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Use of reductant and photosensitizer in photogalvanic cells for solar energy conversion and storage: oxalic acid–methylene blue system

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Abstract

Photogalvanic effect was studied in photogalvanic cell containing oxalic acid as reductant and methylene blue as photosensitizer. The photopotential and photocurrent generated were 312.0 mV and 110.0 μA, respectively. The power of the cell was 12.6 μW at its power point. The observed conversion efficiency was 0.1211% and fill factor was determined as 0.28 against the maximum theoretical value 1.0. The photogalvanic cell can be used in dark for 35 min, showing the storage capacity of the cell against charging time was 140 min. The effects of different parameters on electrical output of the cell were observed and a mechanism has also been proposed for the generation of photocurrent in photogalvanic cell. © 2001 Published by Elsevier Science B.V.

Keywords: Fill factor; Conversion efficiency; Cell performance

1. Introduction

Bacquerel [1,2] in 1839, first observed 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 symmetrically investigated by Rabinnowitch [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 oxalic acid–methylene blue system in the photogalvanic cells for solar energy conversion and storage. The effect has been made to use the low cost materials in the photogalvanic cells for its commercial viability and stable compounds for its longevity. Therefore, the present work was undertaken.

2. Experimental

Oxalic acid (Ranboxy), methylene blue (Qualigens) and sodium hydroxide (s.d. fine) were used in the 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 solution of oxalic acid, methylene blue and sodium hydroxide 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 whole system was first placed in dark till a stable potential was obtained, then the platinum electrode was exposed to a 200 W tungsten lamp (ECE) and the limb containing the SCE was kept in the dark. A water filter was placed between the exposed limb and the light source to cut off infra-red radiations.

The photochemical bleaching of methylene 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. The current–voltage characteristics were determined by applying extra load with the help of carbon pot log 470 K connected in the circuit.

2.1. Effect of variations

The effect of variation in the concentrations of oxalic acid and methylene blue on the electrical output of the cell have been observed and the effect of variation of pH and diffusion length have also been studied. These results are summarized in Tables 1 and 2.

2.2. Current–voltage (i–V) characteristics and conversion efficiency

It was observed that *i*–*V* curve of the cell deviated from its regular rectangular shape (Fig. 1). A point on the *i*–*V*

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Table 1
Effect of variations on oxalic acid–methylene blue system (light intensity: 10.4 mV cm^{-2}; temperature: 303 K)

Variations	Concentration (M)	Photopotential (mV)	Photocurrent (μA)	Power (μW)
Oxalic acid	7.00×10^{-4}	265.0	42.0	11.1
	7.50×10^{-4}	286.0	55.0	15.7
	8.00×10^{-4}	312.0	70	21.8
	8.50×10^{-4}	289.0	54.0	15.6
	9.00×10^{-4}	261.0	38.0	9.9
Methylene blue	2.00×10^{-6}	263.0	52.0	13.6
	2.50×10^{-6}	281.0	60.0	16.8
	3.20×10^{-6}	312.0	70.0	21.8
	3.50×10^{-6}	292.0	55.0	16.0
	4.00×10^{-6}	240.0	42.0	10.0
pH	11.6	260.0	50.0	13.0
	12.0	276.0	61.0	16.8
	12.7	312.0	70.0	21.8
	13.2	281.0	62.0	17.4
	13.8	241.0	48.0	11.5

Table 2

Variations in diffusion length (mm)	Maximum photocurrent, $i_{\max}$ (μA)	Equilibrium photocurrent, i_{eq} (μA)	Rate of initial generation of current (μA min^{-1})
35.0	92.0	60.0	13.4
40.0	104.0	65.0	14.8
45.0	110.0	70.0	15.7
50.0	116.0	75.0	15.8
55.0	124.0	80.0	16.2

curve called the power point (PP) was determined, where the product of potential and current was maximum. The corresponding values 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 0.28 and 0.1211%, respectively, using the following formulae:

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

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

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.

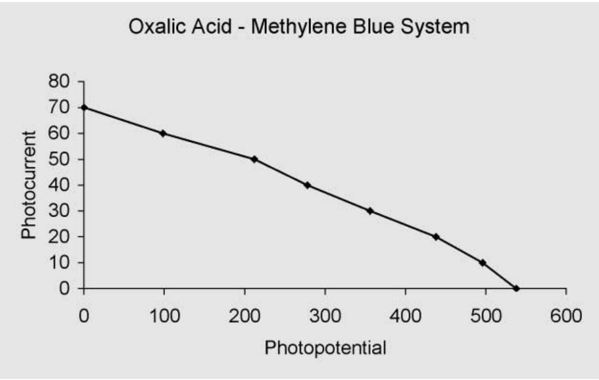

Fig. 1. *i*–*V* characteristics of the cell.

2.3. 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 35.0 min.

2.4. Electroactive species

Various probable process may be considered for the photocurrent generation in photogalvanic cells. The results of the effect of diffusion length [23] on current parameters were studied to know more about the electroactive species. The possible combinations for electroactive species in photogalvanic cell are tabulated as below.

Possible combinations for electroactive species

In illuminated chamber	In dark chamber
MB	Oxidized form of reductant (R^+)
Leuco or semi-MB$^-$	Oxidized form of reductant (R^+)
Leuco or semi-MB$^-$	MB

The oxidized form of reductant is formed only in illuminated chamber and if it is considered to be the electroactive species in 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 leuco or semi-MB and the dye MB in illuminated chamber and dark chamber, respectively. However, the reductant and its oxidized products acts only as electron carrier in the path.

2.5. Mechanism

On the basis of the above investigations the mechanism of the photocurrent generation [24–28] in the photogalvanic cell can be proposed as follows:

Illuminated chamber:

$$\mathrm{MB} \xrightarrow{h\nu} \mathrm{MB}^*, \qquad \mathrm{MB}^* + \mathrm{R} \rightarrow \mathrm{MB}^- + \mathrm{R}^+$$

At electrode,

$$\mathrm{MB}^- \rightarrow \mathrm{MB} + \mathrm{e}^-$$

Dark chamber:

At electrode,

$$\mathrm{MB} + \mathrm{e}^- \rightarrow \mathrm{MB}^-, \qquad \mathrm{MB}^- + \mathrm{R}^+ \rightarrow \mathrm{MB} + \mathrm{R}$$

where MB, MB^-, R and R^+ are methylene blue, its semi or leuco form, reductant and its oxidized form, respectively.

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