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STUDIES OF CATIONIC MICELLES EFFECT ON PHOTO GALVANIC CELLS FOR SOLAR ENERGY CONVERSION AND STORAGE IN CONGO RED-D XYLOSE- CETYL PYRIDINIUM CHLORIDE SYSTEM

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ABSTRACT

The Cetylpyridinium chloride (CPC) has been used as cationic micelle species, Congo Red as photosensitizer and D-Xylose as electron donor for the enhancement of electrical output and performance (storage capacity) of the photogalvanic cell with reduce the cost of construction for commercial viability. The photopotential and photocurrent generated were 930.0mV and 470 μ A, respectively. The observed conversion efficiency and the fill factor were 1.1500% and 0.2356, respectively at the power point of the cell. The photogalvanic cell can be used for 130 minutes in the dark. The effect of different parameters like concentration of micelles; photosensitizer and electron donor, variation of pH, light intensity and diffusion path length were observed. A current- voltage(i-V) characteristics of the photogalvanic cell was studied experimentally and a mechanism has also been proposed for the generation of the photocurrent. All observed results of the system were lower in absence of the micelles species.

Key Words: *Photogalvanic Cell, Micelles, Congo Red, D-Xylose, Conversion Efficiency.*

INTRODUCTION

The flow of current between two unsymmetrical illuminated metal electrodes in sunlight was first observed by *Becquerel* in 1839 and photogalvanic effect was first reported by *Rideal and Williams* in 1925 but, it was systematically investigated by *Rabinowitch 1940* for iron-thionine system. Electron transfer via organic dye molecule and photo- induced electron transfer between micelle and thionine dye through a charge transfer interaction have observed *Mukhopadhyay and Bhowmik 1992*. *Bisquert et al 2004* have reported the physical- chemical principle of dye – sensitized solar cells, and *G.j. Mayer 2005* has presented the molecular approaches to solar energy conversion with coordination compounds. *Ameta et al., 1990, S.khamesra et al, 1991, Pramila and Gangotri 2007*, have used miceller species with different photosensitizer and reductant in photogalvanic system for solar energy conversion and storage. Recently, *Yadav and Lal 2010, R.K.Gunsaria et al 2003, R.K.Gunsaria and J. Hussain 2004*, have developed some interested photogalvanic cells with reasonable electrical output for solar energy conversion and storage.

They have used different photosensitizers, reductant and surfactants in photogalvanic cells but no attention has been paid to use Congo Red – D Xylose -Cetylpyridinium chloride system to system to enhance the electrical output and storage capacity of the cell. Our study reveals that a system of Congo Red – D Xylose -Cetylpyridinium chloride gives higher electrical output with better storage capacity , in addition ,the cell is cost effective which makes it suitable for commercialization in near future , therefore , the present work was undertaken.

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MATERIALS AND METHODS

All the solution were prepared in doubly distilled water and the stock solutions of all the chemicals were prepared direct weighing and were kept in colored container to protect them from light. A mixture of known amounts of solution of Congo Red (Indo dye chem), D-Xylose (LOBA Chem), Cetylpyridinium chloride (LOBA Chem) were taken in an H-shaped glass tube. The total volume of mixture was always kept at 25.0 mL, with make up by doubly distilled water. A platinum electrode ($1.0 \times 1.0 \text{ cm}^2$) was immersed in one limb of the H-tube having a window and a saturated calomel electrode was immersed in the the other limb. The terminals of the electrodes were connected to a digital pH meter and a micro ammeter .

The whole system was first placed in the dark till a stable potential was obtained. Then, the limb having platinum electrode (whole platinum electrode area) was exposed to a 200 W tungsten bulb(Sylvania) while other limb having the saturated calomel electrode was kept in dark. A water filter was used to avoid thermal radiations. On illumination, the photochemical bleaching of photosensitizer was studied potentiometrically. The current-Voltage(i-V) characteristics of the cell were studied by using an external load with the help of a carbon pot(log 470 K) connected in the circuit.

RESULTS AND DISCUSSION

Effect of variation of photo sensitizer and reductant concentration

The electrical output of the cell was affected by variation of photosensitizer (Congo Red) and reductant (D-Xylose) concentration. The results are summarized in Table 1. It was observed that on increasing the concentration of Congo Red ,electrical parameters photo potential(ΔV) and photocurrent(i_{sc}) increases, which reaches a maximum value at a concentration $2.21 \times 10^{-5} \text{ M}$, above which both parameters decrease. A lower concentration of Congo Red ($[\text{Congo Red}] < 2.21 \times 10^{-5} \text{ M}$) resulted into a decrease in electrical parameters because limited number of photosensitizer molecule were available for the excitation and consecutive donation of the electrons to the platinum electrode whereas a higher concentration of Congo Red ($[\text{Congo Red}] < 2.21 \times 10^{-5} \text{ M}$) again resulted into a decrease into electrical output as the intensity of light reaching the photosensitizer molecule near the electrode decreased due to absorption of the major portion of the light by photosensitizer molecules present in the path.

A similar result was observed for variation of concentration of reductant. A lower concentration of reducing agent ($[\text{D-Xylose}] < 1.12 \times 10^{-3} \text{ M}$) resulted into a fall in electrical output because fewer reducing agent molecule were available for electron donation to the photosensitizer molecules whereas a higher concentration of reducing ($[\text{D-Xylose}] < 1.12 \times 10^{-3} \text{ M}$) again resulted in a fall in a electrical output because larger number of reducing agent molecule hinder the photosensitizer molecule from reaching the electrode in the desired time limit.

Effect of variation of micelles concentration

The electrical output of the cell was found increase on increasing the concentration of CPC , reaching a maximum value at the concentration $6.40 \times 10^{-3} \text{ M}$, and then, further increase in their concentration a decrease in electrical output of the cell was observed. The observed results are summarized in Table 1.

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Table 1: Effect of variation of various parameters concentrations on the electrical output

Parameters	Photo potential(mV)	Photocurrent(μ A)	Power(μ A)
	[CPC] x 10^3		
6.24	782.0	308.0	240.86
6.32	855.0	394.0	336.87
6.40	930.0	470.0	437.10
6.48	847.0	385.0	326.10
6.56	775.0	302.0	234.05
	[Congo Red] x 10^5 M		
2.19	796.0	375.0	298.50
2.20	858.0	432.0	370.66
2.21	930.0	470.0	437.10
2.22	863.0	412.0	355.56
2.23	825.0	362.0	298.65
	[D-Xylose] x 10^3		
1.08	815.0	395.0	321.93
1.10	874.0	432.0	377.57
1.12	930.0	470.0	437.10
1.13	882.0	442.0	389.84
1.15	787.0	388.0	305.36
	pH		
12.78	818.0	382.0	312.48
12.79	868.0	425.0	368.90
12.80	930.0	470.0	437.10
12.81	875.0	409.0	357.88
12.82	825.0	368.0	303.60

It was observed that maximum electrical output obtain from the cell around their critical micelle concentration (CMC) of surfactant. It indicates the presence of the some charge transfer interaction between the dye-surfactant and the photoejection of electron from dye-surfactant depends on the charge on micelle. The surfactant has not only solublized the dye molecules to a maximum extent and their cmc value but have stabilizes also the system. In present work, the photogalvanic cell containing micelles system was compared with the cell containing photosensitizer and reductant system only (without micelles).

Effect of variation of pH

It was observed that there is an increase in the electrical output of the cell with increase in pH values and maximum value reaches at a particular pH value(pH=12.80). On further increasing in the pH value , a decrease in the electrical output of the cell was observed. The results are summarized in the Table 1.

It is quite interesting to observe that the pH at the optimum condition for the reductant has a relation with its pKa value, i.e. the desired pH value should be slightly higher then their pKa

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value(pH > pKa) this may be due to the availability of the reductant in an cationic form, which is a better electron donor than its unionized form.

Effect of diffusion path length

The effect of variation of diffusion path length on the electrical output and initial rate of generation of different photocurrent of the cell was studied by using H-shaped cell of different dimensions. The results are summarized in Table 3.

Table 3: Effect of diffusion path length

Diffusion path length D _L (mm) min. ⁻¹)	Maximum photocurrent i _{max} (μA)	Equilibrium photocurrent i _{eq} (μA)	Rate of initial generation of current(μA
35.0	572.0	478.0	15.05
40.0	576.0	474.0	15.16
45.0	580.0	470.0	15.26
50.0	584.0	465.0	15.37
55.0	588.0	461.0	15.47

It was observed that in first few minutes of illumination there was sharp increase in photocurrent and there was a gradual decrease to a stable value of photocurrent. This photocurrent at equilibrium state is known as equilibrium photocurrent (i_{eq}). This kind of photocurrent behavior is due to an initial rapid reaction followed by a slow rate-determining step at later stage. On the basis of effect of diffusion path length on the current parameters, it may be concluded that the leuco or semi reduced form of dyes and itself are the main electroactive species at the illuminated and dark electrodes, respectively. However, the reducing agent and their oxidized products behave as the electron carries in the cell diffusing through the path.

Current –voltage (i-V) characteristics of the cell

The open circuit voltage(V_{oc}) and short circuit current (i_{sc}) of the cell were measured with the help of a digital pH meter (keeping the circuit open) and with a micrometer (keeping the circuit closed), respectively. The potential and current values in between these two extreme values(V_{oc} and i_{sc}) were recorded with the help of a carbon pot (log 470 K) that was in the circuit of the microammeter and through which an external load was applied. The current voltage(i-V) characteristic of the cell is shown Fig.2.

It was observed that i-V curve for the cell deviated from their regular rectangular shape. A point in the i-V curve ,known as power point (pp), was determined where the product of potential and current was maximum. With the help of the curve; fill factor(η) value 0.3233 was calculated using the following formula :

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

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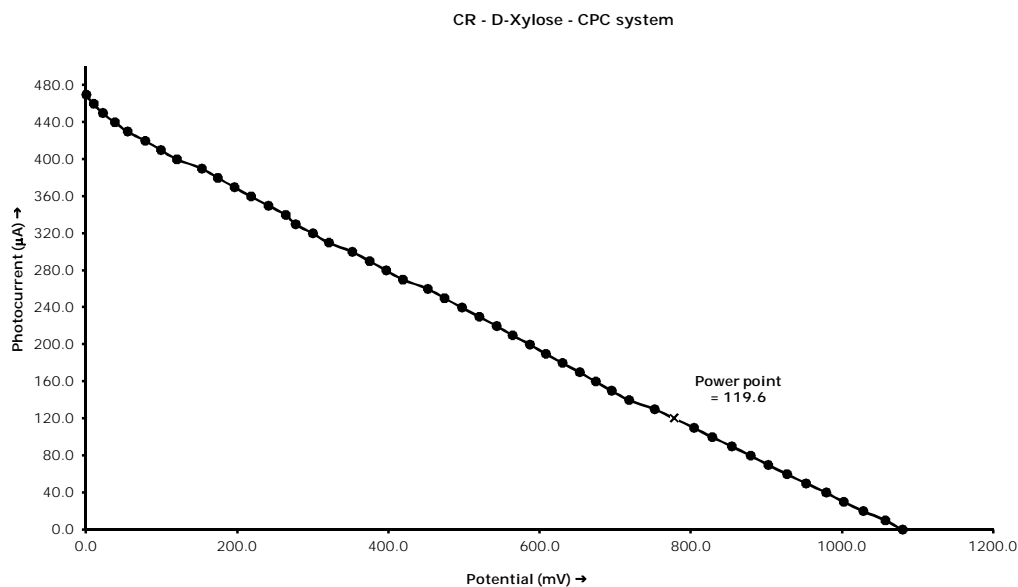


Fig. 2. CURRENT VOLTAGE (i-V) CURVE OF THE CELL

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

The conversion efficiency of cell was determined with help of photocurrent and photo potential values at power point (pp) and the power of incident radiation (light intensity 10.4 mW cm^{-2} which is measured by Solarimeter ,CEL, model SM 203), and it was 1.1500% obtained by using the following formula :

$$\text{Conversion efficiency} \% = \frac{V_{pp} \times i_{pp}}{A \times 10.4 \text{mWcm}^{-2} \times \text{Electrode area (cm}^{-2})} \times 100$$

Performance of the cell

The performance of the cell was studied by applying the desired external load ie resistance (carbon pot log 470 K) used as rheostate to vary the resistance, necessary to have the potential and current corresponding to the power point, after removing the light source of illumination till the output (power) was reduced to half its value (power = $236.0 \mu\text{W}$) at the power point in the dark. The performance was determined in terms of $t_{1/2}$ and it was observed that the cell can be used in the dark 130.0 minutes, which directly indicates the storage capacity of the photogalvanic cell. The observed results are graphically shown in Fig.3.

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CR - D-Xylose - CPC system

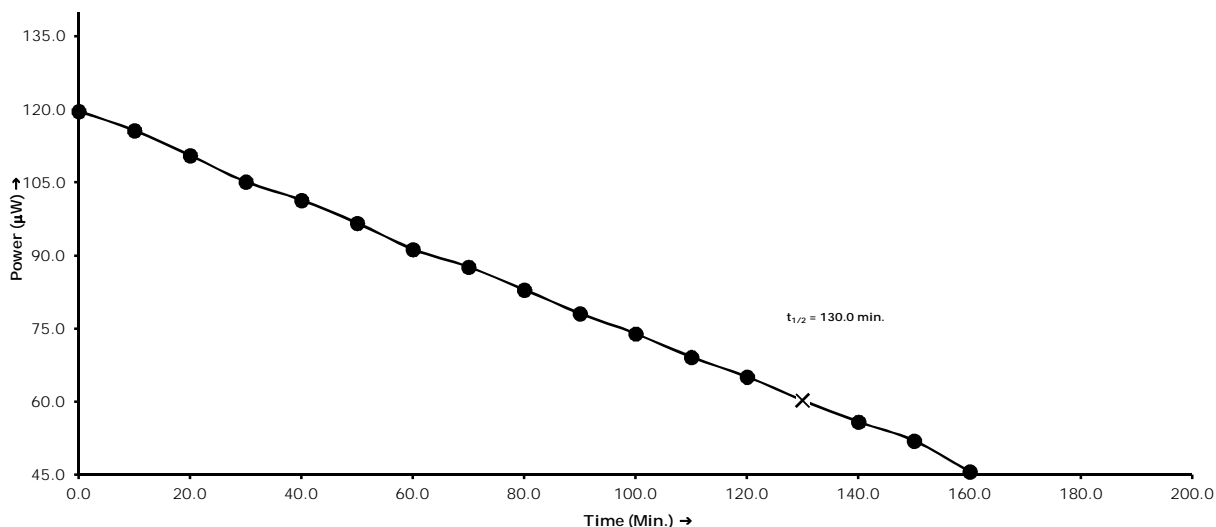
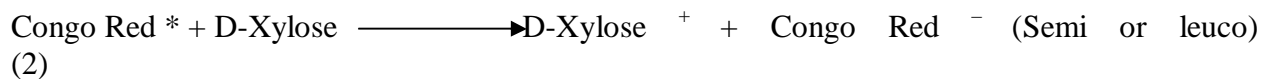
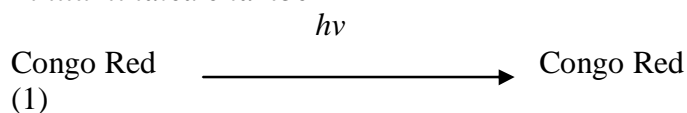


Fig. 3. PERFORMANCE OF THE CELL

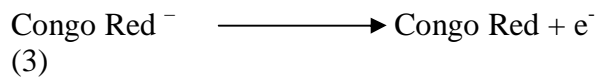
Mechanism

On the basis of above observations, a tentative mechanism has been proposed for the generation of photocurrent in the cell as follows:

In illuminated chamber



At platinum electrode



In dark Chamber

At counter (SC) electrode



Where Congo Red and D-Xylose⁺ are excited form of dye and oxidized form of reductant, respectively.

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Conclusions

On the basis of observed results of the photogalvanic cell containing CPC, Congo Red and D Xylose system, we have observed that the micelles have not only enhanced the conversion efficiency but the performance of the cell also. Exhaustive efforts still have the scope to enhance the electrical output as well as performance of the photogalvanic cells along with reduction in their cost to make commercial viability.

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