

USE OF MICELLES IN PHOTOGALVANIC CELL FOR SOLAR ENERGY CONVERSION AND STORAGE: TOLUIDINE BLUE–GLUCOSE–CETYL PYRIDINIUM CHLORIDE SYSTEM

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INTRODUCTION

Becquerel [1, 2] first observed in 1839 the flow of current between two unsymmetrical illuminated metal electrodes in sunlight. The photogalvanic effect was first reported by Rideal and Williams [3], but it was systematically investigated by Rabinowitch [4, 5]. Hoffman and Lichtin [6] have discussed various problems encountered in the development of this field.

A detailed literature survey reveals that different photosensitizers [7–22] have been used in photogalvanic cells, but no attention has been paid to the use of the toluidine blue–glucose–CPC system in photogalvanic cells for solar energy conversion and storage. Therefore, the present work was undertaken.

EXPERIMENTAL

Toluidine blue (LOBA), glucose (LOBA), cetyl pyridinium chloride (SISCO), and sodium hydroxide (s.d. fine) were used in present work. All the solutions were prepared in doubly distilled water and were kept in amber colored containers to protect them from sunlight. A mixed solution of toluidine blue, glucose sodium hydroxide, and cetyl pyridinium chloride was placed in an H-type glass tube. A platinum electrode ($1.0 \times 1.0 \text{ cm}^2$) was immersed in one arm of the H-tube and a saturated Calomel electrode (SCE) was kept in the other arm. The arm containing the SCE was kept in the dark, and the platinum electrode was exposed to a 200 W tungsten lamp. A water filter was used to cut off infra-red radiations.

The photochemical bleaching of toluidine blue was studied potentiometrically. A digital pH meter (Agronic Model 511) and a microammeter (OSAW, India) were used to measure the potential and current generated by the system, respectively.

EFFECT OF VARIATIONS

The effects of variations in the concentrations of cetyl pyridinium chloride (cationic surfactant), toluidine blue, and glucose on the electrical output of the cell have been observed and the effect of variation of pH and diffusion length have been also studied. These results summarized in Table 1(a) and (b).

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CURRENT-VOLTAGE (*I-V*) CHARACTERISTICS AND CONVERSION EFFICIENCY

It was observed that the *I-V* curve of the cell deviated from its regular rectangular shape. A point on the *I-V* curve called the power point (PP) was determined where the product of potential and current was maximum. The value of potential and current at the power point are represented as V_{pp} and I_{pp} respectively. With the help of the *I-V* curve, the fill factor, and the conversion efficiency of the cell were determined as 0.28 and 0.0433% respectively, using the following formulae:

$$\text{Fill factor} = \frac{V_{pp} \times I_{pp}}{V_{oc} \times I_{sc}}$$

$$\text{Conversion of efficiency} = \frac{V_{pp} \times I_{pp}}{10.4 \text{ mW cm}^{-2}} \times 100\%$$

where V_{pp} , I_{pp} , V_{oc} , and I_{sc} are the potential at power point, current at power point, open circuit voltage, and short circuit current respectively.

Table 1(a). Effect of Variation on T B-Glucose-CPC System.

Light Intensity = 10.4 mW cm ⁻²		Temperature = 303 K		
Variations	Concentration (M)	Photopotential (mV)	Photocurrent (μA)	Power (μW)
CPC	4.0 × 10 ⁻⁴	211.00	35.00	7.88
	5.6 × 10 ⁻⁴	237.00	40.00	9.48
	6.8 × 10 ⁻⁴	222.00	30.00	6.66
TB	2.5 × 10 ⁻⁵	213.00	30.00	6.39
	3.2 × 10 ⁻⁵	237.00	40.00	9.48
	3.5 × 10 ⁻⁵	220.00	36.00	7.92
Glucose	1.5 × 10 ⁻³	234.00	37.00	8.65
	2.0 × 10 ⁻³	237.00	40.00	9.48
	2.5 × 10 ⁻³	211.00	31.00	6.54
pH	10.80	187.00	35.00	6.54
	11.20	237.00	40.00	9.48
	11.30	230.00	37.00	8.51

Table 1(b)

Variations in Diffusion Length (mm)	Maximum Photocurrent (μA) I_{max}	Equilibrium Photocurrent (μA) I_{eq}	Rate of Initial Generation of Current (μA min ⁻¹)
40.00	55.00	42.00	10.80
45.00	56.00	40.00	11.20
50.00	57.00	43.00	11.50

CELL PERFORMANCE

The performance of the cell was studied by applying the external load necessary to maintain current and potential at the power point after removing the source of light until the output (power) fell to half its value at the power point in the dark. It was observed that the cell can be used in the dark at its power point for five minutes.

ROLE OF MICELLES

Alkaitis *et al.* [23] have studied the photoejection of electron from dye-surfactant system suggesting tunneling of photoelectrons from micellar phase to aqueous phase whereas Bhowmik *et al.* [24] have suggested a probability of some charge transfer between micelle and a dye. The usefulness of micelles [25] in photogalvanic cells with respect to their nature have been investigated and found to follow the order anionic micelle > neutral micelle > cationic micelle.

Not only has the conversion efficiency of the cell been enhanced in the presence of an anionic micelle but the cell performance also increased up to a reasonable extent.

The used cetyl pyridinium chloride solublizes the dye more easily and stabilizes the system and may increase the probability of charge transfer between micelle and the dye in the system.

ELECTROACTIVE SPECIES

Various probable processes may be considered for the photo-current generation in photogalvanic cells. The results of the effect of diffusion length [26] on current parameters were utilized to know more about the electroactive species. The possible combinations for electroactive species in photogalvanic cell are tabulated as under.

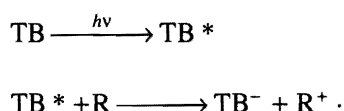
Possible Combinations for Electroactive Species	
In Illuminated chamber	In Dark chamber
TB	Oxidized form of reductant (R ⁺)
Leuco or Semi-TB	Oxidized form of reductant (R ⁺)
Leuco or Semi-TB	TB

The oxidized form of the reductant is formed only in the illuminated chamber and if it is considered to be the electroactive species in the dark chamber, then it must diffuse from the illuminated chamber to the dark chamber to accept an electron from the electrode. As a consequence, the maximum photocurrent (I_{\max}) and rate of increase in photocurrent should decrease with an increase in diffusion length, but this was not observed experimentally. The value I_{eq} was also observed to be independent with respect to change in diffusion length (rather, it decreases slightly). Therefore, it may be concluded that the main electroactive species are the leuco or semi-TB and the dye TB in illuminated chamber and dark chamber, respectively. However, the reductant and its oxidized products act only as electron carrier in the path.

MECHANISM

On the basis of the above investigations the mechanism of the photo-current generation in the photogalvanic cell can be proposed as follows:

Illuminated Chamber

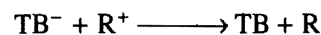


at electrode



Dark Chamber

At electrode



where TB, TB⁻, R, and R⁺ are the toluidine blue, its leuco form reductant and its oxidized form, respectively.

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