azur B) molecules are available for the excitation and consecutive donation of the electrons to the platinum electrode whereas the higher concentration of photosensitizer (Azur B) again resulted into a decrease into electrical output as the intensity of light reaching the dye molecules near the electrode decrease due to absorption of the major portion of the light by dye molecules present in the path.

The reason of the change in electrical output is that the lower concentration of reducing agent resulted into a fall in electrical output because fewer reducing agent molecules are available for electron donation to photosensitizer (Azur B) molecule whereas the higher concentration of reducing agent again resulted into a decrease in electrical output, because the large number of reducing agent molecules hinders the dye molecules from reaching the electrode in the desired time limit.

The reason of the change in electrical output is that the surfactant solubilizes the dye molecules up to highest extent at or around their micelles concentration. The above variations are reported in Table 1.

3.2. Effect of variation of pH on the cell:

The effect of variation in pH on photoelectric parameters of cell is studied. It is found that the cell containing Azur B-EDTA-CTAB to be quite sensitive to the pH of the solution. It is observed that there is an increase in the photoelectric parameters of this cell with the pH value (In the alkaline range). At pH 13.20 a maxima is obtained. On further increase in pH, there is a decrease in photoelectric parameters. It is observed that the pH for the optimum condition has a relation with pKa of the reductant and the desired pH is higher than pKa value (pH>pKa). The reason of the change in electrical output is that the availability of the reductant in its anionic form, which is a better donor form. The above same is reported in Table 1.

**Table 1 Effect of concentration (Azur B, EDTA and CTAB) and pH on the cell**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Photopotential (mV)</th>
<th>Photocurrent (μA)</th>
<th>Power (μW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Azur B) × 10⁻³ M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.82</td>
<td>698</td>
<td>305</td>
<td>212.89</td>
</tr>
<tr>
<td>1.85</td>
<td>742</td>
<td>338</td>
<td>250.8</td>
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<tr>
<td>1.88</td>
<td>795</td>
<td>395</td>
<td>314.03</td>
</tr>
<tr>
<td>1.92</td>
<td>755</td>
<td>344</td>
<td>259.72</td>
</tr>
<tr>
<td>1.95</td>
<td>684</td>
<td>312</td>
<td>213.41</td>
</tr>
<tr>
<td>(EDTA) × 10⁻³ M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.06</td>
<td>713</td>
<td>313</td>
<td>223.77</td>
</tr>
<tr>
<td>1.11</td>
<td>752</td>
<td>346</td>
<td>260.19</td>
</tr>
<tr>
<td>1.16</td>
<td>795</td>
<td>395</td>
<td>314.03</td>
</tr>
<tr>
<td>1.2</td>
<td>747</td>
<td>352</td>
<td>262.94</td>
</tr>
<tr>
<td>1.25</td>
<td>688</td>
<td>309</td>
<td>212.59</td>
</tr>
<tr>
<td>(CTAB) × 10⁻³ M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.63</td>
<td>713</td>
<td>313</td>
<td>223.77</td>
</tr>
<tr>
<td>0.65</td>
<td>752</td>
<td>346</td>
<td>260.19</td>
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<tr>
<td>0.68</td>
<td>795</td>
<td>395</td>
<td>314.03</td>
</tr>
<tr>
<td>0.7</td>
<td>747</td>
<td>352</td>
<td>262.94</td>
</tr>
<tr>
<td>0.72</td>
<td>688</td>
<td>309</td>
<td>212.59</td>
</tr>
<tr>
<td>pH</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>13.04</td>
<td>719</td>
<td>314</td>
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<tr>
<td>13.12</td>
<td>752</td>
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<td>266.82</td>
</tr>
<tr>
<td>13.2</td>
<td>795</td>
<td>395</td>
<td>314.03</td>
</tr>
<tr>
<td>13.28</td>
<td>758</td>
<td>347</td>
<td>263.03</td>
</tr>
<tr>
<td>13.36</td>
<td>702</td>
<td>302</td>
<td>212</td>
</tr>
</tbody>
</table>

(Azur B) = 1.88 x 10⁻³; Light Intensity = 10.4 mW cm⁻²; (EDTA) = 1.16 x 10⁻³ M; Temp. = 303 K; (TX-100) = 0.68 x 10⁻³ M; pH = 13.20
3.3. Effect of temperature and light intensity on the cell

The effect of temperature on the photoelectric parameters of the cell is studied. The effect of light intensity on the photoelectric parameters of the cell is also reported here. It is observed that the photocurrent of the photogalvanic cell is found to be increased with the temperature whereas the photopotential is decreased. Thereafter, the effect of temperature on total possible power output in the Azur B-EDTA-CTAB cell is also studied and it is observed that there a linear change between the both. The reason of the change in electrical output is that internal resistant of the cell decreases at higher temperature resulting into a rise in photocurrent and correspondingly, there will be a fall in photopotential. The same is presented in Figure 2. Similarly, Figure 3 shows rate of change in photoelectric parameter with respect to light intensity. The light intensity is measured in terms of mWcm$^{-2}$ with the help of solarimeter (CEL Model SM 203). It is found that the photocurrent show linear increasing fashion with light intensity whereas the photopotential show an increment in a logarithmic fashion.

![Figure 2](image2.png)

**Figure 2** Variation of photopotential and photocurrent with temperature

![Figure 3](image3.png)

**Figure 3** Variation of photopotential and log V with light intensity

3.4. Current-Voltage (i-V) characteristics of the cell

The short circuit current ($i_{sc}$) and open circuit voltage ($V_{oc}$) of the photogalvanic cells are measured with the help of a multimeter (keeping the circuit closed) and with a digital pH meter (keeping the other circuit open), respectively. The current and potential values in between these two extreme values are recorded with the help of a carbon pot (log 470 K) connected in the circuit of Multimeter, through which an external load is applied. The current-voltage (i-V) characteristics of the photogalvanic cells containing Azur B-EDTA-CTAB cell is graphically shown in Figure 4.

![Figure 4](image4.png)

**Figure 4** Current-Voltage (i-V) curve of the photogalvanic cell

3.5. Storage capacity and conversion efficiency of the cell

The storage capacity of the photogalvanic cell is observed by applying an external load (necessary to have current at power point) after terminating the illumination as soon as the potential reaches a constant value. The storage capacity is determined in terms of $t_{1/2}$, i.e., the time required in the fall of the output (power) to its half at power point in dark. It is observed that the cell can be used in dark for 140.0 minutes, whereas photovoltaic cell cannot be used in the dark even for a second. A photogalvanic cell has the advantage of being used in the dark but at lower conversion efficiency. The results are graphically presented in Figure 5. The conversion of the efficiency of the cell is determined as 1.004% with the help of photocurrent and photopotential values at the power point and the incident power of radiations by using the formula.

\[
\text{Conversion Efficiency} = \frac{V_{pp} x i_{pp}}{V_{oc} x i_{sc}} \times 100\%
\]

![Figure 5](image5.png)

**Figure 5** Performance of the photogalvanic cell
3.6. Performance of the photogalvanic cell

The overall performance of the photogalvanic cell is observed and reached to remarkable level in the performance of photogalvanic cells with respect to electrical output, initial generation of photocurrent, conversion efficiency and storage capacity of the photogalvanic cell. The results so obtained in Azur B-EDTA-CTAB cell are summarized in Table 2.

Table 2 Results obtained in Azur B-EDTA-CTAB

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Parameter</th>
<th>Observed value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dark potential</td>
<td>240.0 mV</td>
</tr>
<tr>
<td>2</td>
<td>Open circuit voltage ($V_{oc}$)</td>
<td>1035.0 mV</td>
</tr>
<tr>
<td>3</td>
<td>Photopotential ($DV$)</td>
<td>795.0 mV</td>
</tr>
<tr>
<td>4</td>
<td>Equilibrium photocurrent ($i_{eq}$)</td>
<td>395.0 mA</td>
</tr>
<tr>
<td>5</td>
<td>Maximum photocurrent ($i_{max}$)</td>
<td>475.0 mA</td>
</tr>
<tr>
<td>6</td>
<td>Initial generation of photocurrent</td>
<td>19.0 mA min⁻¹</td>
</tr>
<tr>
<td>7</td>
<td>Time of illumination</td>
<td>150.0 min</td>
</tr>
<tr>
<td>8</td>
<td>Storage capacity ($t_{1/2}$)</td>
<td>140.0 min</td>
</tr>
<tr>
<td>9</td>
<td>% of storage capacity of cell</td>
<td>0.93%</td>
</tr>
<tr>
<td>10</td>
<td>Conversion efficiency</td>
<td>1.00%</td>
</tr>
<tr>
<td>11</td>
<td>Fill factor (η)</td>
<td>0.2556</td>
</tr>
</tbody>
</table>

4. Mechanism

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

Figure 6 Processes of mechanism in photogalvanic cell

4.1 Illuminated chamber

At platinum electrode:

\[ \text{Dye} \xrightarrow{hv} \text{Dye}^* \]  \hspace{1cm} (4.1)

\[ \text{Dye}^* + R \rightarrow \text{Dye}^- \text{(Semi or leuco)} + R^- \]  \hspace{1cm} (4.2)

4.2 Dark chamber

At calomel electrode:

\[ \text{Dye}^- \rightarrow \text{Dye}^- \text{(Semi or leuco)} \]  \hspace{1cm} (4.3)

\[ \text{Dye}^- + e^- \rightarrow \text{Dye}^- \text{(Semi or leuco)} \]  \hspace{1cm} (4.4)

\[ \text{Dye}^- + R^- \rightarrow \text{Dye}^- + R \]  \hspace{1cm} (4.5)

Where Dye, Dye*, Dye-, R and R^- are the dye, excited form of dye, semi or leuco form of dye, reductant and oxidized form of the reductant, respectively. The same is represented in Figure 6.

5. Conclusion

On the basis of the results, it is concluded that hetrocyclic dye (Azur B) with reductant (EDTA) and surfactant (CTAB) can be used successfully as photosensitizer in a photogalvanic cell. The conversion efficiency and storage capacity of the cell are 1.004% and 140 minutes in dark respectively. It has been observed that the hetrocyclic dye (Azur B) with reductant (EDTA) and surfactant (CTAB) have not only enhanced the electrical parameters but also the storage capacity (performance) and conversion efficiency of the cell. Photovoltaic cells have better conversion efficiency than photogalvanic cells. Photogalvanic cells have the advantages of having in-built storage capacity. Thus, photogalvanic cells show good prospects of becoming commercially viable.

Nomenclature

\[ i_{eq} = \text{photocurrent at equilibrium} \]
\[ i_{max} = \text{maximum photocurrent} \]
\[ i_{pp} = \text{photocurrent at power point} \]
\[ i_{sc} = \text{short circuit current} \]
\[ ml = \text{milliliter} \]
\[ mV = \text{millivolt} \]
\[ M = \text{molarity} \]
\[ pp = \text{power point} \]
\[ t_{1/2} = \text{storage capacity of cell} \]
\[ DV = \text{observed photopotential} \]
\[ V_{oc} = \text{open circuit voltage} \]
\[ V_{pp} = \text{photopotential at power point} \]
\[ \eta = \text{fill factor} \]
\[ mA = \text{microampere} \]
\[ mW = \text{microwatt} \]

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References