

Research Journal of Chemical Sciences _ Vol. **3(3)**, 20-25, March (**2013**)

Study of Photogalvanic Effect in Photogalvanic Cell containing Mixed Surfactant (NaLS+CTAB), Methylene blue as a Photosensitizer and Xylose as Reductant

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Available online at: www.isca.in

Received 31th October 2012, revised 7th November 2012, accepted 17th December 2012

Abstract

Photogalvanic effect was studied in a photogalvanic cell containing methylene blue-xylose-NaLS+CTAB system. The photopotential and photocurrent were observed 655.0 mV and 190.0 μ A respectively. The conversion efficiency of the system was observed 0.4326% and fill factor was determined as 0.2870. The cell performance was observed 90.0 minutes in dark. The effects of different parameters on the electrical output of the cell were observed and current-voltage (i-V) characteristics of the cell were also studied.

Keywords: Photogalvanic effect, methylene blue, xylose, CTAB, Fill factor, conversion efficiency.

Introduction

A large and cheap source of energy is an essential requirement for the development of a growing nation. Today energy is considered as a key for the development of modern era. Energy is the life line of countrys economy and development. No nation can aspire to be modern and developed without the availability of energy for all.

First of all the photogalvanic effect was observed by Rideal and Williams¹ and then was systematically investigated by Rabinowitch²⁻³ and later by various other workers time to time⁴⁻ ¹⁰. Studies in photogalvanic cells for solar energy conversion and storage reported by Ameta et al.^{11–13}. Effect of dyes along with surfactant was studied by Gangotri et al.¹⁴⁻¹⁵. Studies of surfactants in Photogalvanic cell-NaLS-EDTA-Azur-B system studied by Meena et al.¹⁶ Genwa and Gangotri have reported a comparative studies in anionic cationic and nonionic surfactant and Azur B – NTA – CPC system in photogalvanic $cell^{17}$. Gangotri and Bhimwal carried out a comparative study on the performance of photogalvanic cell with different photosensitizer for solar energy conversion and storage¹⁸. Gangotri and Gangotri studied micellar effect of photogalvanics for solar energy conversion and storage using Safranine O-EDTA-CTAB system¹⁹. A detailed Literature survey reveals that different photo sensitizers and reductants have been used in photo galvanic cell.20-27

Material and Methods

Methylene blue as photosensitizer, xylose as reductant and mixed surfactant (NaLS+CTAB) were used in this system. All solutions were prepared in doubly distilled water and were kept in amber coloured containers to protect them from sun light. A mixture of solutions of dye, reluctant, mixed surfactant and sodium hydroxide were taken in an H-type glass tube which is blackened by black carbon paper and white. A shiny platinum foil electrode was immersed in one limb of the H-tube and a saturated calomel electrode (SCE) was immersed in the other limb. The whole system was first placed in the dark till a stable potential was attained, then the limb containing the platinum electrode was exposed to a 200 W tungsten lamp (Philips). A water filter was used to cut off thermal radiation.

A digital pH meter and micro ammeter were used to measure the photopotential and photocurrent generated by the system respectively. The current voltage characteristics were studied by applying an external load with the help of a carbon pot (log 470 K) connected in the circuit. Over all experimental set up is given in figure- 1.

Results and Discussion

Effect of variation of photosensitizer (methylene blue) concentration on the system: Dependence of photopotential and photocurrent on the concentration of photosensitizer (Methylene blue) was studied. It was observed that lower concentration of photosensitizer resulted into a fall in photopotential and photocurrent because fewer photosensitizer (dye – methylene blue) molecules are available for the excitation and consecutive donation of the electrons to the platinum electrode. A greater concentration of dye 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 observed results are summarized in table-1.

Effect of variation of reductant (xylose) concentration on the system: The electrical output of the photogalvanic cell was

affected by the variation of reductant (xylose) concentration on the system. Lower concentration of reducing agent resulted into a fall in electrical output because fewer reducing agent molecules were available for electron donation to photosensitizer (dye - methylene blue) molecule.

Large concentration of reducing agent again resulted into a decrease in electrical output, because the large number of reducing agent molecules hinder the dye molecules from reaching the electrode in the desired time limit. The observed results are summarized in table-1.

Effect of variation of mixed surfactant (NaLS+CTAB) concentration on the system: For photogalvanic cell having methylene blue-xylose-NaLS + CTAB system, the photopotential and photocurrent varied with variation in concentration of mixed surfactants i.e. NaLS and CTAB. In one case concentration of NaLS was kept constant and concentration of CTAB was varied. In other case the concentration of CTAB was kept constant and concentration of NaLS was varied. In both cases a maxima was found for a particular value of NaLS and CTAB concentration above which decrease in electrical output of photogalvanic cell was obtained. The observed results are summarized in table- 1.

Effect of variation of pH on the system: The electrical output of the photogalvanic cell was affected by the variation of pH on the system. It can be observed from the table- 1 that there is an increase in electrical output of the cell with the increase in pH values. At pH 13.20 a maxima was obtained. On further increase in pH, there was a decrease in photopotential and photocurrent. Thus, photogalvanic cells containing the methylene blue-xylose-NaLS+CTAB system were found to be quite sensitive to the pH of the solutions.

It was observed that the pH for the optimum condition has a relation with pKa of the reductant and the desired pH is higher than in pKa value (pH>pKa). The reason may be the availability of the reductant in its anionic form, which is a better donor form. The observed results are summarized in table-1.

Effect of diffusion length: Effect of variation of diffusion length (distance between the two electrodes) on the current parameter of the cell (imax) has been studied using H-shaped cells of different dimensions. It is observed that in the first few minutes of illuminations there is sharp increase in the photocurrent. As a consequence, the maximum photocurrent (i_{max}) of photocurrent increase with increase in diffusion length, but this is not observed experimentally. Therefore, it may be concluded that the main electroactive species are the leuco or semi-leuco form of dye (photosensitizer) and the dye in illuminated and dark chamber respectively. The reductant and its oxidation product act only as electron carriers in the path. The results are summarised in table-2.

Effect of electrode area: The effect of electrode area on the current parameters of the cell has also been studied. It was

observed that with the increase in the electrode area the value of maximum potential (i_{max}) is found to increase. The results are summarised in table- 3.

Current-voltage (i-V) characteristics of the photogalvanic cell: The photogalvanic cell containing methylene blue-xylose-NaLS+CTAB system, the short circuit current (isc) and open circuit voltage (Voc) of the photogalvanic cells were measured with the help of a microammeter (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 were recorded with the help of a carbon pot (log 470 K) connected in the circuit of microammeter, through which an external load was applied. The Current–Voltage (i-V) characteristics of the photogalvanic cell containing Methylene blue-Xylose-NaLS+CTAB system is reported in figure- 2.

It was observed that current-voltage (i-V) curve deviated from their regular rectangular shapes. A point in i-V curve, called power point (pp) was determined where the product of current and potential was maximum and the fill-factor was calculated using the following formula :

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

Where V_{pp} and i_{pp} represent the value of potential and current at power point, respectively and Voc, isc represent open circuit voltage and short circuit current, respectively. The value of fill factor $(\eta) = 0.2870$ was obtained and the power point of cell $(pp) = 44.99 \mu W$ was determined on the system.

Cell performance and conversion efficiency: The performance of the photogalvanic cell was observed by applying an external load (necessary to have current at power point) after termination the illumination as soon as the potential reaches a constant value. The performance was determined in terms of $t_{1/2}$, (figure-3) i.e., the time required in fall of the output (power) to its half at power point in dark. It was observed that the cell can be used in dark for 90 minutes. The conversion efficiency of the cell was determined as 0.4326% using the following formula:

Conversion efficiency = $\frac{V_{pp} \times i_{pp}}{A \ 10.4 m W cm^{-2}} \times 100\%$ (2)

Where V_{pp}, i_{pp} and A are photopotential at power point, Photocurrent at power point and electrode area respectively.

Mechasnism: On the basis of above investigations the mechanism of the photocurrent generation in the photogalvanic cell may be proposed as follows:

Illuminate Chamber

hv (i)

Dye \longrightarrow Dye * Dye * + R \longrightarrow Dye '(semi or leuco) + R⁺ (ii) At platinum electrode

$$Dye^{-} \longrightarrow Dye + e^{-}$$
(iii)

Dark Chember

At counter electrode :		
$Dye + e^- \longrightarrow$	Dye (semi or leuco)	(iv)
$Dye^{-} + R^{+} \longrightarrow$	Dye + R	(v)

Here Dye, Dye⁻, R and R⁺ are the dye (methylene blue), its leuco form, reductant (xylose) and its oxidized form, respectively.

Table- 1					
Effect of Variation of Methylene blu	e, Xylose, NaLS, CTAB and pH				
Parameters	Photopotential	Photocurrent			
	(mV)	(µA)			
[Methylene blue] ×10 ⁻⁵ M					
3.60	564.0	138.0			
3.80	602.0	162.0			
4.00	4.00 655.0				
4.20	612.0	165.0			
4.40	556.0	142.0			
$[Xylose] \times 10^{-3} M$					
1.96	572.0	138.0			
1.98	618.0	162.0			
2.00	655.0	190.0			
2.02	612.0	165.0			
2.04	558.0	142.0			
[NaLS] × 10 ⁻³ M					
6.36	578.0	138.0			
6.38	613.0	162.0			
6.40	655.0	190.0			
6.42	615.0	165.0			
6.44	568.0	142.0			
$[CTAB] \times 10^{-4} M$					
6.80	578.0	138.0			
7.00	613.0	162.0			
7.20	655.0	190.0			
7.40	615.0	165.0			
7.60	568.0	142.0			
рН					
13.04	557.0	138.0			
13.12	608.0	162.0			
13.20	655.0	190.0			
13.28	613.0	165.0			
13.36	552.0	142.0			

Light Intensity = 10.4 mWcm^{-2} , Temp. = 303 K

Effect of diffusion length						
Diffusion length (mm)	Maximum photocurrent i _{max} (µA)	Equilibrium photocurrent i _{eq} (µA)	Rate of initial generation of photocurrent (μA min ⁻¹)			
35.0	208.0	198.0	5.78			
40.0	214.0	194.0	5.94			
45.0	220.0	190.0	6.11			
50.0	228.0	188.0	6.33			
55.0	235.0	182.0	6.53			

Table– 2 Effect of diffusion length

[Methylene blue] = 4.0×10^{-5} M, Light Intensity = 10.4 mW cm⁻², [Xylose] = 2.0×10^{-3} M, Temperature = 303 K, [NaLS] = 6.40×10^{-3} M, pH = 13.20, [CTAB] = 7.2×10^{-4} M

Effect of electrode area							
Methylene blue-Xylose-NaLS+CTAB	Electrode Area (cm ²)						
System	0.70	0.85	1.00	1.15	1.30		
Maximum photocurrent i _{max} (μA)	209.0	215.0	220.0	226.0	232.0		
Equilibrium photocurrent $i_{eq} (\mu A)$	197.0	194.0	190.0	187.0	183.0		

Table- 3 ffect of electrode area

[Methylene blue] = 4.0×10^{-5} M, Light Intensity = 10.4 mW cm⁻², [Xylose] = 2.0×10^{-3} M, Temperature = 303 K, [NaLS] = 6.40×10^{-3} M, pH = 13.20, [CTAB] = 7.2×10^{-4} M



Figure- 1 Experimental set up

Conclusion

The photogalvanic conversion of solar energy has attracted attention of scientists towards solar energy conversion and storage. The charging of cell occurs only in presence of illuminating source. The discharging of cell takes place only when we apply the external circuit for electron transfer. As long as there is no external circuit, the cell will keep light energy stored. The photogalvanic cell have inbuilt storage capacity and stored energy can be used in absence of light where as photovoltaic cells needs extra hardware as batteries for energy storage, photogalvanic cells are economic than photovoltaic cells because low cost materials are used in these cells. The conversion efficiency, $t_{1/2}$ and fill factor are recorded as 0.4326%, 90.0 min. and 0.2870 respectively in methylene blue-xylose-NaLS+CTAB system.

Acknowledgments

Authors are thankful to Prof. Mrs. (Dr.) Sunita Kumbhat, Head, Department of Chemistry, J.N.V. University, Jodhpur for providing necessary facilities and one of the author (Mohan Lal) is specially thanks to Dr. K.R. Genwa and Dr. P. Koli for critical and scientific analysis during practical works.



Methylene-Xylose-NaLS+CTAB System

Figure-2 Current voltage (i-v) curve of the cell



Performance of the cell

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