Research Article

ROLE OF REDUCTANT AND DYE SENSITIZER FOR SOLAR ENERGY CONVERSION AND STORAGE IN PHOTOGALVANIC CELL: INDIGO CARMINE - ASCORBIC ACID SYSTEM

*Syed Shadaab Nadeem and R.K. Gunsaria
Department of Chemistry, Govt. P. G. College, Tonk (Rajasthan)-304001(India)
*Author for Correspondence

ABSTRACT
Photogalvanic cell containing Indigo Carmine as dye sensitizer and Ascorbic acid as electron donor for the enhancement of the electrical output and performance (storage capacity) of the photogalvanic cell with reduce the cost of construction for commercial viability. The photopotential and photocurrent observed were 580.0 mV and 160.0 µA respectively. The conversion efficiency of the system was observed 0.45% and fill factor was determined as 0.27. The cell performance was observed 40.0 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.

Key Words: Fill Factor, Ascorbic Acid, Photogalvanic Cell, Electrical Output, Parameters

INTRODUCTION
Energy is one of the fundamental elements of our universe. It is the basis of human life. Earlier man used muscle power, then fire and animals in daily tasks. The quality of human life depends on the availability of energy.
Photogalvanic effect was first reported by Rideal and Williams (1925), but it was systematically investigated by Rabinowitch (1940) and later by other workers i.e. Gomer (1975), Clark and Eckert (1975), Albery and Archer (1976), Memming (1980) and Bhardwaj *et al.,* (1981) get momentum in the field of energy production. Gangotri (2003) used surfactant in photogalvanic cell for solar energy conversion and storage. Gunsaria and Hussain (2004a) reported photogalvanic systems with increased output using various photosensitizers with surfactants and Gunsaria and Hussain (2004b) also reported role of reductant, photosensitizer and surfactant for solar energy conversion and storage. Gunsaria *et al.,* (2005) studied role of reductant and photosensitizers in solar energy conversion and storage. Pramila and Gangotri (2007) and Gangotri and Gangotri (2009) have used micellar species with different photosensitizers and reductant in photogalvanic cells. Gangotri an Indora (2010) studied in mixed reductant with dye. Gunsaria and Meena (2012) and Gunsaria *et al.,* (2012), have developed photogalvanic cells with reasonable electrical output for solar energy conversion and storage. A detailed survey of literature reveals that no attention has been paid to electrochemical behaviour of Indigo Carmine - Ascorbic Acid has also been investigated at platinum electrode in presence of these reducing agents; therefore, the present work has been undertaken.

MATERIALS AND METHODS
Indigo Carmine (Ases Chemicals, Jodhpur), Ascorbic acid (Ranbaxy) and NaOH (Ranbaxy) were used in the present work. All solutions were prepared by direct weighing in double distilled water and kept in amber color container to protect them from direct light. Role of reductant and dye sensitizer in photogalvanic cell was studied using H- shaped glass tube which contained known amount of the solution of Indigo Carmine, Ascorbic acid, NaOH and double distilled water so as to keep total volume of the mixture constant at 25.0 ml. NaOH was used to maintain the pH of solution. A Platinum electrode $(1.0 \times 1.0 \text{ cm}^2)$ was dipped in one limb and a saturated calomel electrode (SCE) was immersed in another limb of the H- tube. Hence in present system, the platinum electrode was a working electrode and SCE acted as counter electrode. The terminals of the electrodes were then connected to a digital pH meter (Systronics Model- 335). The entire system was first placed in dark until a stable potential is reached,

Research Article

then the limb containing platinum electrode exposed to the light source (Tungsten lamp). The light intensity varied by employing tungsten lamp (Sylvania) of different wattage. A water filter was placed between the illuminated chamber and the light source to cut off thermal radiations. A microammeter (Newtech Model - 65) connected through a key was used to close one circuit and open the other with resistance (a carbon pot log 470 K) so as to measure the photocurrent of the solution. On illumination, the photochemical bleaching of Indigo Carmine was studied potentiometrically.

RESULTS AND DISCUSSION

Effect Of Variation Of Dye Sensitizer (Indigo Carmine) And Reductant (Ascorbic Acid) Concentration

Table 1 shows the effect of dye sensitizer and reductant concentration. It shows that the photopotential and photocurrent in Indigo Carmine - Ascorbic acid System and for better performance of the photogalvanic cell, proper concentration of dye sensitizer needed. The photopotential (ΔV) and photocurrent (i_{sc}) increased with increase in Indigo Carmine concentration. A maximum was obtained at certain dye sensitizer concentration (4.80×10^{-6} M). On further increase in the concentration of dye sensitizer, a fall in the electrical output was observed. At the lower concentration range of dye sensitizer, there are only a few dye sensitizer molecules to absorb the major portion of the light and therefore, there was a low electrical output. Whereas higher concentration of dye sensitizer again caused decrease in electrical output due to decreased intensity of light reaching the dye molecules near the electrode due to absorption of the major portion of the light by the dye sensitizer molecules present in the path and hence, there is corresponding fall in the electrical output of the cell.

The electrical output of the cell was affected by the variation of reductant (ascorbic acid) concentration. It was observed that photopotential (ΔV) and photocurrent (i_{sc}) was found to increase to maximum value at 4.80×10^{-4} M and then decrease in electrical output because fewer reductant molecules were available for electron donation to dye sensitizer molecules. Higher concentration of reductant again resulted in a decrease in electrical output, because large numbers of reductant molecules hinders the dye sensitizer molecules reaching close to electrode in the desired time limit.

Effect of Variation of pH

Cell performance was quite sensitive to the pH of the solution. The increasing in pH value (at alkaline range) increased the photopotential and the photocurrent of this system. At pH = 12.68, a maximum value was obtained. On further increasing the pH there was a decrease in photopotential and photocurrent. It was observed that optimum pH for a reductant has a relation with its pKa value i.e. the desired pH should be slightly higher than their pKa values (pH > pKa). The reason may be the availability of reductant in its anionic form, which is better donor form. The results showing the effect of pH are summarized in Table 1. All results were observed at pH = 12.68, temperature =303K, and light intensity=10.4 mWcm^{-2} except the variable parameter.

Effect of diffusion path length

The effect of diffusion path length variation on the electrical output and initial rate of generation of photocurrent of the cell was studied by using H-shaped cell of different dimensions. In the first few minutes of illumination there was a sharp increase in photocurrent and subsequently there was a gradual decrease to a stable value of photocurrent. This photocurrent at equilibrium state is known as equilibrium photocurrent (i_{eq}). This kind of photocurrent behaviour is due to an initial rapid reaction followed by a slow rate-determining step at later stage. On the basis of effect of diffusion path length on the current parameters, it may be concluded that the leuco or semi reduced form of dyes and dyes itself are the main electroactive species at the illuminated and the dark electrodes, respectively. However, the reducing agent and their oxidized products behaved as the electron carriers in the cell diffusing through the path. The results are summarized in Table 2 and 3. Effects of diffusion path length are shown in Fig.1.

Research Article

Table 1: Effect of variation of various concentrations on the electrical output

Concentration	Photopotential (mV)	Photocurrent (µA)	Power (µW)
[Indigo Carmine] $\times 10^{-6}$ M			
3.20	397.0	99.0	39.30
4.00	479.0	120.0	57.48
4.80	580.0	160.0	92.80
5.60	451.0	103.0	46.45
6.40	343.0	63.0	21.61
[Ascorbic acid] $\times 10^{-4}$ M			
3.20	379.0	94.0	35.62
4.00	424.0	115.0	48.76
4.80	580.0	160.0	92.80
5.60	451.0	111.0	50.06
6.40	312.0	76.0	23.71
pH			
12.62	383.0	88.0	33.70
12.65	465.0	126.0	58.59
12.68	580.0	160.0	92.80
12.71	437.0	109.0	47.63
12.74	328.0	83.0	27.22

Table 2: Effect of diffusion path length

Diffusion Length D_L (mm)	Maximum Photocurrent i_{max} (µA)	Equilibrium Photocurrent i_{eq} (µA)	Rate of initial Generation of Current (µA min^{-1})
35.0	190.0	163.0	10.5
40.0	233.0	161.0	16.6
45.0	276.0	160.0	22.3
50.0	326.0	158.0	31.2
55.0	371.0	157.0	41.9

Table 3: Probable process and combination for electroactive species

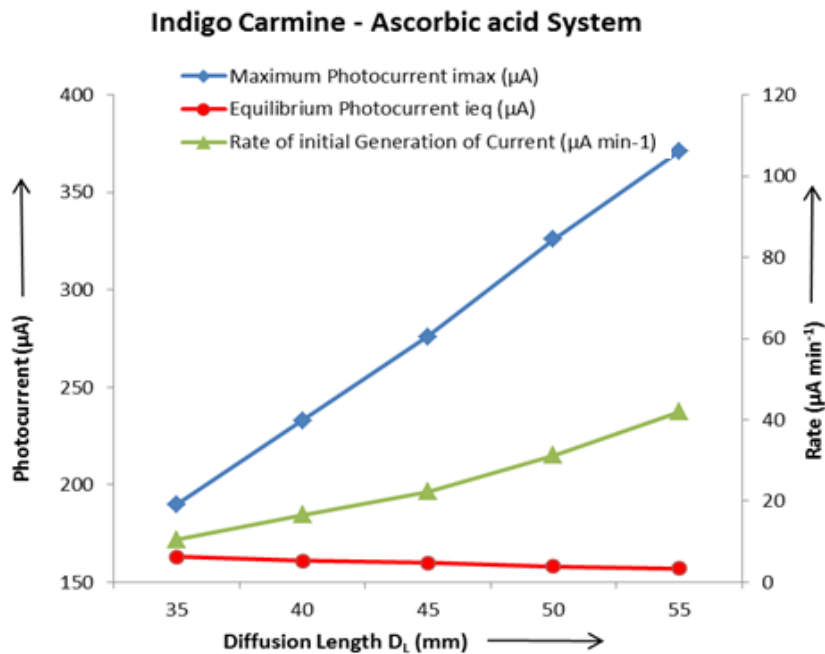| In Illuminated Chamber	In Dark Chamber
Indigo Carmine Dyes	Oxidized form of the reductant (R^+)
Semi or leuco form of dye$^-$	Oxidized form of reductant (R^+)
Semi or leuco form of dye$^-$	Indigo Carmine Dyes

Research Article

Figure 1: Effect of diffusion path length of the cell

Effect of variation of light intensity
The effect of light intensity was studied by using tungsten lamps of different wattage. It was observed that photocurrent (i_{sc}) showed a linear increasing behavior with the increase in light intensity whereas photopotential (ΔV) increased in logarithmic manner. This increasing behavior of electrical output with increase in light intensity was due to increase in number of photons with increase in light intensity. The results are summarized in Table 4 and the observed results showing dependence of light intensity on photopotential (ΔV) and photocurrent (i_{sc}) of the cell are depicted in Fig.2.
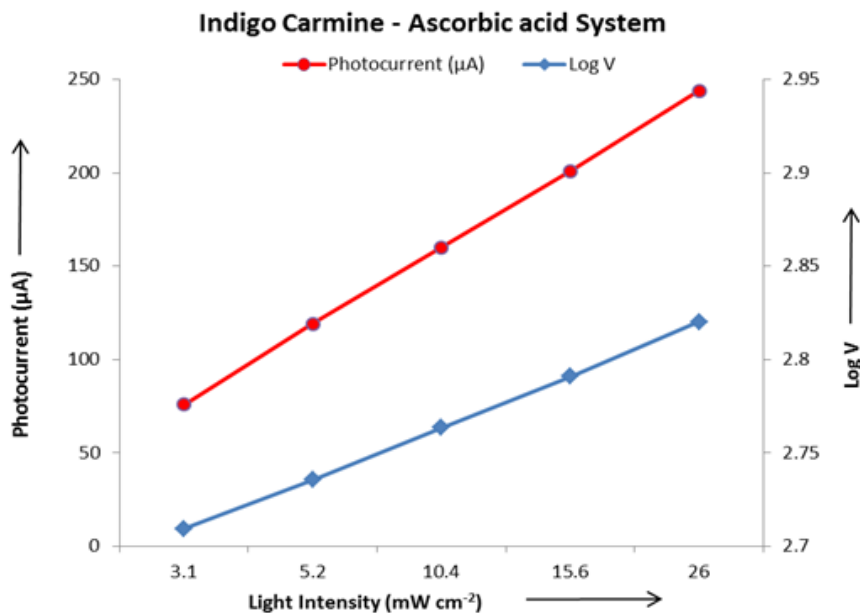

Figure 2: Variations of Photocurrent and Log V with Light Intensity on the cell

Research Article

Table 4: Effect of light intensity on the system

Indigo Carmine – Ascorbic acid System	Light Intensity (mWcm^{-2})				
	3.1	5.2	10.4	15.6	26.0
Photopotential (mV)	512.0	544.0	580.0	618.0	661.0
Photocurrent (µA)	76.0	119.0	160.0	201.0	244.0
Log V	2.70	2.73	2.76	2.79	2.82

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

The open circuit voltage (V_{oc}) and short circuit current (i_{sc}) 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 microammeter (keeping the circuit closed), respectively. The potential and current between two extreme values (V_{pp} and i_{pp}) were recorded with the help of a carbon pot (log 407K) connected in circuit with microammeter. It was observed that i-V curve deviated from its regular rectangular shape. A point in the i-V curve, called Power point (pp), was determined where the product of current and potential was maximum.
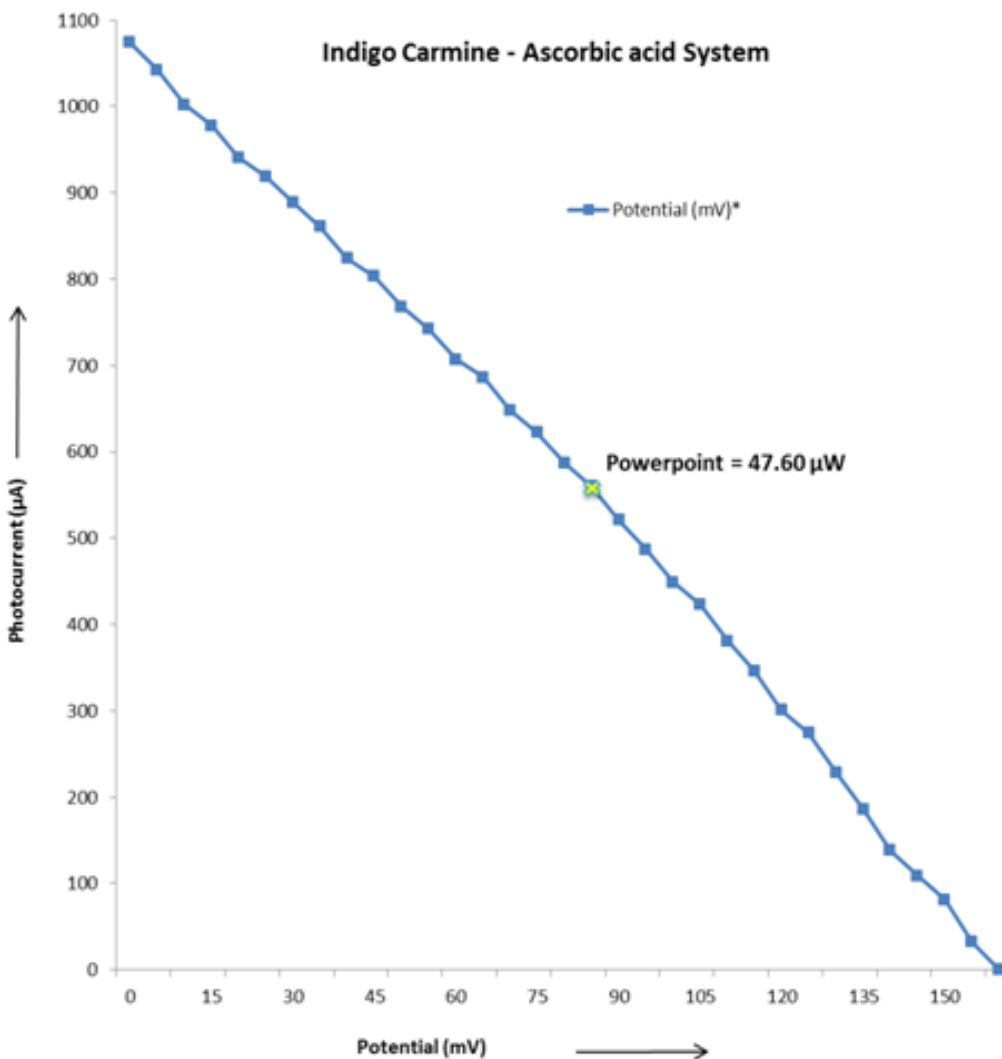

Figure 3: Current – Voltage (i-V) characteristics of the cell

Research Article

The i-V characteristics curve of cell is shown in Fig. 3. With the help of i-V curve, the fill-factor was calculated as 0.27 using the formula:

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

In the above formula, V_{pp} and i_{pp} represent the value of potential and current at Power point, respectively while V_{oc} and i_{sc} represent open circuit and short circuit current, respectively. The current voltage (i-V) characteristic of the cell is shown in Fig. 3.

Conversion efficiency of the cell
The conversion efficiency of cell was calculated using photocurrent and photopotential values at Power point (pp) and the power of incident radiation (light intensity 10.4 mWcm^{-2}, measured by Solarimeter Model - 501 Cell), as per following formula. The conversion efficiency of cell is 0.45%.

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

Storage capacity (Performance) of the cell
The performance was determined in term of $t_{1/2}$ i.e. the time required in fall of the output (power = 47.60 µW) to its half at Power point in dark. It was obtained with time- power curve (Fig.4.). It was observed that the cell can be used in dark at its Power point for 40.0 min using Indigo Carmine - Ascorbic Acid System.
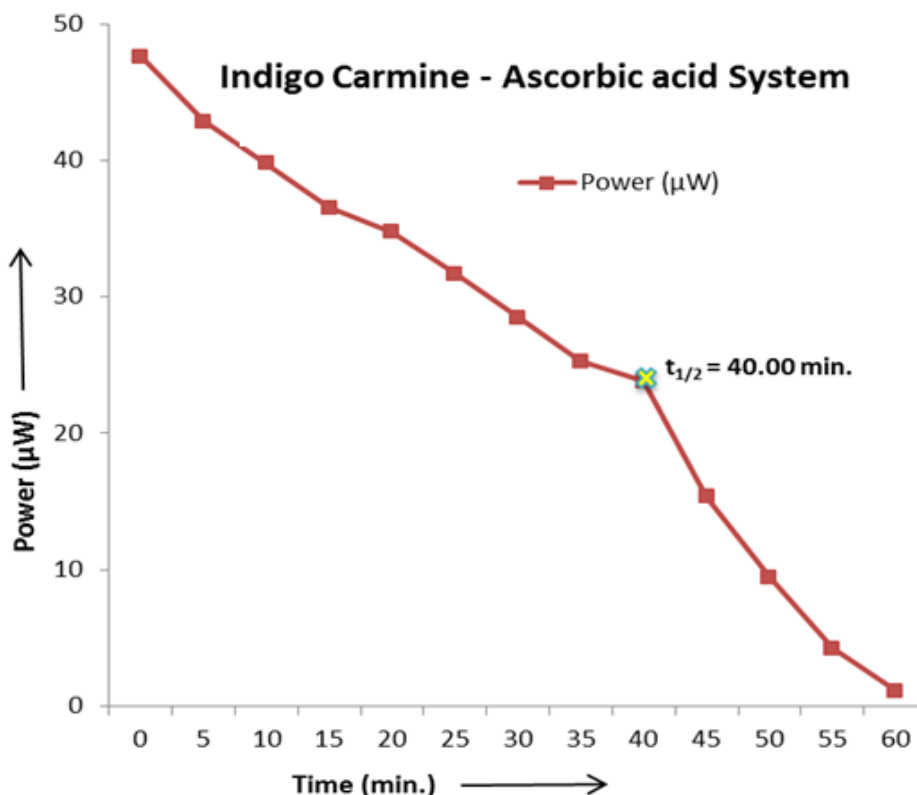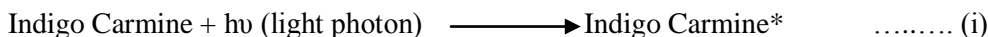

Figure 4: Performance of the cell

MECHANISM
On the basis of above observations, a tentative mechanism for the generation of photocurrent in the cell is proposed here:

Illumination chamber
On illumination, the dye (dye sensitizer) molecules get excited;

Research Article

$$\text{Indigo Carmine} + h\upsilon \text{ (light photon)} \longrightarrow \text{Indigo Carmine*} \qquad .... \text{ (i)}$$

The excited dye molecules accept an electron from reductant and get converted into semi or leuco form of dye and the reductant get converted into its oxidized form.

$$\text{Indigo Carmine*} + R \longrightarrow \text{Indigo Carmine}^- \text{(semi or leuco)} + R^+ \qquad .... \text{ (ii)}$$
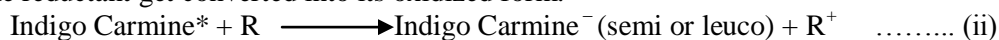
At platinum electrode:

The semi or leuco form of dye molecules lose an electron and get converted into original dye molecule.

$$\text{Indigo Carmine}^- \longrightarrow \text{Indigo Carmine} + e^- \qquad .... \text{ (iii)}$$

Dark chamber

At counter electrode:

$$\text{Indigo Carmine} + e^- \longrightarrow \text{Indigo Carmine}^- \text{(semi or leuco)} \qquad .... \text{ (iv)}$$

Finally semi/leuco form of dye and oxidized form of reductant combine to give original dye and reductant molecule and the cycle continues will go on:

$$\text{Indigo Carmine}^- + R^+ \longrightarrow \text{Indigo Carmine} + R \qquad .... \text{ (v)}$$

Here Dye, Dye*, Dye$^-$, R and R$^+$ are the dye, its excited form, leuco form, reductant and its oxidized form, respectively. Scheme of mechanism is shown in Fig.5.
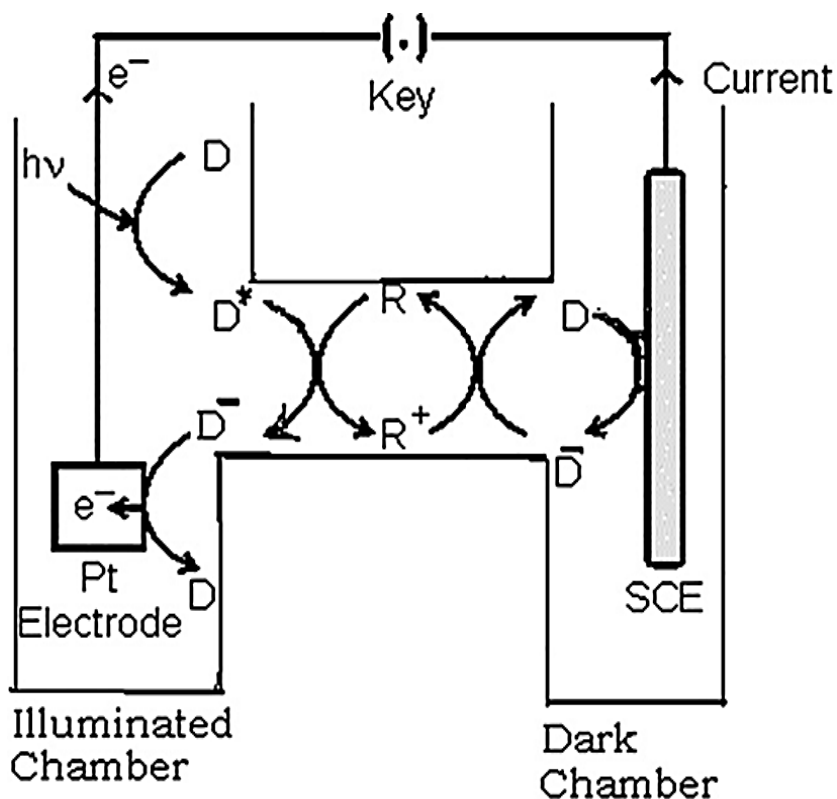

Figure 5: Mechanism of photo generation of current in photogalvanic cell. SCE, Saturated Calomel Electrode; D, Dye (Dye sensitizer); D*, Oxidized form of Dye; R$^+$, Oxidized form of reductant; e$^-$, Electron

Conclusion

Photovoltaic cells and photogalvanic cells are considered as viable medium to counter energy crises. At present photovoltaic cells are used in solar energy utilization but they have disadvantage of low storage capacity. Photogalvanic cells have an advantage to have inbuilt storage capacity. The photogalvanic cells are made from low cost materials and they are pollution free. The investigators are working to reduce the cost and enhance the performance of photogalvanic systems. On the basis of results obtained in the

Research Article

present photogalvanic cell using Indigo Carmine - Ascorbic acid System, it is concluded that value of conversion efficiency, storage capacity and fill factor observed are reasonable and this system can be used in photogalvanic cell for solar energy conversion and storage device. Our study also shows that the photogalvanic cells must have reductant and dye sensitizer (photo sensitizer) to enhance the electrical output, conversion efficiency and storage of solar energy.

ACKNOWLEDGEMENT

REFERENCES
Albery WJ and Archer MD (1977). Optimum efficiency of photogalvanic cells for solar energy conversion. *Nature* **270** 399-402.
Bhardwaj R, Pan RL and Gross EL (1981). Solar energy conversion by chloroplast photoelectrochemical cells. *Nature* **289** 396-398.
Clark WDK AND Eckert JA (1975). Photogalvanic cells. *Solar Energy* **17** 147-152.
Gomer R (1975). Photogalvanic Cell. *Electrochimica Acta* **20** 13-20.
Gangotri KM, Gunsaria RK and Meena RC (2003). Use of Surfactant in Photogalvanic Cell for Solar Energy Conversion and Storage: NaLS-Glycerol-Azur A. *Afinidad* **60** 563-567.
Gunsaria RK and Hussain J (2004a). Use of surfactant in photogalvanic cell for cell energy conversion and storage. Tx-100-Glycerol-Azure-C System. *Asian Journal of Chemistry* **16**(1) 375-384.
Gunsaria RK and Hussain J (2004b). Role of Reductant,Photosensitizer and surfactant for solar energy conversion and storage.EDTA-AzureA-NaLS System. *Asian Journal of Chemistry* **16**(1) 385-392.
Gunsaria RK, Sindal RS, Chandra M and Meena RC (2005). Role of reductant and photosensitizers in solar energy conversion and storage. Oxalic acid – Brilliant Cresyl System *The Arabian Journal for Science and Engineering* **31** 177-183**.**
Gangotri KM and Gangotri P (2009). Studies of the micellar effect on photogalvanics: Solar energy conversion and storage–EDTA-Safranine O-Tween-80 system. *Energy and Fuels* **23** 2767-2772.
Gangotri KM and Indora V (2010). Studies in the photogalvanic effect in mixed reductant for solar energy conversion and storage: Dextrose and Ethylenediaminetetraacetic acid-Azur A system. *Solar Energy* **84**(2) 271-276.
Gunsaria RK, Nadeem SS and Meena RN (2012). Studies of cationic micelles effect on photogalvanic cells for solar energy conversion and storage in Congo red – D-Xylose – Cetyl pyridinium chloride system. *International Journal of Basic and Applied Chemical Science* **2**(1) 77-83.
Gunsaria RK and Meena RN (2012). Glycerol-Azure A-NaLS System: *Journal of Chemical, Biological and Physical Sciences* Section *C: Physical Sciences* **2**(3) 1506-1514.
Memming R (1980). Solar energy conversion by photoelectrochemical processes. *Electrochimia Acta* **25**(1) 77-88.
Pramila S and Gangotri KM (2007). Use of anionic micelles in photogalvanic cell for solar energy conversion and storage: Dioctylsulfosuccinate – Mannitol - Safranine system. *Energy Sources Part A* **29** 1253-1257.
Rideal EK and Williams DC (1925). The Action of Light on the Ferrous Iodine- Iodide Equilibrium. *Journal of the Chemical Society* **127** 258-269.
Rabinowitch E (1940). The photogalvanic Effect I: the Photochemical Properties of the Thionine-iron System. *Journal Chemical Physics* **8** 551-559.
Rabinowitch E (1940). The Photogalvanic Effect II: the Photogalvanic Properties of the Thionine-iron System. *Journal Chemical Physics* **8** 560-566.