

A XYLIDINE PONCEAU DYE BASED PHOTOGALVANIC **CELL: ENERGY CONVERSION FOR SUSTAINABLE** DEVELOPMENT

K. R. Genwa^[a]* and C. P. Sagar^[a]

Keywords: xylidine ponceau, conversion efficiency, storage performance, Tween 60, fill factor, photogalvanic cell, ascorbic acid

The photogalvanic behavior of Xylidine ponceau dye was studied in Xylidine ponceau - Tween 60 - ascorbic acid system. The experimental studies were performed at different pH conditions and dye concentrations. The effects of electrode area, light intensity and diffusion length on cell electrical parameter are studied in various experimental conditions. Cell generates maximum power of 68.77 µW in ideal conditions, conversion efficiency was calculated by observed photopotential and photocurrent values at power point.

Corresponding Authors

Fax: +91- 291- 2720840; E-Mail: krg2004@rediffmail.com Department of Chemistry, Jai Narain Vyas University, Jodhpur – 342005 (INDIA)

INTRODUCTION

The source for the renewable energies is the sun and is linked either directly or indirectly to the power of the earth's internal and external changes. The sun's heat and the earth's surface temperatures cause heating and cooling of air masses that become powerful winds. Electricity generation from renewables is assuming increasing importance in the context of large negative environmental externalities caused by electricity generation. The utility of solar energy is one from many renewable sources of energy especially in photogalvanic cells, so the photogalvanic cells are worthwhile source of energy and have future applications and uses. The photogalvanic effect was first reported by Rideal and Williams², but Rabinowitch³⁻⁴ made the first photogalvanic cell using thionine-iron system. Later on Kaneko and Yamada⁵ were reported the photopotential and photocurrent induced by tolusafranine- ethylenediaminetetraacetic acid system and Kaneko and Wohrle⁶ used cation radical formed electrochemically in the presence of oxygen. Murthy et al.7-9 studied photogalvanic effect in system containing blue, methylene riboflavin ethylenediaminetetraacetic acid and toluidine blue and shown the importance of the determination electrochemical properties of dyes and flat band potentials of a few thin film semiconductor electrodes. Rohatgi Mukherjee et al. 10-11 were studied photo voltage generation of the phenosafranine-EDTA system in photogalvanic cell on temperature effect. Folcher and Paris 12, Alfredo et al. 13 reported the electron transfer via organic dye for solar energy conversion. Pan et al. ¹⁴, Jana and Bhowmik ¹⁵⁻¹⁶ were calculated solar energy efficiency (SEE) and other cell characteristics of mixed dye-solar cell is larger in comparison to the cell with single dye. whereas Bayer et al.¹⁷, Matsumoto et al.¹⁸⁻¹⁹, Shiroishi et al.²⁰ have studied some interesting photogalvanic systems with reasonable power. Bisquert et al.²¹, Bisquert and Belmonte²² and Bisquert et al.²³ have reviewed the importance's analysis of galvanostatically synthesized polypyrole films, correlation of ionic difference and capacitance parameters with the

electrode morphology, whereas Mayer²⁴ has presented the molecular approaches to solar energy conversion.

Gangotri and Bhimwal²⁵ studied the performance of photogalvanic cell for solar energy conversion and storage in methyl orange -D xylose NaLS systems whereas Gangotri and Bhati²⁶ was studied photogalvanic cells having different surfactants, reductants and photosensitizers and tried to get the better electrical output and storage capacity. Sharma et al. 27-28 used Brilliant cresyl blue - Fructose and rodamine B - fructose systems for enhancement of solar energy conversion and storage capacity of photogalvanic solar cells. Recently, attention has been paid to use of some new dyes as photosensitizer in photogalvanic systems and surfactants as stabilizing agents²⁹⁻³⁰. In the present work, electrical output of Tween 60 – Xylidine ponceau – Ascorbic acid system examined experimentally to increase storage performance of cell and to development cost effective photogalvanic cell system for sustainable development.

Experimental

Xylidine ponceau (scheme I) is a solid red power with a absorption of 480 nm, its molecular formula is C₁₈H₁₄N₂Na₂O₇S₂, molecular weight is 480.42 and it is soluble in water.

Scheme I

Tween 60 (Polyoxyethylene sorbitan monostearate) (Scheme II) is a pale yellow semisolid liquid, molecular formula is C₂₄H₄₆O₆(C₂H₄O)_n, molecular weight is 1312 and it is soluble in water.

Scheme II

Ascorbic acid (scheme III) is white to slightly yellowish crystalline powder its molecular formula is $C_6H_8O_6$, molecular weight is 176.13 and it is soluble in water.

Scheme III

Photogalvanic effect of dye was studied using H- shaped glass tube which consist known amount of the solution of Xylidine ponceau (5.6x10⁻⁵ M), Tween 60 (1.08x10⁻³ M), Ascorbic acid (2.08x10⁻³ M) and NaOH (1.0 N). A Platinum electrode (1.0x1.0 cm²) was dipped in one limb and a saturated calomel electrode (SCE) is immersed in another limb of the H- tube. The terminals of the electrodes were then connected to a digital pH meter and the whole cell is placed in dark. The photopotential was measured in dark when the cell attains a stable potential. The limb containing platinum electrode was focused to the light source (projector Tungsten lamp). The light intensity was varied by employing tungsten lamp of 200 W and solarimeter. A water filter placed between the illuminated chamber and the light source to cut off thermal radiations. Photopotential and photocurrent were measured by digital pH meter (Systronics model 335) and digital ammeter (Osaw). Absorption spectra were recorded using Spectrophotometer (Systronics 106) with the matched pair of silica cuvetts (path length 1cm). All spectral measurements were duplicated in a constant temperature water bath maintained with in ±1 °C and mean values were processed for data analysis.

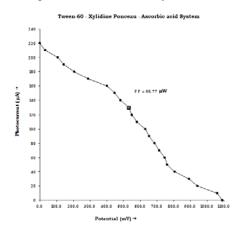


Figure 1. Absorption spectrum of dye and dye + surfactant

The dye shows absorption peak (λ_{max}) in visible region with maximum at 480 nm. Maximum absorption is recorded at Xylidine ponceau - Tween 60 combination of concentration $5.6 \times 10^{-5} \, M + 1.08 \times 10^{-3} \, M$. The changes in the spectra are shown in Figure 1.

Results and discussion

Effect of variation of dye, surfactant, and reductant concentration

Effect of dye, surfactant and reductant concentration on photopotential and photocurrent are summarized in Table 1. In Tween 60 – Xylidine ponceau – Ascorbic acid system for the better performance of the photogalvanic cell proper concentration of dye needed. It was observed that photopotential and photocurrent increased with increase in concentration of the xylidine ponceau. A maxima was obtained at certain dye concentration (5.6x10⁻⁵ M). On further increasing in dye concentration, a decrease in the electrical output was observed. On the lower concentration range of dye, there are limited number of dye molecules to absorb the major portion of the light in the path and therefore, minimum electrical output observed, where as high concentration of dye intensity of light reaching the molecule near the electrode decreased due to absorption of the major portion of the light by the dye molecules present in the path. Therefore corresponding fall in the power of the cell was observed.

Table 1. Effect of variation of Xylidine ponceau, Tween 60 and Ascorbic acid concentration

Concentration	Photopotential, mV	Photocurrent, µA		
[Xylidine ponceau] x 10 ⁻⁵ M				
4.8	712	154		
5.2	769	179		
5.6	880	197		
6.0	760	181		
6.4	725	160		
	[T (0] 10 ⁻³ M			
[Tween 60] x 10 ⁻³ M				
0.28	620	97		
0.28	778	143		
1.08	880	197		
1.48	730	170		
1.88	590	128		
1.00	390	120		
[ascorbic acid] x 10 ⁻³ M				
1.28	663	142		
1.68	790	176		
2.08	880	197		
2.48	810	180		
2.88	720	168		

 a Light Intensity = 10.4 mW cm⁻², b Temp. = 303 K, c pH = 10.80

Tween 60 is used as a surfactant in the photogalvanic cell system. The photopotential and photocurrent of the cell was increased on increasing the concentration of Tween 60. A maxima was obtained at a certain value (1.08x10⁻³ M) and decrease on further increase in surfactant concentration. The miceller systems have the ability to solubilize a variety of molecules and substantial catalytic effect on chemical reaction. Photopotential and photocurrent was found to increase with increase in reductant (ascorbic acid) concentration to maximum value of photopotential of 880.0 mV and photocurrent of 197.0 μA and then decrease in electrical output because fever reductant molecule were available for electron donation to photosensitizer (dye) molecule. Higher concentration of reductant again resulted in a decrease in electrical output, due to the large number of reductant molecules hinder the dye molecule from reaching electrode in the desired time limit.

Effect of variation of pH

Photogalvanic cell containing Tween 60 - Xylidine ponceau – ascorbic acid system was found to be quite sensitive to pH of the solution. The photopotential and photocurrent is increased with increase pH value (in alkaline range) of the cell. At pH 10.80, maximum photopotential and photocurrent of 880.0 mV, 197.0 µA recorded, further increase in pH, photopotential and photocurrent decreased. The results showing the effect of pH are summarized in Table 2.

Table 2. Effect of pH on photogalvanic parameters

pН	Photopotential, mV	Photocurrent, μA
10.72	690	92
10.76	760	135
10.80	880	197
10.84	762	170
10.88	670	108

 $^{^{}a}$ [Tween 60] = 1.08 x 10⁻³ M, b [Xylidine ponceau] = 5.6 x 10⁻⁵ M, c [ascorbic Acid] = 2.08 x 10⁻³ M, d Light Intensity = 10.4 mW cm⁻², c Temp. = 303 K

Table 3. Effect of diffusion length

$\begin{array}{c} \textbf{Diffusion} \\ \textbf{length } \textbf{D}_{L}, \\ \textbf{mm} \end{array}$	Maximum pho- tocurrent, i _{max} , μΑ	Rate of initial generation of current, µA min ⁻¹
50	191	9.55
55	202	10.15
60	215	10.75
65	228	11.40
70	242	12.10

^a[Tween 60] = $1.08 \times 10^{-3} M_3$ ^b[Xylidine ponceau] = $5.6 \times 10^{-5} M_3$ ^c[ascorbic Acid] = $2.08 \times 10^{-3} M_3$ ^dLight Intensity = 10.4 mW cm^{-2} , ^eTemp. = 303 K

Effect of diffusion length

Effect of variation of diffusion length (distance between two electrodes) on the current parameters (i_{max} , i_{eq}) and initial rate of generation of photocurrent are studied using

H-Shaped cell of different diameters. Results are reported in Table 3. It is observed that in the first few minutes of illumination there is sharp increase in the photocurrent (i_{max}). The conductivity of electroactive species depends on its population between electrodes. As diffusion length increased, the volume of dye solution and intern population of dye molecule(Xylidine ponceau) increased leading higher i_{max} the electroactive nature of dye/dye is provide by the fact that i_{max} increase with diffusion length. There for it may be concluded that the main electro active species are the leuco or semi form of dye- and the dye in the illumination and the dark chamber respectively.

Effect of variation of electrode area and light intensity

The effect of variation of electrode area on the current parameters of the cell also studied using thin platinum electrodes of different diameters. Experimentally, it was observed that with increase electrode area the value of maximum photocurrent (i_{max}) was found to increase and (i_{eq}) is all most independent to change in electrode cell. The results are summarized in Table 4.

Table 4. Effect of electrode area on photocurrents

Electrode area,	Maximum photo-	Equilibrium pho-
cm ²	current, i_{max} , μA	tocurrent, $I_{\rm eq}$, $\mu { m A}$
0.25	188	171
0.64	198	183
1.00	215	197
1.21	231	207
1.96	246	228

 a [Tween 60] = 1.08 x 10⁻³ M, b [Xylidine ponceau] = 5.6 x 10⁻⁵ M, c [ascorbic Acid] = 2.08 x 10⁻³ M, d Light intensity = 10.4 mW cm⁻², e Temp. = 303 K

The intensity of light is also affects the electrical output of the cell. This effect was observed by varying intensity using solar intensity meter. Effect of light intensity graphically represented in Figure 2. It was observed that photocurrent showed a linear increasing behavior with the increase in light intensity whereas photopotential increase in logarithmic manner.

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

The open circuit voltage ($V_{\rm oc}$ 1091.0 mV) and short circuit current ($i_{\rm sc}$ 197.0 μ A) of the photogalvanic cell were measured under the continuous illumination of light, with the help of digital pH meter (keeping the circuit open) and a micro ammeter (keeping the circuit closed), respectively. The external parameters (photopotential and photocurrent) of the photogalvanic cell in between this two extreme values ($V_{\rm pp}$ and $i_{\rm pp}$) were recorded with the help of a carbon pot (log 407 K) connected in the circuit of micro ammeter, through which an external load applied on it (Figure 3). A point in the i-V curve, called power point (pp), was determined where the product of current and potential was maximum and the Fill-factor (ff) was calculated as 0.33 and conversion efficiency (η) of the cell was determined as 0.6613% using the following relationship

$$ff = \frac{V_{\rm pp}i_{\rm pp}}{V_{\rm oc}i_{\rm sc}} \tag{1}$$

$$\eta = \frac{V_{\rm pp}i_{\rm pp}}{10.4 \cdot A} 100 \tag{2}$$

where $V_{\rm pp}$, $i_{\rm pp}$ and A are photopotential at power point, photocurrent at power point and electrode area, respectively.

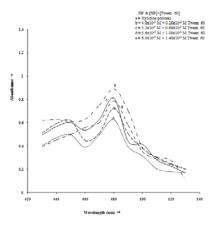


Figure 2. Variation of photocurrent and log V with light intensity

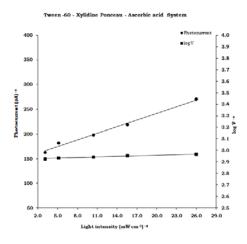


Figure 3. Current - potential (i-V) curve of the cell

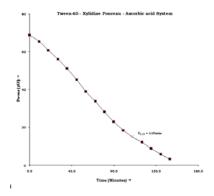


Figure 4. Time - power curve of the cell

Storage capacity (performance) of the cell

The performance of the photogalvanic cells containing the Tween 60 – Xylidine ponceau - ascorbic acid system 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 for 110.0 minutes (Figure 4).

Mechanism

The mechanism is photocurrent given in the photogalvanic cell may be proposed as follow:

In illuminated chamber

On irradiation, dye molecule get excited

$$Dye \xrightarrow{hv} Dye^*$$
 (3)

The excited dye molecule accept an electron from reductant and convert into semi or luco form of dye, and the reductant into its excited state state form

$$Dye^* + R \rightarrow Dye^- + R^+ \tag{4}$$

At platinum electrode

The semi or luco form of dye loses an electron and converted into original dye molecule

$$Dye^{-} \rightarrow Dye + e^{-} \tag{5}$$

Dark chamber

At counter electrode (SCE)

$$Dye + e^{-} \rightarrow Dye^{-}$$
 (6)

Finally luco/semi form of dye and oxidized form of reductant combine to give original dye and reductant molecule

$$Dye^{-} + R^{+} \rightarrow Dye + R \tag{7}$$

where Dye, Dye*, Dye⁻, R and R⁺ represents the dye, excited form of dye, reduced form of dye, reductant and oxidized form of reductant, respectively.

Acknowledgements

The authors are thankful to UGC, New Delhi for providing financial assistance under UGC Major Research Project (No. 40-55/2011 (SR) dated 5 July 2011).

References

- ¹Rubbia, C., Opening remarks at the 18th IAEA Fusion Energy Conference Sorrento, Italy, 4th October **2000**.
- ²Rideal, E. K., Williams, E. G., *J. Chem. Soc. Trans.*, **1925**, *127*, 258.
- ³Rabinowitch, E., J. Chem. Phys., 1940, 8, 551.
- ⁴Rabinowitch, E., *J. Chem. Phys.*, **1940**, 8, 560.
- ⁵Kaneko, M., Yamada, A., J. Phys. Chem., 1977, 81, 1213.
- ⁶Kaneko, M., Wohrle, D., J. Electroanal. Chem., 1991, 307, 209.
- ⁷Murthy, A. S. N., Reddy, K. S., *Int. J. Energy Res.*, **1979**, *3*, 205.
- ⁸Murthy, A. S. N., Dak, A. C., Reddy, K. S., Int. J. Energy Res., 1980, 4, 339.
- ⁹Murthy, A. S. N., Reddy, K. S., *Solar Energy*, **1983**, *30*, 39.
- ¹⁰Rohatgi-Mukherji, K. K., Roy, M., Bhowmik, B. B., *Solar Energy*, **1983**, *31*, 417.
- ¹¹Rohatgi-Mukherjee, K. K., M. Bagchi, M., Bhowmik, B. B., Electrochim. Acta, 1983, 28, 293.
- ¹²Folcher, G., Paris, J., J. USA Patent, **1983,**US 4,391,881
- ¹³Alfredo, O., Georgina, P., Sebasteian, P. J., Solar Energy Material Solar Cells, 1990, 59, 137.
- ¹⁴Pan, R. L., Bhardwaj, R., Gross, E. L., J. Chem. Tech. Biotech. Chemtech., **1983**, *33*, 39.
- ¹⁵Jana, A. K., Bhowmik, B. B., J. Photochem. Photobiol. A: Chem., 1997, 110, 41.

- ¹⁶Jana, A. K., J. Photochem. and Photobiol. A: Chem., 2000, 132, 1.
- ¹⁷Bayer, L.S., Erogle, I., Turker, L., *Int. J. Energy Res.*, **2001**, 25, 207.
- ¹⁸Erabi, T., Matsumoto, K., Fujimura, K., Nomura, K., Wada, M., Electrochemistry, 1997, 65, 673.
- ¹⁹Matsumoto, K., Fujioka, S., Mii, Y., Wada, M., Erabi, T., Electrochemistry, 2001, 69, 340.
- ²⁰Shiroishi, H., Kaburagi, Y., Seo, M., Hoshi, T., Nomura, T., Tokita, S., Kaneko, M., J. Chemical Software, 2002, 8, 47.
- ²¹Bisquert, J., Belmonte, G. G., Santiago, F. F., Bueno, P. R., Electrochem. Commun., 1999, 1, 429.
- ²²Bisquert, J., Belmonte, G. G., *Electrochim. Acta*, **2002**, *47*, 4263.
- ²³Bisquert, J., Belmonte G. G., Pitarch, A., *ChemPhysChem.*, **2003**, 4, 287.
- ²⁴Meyer, G. J., *Inorg. Chem.*, **2005**, *44*, 6852.
- ²⁵Gangotri, K. M., Bhimwal, M. K., Energy Sources Part-A, 2011, 23, 2058.
- ²⁶Gangotri, K. M., Bhati, K. K., Int. J. Electrical Power Energy Systems, 2011, 33, 155.
- ²⁷Sharma, U., Koli, P., Gangotri, K. M., Fuel, **2011**, 90, 3336
- ²⁸Sharma, U., Koli, P., Gangotri, K. M., Renewable Energy, 2012, 37, 250.
- ²⁹Genwa, K. R., Kumar, A., *Energy Sources Part A*, **2012**, *34*, 1261.
- ³⁰Genwa, K. R., Singh, K., Smart Grid and Renewable Energy, 2013, 4, 306.

Received: 08.10.2013. Accepted: 21.11.2013.