Photogalvanic Effect in Aqueous Bromothymol Blue - Triton X-100 - Oxalic acid Systems: Conversion of Sun Light into Electricity

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ABSTRACT

The photogalvanic effect in electrochemical cells, employing Bromothymol blue as photosensitizer, Triton X-100 as surfactant and Oxalic acid as electron donor, was experimentally investigated. Seven different standard H-cell configurations were set-up by modifying the electrolyte. Long-term open-circuit voltage measurements were conducted in order to test the stability of the cells. Light on-off reproducibility experiments were also carried out during lengthy cell operations. The photopotential and photocurrent generated by this cell were 910 mV and 180 µA, respectively. The effect of various parameters likes pH, light intensity, diffusion length, reductant concentration, dye concentration, etc. on the electrical output of the cell has been studied. The current voltage (i-V) characteristics of the cell have also been observed and a tentative mechanism for the generation of photocurrent has been proposed. Performance of the cell was determined in dark at its power point.

Keywords: Bromothymol blue, Triton X-100, Photopotential, Photocurrent, Diffusion Length.

INTRODUCTION

Global energy consumption has increased two fold since last 40 years from IEA Key World Energy Statistics [1]. In 1960, the global energy consumption rate was 3.3 Gtoe, while in 1990 this rate hit 8.8 Gtoe. This indicates an average annual growth of 3.3% and a total increase of 166%. Presently, the global energy consumption rate is 10 Gtoe/year is predicted that this rate would amount to 14Gtoe/year by 2020[2]. These rates indicate that the global energy consumption rate is on the rise in years to come. This has highlighted the important issue, whether fossil fuel energy resources can meet the global energy demand for survival and development in the coming decades? While the concern for pollution and global warming

is over shadowing all planning and decision makings. Two major reasons can be noted, that give rise to the development to falter native energy sources that are both clean (1)What is used a fossil fuel is concentrated chemical type, and now a days is more valuable than being burning for energy. (2) The emergence of sustainable Development concepts and issue, global warming, health problems due to pollution. These and other issues have caused undertaking enormous effort by the global community to find alternative energy sources to control carbon dioxide emission, preserve the environment and get better value from fossil fuel sources. Alternative energy sources have been in the centre of attention for many research and development activities in many different countries. In particular they are turning to renewable energies to meet their growing energy demands and have taken actions in the development and application of renewable energy technologies for sustainable development. As a percent of installed capacity, renewable energies increased by about 50% between 2000 and 2008. The share of new renewable in global electricity production is also increasing [3].

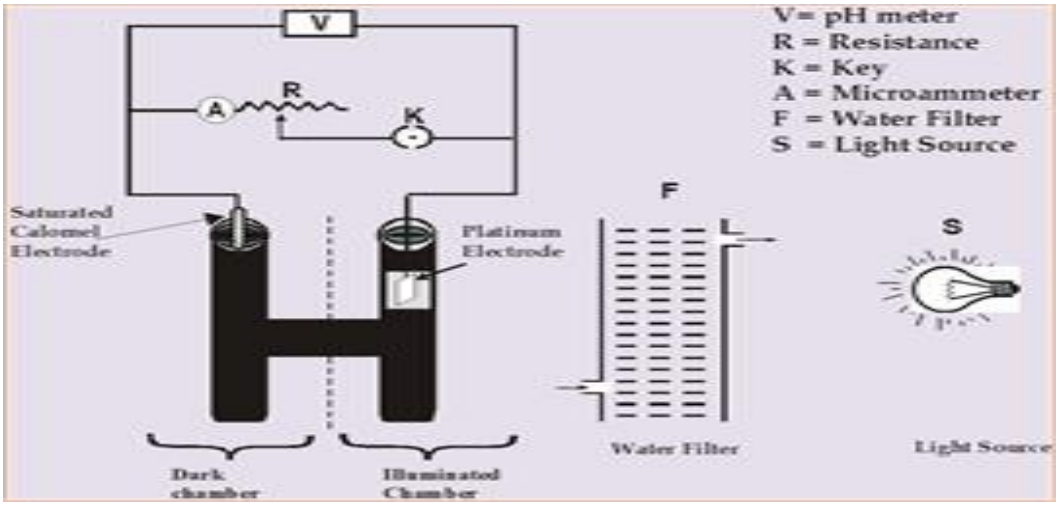
Becquerel, 1839 first observed the flow of current between two unsymmetrical illuminated metal electrodes in sunlight [4]. The photogalvanic effect was first of all reported by Rideal and Williams, 1925 [5] but it was systematically investigated by Rabinowith,1940 [6]. Later on, Kaneko and Yamada, 1977, Murthy et.al, 1980, Rohatgi Mukherjee et.al, 1983, Ameta et.al, 1958, 1989 and Gangotri et.al, 1996,1997 have reported some interesting photogalvanic systems [7-11]. The theoretical conversion efficiency of a photogalvanic cell is about 18% but the observed conversion efficiencies are quite low due to lower stability of dyes, back-electron transfer, aggregation of dye molecules around electrode, etc. Hoffman and Lichtin, have discussed various problems encountered in the development of this field [12].

A detailed literature survey [13-25] reveals that different surfactants, photosensitizers and reductants have been used in photogalvanic cells, but no attention has been paid to the use of the Triton X-100 – BTB (Bromothymol blue) -Oxalic acid system in the photogalvanic cells for solar energy conversion and storage. Therefore, the present work was undertaken.

TECHNIQUE USED

The whole system was first placed in dark till a stable potential was obtained, then the platinum electrode was exposed to a 200 W tungsten lamp (ECE). A water filter was used to cut off infrared radiations. The photochemical bleaching of Bromothymol blue was studied potentiometrically. A digital pH meter (Systronics Model – 335) and a micro-ammeter

(INCO Model No. 65) were used to measure the potential and current generated by the system, respectively. Experimental setup is given in figure.



RESULTS AND DISCUSSION

Effect of variation of Triton X-100 concentration, effect of variation of dye concentrations, effect of variation of oxalic acid concentrations, effect of variation of pH is given in following table.

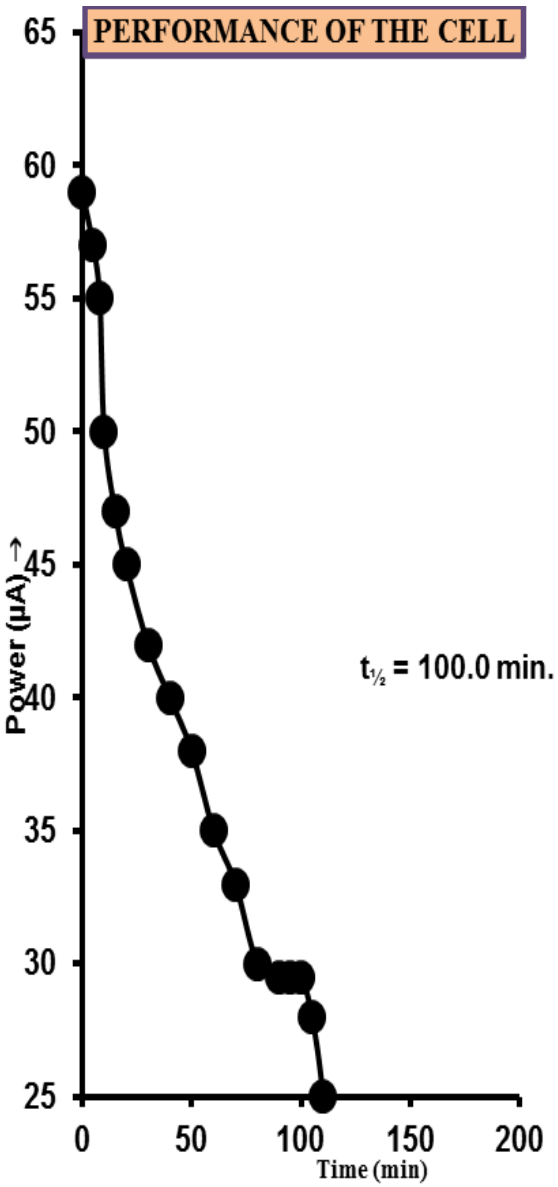
Effect of Variation of Triton X-100 Concentration							
[**Triton X-100**] x 10^4M	2.0	2.5	2.8	**3.0**	3.2	3.5	4.0
Photopotential (mV)	470.0	518.0	603.0	**910.0**	598.0	493.0	460.0
Photocurrent (μA)	100.0	120.0	128.0	**180.0**	131.0	123.0	90.0
Power (μW)	47.0	62.16	77.18	**163.8**	78.33	60.63	45.5
Effect of Variation of Dye Concentrations							
[BTB] x 10^5M	2.5	3.0	3.5	**4.0**	4.5	5.0	5.5
Photopotential (mV)	440.0	560.0	703.0	**910.0**	623.0	583.0	460.0
Photocurrent (μA)	100.0	131.0	140.0	**180.0**	138.0	129.0	99.0
Power (μW)	44.0	73.36	98.40	**163.8**	85.97	75.20	45.54
Effect of Variation of Oxalic Acid Concentrations							
[Oxalic Acid] x 10^3M	2.4	2.6	2.8	**3.0**	3.2	3.4	3.6
Photopotential (mV)	390.0	470.0	610.0	**910.0**	605.0	497.0	395.0
Photocurrent (μA)	95.0	131.0	136.0	**180.0**	137.0	132.0	97.0
Power (μW)	37.05	61.57	82.96	**163.8**	82.88	65.60	38.31
Effect of Variation of pH							
pH	11.8	12.0	12.2	**12.4**	12.5	12.6	12.8
Photopotential (mV)	350.0	413.0	600.0	**910.0**	623.0	440.0	375.0
Photocurrent (μA)	90.0	120.0	138.0	**180.0**	140.0	113.0	92.0
Power (μW)	31.50	49.56	82.80	**163.8**	87.22	49.72	34.50

I-V CHARACTERISTICS OF THE CELL

With the help of a micro-ammeter (keeping the circuit closed) and digital pH meter (keeping the other circuit open) the short circuit current (i_{sc}) and open circuit voltage (V_{oc}) of the photogalvanic cells are measured, respectively. The potential and current values in between these two extreme values are recorded with the help of a carbon pot (log 470 K) connected in the circuit of multi-meter, an external load is applied on it.

i-V Characteristics		
Potential* (mV)	**Photocurrent (μA)**	**Fill Factor (η)**
910.0	0.0	
900.0	10.0	
880.0	20.0	
860.0	30.0	
840.0	40.0	
760.0	50.0	
700.0	60.0	
690.0	70.0	
670.0	80.0	
650.0	85.0	
630.0	90.0	
620.0	95.0	
590.0	**100.0**	**0.36**
530.0	105.0	
450.0	110.0	
400.0	115.0	
350.0	120.0	
296.0	125.0	
220.0	130.0	
195.0	135.0	
140.0	145.0	
105.0	155.0	
80.0	160.0	
60.0	165.0	
45.0	170.0	
25.0	175.0	
0.0	180.0	

PERFORMANCE OF THE CELL



The performance of the photogalvanic cells was studied by applying the desired external load necessary to have the potential and the current corresponding to power point,

after removing the source of illumination till the output (power) its half value at the power point in the dark. The performance of the cell was determined in terms of $t_{1/2}$ i.e. time required in fall of the output (power) to its half value at power point in dark. It was observed that cell can be used in the dark at its power point for 100 minutes. Performance of the cell is graphically represented in figure.

EFFECT OF DIFFUSION LENGTH

The effect of variation of diffusion length (distance between the two electrodes) on the current parameters of the cell was studied using H-cells of different dimension.

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

Diffusion length D_L (mm)	Maximum Photocurrent i_{max} (μA)	Equilibrium Photocurrent i_{eq} (μA)	Rate of initial generation of current (μA min^{-1})
30.0	188.0	175.0	18.0
35.0	190.0	178.0	19.0
40.0	195.0	179.0	20.6
45.0	200.0	180.0	22.0
50.0	205.0	177.0	24.5
55.0	210.0	175.0	26.1
60.0	215.0	173.0	27.1

On the basis of the effect of diffusion path length on the current parameters, as investigated by Kaneko and Yamada (1977) it may be concluded that the leuco or semi reduced form of dyes, and the dyes itself are the main electro active species at the illuminated and the dark electrodes, respectively. However, the reducing agents and its oxidized products behave as the electron carriers in the cell diffusing through the path.

ELECTRO ACTIVE SPECIES

Various probable processes may be considered for the photocurrent generation in photogalvanic cells. The results of the effect of diffusion length on the current parameters were utilized to know more about the electro active species. The possible combinations for electro active species in photogalvanic cell are given below.

In Illuminated Chamber	In Dark Chamber
[BTB]	Oxidized form of the Reductant (R^+)
Leuco-or Semi [BTB^-]	Oxidized form of the Reductant (R^+)
Leuco-or Semi [BTB]	[BTB]

The oxidized form of the reductant is formed only in the illuminated chamber and if it is considered to be the electro active species in the dark chamber, then it must diffuse from the illuminated chamber to the dark chamber to accept an electron from the electrode. As a consequence, the maximum photocurrent (i_{max}) and rate of increase in photocurrent should decrease with an increase in diffusion length, but this was not observed experimentally. The value of the photocurrent at equilibrium (i_{eq}) was also observed to be independent with respect to change in diffusion length. Therefore it may be concluded that the main electro active species are the leuco or semi $[BTB]^-$, and the dye [BTB] in illuminated chamber and dark chamber respectively. The reductant and its oxidized products act only as electron carrier in the path.

Conversion Efficiency of the Cell

The conversion efficiency of photogalvanic systems was calculated using the output at power point and the power of incident radiation and conversion efficiency as 0.57% using the formula.

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

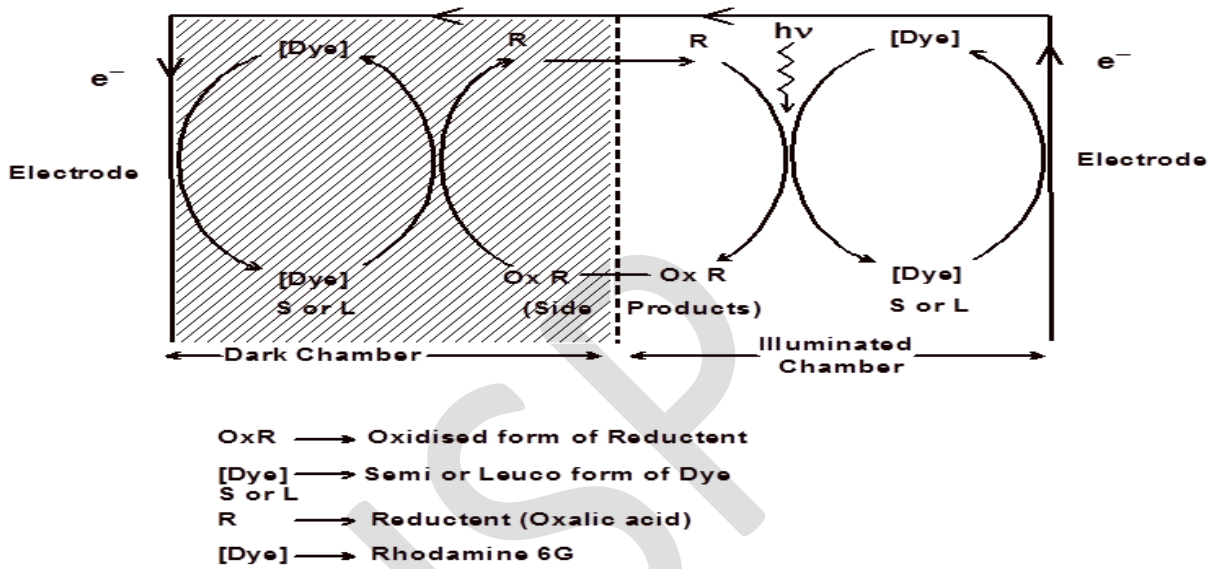
MECHANISM

Light energy is converted in to chemical energy by driving a suitable redox reaction against the potential gradient. Tentative reaction mechanism in our system proposed as:

Illuminated chamber: On irradiation, dye molecules get excited. The excited dye molecules accept an electron from reductant and converted into semi or leuco form of dye,

and the reductant into its excited form. At platinum electrode the semi or leuco form of dye loses an electron and gets converted into original dye molecule.

Dark chamber: At calomel electrode dye molecule accepts an electron from electrode and gets converted into semi or leuco form. Finally leuco/semi form of dye and oxidized form of reductant combine to give original dye and reductant molecule. This cycle of mechanism is repeated again and again leading production of current continuously.



CONCLUSION

Photogalvanic cells containing surfactant-photosensitizer -reductant the electrical output has increased 1.5 to 2.0 times as the observation shows. It is observed that by the addition of surfactant, conversion efficiency as well as storage of solar energy has been increased. Efforts will be made in future to make it more efficient.

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