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Photogalvanic Performance of DSS-Indigo Carmine-EDTA Cell Materials

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In the present work, the studies in photogalvanics of indigo carmine dye with EDTA reductant and dioctyl sodium sulphosuccinate surfactant in alkaline medium has been done with aim of finding relatively better combination photosensitizer, reductant and surfactant for improvement in electrical performance of these cells. The photopotential and photocurrent were observed 920 mV and 410 µA, respectively. The conversion efficiency of the system was determined as 0.9377 % and fill factor 0.2530. The cell performance was observed 120 min 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 in this dye surfactant cell combination.

Keywords: Photogalvanic effect, Indigo carmine, EDTA, Dioctyl sodium sulphosuccinate, Fill factor, conversion efficiency.

INTRODUCTION

The rate of depletion of natural sources of energy has compelled the scientific community to explore the renewable source of energy having highest promising nature to feed the whole world and get all of the solution like energy crisis. The scientist have put up their own efforts in this direction and have applied the solar energy can be only option to cope up with this situation.

Sources and the methods of production of environment friendly renewable energy based have been observed to ensure high quality useful energy (electrical energy).among the many environment friendly energy sources, solar energy is prominent source. Solar energy can be harnessed by direct and indirect methods. The solar energy-thermal energy and photon (light) energy is direct harnessed for generating useful energy [1-4]. The photogalvanic cell was used as a converter device which converts solar energy (photon) in to electrical energy. Photogalvanic cell are relativity low-cost, clean and potential source of renewable energy. The difference between photogalvanic and photovoltaic cell is in the locus of the photochemical change. The photochemical changes occur in electrolyte. It is, therefore more easily identifiable and the storage capacity of the cell can be larger in photogalvanic cell. On the other hand, photochemical changes take place in the surface layers of the electrode (illuminated) in photovoltaic cell.

Rideal and Williams [5] reported the photogalvanic effect, but it was systematically investigated by Rabinowitch [6-8]. Wendell and Clark [9,10] reported this effect with same manner. The origin of the photovoltaic phenomena is called Becqueral effect [11,12], which was first observed in 1839. Rabinowitch suggested that the photogalvanic effect might be used to converts sunlight into electricity. Later on role of dyes, reductants and range of surfactant were used for the betterment of photogalvanic conversion efficiency of series of cells [13-19]. Some recent results shown termindous improvements in cell outputs [20,21] but, to make photogalvanic cell more efficient and practically applicable in daily life. Some new dye surfactant combinations and gradients have to be used for fabrication of photogalvanic cells. To explore this suggestion various photogalvanic cells with different dyes and reductant have been studied. To this end solar energy conversion efficiency and photocurrent of D-xylose-methylene blue system [22] was found 0.5313 % and 210 µA, respectively. Bismark brown-fructose [23] system and EDTA-Safranine O-CTAB [24] system studied with conversion efficiency and photocurrent of 0.708 %, 320 µA and 0.1469 %, 185 µA, respectively. These results show the importance of the present DSS-Indigo Carmine-EDTA system which has much better conversion efficiency of 0.9377 % with 410 µA photocurrent.

EXPERIMENTAL

Indigo carmine AR of (Ases Chemical Works, Jodhpur, India) as photosensitizer, ethylene diamine tetra acetic acid (98 % minimum assay-purity, Ases Chemical Works, Jodhpur, India) as reductant and dioctyl sodium sulphosuccinate (DSS, 98 % minimum assay-purity, Ases Chemical Works, Jodhpur,

India) as surfactant, NaOH (98 % assay-purity, Ases Chemical Works, Jodhpur, India) as alkaline medium and oxalic acid (99.5 % minimum assay-purity, Ases Chemical Works, Jodhpur, India) for standardization of NaOH have been used in experimental work. Indigo Carmine ($C_{16}H_8N_2Na_2O_8S_2$), 466.36 (m.w.), 608 nm (λ_{max}), 73015 (Colour Index No.). The solutions prepared of Indigo Carmine AR (10^{-5} M), ethylene diamine tetra acetic acid (10^{-3} M), dioctyl sodium sulphosuccinate (10^{-3} M), All solution were prepared in doubly distilled water and were kept in amber coloured containers to protect them from sun light.

Experimental set up: A mixture of solutions of photosensitizer, reductant, surfactant and sodium hydroxide were taken in an H-type glass tube which is blackened (by black carbon paper and white), but a window is left in one arm. The arm with window acts as illuminated chamber and other arm without window act as dark chamber. The total volume of solution is always kept 25 mL making up by doubly distilled water. A shiny platinum foil electrode (as negative terminal) was immersed in one limb (illuminated chamber against window) and a Calomel electrode-CE (as positive terminal) was immersed in the other limb (dark chamber) of the H-tube. The terminals of the electrodes are connected to a digital pH meter.

Initially, 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. On illumination, the photopotential (V) and photocurrent (i) are generated by the system.

Mechanism of photocurrent generation and storage capacity: In illuminated region of the cell, a photon excites an electron from a ground state orbital to higher energy orbital (*i.e.*, excited singlet state which through inter-system crossing (ISC) collapses to excited triplet state) of indigo carmine dye photosensitizer. The formation of excited state leaves vacancy in ground state that can be filled by an electron donor like ethylene diamine tetra acetic acid reductant. The net result is that an excess electron is produced in higher energy state of dye molecule, which can be donated to an electron acceptor as Pt electrode, electron from platinum electrode flow through circuit to SCE showing conversion of light into electricity. At SCE, the dye molecule in solution accepts electron. This way, the photogalvanic cell enables solar energy conversion into solar power with inherent storage capacity.

Thus, the mechanism of the photocurrent generation in the photogalvanic cell may be proposed as follows:

Illuminate chamber (anode):

$$Dye \xrightarrow{hv} Dye^* \quad (i)$$

$$Dye^* + R \longrightarrow Dye^- \text{ (semi or leuco)} + R^+ \quad (ii)$$

At platinum electrode:

$$Dye^- \longrightarrow Dye + e^- \quad (iii)$$

Dark chember (saturated calomel electrode-SCE as cathode):

At counter electrode:

$$Dye + e^- \longrightarrow Dye \text{ (semi or leuco)} \quad (iv)$$

$$Dye^- + R^+ \longrightarrow Dye + R \quad (v)$$

Here Dye, Dye^-, R and R^+ are the dye (indigo carmine), its leuco form, reductant (EDTA) and its oxidized form, respectively.

RESULTS AND DISCUSSION

Effect of variation of photosensitizer (indigo carmine) concentration on the system: The variation in photopotential and photocurrent with the change in concentration of photosensitizer (indigo carmine) was studied. A cell has total 25 mL (including dye, EDTA, DSS, NaOH and doubly distilled water) solution. The increase in cell parameters like photopotential and photocurrent was observed with increase in concentration of the dye up to 2.12×10^{-5} M and beyond this concentration, the decrease in these parameters was observed (Table-1). Thus, a maximum was observed for a particular value of indigo carmine concentration (2.12×10^{-5} M), above which a decrease in electrical output of the cell was observed, as the intensity of light reaching the dye molecules near the electrode decreases due to absorption of the major portion of the light by dye molecules present in the path. The concentration of dye (lower than 2.12×10^{-5} M) resulted into a fall in photopotential and photocurrent because fewer photosensitizer (dye – indigo carmine) molecules are available for the excitation and consecutive donation of the electrons to the platinum electrode. The effect of photopotential and photocurrent on the concentration of photosensitizer (indigo carmine) is shown in Fig. 1.

Effect of variation of reductant (EDTA) concentration on the system: The effect of concentration of reductant on the photopotential and photocurrent was studied. The increase in cell parameters like photopotential and photocurrent was observed with increase in concentration of the ethylene diamine

TABLE-1
EFFECT OF VARIATION OF INDIGO CARMINE, EDTA, DSS AND pH
Light intensity = 10.4 mW cm^{-2}; Temp. = 303 K

Parameters	Photopotential (mV)	Photocurrent (μA)
[Indigo carmine] × 10^{-5} M		
1.82	699	283.0
1.97	815	349.0
2.12	920	410.0
2.27	798	345.0
2.42	705	287.0
[EDTA] × 10^{-3} M		
1.58	702	278.0
1.61	825	344.0
1.64	920	410.0
1.67	836	356.0
1.70	714	279.0
[DSS] × 10^{-3} M		
1.48	709	282.0
1.50	838	354.0
1.52	920	410.0
1.54	834	349.0
1.56	716	286.0
pH		
12.68	695	287.0
12.72	827	351.0
12.76	920	410.0
12.80	823	348.0
12.84	702	274.0

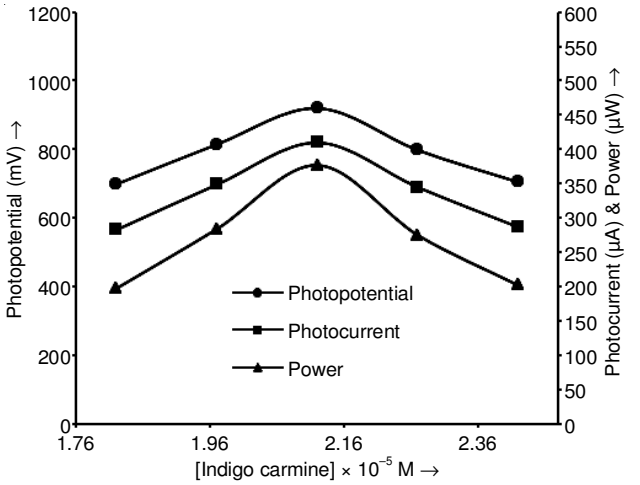

Fig. 1. Variation of photopotential, photocurrent and power with indigo carmine concentration

tetra acetic acid up to 1.64×10^{-3} M and beyond this concentration, the decrease in these parameters was observed (Table-1). Thus, a maximum was observed for a particular value of ethylene diamine tetra acetic acid concentration (1.64×10^{-3} M), above which a decrease in electrical output of the cell was observed, as the higher concentration of ethylene diamine tetra acetic acid will promote back electron transfer from dye molecule to reductant molecule and also hinder the motion of the dye molecule toward the electrodes. And concentration of reductant (lower then 1.64×10^{-3} M) resulted into a fall in photopotential and photocurrent because of fewer reductant (ethylene diamine tetra acetic acid) molecules to donate electrons to dye molecules. The effect of photopotential and photocurrent on the concentration of reductant (EDTA) is shown in Fig. 2.

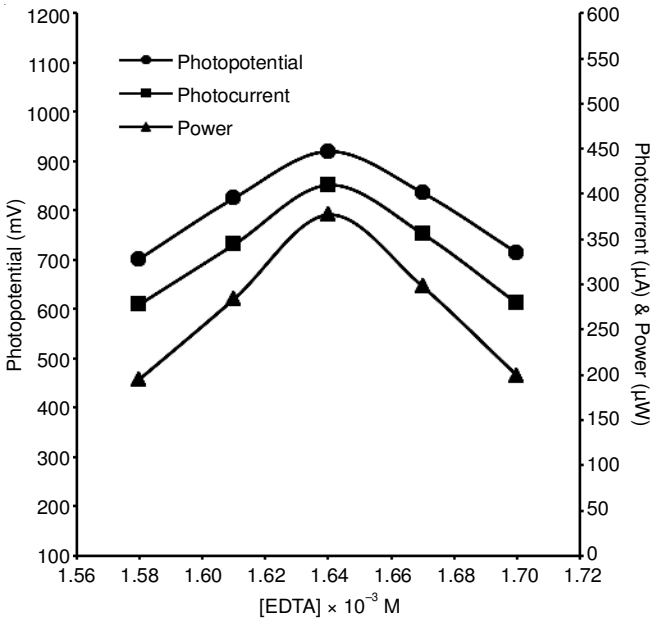

Fig. 2. Variation of photopotential, photocurrent and power with EDTA concentration

Effect of variation of surfactant (DSS) concentration on the system: The effect of photopotential and photocurrent on the concentration of surfactant (DSS) was studied. The increase in cell parameters like photopotential and photocurrent was observed with increase in concentration of the DSS up to 1.52×10^{-3} M and beyond this concentration, the decrease in these parameters was observed (Table-1). Thus, a maximum was observed for a particular value of DSS concentration (1.52×10^{-3} M), above which a decrease in electrical output of the cell was observed, as the higher concentration of DSS will hinder the motion of dye molecules towards the electrodes. And concentration of surfactant (lower than 1.52×10^{-3} M) resulted into a fall in photopotential and photocurrent because of fewer surfactant (DSS) molecules to available electron transfer and solubility and stability of dye molecules. The effect of photopotential and photocurrent on the concentration of surfactant (DSS) is shown in Fig. 3.

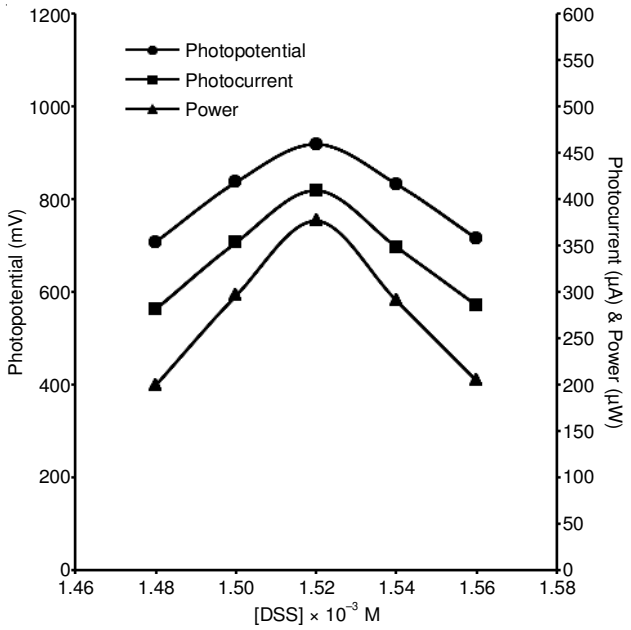

Fig. 3. Variation of photopotential, photocurrent and power with DSS concentration

Effect of variation of pH on the system: The effect of photopotential and photocurrent on the variation of initial pH was studied. The increase in cell parameters like photopotential and photocurrent was observed with increase in pH up to 12.76 and beyond this pH, the decrease in these parameters was observed (Table-1). Thus, a maximum was observed for a particular value of pH (12.76), above which a decrease in electrical output of the cell was observed. The performances of the photogalvanic cell containing the indigo carmine-EDTA-DSS system were found poor in acidic solutions. It may be due to proton attachment to hetero atom and double bond in dye and reductant leading to poor electron donating power of dye and reductant to Pt electrode.

In alkaline medium, this effect is not observed. There is an enhancement in electron power donation due to anion formation of dye and reductant. Above pH 12.76, OH^- (from NaOH used in this system) may combine with cationic reductant (formed on electron donation from reductant to dye) inhibiting regeneration of reductant in original form, leading to poor performance of the cell. The effect of photopotential and photocurrent on the variation of initial pH is shown in Fig. 4.

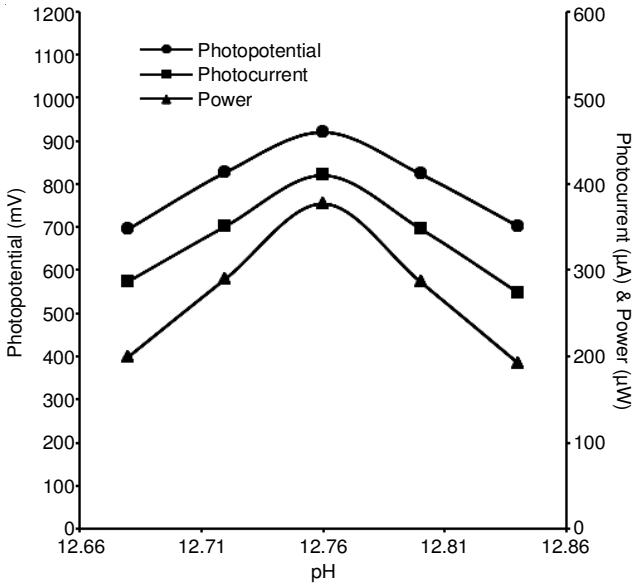

Fig. 4. Variation of photopotential, photocurrent and power with pH

Effect of diffusion length: The effect of variation of diffusion length (distance between the two electrodes) on the current parameter of the cell (i_{max}) 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. The increase in photocurrent was observed with increase with diffusion length up to 45 mm and beyond this diffusion length, the decrease in photocurrent was observed (Table-2). Thus, a maximum photocurrent was observed for a particular value of diffusion length (45 mm), above which a decrease in photocurrent of the cell was observed, as the photocurrent of dye increases due to increase in volume of solution between electrodes. As diffusion length is decrease, concentration gradient factor is reduced and photocurrent is decreased.

TABLE-2
EFFECT OF DIFFUSION LENGTH
[Indigo carmine] = 2.12×10^{-5} M; Light intensity = 10.4 mW cm^{-2}; [EDTA] = 1.64×10^{-3} M; Temperature = 303 K; [DSS] = 1.52×10^{-3} M; pH = 12.76

Diffusion length (mm)	Maximum photocurrent i_{max} (μA)	Equilibrium photocurrent i_{eq} (μA)	Rate of initial generation of photocurrent (μA min^{-1})
35	456	419	18.24
40	461	415	18.44
45	465	410	18.60
50	469	405	18.76
55	475	399	19.00

Effect of electrode area: The effect of variation of Pt electrode area on cell was studied. Under the observed effect of electron area, the current parameter was found highest for electrode area 1 cm^2. For electrode area (larger than 1 cm^2), the cell current parameter was found decreasing with increase in electrode area (Table-3). The photogalvanic cells are based on ion diffusion mechanism, the better cell parameters were observed for small electrode owing to relativity less hindrance to diffusion of ions.

Current–voltage (i-V) characteristics of the photogalvanic cell: The photogalvanic cell containing indigo carmine-EDTA-DSS system, the (i-V) characteristic of the cell has been studied. After charging of the cell, the short circuit current (i_{sc}) and open circuit voltage (V_{oc}) of the photogalvanic cells were measured with the help of potential (calculated by digital pH meter keeping the circuit open) at different direct current (calculated by microameter keeping the circuit closed) by varying resistance (calculated by Ohm law) of the circuit. It was observed that current-voltage (i-V) curve deviated from their regular rectangular shapes The cell is operated at highest power (p_{pp}) at corresponding external load, current (i_{pp}) and potential (V_{pp}) to study its performance by observing change in current and potential with time and the fill-factor was calculated using the following formula :

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

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

The value of fill factor calculated as 0.2530 and the power point of cell (pp) as 97.52 mW. The current–voltage (i-V) characteristics of the photogalvanic cell containing indigo carmine-EDTA-DSS system is shown in Fig. 5.

Cell performance and conversion efficiency: The performance of the photogalvanic cell was studied in term of half change time ($t_{1/2}$) and conversion efficiency (CE) in dark. The time taken for fall in the power of the cell to its half value of power at power point is called $t_{1/2}$ (which is measure of storage capacity of the cell).

It was observed that the cell can be used in dark for 120 min (Fig. 6). The conversion efficiency of the cell was determined as 0.9377 % using the formula:

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

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

Conclusion

The use of indigo carmine dye photosensitizer-EDTA reductant-DSS surfactant combination in photogalvanic conversion of solar energy. The result of this study have proposed a number of idea with reference to fabricate a cell, its

TABLE-3
EFFECT OF ELECTRODE AREA
[Indigo carmine] = 2.12×10^{-5} M; Light intensity = 10.4 mW cm^{-2}; [EDTA] = 1.64×10^{-3} M; Temp. = 303 K; [DSS] = 1.52×10^{-3} M; pH = 12.76

	Electrode area (cm^2)				
Indigo carmine-EDTA-DSS system	0.7	0.85	1.0	1.15	1.3
Maximum photocurrent i_{max} (mA)	455.0	460.00	465.0	470.00	475.0
Equilibrium photocurrent i_{eq} (mA)	420.0	415.00	410.0	405.00	400.0

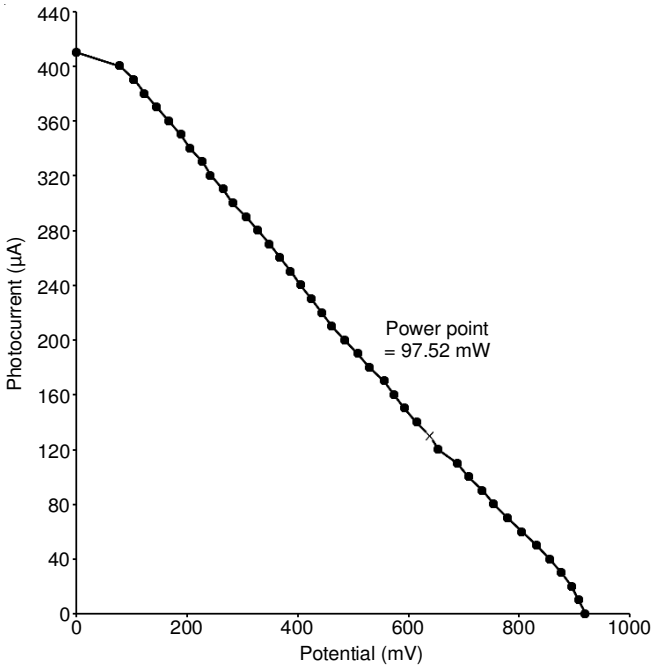

Fig. 5. Current-voltage (i-V) curve of the cell

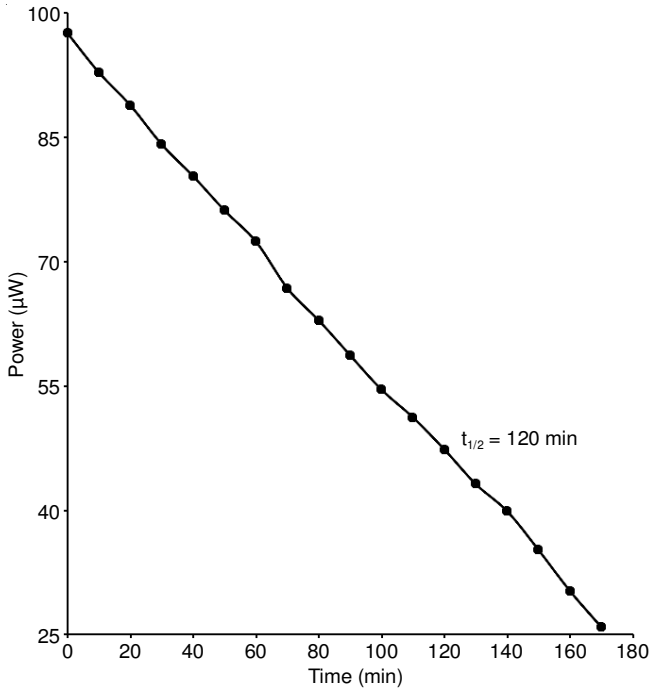

Fig. 6. Performance of the cell

mechanism and factors that affect electrical output. Photovoltaic cells have better conversion efficiency than photogalvanic cells. Photogalvanic cells have the advantage of having inbuilt storage capacity and are more 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 0.9377 %, 120 min and 0.2530, respectively in indigo carmine-EDTA-DSS system.

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