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Study on effect of reductant in Photosensitizer for Solar energy Conversion and Storage: Bismark brown – Oxalic acid system

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Abstract: An efficient photogalvanic cell containing oxalic acid as an electron donar, a dye Bismark brown as photosensitizer has been investigated for solar energy and storage. The photopotential, photocurrent and power generated by the photogalvanic cell were 888.0mV, 620.0µA and 550.0 µW respectively. The determined conversion efficiency of cell was determined as 0.4704% and fill factor was 0.557. The current voltage characteristics of the cell have also been studied. The effect of diffusion parameters on the electrical output of the cell was investigated and a mechanism for the generation of photocurrent in this photogalvanic cell has also been proposed.

Key Words: Current-Voltage characteristics, Fill Factor, Conversion Efficiency.

1. Introduction

All activity requires energy can be obtained from two types of sources- renewable and non renewable. Non- renewable sources are fossil fuels, coal, crude oil, etc. Renewable sources are Sun radiations, wind, biomass, etc. Non- renewable sources are limited and polluting in nature. Sun is the most powerful source of energy. The solar energy can be harnessed through photogalvanic effect. The photogalvanic effect was first of all observed by Rideal and Willams[1] but it was systematically Studied by Rabinowitch[2,3]. Solar energy conversion and storage has also been studied by the Ramkumar et al[4,] Nozik[5], Bayer et al[6] , Miyasaka,[7] and Gratzel[8]. Optimum efficiency of photogalvanic cell for solar energy conversion has been studied by James et al[9]. Michael Gratzel[10-11]observed that solar energy can be directly stored by photocapacitor. Conversion of sun-light into electricity by dye sensitized solar cell have also been studied by Quing et al[12], Jana.[13,] Trupke et al [14], Herve et al[15] , Hao et al.[16],and koumura et al.[17].

A low cost and high efficiency dye sensitized solar cell based on TiO_2 films have been studied by Burke et al.[18] Control mechanism of charge transfer and recombination in dye sensitized solar cell have been studied by Hegberg et al.[19], Margaret et al.[20], and Blijnyuke et al.[21].

Characteristics of high efficiency dye sensitized solar cell studied by the Gangotri and Lal[22] showed the enhancement of the power output of solar cell consisting of mixed dye.

Gangotri and meena[23] have used EDTA as a reductant and mixed dye methylene blue and toluidine blue in photogalvanic effect. Gangotri and Lal[24-25] have used oxalic acid as a reductant and methylene blue as photosensitizer in the photogalvanic cell for solar energy conversion and storage.

Gangotri and Pramila[26] used anionic micelles in photogalvanic cell for solar energy conversion and storage. Suresh C. Ameta et. al.[27] used NaLS in photogalvanic cell for solar energy conversion and storage. Gangotri and C. Lal[28] have used EDTA as a reductant and methylene blue and thionine as photosensitizer in photogalvanic cell for solar energy conversion and storage. Genwa et.al[29].have comparatively studied the photogalvanic effect by using Toluidine Blue and Malackite Green as photosensitizer with Arabinose-NaLS system

2. Experimental

A mixture of photosensitizers - Bismark brown, Oxalic acid (Ranbaxy), and sodium hydroxide (s.d.fine) were used in the present work. All solutions were prepared in doubly distilled water and were kept in amber coloured containers to protect them from sunlight. A mixture of Bismark brown, Oxalic acid and sodium hydroxide was taken in an H-type glass tube. A platinum electrode (1.0 x 1.0 cm^2) was immersed in one limb of the H-tube and a saturated calomel electrode (SCE) was immersed in the other limb. 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 between bulb and H-Cell to cut off thermal radiations from reaching the cell.

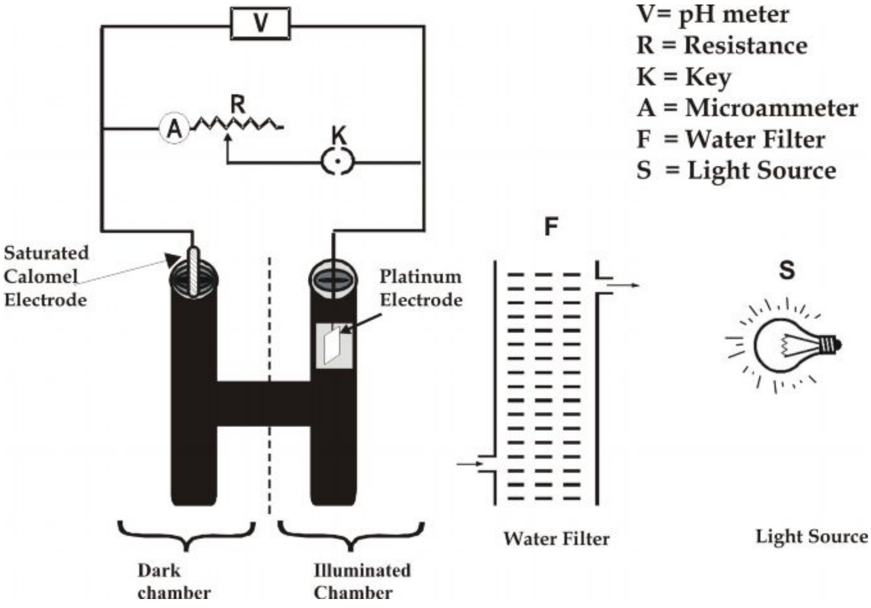
Photochemical bleaching of the dye was studied potentiometrically. A digital pH meter (Systronics 335) and a microammeter (INCO-65) were used to measure the potential and current generated by the system respectively. The current voltage characteristics were studied by applying an external load with the help of a carbon pot (log 470 K) connected in the circuit (**Figure- 1).**

3. Results and discussion

3.1 Effect of Variation of concentration of photosensitizer

In Bismark brown- Oxalic acid system it was observed that with the increase in the total concentration of the photosensitizer, the photopotential was found to increase till it reaches a maximum value. On further increase in the total concentration of photosensitizer, a decrease in the electrical output of the cell was observed.

The fall in power output was also resulted with decrease in concentration of dye due to less number of molecules available for electron donation to Pt electrode on the other hand the passage of radiations may be hindered by the higher concentration of mixed dyes to reach the electrode in the desired amount and it will also result in to a decrease in electrical output. The effect of variation of mixed photosensitizer concentration on the photopotential and photocurrent of system is given in table.1 and graphically represented in Figure 1.



Experimental set-up of photogalvnic cell

Table – 1 : Effect of Variation of Bismark Brown Concentration

[Bismark brown] = 3.28 x 10^{-5} M Light Intensity = 10.4 mW cm^{-2}
[Oxalic acid] = 2.64 x 10^{-3} Temperature = 303 K
PH = 12.74

Bismark brown- Oxalic acid - system	[Bismark brown] x 10^{-5} M				
	1.20	1.60	2.00	2.40	2.80
Photopotential (mv)	227.0	513.0	675.0	425.0	327.0
Photocurrent (μA)	50.0	75.0	130.0	110.0	60.0
Power (μW)	11.350	38.475	87.750	46.750	19.620

Table – 2 :Effect of Variation of Reductant (Oxalic Acid) Concentration

[Bismark brown] = 3.28 x 10^{-5} M Light Intensity = 10.4 mW cm^{-2}
Temperature=303K pH = 12.74

Bismark brown- Oxalic acid system	[Oxalic acid] x 10^{-3} M				
	2.52	2.60	2.64	2.68	2.72
Photopotential (mV)	778.0	845.0	888.0	838.0	785.0
Photocurrent(μA)	544.0	582.0	620.0	578.0	538.0
Power(μW)	423.23	491.79	550.56	484.36	422.33

Table – 3: Effect of Variation of pH

[Bismark brown] = 3.28 x 10^{-5} M Light Intensity = 10.4 Mw cm^{2}
[Oxalic acid] = 2.64 x 10^{-3}M Temperature = 303 K

Bismark brown- Oxalic acid system	PH				
	12.83	12.86	12.74	12.9	12.92
Photopotential (mV)	755.0	822.0	888.0	834.0	764.0
Photocurrent(μA)	535.0	588.0	620.0	578.0	528.0
Power(μW)	403.92	483.33	550.58	482.05	403.39

3.2 Effect of Variation of reductant (Oxalic acid) concentration

With the increase in concentration of the reductant the photopotential and photocurrent were found to increase until they reach a maximum value. On further increase in concentration of reductant the decrease in electrical output of the cell was found. The effect of variation of the reductant concentration on photopotential and photocurrent of is given in Table 2 and graphically Bismark brown- Oxalic acid system represented in Figure 2.

3.4 Effect of Variation of pH

Photogalvanic cell containing was found to be quite sensitive to pH of the Bismark brown- Oxalic acid system solution. The system shows an increase in the photopotential and photocurrent of the cell with increase in pH value (in alkaline range). At pH 12.88 a maxima was achieved. On further increase in pH, there was a decrease in photopotential and photocurrent. The effect of variation of pH on photopotential and photocurrent is given in table 3 and graphically represented in Figure 3.

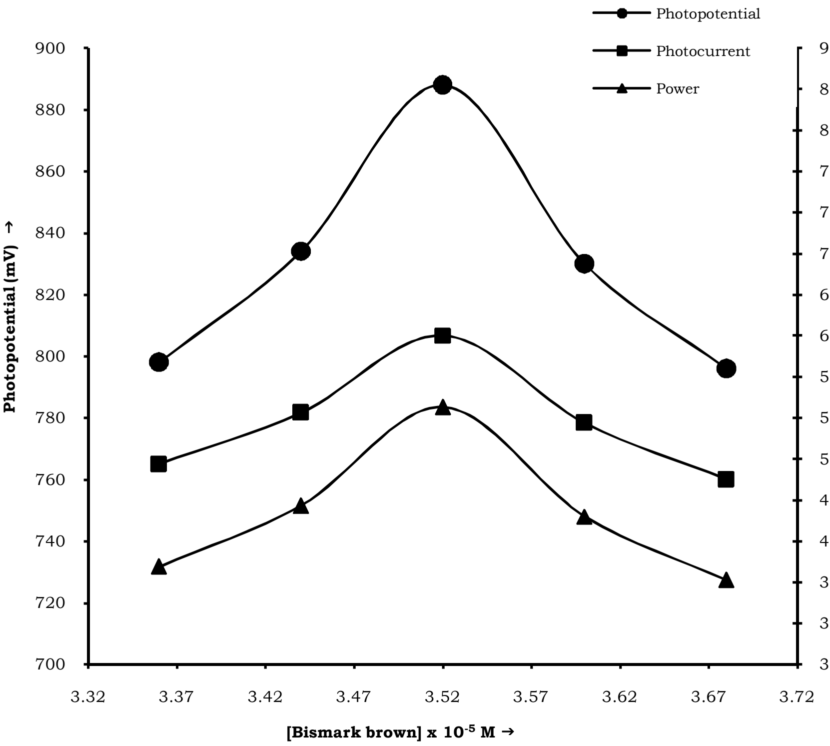


Fig. 1 VARIATION OF PHOTOPOTENTIAL, PHOTOCURRENT AND POWER WITH BISMARK BROWN CONCENTRATION

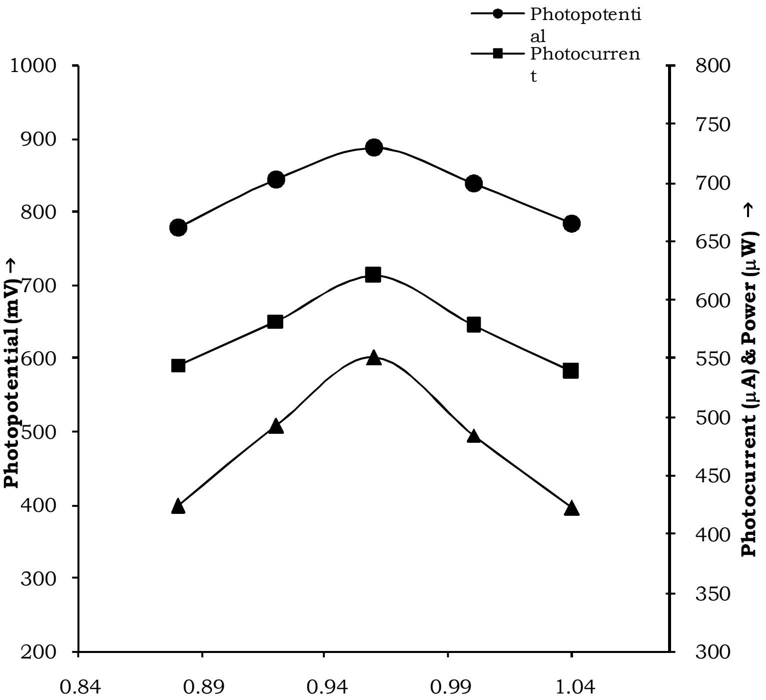


Fig. 2 VARIATION OF PHOTOPOTENTIAL, PHOTOCURRENT AND POWER WITH OXALIC ACID CONCENTRATION

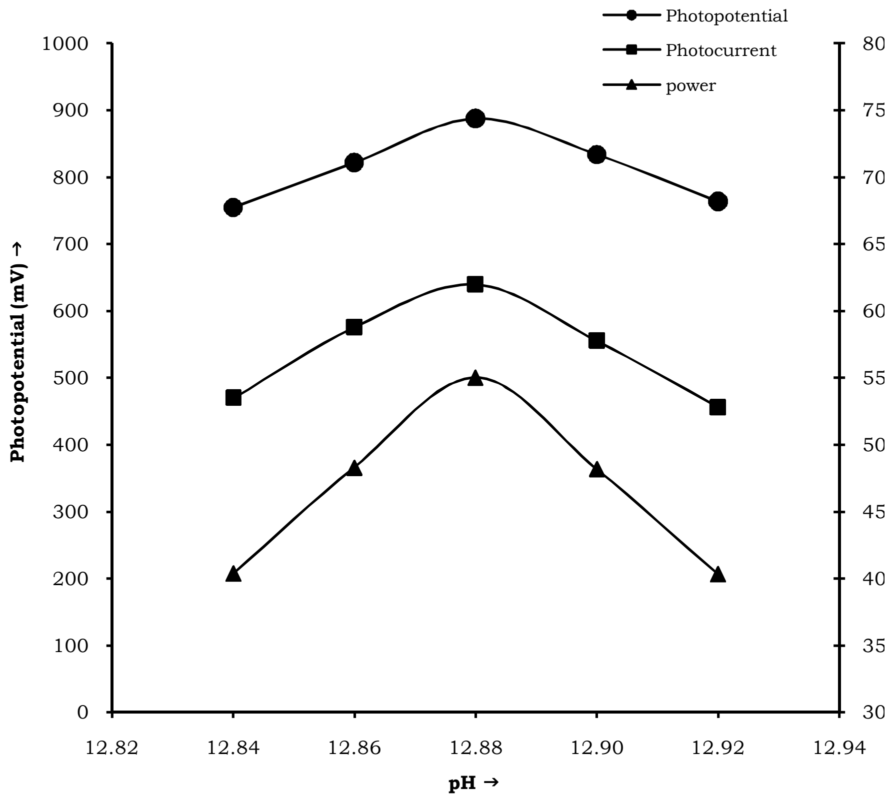


Fig. 3 VARIATION OF PHOTOPOTENTIAL, PHOTOCURRENT POWER WITH pH

3.5 i-V Characteristics of the Cell

The short circuit current (i_{sc}) and open circuit voltage (V_{oc}) of the cells were measured with the help of a microammeter (keeping the circuit closed) and with a digital pH meter (keeping the other circuit open), respectively. The current and potential values in between these two extreme values were recorded with the help of a carbon pot (log 470 K) connected in the circuit of micro-ammeter, through which an external load was applied. The i-V characteristics of the cell containing Bismark brown- Oxalic acid system is given in table 4 and graphically represented in Figure 4.

It was observed that i-V curve deviated from their regular rectangular shapes. A point in i-V curve, called power point was determined where the product of current and potential was maximum and the fill factor was calculated as 0.557 using the formula:-

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

Where V_{pp} and i_{pp} represent the value of potential and current at power point respectively.

3.6 The performance of the photogalvanic cell

The performance of the photogalvanic cell was observed by applying an external load (necessary to have current at power point) after termination the illumination as soon as the potential reaches a constant value. The performance was determined in terms of $t_{1/2}$, (fig. 6) i.e., the time required in fall of the output (power) to its half at power point in dark. It was observed that the cell can be used in dark for 65.0 minutes. The results are summarised in table 5 and is graphically represented in Figure 5.

3.7 Conversion Efficiency

The conversion efficiency of the cell was determined as 0.4704 % using the following formula:

$$\text{Conversion efficiency} = \frac{V_{pp} \times i_{pp}}{10.4 mWcm^{-2}} \times 100\%$$

................(2)

Table – 4: Current-Voltage (i-V) Characteristics of the Cell

[Bismark brown] = 3.28×10^{-5} M Light Intensity = 10.4 Mw cm^2
[Oxalic acid] = 2.64×10^{-4}M Temperature = 303 K
PH=12.74

Potential * (mV)	Photocurrent (μA)	Fill Factor (η)
1072.0	0.0	
1066.0	10.0	
1053.0	20.0	
1037.0	30.0	
1013.0	40.0	
1008.0	50.0	
999.0	60.0	
981.0	70.0	
963.0	80.0	
957.0	90.0	
933.0	100.0	
922.0	110.0	
903.0	120.0	
883.0	130.0	
863.0	140.0	
854.0	150.0	
848.0	160.0	
838.0	170.0	
812.0	180.0	
790.0	190.0	
782.0	200.0	
758.0	210.0	
738.0	220.0	
724.0	230.0	
719.0	240.0	
702.0	250.0	
668.0	260.0	
653.0	270.0	
642.0	280.0	
623.0	290.0	
604.0	300.0	
592.0	310.0	
582.0	320.0	
578.0	330.0	
560.0	340.0	
559.0	350.0	0.557
528.0	360.0	
478.0	370.0	
459.0	380.0	
440.0	390.0	
422.0	400.0	
408.0	410.0	
398.0	420.0	
379.0	430.0	
353.0	440.0	
333.0	450.0	
319.0	460.0	
282.0	470.0	
268.0	480.0	

243.0	490.0
223.0	500.0
217.0	510.0
203.0	520.0
190.0	530.0
160.0	540.0
140.0	550.0
123.0	560.0
111.0	570.0
93.0	580.0
81.0	590.0
78.0	600.0
62.0	610.0
0.00	620.0

*** Absolute Values.**

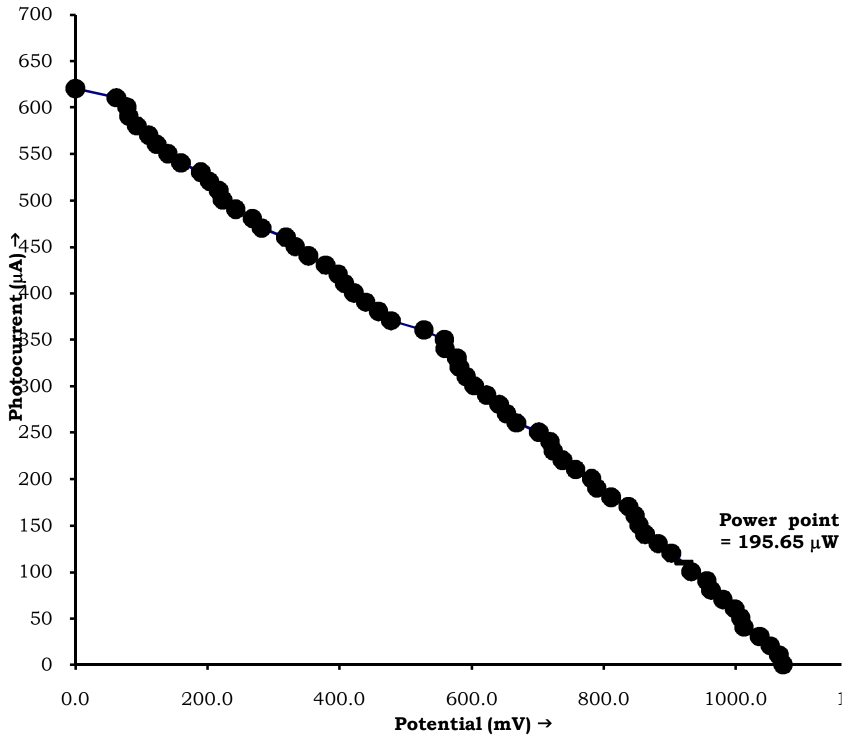


Fig. 4 CURRENT-VOLTAGE (i-V) CURVE OF THE CELL

4. Mechanism

On the basis of above investigations the mechanism of the photocurrent generation in the photogalvanic cell may be proposed as follows:

Illuminated Chamber

$$\text{Dye} \longrightarrow \text{Dye}^* \qquad \text{...... (i)}$$

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

At platinum electrode :

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

Dark Chamber

At counter electrode:

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

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

Here Dye, Dye $^-$, R and R^+ are the dye, its leuco form, reductant and its oxidized form, respectively.

Table – 5: Performance of the cell

[Bismark brown] = 3.28 x 10^{-5} M Light Intensity = 10.4 Mw cm^2
[Oxalic acid] = 2.64 x 10^{-3}M Temperature = 303 K
PH=12.74

Time (Min)	Power (μW)
0.0	195.65
5.0	168.98
10.0	158.79
15.0	146.52
20.0	141.70
25.0	130.20
30.0	124.44
35.0	121.50
40.0	117.11
45.0	111.36
50.0	108.30
55.0	104.72
60.0	101.20
65.0	96.93
70.0	93.28
75.0	91.37
80.0	89.32
85.0	87.15
90.0	85.25

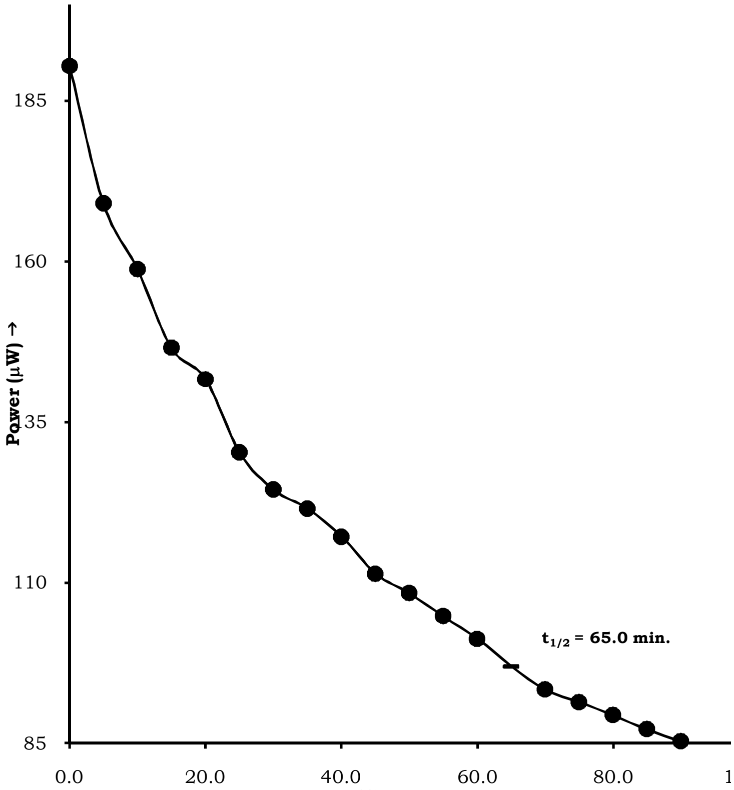


Fig. 5 PERFORMANCE OF THE CELL

5. Conclusion

Scientists have been studying the harvesting of solar energy in various forms of solar cells like photoelectrochemical, photovoltaic and photogalvanic cells. Photovoltaic cells are widely used in most countries for conversion and storage of solar energy but owing to their nil storage capacity, photogalvanic cells are emerging as thrust research area as they have the added advantage of inherent storage capacity. The use of photosensitizer Bismark brown - Oxalic acid System not only enhances the electrical output of the cell but also increases the conversion efficiency and storage capacity in comparison to the photogalvanic cell using single photosensitizer. Efforts will be made in future to make it more efficient.

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