Use of Surfactant in Photogalvanic Cell for Solar Energy Conversion and Storage: TX-100-Glycerol-Azure-C System

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The photovoltaic cells involve direct excitation of an electron by a photon and thus producing electricity. The photovoltaic cells have high conversion efficiency but lack of storage capacity whereas the photogalvanic cells are based on some chemical reactions which give rise to high energy products on excitation by photon and these energy-rich products lose energy electrochemically. The efforts have been made to rich a desired amount of conversion efficiency and storage capacity by the addition of surfactants. The photogalvanic cells containing glycerol as reductant. Azure-C as photosensitizer and Triton X-100 as neutral surfactant have been investigated for solar energy and storage. The photopotential, photocurrent and power generated by this photogalvanic cell were 675.0 mV, 130.0 μA and 87.750 μW respectively. The conversion efficiency of the cell was determined as 0.4704% and fill factor was 0.4351. The current voltage characteristics of the cell have also been studied. The effect of different parameters of electrical output of the cell was investigated and a mechanism for the generation of the photocurrent in this photogalvanic cell has also been proposed.

Key Words: Photogalvanic cell, Solar energy, Triton-X-100-Glycerol-Azure-C.

INTRODUCTION

Growing industrial activity and rising standard of living throughout the world make an increase in consumption of energy. This process leads to rapid exhaustion of the natural sources like oil, petrol, diesel, coal and natural gas. This has created a situation of energy crisis on one hand and increasing global warming and environmental pollution on the other as well. The conversion of solar energy into electricity has attracted the attention of scientists all over the globe to meet the existing challenge of energy crisis with renewable source of energy, having promising future prospects and polluting devices.

Solar energy fits the bill to meet all requisite situations and some solar cells like photovoltaic cells, photoelectrochemical cell, photogalvanic cell etc. have been developed.

Photogalvanic effect was first discovered in 1925 by Rideal and Williams¹,

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376 Gunsaria et al. Asian J. Chem.

but it was systematically investigated by Rabinowitch²⁻³. Later o,n this kind of work was followed by various workers⁴⁻¹¹. Various problems of this field have been discussed by Hoffman and Lichtin¹². Theoretical conversion efficiency of a photogalvanic cell is about 18% but the observed conversion efficiency is quite low. The back electron transfer, lower stability of dyes, aggregation of dye molecules around the electrode, etc. are the possible main reasons for this drawback.

A detailed survey of the literature reveals the photogalvanic cells¹³⁻²⁴ have been prepared with different systems. In order to increase the conversion efficiency and storage capacity of photogalvanic cells, a neutral surfactant Triton X-100 has been used with Azure-C and glycerol in the present work.

EXPERIMENTAL

Glycerol (Ranbaxy), Azure-C (Sigma) and NaOH (Qualigens) were used in the present work. All the solutions were prepared in doubly distilled water. A mixture of solutions of Triton X-100, glycerol, Azure-C and sodium hydroxide was taken in an H-type cell. Platinum electrode (1 × 1 cm²) was dipped in one limb of the cell and saturated calomel electrode (SCE) in the other. The whole system was first placed in the dark until a stable potential was obtained and then the platinum electrode was exposed to a 200 W tungsten lamp (Sylvania) and the other limb containing SCE was kept in the dark as a reference electrode and connected with digital pH-meter (Agronic model 511) and micrometer (Osaw, India) through a key and resistance to keep the circuit close and open devices and ultimately magnified with solar radiations. The i-V characteristics in the circuit were determined to get a complete picture of conversion of chemical energy into electrical energy.

RESULTS AND DISCUSSION

Effect of variation of neutral surfactant (TX-100) concentration

The effect of variation of neutral surfactant (TX-100) concentration was investigated in TX-100. glycerol-Azure-C system. It was observed that electrical output of the cell was found to increase on increasing the concentration of neutral surfactant reaching a maximum value. On further increase in their concentration, a fall in photopotential, photocurrent and power of the photogalvanic cell was observed.

The possible reason for lowering in electrical output on higher and lower concentrations of surfactant is due to its most active form around its critical micelle concentration. It was found that a maximum electrical output was obtained at 2.0×10^{-4} M concentration of neutral surfactant (TX-100) because two important factors are responsible: first may be due to the better stabilization of dye molecules by neutral surfactant because Azure-C is cationic in nature. Secondly, the molecules by natural surfactant will drastically increase the probability of photo-ejection of electrons from micelle aggregates into the aqueous phase. The obtained results are given in Table-1 and graphically represented in Fig. 1.

It is clear from all the tables that electrical output increases around the critical micelle concentration (CMC) of the surfactant.

TABLE-1 EFFECT OF VARIATION OF NEUTRAL SURFACTANT (TX-100) CONCENTRATION

[Azure-C] = 3.28×10^{-5} M	$[Glycerol] = 2.64 \times 10^{-3} M$
pH = 12.74	Light intensity = 10.4 mW cm^{-2}
•	Temp. = 303 K

$[TX-100] \times 10^{-4} M$	Photopotential (mV)	Photocurrent (µA)	P ow er (µW)
1.2	227.0	50.0	11.350
1.6	513.0	75.0	38.475
2.0	675.0	130.0	87.750
2.4	425.0	110.0	46.750
2.8	327.0	60.0	19.620

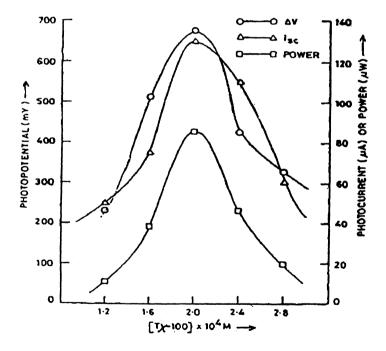


Fig. 1. Variation of photopotential, photocurrent and power with [TX-100] concentration

Effect of variation of reductant [glycerol]

The decrease in reductant concentration resulted into fall in photopotential and photocurrent due to low electron donating activity by the number of reductant molecules available. Further, increase in the concentration of reductant and electrical output was not increased but decreased. Glycerol has a large number

of molecules at higher concentration and fewer number of molecules at lower concentration does not pursue the electron donation to the dye molecules. The results were summarized in Table-2.

TABLE-2
EFFECT OF VARIATION OF REDUCTANT (GLYCEROL) CONCENTRATION

$[Azure-C] = 3.28 \times 10^{-5} M$	$[TX-100] = 2.00 \times 10^{-4} M$
pH = 12.74	Light intensity = 10.4 mW cm^{-2}
•	Temp. = 303 K

[Glycerol] × 10 ⁻³ M	Photopotential (mV)	Photocurrent (µA)	Power (µW)
2.52	232.0	80.0	18.560
2.60	442.0	110.0	48.620
2.64	675.0	130.0	87.750
2.68	532.0	70.0	37.240
2.72	417.0	55.0	22.935

Effect of variation of dye [Azure-C]

The decrease in dye concentration resulted into fall in electrical output of the cell due to fewer number of dye molecules available for the excitation and consecutive donation of the electrons to the platinum electrode.

Higher concentration of dye resulted into a decrease in electrode output as the intensity of light reaching the dye molecule near the electrode decreases due to absorption of light by dye molecules present in the path, thus not permitting the desired intensity to reach the dye near the electrode. The results are presented in Table-3.

TABLE-3
EFFECT OF VARIATION OF DYE (AZURE-C) CONCENTRATION

$[TX-100] = 2.00 \times 10^{-4} M$	$[Glycerol] = 2.64 \times 10^{-3} M$
pH = 12.74	Light intensity = 10.4 mW cm^{-2}
	Temp. = 303 K

[Azure C] \times 10 ⁻⁵ M	Photopotential (mV)	Photocurrent (µA)	Power (µW)
3.04	344.0	65.0	22.360
3.20	517.0	55.0	43.945
3.28	675.0	130.0	87.750
3.36	343.0	75.0	25.725
3.44	220.0	40.0	8.800

Effect of variation of pH

It was observed that the photogalvanic cell containing TX-100-glycerol-Azure-C is very sensitive to pH value and a maximum value of electrical output at

pH = 12.74 was obtained. The optimum condition for each system has a relation with the nature of neutral surfactant. This may be due to the availability of the reductant glycerol in a better form. The observations are summarized in Table-4.

TABLE-4 EFFECT OF VARIATION OF pH

[Azure C] = 3.28×10^{-5} M	[
$[TX-100] = 2.00 \times 10^{-4} M$	I
pH = 12.74	

 $[Glycerol] = 2.64 \times 10^{-3} M$ Light intensity = 10.4 mW cm^{-2} Temp. = 303 K

рН	Photopotential (mV)	Photocurrent (µA)	Power (µW)
12.62	372.0	90.0	33.480
12.68	540.0	100.0	54.000
12.74	675.0	130.0	87.750
12.80	414.0	80.0	33.120
12.85	388.0	65.0	25.220

Effect of diffusion path length

The effect of variation of diffusion length (distance between the two electrodes) on the current parameters of the cell (i_{max}, i_{eq}) and rate of the initial generation of photocurrent) was studied using H-cell of different dimensions.

It was observed that there was a sharp increase in photocurrent i_{max} in the first few minutes of illumination and then there was a gradual decrease to a stable value of photocurrent. This photocurrent at equilibrium is represented as (ieq). This kind of photocurrent behaviour is an initial rapid reaction followed by a slow rate determining step at a large stage. The results are summarized in Table-5.

TABLE-5 EFFECT OF DIFFUSION LENGTH

$[Azure-C] = 3.28 \times 10^{-5} M$
$[TX-100] = 2.00 \times 10^{-4} M$
pH = 12.74

[Glycerol] = $2.64 \times 10^{-3} \text{ M}$ Light intensity = 10.4 mW cm^{-2} Temp. = 303 K

Diffusion length DL (mm)	Maximum photocurrent i _{max} (μA)	Equilibrium photocurrent i _{eq} (µA)	Rate of initial generation of photocurrent (µA min ⁻¹)
35.0	165.0	140.0	10.5
40.0	175.0	134.0	10.8
45.0	185.0	130.0	11.5
50.0	195.0	125.0	₂ 12.0
55.0	200.0	120.0	12.5

Current voltage (i-V) characteristics of the cell

The short circuit (i_{sc}) and open circuit (V_{oc}) of the photogalvanic cell were

measured with a micrometer (circuit closed) and with a digital pH-meter (circuit open), respectively. The current and potential values in between these two extreme values (V_{∞} and i_{sc}) were recorded with the help of a carbon pot (log 470k) connected into micrometer through which an external load was applied.

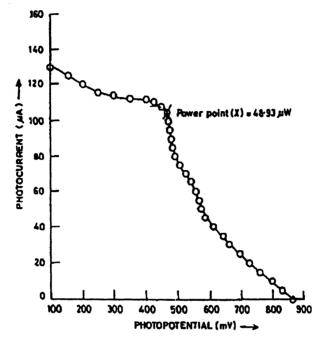


Fig. 2. Current potential (i-V) curve of the cell

It was observed that i-V curve deviated from its ideal regular rectangular shape. A point on the i-V curve, called power point (pp), was determined where the product of potential and current was maximum and the corresponding values of potential and current V_{pp} and i_{pp} respectively, with the help of i-V curve as graphically represented in Fig. 2, the fill factor was determined as 0.4351 using the formula:

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

on the basis of the optimum conditions the system was directly exposed to sunlight and conversion data are summarized compared with the result when cell contains no surfactant.

Conversion efficiency

With the help of current and potential values at power point and the incident power of radiations the conversion efficiency of the cell was determined as 0.4704% using the formula

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

Sunlight conversion data with surfactant and without surfactant are given in Table-6.

TABLE-6 CONVERSION EFFICIENCY AND SUNLIGHT CONVERSION DATA

$[Azure-C] = 3.28 \times 10^{-5} M$	[Glycerol] = $2.64 \times 10^{-3} \text{ M}$
$[TX-100] = 2.00 \times 10^{-4} M$	Light intensity = 10.4 mW cm^{-2}
pH = 12.74	Temp. = 303 K

TX-100-glycerol- azure-C system	Conversion efficiency (%)	Sunlight conversion data	
		Photopotential (mV)	Photocurrent (µA)
Triton X-100	0.4704	1500.0	365.0
No surfactant	0.2839	540.0	180.0

Performance of the cell

The performance of the cell was studied by applying the external load necessary to have the current and potential at the power point after removing the source of light. It was observed that the cell can be used in the dark for 38 min only, whereas in absence of surfactant the cell can be used only for 25 min. It is graphically given in Fig. 3.

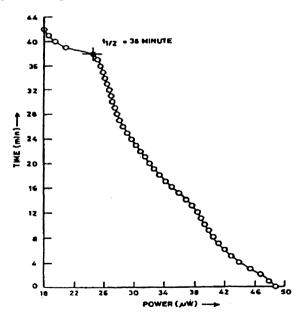


Fig. 3. Performance of the cell

Electroactive Species

On illumination there was a rapid fall in potential and after some time a

constant value was obtained (on removing the source of light). The change in potential was reversed but it never reached the initial value. It suggests that the main reversible photochemical reaction is also accompanied by an irreversible side reaction. Electroactive species are the dyes and leuco or semi-dyes at the illuminated and dark electrodes respectively.

According to observed results the most probable rate determining process for (i_{eq}) should be the recycling reaction of oxidation product (of the reducing agent) and the semi or leuco-dye (photosensitizer). Some experimental evidences have been obtained by Wyart Remy *et al.*²⁵ and Wildes and Lichtin²⁶ in favour of participation of leuco form of the dye as electroactive species. The various combination actions of electroactive species are given in Table-7.

TABLE-7

In illuminated chamber	In dark chamber.
Dye	Oxidized form of the reductant (R ⁺)
Luco or semi-dye	Oxidized form of the reductant (R ⁺)
Luco or semi-dye	Dye

Mechanism

On the basis of the above investigation, photocurrent generation in the photogalvanic cell²⁷ can be proposed as follows and the mechanism of the photocurrent generation in the photogalvanic cell is represented in Fig. 4 also.

Illuminated chamber

$$AC \xrightarrow{hv} AC^*$$

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

At platinum electrode

$$AC^- \longrightarrow AC + e^-$$

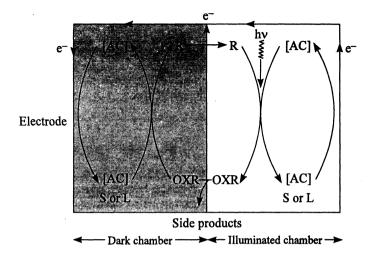
Dark chamber

$$AC + e^{-} \longrightarrow AC^{-}$$
 (semi or leuco)
 $AC^{-} + R^{+} \longrightarrow AC + R$

when AC, AC⁻, R and R⁺ are Azure-C, leuco or semi-leuco form of Azure-C, reductant and oxidized form of reductant (glycerol), respectively.

Conclusion

The photogalvanic cell containing neutral surfactant. Triton X-100 has not only increased the conversion efficiency but also increased the storage capacity to a remarkable extent.



[AC] = Azure-C [AC]_{S or L} = Semi or leuco form; R = Reductant; OxR = Oxidized form of reductant

Fig. 4. Mechanism for photocurrent generation in photogalvanic cell

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384 Gunsaria et al. Asian J. Chem.

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