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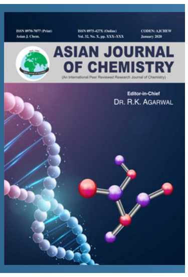

Enhanced Efficiency of Photogalvanic Cell based on Mixed Triphenylmethane Dyes

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The study focused on the enhancement of solar power generation and storage capacity of a photogalvanic cell ethylene diaminetetraacetic acid as reductant, xylene cyanol FF and patent blue as photosensitizers. This chemical system with changed concentrations, a combination electrode and a very small Pt electrode was used to fabricate a modified photogalvanic cell. The modified cell showed greatly enhanced performance in terms of photopotential (868.0 mV), photocurrent (230.0 µA), efficiency (0.64 %) and the maximum output (power) of the cell was found to be 199.64 W. The photogalvanic cell can be used at this power level for 115 min in the dark due to the storage capacity of the cell. The effects of various parameters such as pH, reductant concentration, dye concentration, diffusion length, light intensity, and electrode area on electrical output of the cell were also investigated. The current-voltage (i-v) characteristics of the cell have been studied and a mechanism for the photocurrent generation in photogalvanic cell has also been proposed.

Keywords: Photogalvanic cell, Xylene Cyanol FF, Patent Blue, Conversion efficiency.

INTRODUCTION

Energy generation from the clean source is now become one of the major concern due to increasing global warming. In order to maintain the quality of environment, the biggest challenges among the scientific community is to generate clean source of energy other than fossil fuels, without disturbing the climate. Sun light is accessible in plenty and can be harnessed through photo-electrochemical solar energy conversion systems. This is one of the most rapidly developing field of research which is attracting scientists from various disciplines. Photo-electrochemical process is a viable mean of converting the solar energy directly into electricity.

Photogalvanic cells devices have a potential by providing the energy requirements in cheap, renewable and eco-friendly way. For this purpose, several functional materials have been used in various solar power techniques including photogalvanic cells [1,2]. The photogalvanic cells generally consist of dilute solutions of photo-sensitizers, reductant, NaOH and surfactants. Further, the construction of photogalvanic cell is very simple as it uses easily available and simple materials like dye. Whereas other techniques are quite complex due to their complex fabrication and the involvement of costly materials like gallium arsenide, polycrystalline silicon, carbon nanotubes, fullerene, graphene, *etc*.

Although the existence photogalvanic effect was apparently discovered in 1925, it was first seriously considered by Rabinowitch [3], who has investigated the thionine-iron system. His work has been followed by various workers with several modifications [4-10]. It is observed that these cells exploited photosensitizer (dye), reductant, alkali/acid and with or without surfactant for solar energy conversion and storage. Although, initial research works of photogalvanic cell were based on dye and reversible reductant systems, especially thionine-iron system, but later on various higher intense colour dyes and irreversible reductant were used for the same.

Photogalvanic cells using different dyes, reductant and surfactant, it was observed that photo-chemical solar energy conversion and storage depend mainly on structures, reduction potential and absorption maxima of dyes used for the cell. To utilize a broader solar spectrum, a mixed dye system instead of a single dye is used in solar cells [11,12]. An improvement in power output of photogalvanic cells consisting of mixed dyes was observed as compared to cells based on single dye system [13-15]. Dube [16] has used mixed azur dyes system in photogalvanic cells for enhancement of conversion efficiency and noticed that mixed dyes raised the absorption capability of solution for solar energy and hence a broad area of solar light is absorbed by dye. Later on, various mixed dye system *viz.* toludine blue-azur B-EDTA system [17], thionine-azur B-EDTA system [11], brilliant green-celestine blue-EDTA system [18], toludine blue-thionine-EDTA system [19], brilliant green-fast green-EDTA system [14], *etc.* of the photogalvanic cells have been studied. Because of low cost, higher wavelength, and photoreduced properties, these dyes have been chosen for this work. Mixed dyes (combination of two or more dyes) were used to use the broad solar spectrum of visible region of solar radiation for generation of better electrical output [20,21]. An enhancement in electrical output of the cell consisting of mixed dyes was observed when compared with the cell with single dye [22].

In the present work, performance characteristics of photogalvanic cells containing mixed dyes *viz.* xylene cyanol FF, patent blue as photosensitizer with a reducing agent ethylene diamine tetraacetic acid (EDTA) have been experimentally examined. Effect of various parameters such as pH, reductant and dye concentration, diffusion length and electrode area on electrical output were also determined.

EXPERIMENTAL

The dyes xylene cyanol FF (green colour, λ = 625 nm, m.w. 482.63, m.f. $C_{27}H_{34}N_2O_4S$) and patent blue (blue colour, λ = 642 nm, m.w. 363.80, m.f. $C_{17}H_{18}N_3O_4Cl$) were procured from Aldrich-Sigma, USA. Ethylenediamine tetraacetic acid (EDTA), disodium salt dihydrate (Merck) and sodium hydroxide (Qualigens) of analytical reagent grade were used. All the solutions were prepared in double distilled water. The pH of solution was adjusted by addition of 0.1 N solution of NaOH standardized against oxalic acid solution.

Experimental setup of photogalvanic cell consists of a H-shaped cell, a Pt electrode, a bulb and the water filter. Photogalvanic solution is placed in a blackened H-shaped glass cell. Photogalvanic cell consist of platinum foils used as a working electrode and a saturated calomel electrode (SCE) as a reference electrode. Tungsten lamp (Philips) of 200 W with an intensity of 10.4 mW cm^{-2} on the surface of the cell was used as a light source. Intensity of the light was measured with the help of Solarimeter Model-501CEL meter. Distance between the light source and illuminated electrode is fixed at 14 cm. Water filter is used for obstructing infrared radiations.

The working of the experimental setup was formed according the previous reported method [14], by placing a setup in dark to obtain a stable potential. The H-shaped glass cell is divided into two separate chambers-dark chamber (arm having SCE) and illuminated chamber (arm having platinum electrode just before the window). Platinum electrode was exposed to the tungsten lamp. Photochemical bleaching of xylene cyanol FF and patent blue was initiated on illumination. The I-V characteristics of the cell were studied by applying external loads using a variable resistors-carbon pot Log 500 K. Cell performance is studied in terms of half change time ($t_{0.5}$), conversion efficiency (CE) and fill factor (FF) in dark. The CE and FF were calculated from the following equations:

$$\text{Conversion efficiency (CE, \%)} = \frac{V_{pp} \times i_{pp}}{10.4\ \text{mW/cm}^2} \times 100$$

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

where, P_{pp} is the power at power point at corresponding external load; i_{pp} is the current at power point; V_{pp} is the potential at power point; i_{sc} is the short-circuit current and V_{oc} is the open-circuit potential.

RESULTS AND DISCUSSION

Mechanism of generation of photocurrent: On the basis of investigation of diffusion path length, it may be concluded that semi- or leuco-mixed dyes and the mixed dyes itself are the electroactive species at the illuminated and dark electrode, respectively. The participation of leuco-form of dye as an electroactive specie has been experimentally confirmed by Wildes and Lichtin [23]. The semi- or leuco-mixed dyes give electrons to platinum electrode connected through external circuit with SCE at which dyes accept electrons. Finally, leuco/semi-form of dyes and oxidized form of reductant (EDTA) may combine to produce mixed dyes and reductant molecules in the dark chamber. The energy stored in the charge separated form-semi or leuco can be converted into the electrical energy. The mechanism of photo-current generation in the photogalvanic cell is as follows:

In illuminated chamber: On irradiation, dye molecules get excited.

$$\text{XCFF} + \text{PB} \xrightarrow{h\nu} \text{XCFF}^* + \text{PB}^* \quad (1)$$

where XCFF = xylene cyanol FF, and PB = patent blue dye

Excited dye molecules accept electrons from reductant and were converted to the semi- or leuco- form of mixed dyes and the reductant converts to its oxidized form:

$$\text{XCFF}^* + \text{PB}^* + 2\text{R} \longrightarrow \text{XCFF}^- + \text{PB}^- + 2\text{R}^+ \quad (2)$$

where R = reductant (EDTA).

At the working electrode: The semi- or leuco- form of mixed dye looses an electron and converted into the original dye molecules.

$$\text{XCFF}^- + \text{PB}^- \longrightarrow \text{XCFF} + \text{PB} + 2\text{e} \quad (3)$$

In dark chamber: At the counter electrode (SCE), the dye molecules accept electrons from the electrode and were converted to the semi- or leuco-forms:

$$\text{XCFF} + \text{PB} + 2\text{e}^- \longrightarrow \text{XCFF}^- + \text{PB}^- \quad (4)$$

Finally, the leuco-/semi-form of dyes and oxidized forms of the reductant combine to regenerate the original dyes and reductant molecules.

$$\text{XCFF}^- + \text{PB}^- + 2\text{R}^+ \longrightarrow \text{XCFF} + \text{PB} + 2\text{R} \quad (5)$$

where $XCFF^* + PB^*$, $XCFF^- + PB^-$ are the excited and the leuco/semi-leuco forms of xylene cyanol FF + patent blue and R and R^+ are the reductant and its oxidized form.

The system at its optimum condition was exposed to the sunlight. It was observed that I-V curve deviates from its ideal regular rectangular shape as shown in Fig. 1.

Effect of variation of pH: Photogalvanic cell containing EDTA-xylene cyanol FF-patent blue system was found to be

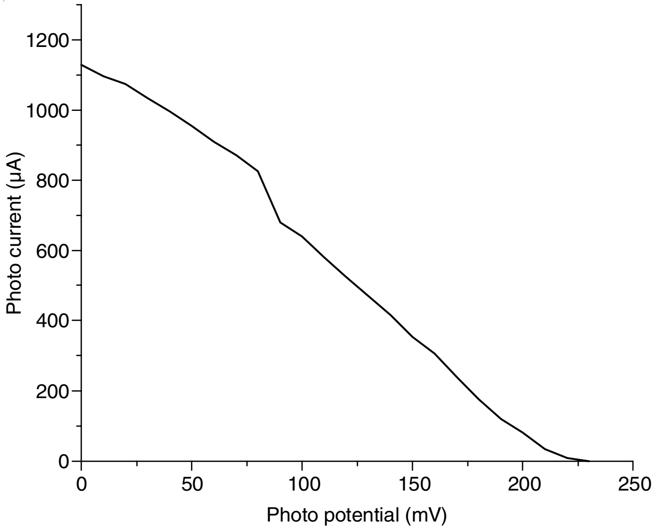

Fig. 1. Current-potential (I–V) curve of photogalvanic cell based on mixed triphenylmethane dyes

sensitive to the pH of solution. An increase in electrical output of the cell was noticed up to a pH value of 12.8, beyond that a drop in electrical output was observed (Table-1).

Maximum photo-potential of 868 mV and photo-current of 230 µA were recorded at pH 12.8. The pH for the optimum condition has a relationship with pK_a of the reductant and the desired pH is higher than its pK_a value ($pH > pK_a$). It was probably due to the availability of reductant in its anionic form which is a better donor form [24].

Effect of EDTA concentration: The electrical output of the cell depends on the variation in concentration of reducing agent EDTA. The optimum concentration of reducing agent EDTA was recorded at 9.3×10^{-3} M giving best photo-potential of 868 mV and photo-current of 230 µA. The concentration of EDTA below this optimum value results in a decrease in the electrical output as fewer reducing agent molecules were available for electron donation to the dye molecules (Table-2). A high concentration also leads to a decrease in electrical output as more number of molecules hinder the movement of dye molecules towards the electrodes [25,26]. It is difficult to visualize the role of oxidized and reduced forms of EDTA as electrode active species because the photo-chemical oxidation of EDTA is reversible and oxidized and reduced forms have not been characterized. The reactants normally undergo irreversible photo-chemical degradation. Hence, it is assumed that no side reactions were occured.

Effect of mixed dyes concentration: Dependence of photo-potential and photo-current on concentration of the dyes was also investigated. Best photo-potential and photo-current values were obtained at the concentration of 2.59×10^{-5} M (XCFF) and 1.6×10^{-5} M (PB), respectively. A lower concentration, a decrease in the photo-potential and photo-current was observed, as fewer dye molecules were available for excitation and consecutive donation of electrons to the platinum electrode (Table-3). Similarly, at higher concentrations, dye molecules do not permit the desired light intensity to reach the photosensitizer molecules near the electrodes.

TABLE-1
EFFECT OF VARIATION IN pH VALUE
[XCFF] = 2.59×10^{-5} M; [EDTA] = 9.3×10^{-3} M; [PB] = 1.6×10^{-5} M; Light intensity = 10.4 mW cm^2; Temp. = 303 K

pH	12.0	12.2	12.4	12.6	12.8	13.0	13.2	13.4	13.6
Photo-potential (mV)	430	570	680	795	868	790	620	520	440
Photocurrent (µA)	70	140	190	208	230	205	180	110	60
Power (µW)	30.10	79.80	129.20	165.36	199.64	161.95	111.60	57.20	26.40

TABLE-2
EFFECT OF VARIATION IN EDTA CONCENTRATION
[XCFF] = 2.59×10^{-5} M; [PB] = 1.6×10^{-5} M; Light intensity = 10.4 mW cm^2; pH = 12.8; Temp. = 303 K

[EDTA] × 10^{-3} M	8.5	8.7	8.9	9.1	9.3	9.5	9.7	9.9	10.1
Photo-potential (mV)	410	512	660	740	868	710	625	535	465
Photocurrent (µA)	32	92	188	211	230	209	190	88	46
Power (µW)	13.12	47.10	124.08	156.14	199.64	148.39	118.75	47.08	21.39

TABLE-3A
EFFECT OF VARIATION IN XCFF CONCENTRATION
[EDTA] = 9.3×10^{-3} M; [PB] = 1.6×10^{-5} M; Light intensity = 10.4 mW cm^2; pH = 12.8; Temp. = 303 K

[XCFF] × 10^{-5} M	1.79	1.99	2.19	2.39	2.59	2.79	2.99	3.19	3.39
Photo-potential (mV)	628	729	786	836	868	815	691	534	503
Photocurrent (µA)	102	133	160	205	230	184	133	102	92
Power (µW)	64.06	96.96	125.76	171.38	199.64	149.96	91.90	54.46	46.27

TABLE-3B
EFFECT OF VARIATION OF PB CONCENTRATION
[XCFF] = 2.59×10^{-5} M; [EDTA] = 9.3×10^{-3} M; Light intensity = 10.4 mW cm^2; pH = 12.8; Temp. = 303 K

[PB] × 10^{-5} M	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4
Photo-potential (mV)	503	660	817	836	868	786	679	628	597
Photocurrent (µA)	82	102	133	195	230	174	143	127	112.0
Power (µW)	41.25	67.32	108.66	163.02	199.64	136.76	97.09	79.76	66.86

Effect of variation in diffusion length: The effect of variation in diffusion length on the current parameters i_{max}, i_{eq} and rate of initial generation of current of the cell was also investigated using H-shaped cells of different dimensions. A sharp increase in photo-current (i_{max}) was observed in first few minutes of the illumination followed by a gradual decrease in the photo-current till a stable value of 230 µA was attained (Table-4). A spontaneous increase in the photocurrent on illumination is a indicative of the fact that an initial rapid reaction was followed by a slow stable rate.

TABLE-4
EFFECT OF VARIATION IN DIFFUSION LENGTH
[XCFF] = 2.59×10^{-5} M; [EDTA] = 9.3×10^{-3} M; [PB] = 1.6×10^{-5} M; Light intensity = 10.4 mW cm^2; pH = 12.8; Temp. = 303 K

Diffusion length (mm)	Maximum photocurrent i_{max} (µA)	Equilibrium photocurrent i_{eq}(µA)	Rate of initial generation of current (µA min^{-1})
35.0	240.0	238.0	13.4
40.0	245.0	233.0	14.2
45.0	246.0	230.0	15.0
50.0	250.0	229.0	15.6
55.0	256.0	227.0	15.9

The oxidized form of reductant was formed only in the illuminated chamber and if it was present in the dark chamber as electroactive species, then it must diffuse from the illuminated chamber to the dark chamber to accept an electron from the electrode. As a consequence, a maximum photo-current and rate of increase of photo-current should decrease with the increase in diffusion length. However, it was not observed during the experiment. The value of photocurrent at equilibrium (i_{eq}) was found to be independent to the change in diffusion length, rather it decreases slightly. On illumination, current, i_{max} increases rapidly. Electroactive species take a bit longer time to reach at the electrode surface as the diffusion length increases. This gives ample time for the reaction to take place, causing increase in i_{max}. Since, the volume of reaction solution increase and the area of electrode is unchanged, no increase in i_{eq} was observed.

Effect of variation in electrode area: Thin platinum electrodes of different diameters were used to determine the effect of variation in electrode area on photogeneration. A maximum photo-current of 252 µA was recorded. The value of maximum photo-current (i_{max}) increases with an increase in the electrode area. However, photo-current at equilibrium, i_{eq} of 230 µA was almost independent to any change in electrode area. The dye molecules were transported towards the charged illuminated electrode by diffusion and a static layer was gradually developed near the electrode surface. A loose complex between the mixed dye and EDTA was formed on the electrode surface with could be a charge transfer type with increased donor capacity. The effect of variation of electrode area on i_{max} and i_{eq} is shown in Table-5.

Current-potential (I-V) characteristics of the cell: The short circuit current i_{sc} = 230 µA and open circuit voltage V_{oc} = 868 mV of the cell were measured. The current and potential values between these two extremes (V_{oc} and i_{sc}) were recorded with the help of a resistor-carbon pot Log 500 K connected in the circuit of microammeter through which external load was applied. A point in the I-V curve called power point (pp) was determined, where the product of potential and current was maximum as shown in Fig. 1. A fill factor of 0.24 and a conversion efficiency of 0.64 % was obtained with the tungsten lamp of 200 W. The lamp has a light intensity approximately 15 times less as compared to the direct sunlight. Hence, a theoretical conversion efficiency of the order of 9.6 % may be expected in the presence of natural sunlight. Lower conversion efficiency recorded during the experimentation in comparison to the theoretical one is primarily assigned to the lower stability of dyes, back electron transfer and the aggregation of dye molecules around the electrode [27].

TABLE-5
EFFECT OF VARIATION IN ELECTRODE AREA
[XCFF] = 2.59×10^{-5} M; [EDTA] = 9.3×10^{-3} M; [PB] = 1.6×10^{-5} M; Light intensity = 10.4 mW cm^2; pH = 12.8; Temp. = 303 K

Electrode area (cm^2)	0.36	0.64	1.00	1.44	1.69
Maximum photocurrent i_{max} (µA)	236	240	244	248	252
Equilibrium photocurrent i_{eq}(µA)	214	222	230	220	215

Performance of the cell: The performance of photogalvanic cell containing EDTA-mixed dyes system was monitored by applying desired external load to have the current and potential corresponding to the power point after removing the source of illumination till the power output was reduced to a half of its original value at the power point in dark. The performance of the cell was determined in terms of half change time ($t_{0.5}$), *i.e.* time required for the fall of the output to its half value at the power point in the dark. Mixed dyes system studied in this work has a better performance due to its lower charging time of 135 min and has an improved storage capacity of 115 min. The performance of the cell is graphically shown in Fig. 2.

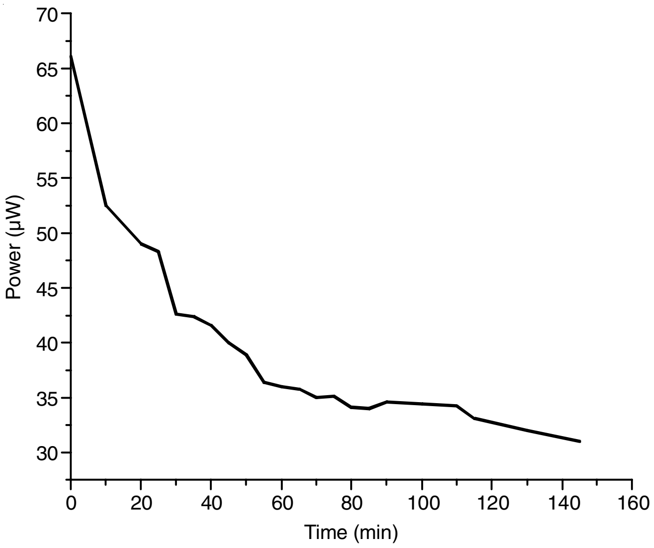

Fig. 2. Performance of photogalvanic cell based on mixed triphenylmethane dyes

The absorption spectra of single dyes and mixed dyes by combining two single dyes were recorded to show a frequency range in which energy is absorbed. Spectra were recorded on a double-beam spectrophotometer (Systronic-2203). The absorption spectra for a single dye system *viz.* PB-EDTA abd XCFF-EDTA are shown in Fig. 3a-b. An absorption spectrum of XCFF-PB-EDTA (Fig. 3c) shows a wavelength of 642 nm at which

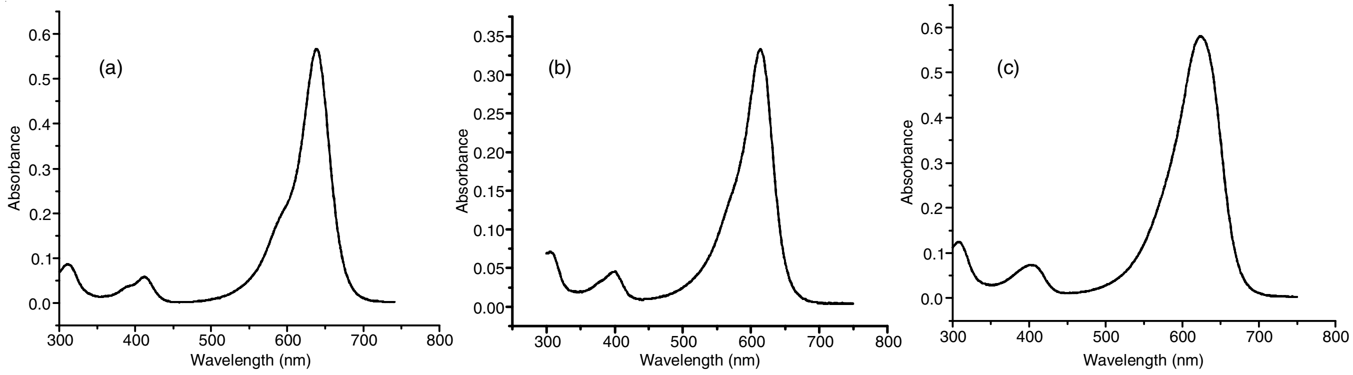

Fig. 3. Absorption spectra of (a) PB-EDTA, (b) XCFF-EDTA and (c) XCFF-PB-EDTA photogalvanic systems

the energy was absorbed. It suggests that a better absorbance range is expected for mixed dye system XCFF-PB-EDTA at the optimized conditions.

Conclusion

Performance characteristics of photogalvanic cells containing mixed dyes xylene cyanol FF, patent blue using EDTA as reducing agent were analyzed experimentally. Photo-potential of 868 mV and photo-current of 230 µA was experimentally recorded. Power convesion efficiency of EDTA-xylene cyanol FF-patent blue photogalvanic cell was estimated as 0.64%. The combination used in the present study offers a promising alternative to the existing dye systems as a better performance of photogalvanic cell. More investigation of such systems are required to further improve the conversion efficiency and storage potential of such photogalvanic cells.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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