ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 123 (1999) 93–97

Journal of Photochemistry and Photobiology A:Chemistry

Use of micelles in photogalvanic cells for solar energy conversion and storage: cetyl trimethyl ammonium bromide-glucose-toluidine blue system

K.M. Gangotri*,[1], R.C. Meena, Rajni Meena

Department of Chemistry, Jai Narain Vyas University, Jodhpur 342005, Rajasthan, India

Received 12 January 1997; received in revised form 25 December 1998; accepted 3 February 1999

Abstract

Photogalvanic effect was studied in photogalvanic cell containing cetyl trimethyl ammonium bromide as micellar species, glucose as reductant and toluidine blue as photosensitizer. The photopotential and photocurrent generated were 175 mV and 35 μA, respectively. The observed conversion efficiency was 0.0578% and the maximum power of cell was 6.26 μW. The storage capacity of the cell was 6 min in dark. The effect of different parameters on electrical output of the cell was observed and a mechanism has also been proposed for the generation of photocurrent in photogalvanic cells. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cetyl trimethyl ammonium bromide; Fill factor; Conversion efficiency; Power point

1. Introduction

The photogeneration of electricity has attracted attention of scientists as viable media for solar energy conversion with a bright future prospects.

Becquerel [1,2] first observed in 1839 the flow of current between two unsymmetrical illuminated metal electrodes in sunlight. The photogalvanic effect was first of all reported by Rideal and Williams [3] but it was systematically investigated by Rabinowitch [4,5]. Later on Kaneka and Yamada [6], Murthy et al. [7], Rohtagi Mukherjee et al. [8], Ameta et al. [9–11] and Gangotri et al. [12–14] have reported some interesting photogalvanic systems. Theoretical conversion efficiency of photogalvanic cell is about 18% but the observed conversion efficiencies are quite low due to low stability of dyes, back electron transfer, aggregation of dye molecules around electrodes etc. Hoffman and Lichtin [15] have discussed various problems encountered in the development of this field.

A detailed literature [16–27] survey reveals that different photosensitizers and reductants have been used in photogalvanic cells, but no attention has been paid to use of the CTAB–toluidine blue–glucose system in the photogalvanic cell for solar energy conversion and storage. Therefore, the present work was undertaken.

2. Experimental

Cetyl trimethyl ammonium bromide (SISCO), glucose (LOBA), toluidine blue (LOBA), 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 coloured containers to protect them from sunlight. A mixture of solutions of CTAB, glucose, toluidine blue and sodium hydroxide was taken in an H-type glass tube. A platinum electrode ($1.0 \times 1.0\,\mathrm{cm}^2$) was immersed into one arm of the H-tube and a saturated calomel electrode (SCE) was kept in the other. The whole system was first placed in dark till a stable potential was obtained, then 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.

---

*Corresponding author.

[1] Pressent address: C-38 University Jaswant Campus, Jodhpur 342001, Rajasthan, India.

1010-6030/99/$ – see front matter © 1999 Elsevier Science S.A. All rights reserved.

PII: S1010-6030(99)00034-9

Table 1
Effect of variation of (cetyl trimethyl ammonium bromide] concentration)

(TB.) = 3.20×10^{-5} M; pH = 11.4; Temp = 303 K	(Glucose) = 2.00×10^{-3} M; Light intensity = 10.4 mW cm^{-2}				
	(CTAB) × 10^{-3} M				
	0.92	1.20	1.60	2.00	2.50
Photopotential (mV)	145.0	162.0	179.0	178.0	160.0
Photocurrent (μA)	25.0	30.0	35.0	33.0	29.0
Power (μW)	3.62	4.86	6.26	5.87	4.64

3. Results and discussion

3.1. *Effect of variation of (cetyl trimethyl ammonium bromide) concentration*

It was observed that electrical output of the cell was found to increase on increasing the concentration of surfactant (micellar species) reaching a maximum value. On further increase in their concentration, fall in photopotential, photocurrent and power of the photogalvanic cell was observed and it is summarized in Table 1.

3.2. *Effect of variation of pH*

The electrical output of the cell was affected by the variation in pH of the system. It is observed from Table 2 that there is an increase in electrical output of the cell with the increase in pH values. At pH 11.4 a maxima was obtained. On further increase in pH, there was a decrease in photopotential and photocurrent. Thus, photogalvanic cells containing the cetyl trimethyl ammonium bromide-glucose-toluidine blue system were found to be quite sensitive to the pH of the solutions.

It was observed that the pH for the optimum condition has a relation with pKa of the reductant and the desired pH is higher than its pKa value (pH > pKa). The reason may be the availability of reductant in its anionic form, which is a better donor form.

3.3. *Effect of variations of (glucose) concentration*

The electrical output of the cell was affected by the variation of reducing agent concentration (glucose) in the system; the results are summarized in Table 3.

Lower concentrations of reducing agents resulted in a fall in electrical output because fewer reducing agent molecules were available for electron donation to dye molecules.

Large concentration of reducing agent again resulted into a decrease in electrical output, because the large number of reducing agent molecules hinder the dye molecules reaching the electrode in the desired time limit.

3.4. *Effect of variation of (toluidine blue) concentration*

Dependence of photopotential and photocurrent on the concentration of dye was studied and the results are summarized in Table 4.

Lower concentration of dye resulted into a fall in photopotential and photocurrent because fewer dye molecules are available for the excitation and consecutive donation of the

Table 2
Effect of variation of pH

(TB.) = 3.20×10^{-5} M; Temp = 303 K	(CTAB) = 1.60×10^{-3} M		(Glucose) = 2.00×10^{-3} M; Light intensity = 10.4 mW cm^{-2}		
	pH				
	10.8	11.0	11.4	11.5	11.6
Photopotential (mV)	103.0	161.0	179.0	159.0	115.0
Photocurrent (μA)	18.0	30.0	35.0	29.0	15.0
Power (μW)	1.85	4.83	6.26	4.61	1.72

Table 3
Effect of variation of (glucose) concentration

(TB.) = 3.20×10^{-5} M; pH = 11.4	(CTAB) = 1.6×10^{-3} M (Glucose) × 10^{3} M		Light intensity = 10.4 mW cm^{-2}; Temp = 303 K		
	1.00	1.50	2.00	2.50	3.25
Photopotential (mV)	140.0	170.0	179.0	148.0	131.0
Photocurrent (μA)	26.0	29.0	35.0	31.0	24.0
Power (μW)	3.64	4.93	6.26	4.58	3.14

Table 4
Effect of variation of (toluidine blue) concentration

(Glucose) = 2.00 $\times 10^{-3}$ M; pH = 11.4	(CTAB) = 1.6 $\times$ 10^{-3} M (TB) $\times$ 10^{5} M		Light intensity = 10.4 mW cm^{-2}; Temp = 303 K		
	2.00	2.50	3.20	3.50	4.00
Photopotential (mV)	151.0	171.0	179.0	160.0	138.0
Photocurrent (μA)	29.0	33.0	35.0	30.0	22.0
Power (μW)	4.37	5.64	6.26	4.80	3.03

Table 5
Effect of diffusion length

(TB.) = 3.20 $\times$ 10^{-5} M; pH = 11.4	(CTAB) = 1.60 $\times$ 10^{-3} M		(Glucose) = 2.00 $\times$ 10^{-3} M; Light intensity = 10.4 mW cm^{-2}; Temp = 303 K
Diffusion path 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	44.0	36.0	8.5
40.0	45.0	36.0	8.7
45.0	46.0	35.0	9.2
50.0	47.0	34.0	9.6
55.0	47.0	34.0	9.8

electrons to the platinum electrode. The greater concentration of dye again resulted into a decrease in electrical output as the intensity of light reaching the dye molecule near the electrode decreases due to absorption of the major portion of the light by dye molecules present in path.

3.5. Effect of diffusion length

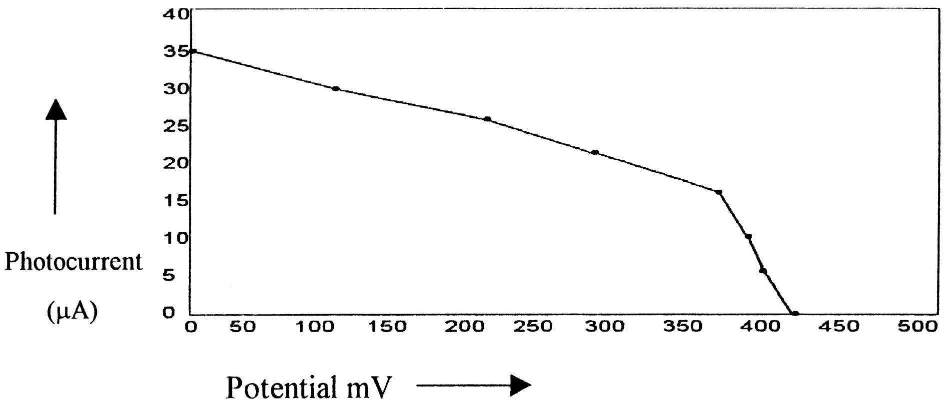
The effect of variation of diffusion length (distance between the two electrodes) on the current parameters of the cell was studied using H-cells of different dimension. The results are reported in Table 5.

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 (i_{eq}). This kind of photocurrent behaviour is an initial rapid reaction followed by a slow rate determining step at a later stage.

On the basis of the effect of diffusion path length on the current parameters, as investigated by Kaneko and Yamada [6] it may be concluded that the leuco or semi reduced form of dye, and the dye itself are the main electroactive species at the illuminated and the dark electrodes, respectively. However, the reducing agents and its oxidized products behave as the electron carriers in the cell diffusing through the path.

3.6. Current-voltage (i-V) characteristics and conversion efficiency

It was observed that i–V curve of the cell deviated from its regular rectangular shape as given in the figure.



Current-voltage (i-v) Curve of the Cell

Table 6
Conversion Efficiency and Sunlight Conversion Data

(TB)3.20×10^{-5} M; (glucose) 2.00×10^{-3} M; (CTAB) 1.60×10^{-3} M; pH = 11.4 Temp = 303 K; Light Intensity = 10.4 mW cm^{-2}	Conversion efficiency %	Sunlight conversion data	
		Photopotential (mV)	Photocurrent (µA)
Without micelle	0.0282	252.0	43.0
CTAB	0.0578	268.0	51.0

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 i–V curve the fill factor, and the conversion efficiency of cell were determined as 0.41 and 0.0578%, respectively, using the following formulae

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

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

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. The system (at its optimum condition) was exposed to sunlight. The conversion data for the photogalvanic cell is reported in Table 6.

3.7. 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) to its half 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 6 min.

4. Role of micelles

The usefulness of micelles [28] in photogalvanic cells with respect to their nature have been investigated and found to follow the order anionic micelle > neutral micelle > cationic micelle. Alkaties et al. [29] have studied the photoejection of electron from dye-surfactant system suggesting tunneling of photoelectrons from micellar phase to aqueous phase whereas Mukhopadhayay and Bhowmik [30] have suggested a probability of some charge transfer between micelle and a dye.

The photogalvanic cell containing toluidine blue and glucose (without micelles) shows the conversion efficiency 0.0282%, whereas the cetyl trimethyl ammonium bromide (micelles) have increased the conversion efficiency i.e., 0.0578% of the photogalvanic cells. The used cetyl trimethyl ammonium bromide solubilises the dye more easily and stabilizes the system and may increase the probability of charge transfer between micelle and the dye in the system.

Table 7
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

5. Electroactive species

Various probable processes may be considered for the photocurrent generation in photogalvanic cells. The results of the effect of diffusion length on current parameters were utilized to know more about the electroactive species. The possible combinations for electroactive species in photogalvanic cell are tabulated in Table 7.

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.

6. Mechanism

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

Illuminated chamber

Bulk solution

$$\mathrm{TB} \xrightarrow{h\nu} \mathrm{TB}^* \qquad (1)$$

$$\mathrm{TB}^* + \mathrm{R} \rightarrow \mathrm{TB}^- + \mathrm{R}^+ \qquad (2)$$

At electrode

$$\mathrm{TB}^- \rightarrow \mathrm{TB} + \mathrm{e}^- \qquad (3)$$

Dark chamber

At electrode

$$\mathrm{TB} + \mathrm{e}^- \rightarrow \mathrm{TB}^- \tag{4}$$

Bulk solution

$$\mathrm{TB}^- + \mathrm{R}^+ \rightarrow \mathrm{TB} + \mathrm{R} \tag{5}$$

Where TB, TB^-, R and R^+ are the toluidine blue and its leuco or semi leuco forms, reductant and its oxidized form, respectively.

Acknowledgements

The authors are grateful to the Professor and Head of the Department of Chemistry, Jai Narain Vyas University, Jodhpur for providing the necessary laboratory facilities. Thanks are also due to Shri Pooran Koli, Department of Chemistry for his critical discussions and Shri Shanker Lal Meena for interpretation of observations. Authors are thankful to the UGC for financial assistance.

References

[1] K. Becquerel, C.R. Acad. Sci. Paris 9 (1839) 14.
[2] K. Becquerel, C.R. Acad. Sci. Paris 9 (1839) 561.
[3] E.K. Rideal, D.C. Williams, J. Chem. Soc. 1925, 258.
[4] E. Rabinowitch, J. Chem. Phys. 8 (1940) 551.
[5] E. Rabinowitch, J. Chem. Phys. 8 (1940) 560.
[6] A. Kaneko, Yamada, J. Phys. Chem. 81 (1977) 1213.
[7] A.S.N. Murthy, H.C. Dak, K.S. Reddy, Int. J. Energy Res. 4 (1980) 339.
[8] K.K. Rohtagi Mukherjee, M. Roy, B.B. Bhowmik, Solar Energy 31 (1983) 417.
[9] S.C. Ameta, P.K. Jain, A.K. Janu, R. Ameta, The Energy J. (UK) 58 (1985) 8.
[10] S.C. Ameta, S. Khamsera, S. Lodha, R. Ameta, J. Photochem. Photobiol. 48 (1989) 8.
[11] S.C. Ameta, A.K. Chittora, K.M. Gangotri, S. Khamesra, Z. Phy. Chem. (Leipzig) 270 (1989) 607.
[12] K.M. Gangotri, P. Kalla, K.R. Genwa, C. Lal, O.P. Regar, R. Meena, J. Ind. Council Chem. 2 (1994) 19.
[13] K.M. Gangotri, O.P. Regar, C. Lal, P. Kalla, K.R. Genwa, R. Meena, Int. J. Energy Res. 20 (1996) 581.
[14] K.M. Gangotri, O.P. Regar, C. Lal, K.R. Genwa, P. Kalla, R. Meena, Arab. J. Sci. Engg 22 (1997) 115.
[15] M.Z. Hoffman, N.N. Lichtin, in: R.R. Hantala, R.B. King, C. Kutal Clifton (Eds.), Solar Energy , N.J. Publisher, p. 153.
[16] M. Eisenberg, H.P. Silverman, Electrochem Acta 5 (1961) 1.
[17] A.S.N. Murthy, K.S. Reddy, International Solar Energy Conference, New Delhi, 1978, p. 47.
[18] T. Yamase, Photochem Photobiol. 34 (1981) 111.
[19] T. Tamilasaran, P. Natarajan, Indian J. Chem. 20A (1983) 213.
[20] A.S.N. Murthy, K.S. Reddy, Solar Energy 30 (1983) 39.
[21] S.C. Ameta, G.C. Dubey, T.D. Dubey, R. Ameta, Z. Phys. Chem. (Leipzig) 266 (1985) 200.
[22] S.C. Ameta, T.D. Dubey, G.C. Dubey, R. Ameta, Z. Phys. Chem. (Leipzig) 265 (1984) 838.
[23] S.C. Ameta, R. Ameta, S. Seth, T.D. Dubey, Afinidad XIV (1988) 264.
[24] S.C. Ameta, R. Ameta, S. Seth, G.C. Dubey, Z. Phys. Chem. (Leipzig) 270 (1989) 923.
[25] S.C. Ameta, R. Khamesra, K.M. Gangotri, S. Seth, Z. Phys. Chem. (Leipzig) 271 (1990) 427.
[26] S.C. Ameta, R.C. Ameta, R. Bhardwaj, S. Sahasi, P.K. Jain, Izrestiva, USSR, (1991), p. 15.
[27] S.C. Ameta, S. Khamesra, A.K. Chittora, K.M. Gangotari, Int. J. Energy Res. 13 (1989) 643.
[28] S.C. Ameta, S. Khamesra, M. Bala, K.M. Gangotari, Philli. J. Sc. 119 (1990) 371.
[29] S.A. Alkaties, M. Gratzel, A. Henglein, Berg. Beusenges Phys. Chem. 79 (1975) 541.
[30] M. Mukhopadhyay, B.B. Bhowmik, J. Photochem. Photobiol 69 (1992) 223.