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USE OF DYES IN PHOTOGALVANIC CELL FOR SOLAR ENERGY CONVERSION AND STORAGE : BISMARCK BROWN AND ASCORBIC ACID SYSTEM

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ABSTRACT

Photogalvanic effect was studied in photogalvanic cell containing ascorbic acid as reductant and bismarck brown as photosensitizer. The photopotential and photocurrent generated were 915.0 mV and 205.0 μA, respectively. The observed conversion efficiency was 0.8990% and the maximum power of cell was 92.4 μW. The storage capacity of the cell was 38 minutes in dark. The effects of different parameters on electrical output of the cell were observed and a mechanism has been proposed for the generation of photocurrent in photogalvanic cell.

Key words: Bismarck brown, Ascorbic acid, Fill factor, Conversion efficiency, Power point, Storage capacity.

INTRODUCTION

The photogeneration of electricity has attracted attention of scientists as a viable media for solar energy conversion with bright future prospects; Becquerel[1,2] first observed in 1839, the flow of current between two unsymmetrical illuminated electrodes in sunlight. The photogalvanic effect was systematically investigated by Rabinowitch[3,4] in iron-thionine system. Later on, it was followed by many workers time to time (Fujishima and Honda[5], Kaneko and Yamada[6], Fox and Kabir-ud-din[7], Murthy and Reddy[8-10]). Rohatgi – Mukherjee et al.[11] have reported some interesting photogalvanic systems. Theoretical conversion efficiency of photogalvanic cells 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 electrode, etc.

A detailed literature survey reveals that different photosensitizers and reductants

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have been used in photogalvanic cells by many workers (Ameta[12,13], Gongotri et al.[14-16], Meena et al.[17-19], Chhagan Lal[20]) but no attention has been paid to use of the bismarck brown as photo sensitizer and ascorbic acid as reductant in the photogalvanic cells for solar energy conversion and storage.

EXPERIMENTAL

Bismarck brown (LOBA), ascorbic acid (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 bismarck brown, ascorbic acid and sodium hydroxide was taken in an H-type glass tube. A platinum electrode (1.0×1.0 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 and then the arm containing the SCE was kept in dark and the platinum electrode was exposed to a 200W tungsten lamp. A water filter was used to cut off infrared radiations. The photochemical bleaching of bismarck brown was studied potentiometrically. A digital pH meter (Systronics 802) and a micro ammeter (New Tech, India) were used to measure the potential and current generated by the system respectively.

RESULTS AND DISCUSSION

Effect of pH : The electrical output of the cell was affected by the variation in pH of the system.

Table 1. Effect of variation of pH

	pH				
	12.0	**12.4**	**12.7**	**13.1**	**13.4**
Photopotential (mV)	815	864	915	872	853
Photocurrent (mA)	114	135	155	142	125

It can be observed from Table 1 that there is an increase in electrical output of the cell with the increase in pH values. At pH 12.7, a maxima was obtained. On further increase in pH, there was a decrease in photopotential and photocurrent. Thus, photogalvanic cells containing the bismarck brown and ascorbic acid 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 then its pKa value (pH > pKa). The reason may be the availability of reductant in its anionic form, which is a better donor form.

Effect of ascorbic acid concentration : The electrical output of the cell was affected by the variation of reducing agent concentration [Ascorbic Acid] in the system. The results are summarized in Table 2. Lower concentrations of reducing agents resulted into a fall in electrical output because less reducing agent molecules were available for electron donation to bismarck brown molecules. Large concentration of reducing agent again resulted into a decrease in electrical output, because the large number of reducing agent molecule hinders the dyes molecules reaching the electrode in the desired time limit.

Table 2. Effect of variation of ascorbic acid concentration

	[Ascorbic acid] × 10^{-3} M				
	4.0	**4.8**	**5.6**	**6.4**	**7.2**
Photopotential (mV)	774	867	915	873	855
Photocurrent (mA)	110	130	155	140	120

Effect of bismarck brown : Concentrations dependence of photopotential and photocurrent on the concentration of bismarck brown was studied and the results are summarized in Table 3. Lower concentration of dye resulted into a fall in photo potential and photocurrent because less dye molecules are available for the excitation and consecutive donation of the electrons to the platinum electrode. The greater concentration of dyes again resulted in a decrease in electrical output as the intensity of light reaching the dye molecules near the electrode decreases due to absorption of the major portion of the light by dyes molecules present in path.

Table 3. Effect of Bismarck brown concentration

	[Bismarck brown] × 10^{6} M				
	3.2	**4.8**	**6.4**	**8.0**	**9.6**
Photopotential (mV)	855	890	915	887	865
Photocurrent (μA)	120	143	155	141	125

Effect of diffusion length : The effect of variation of diffusion length (distance between the two electrodes) on the current parameter of the cell was studied using H-cells of different dimensions. The results are reported in Table 4.

Table 4. Effect of Diffusion length

Diffusion path length, D_L (mm)	Maximum photocurrent (mA) i_{max}	Equilibrium photocurrent (mA) i_{eq}	Rate of initial generation of current (mA min^{-1})
35	180	135	17.6
40	186	140	18.2
45	198	155	19.2
50	205	155	20.4
55	210	162	21.0

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 indicates an initial rapid reaction followed by slow rate determining step at a later stage. On the basis of the effect of diffusion path length on the current parameter, it may be concluded that the leuco– or semi– reduced form of dyes and the dye itself are the main electro active 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.

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 cells are tabulated in Table 5. 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 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 reduced– dye and the dye in illuminated chamber and dark chamber, respectively. However, the reductant and its oxidized products act only as electron carrier in the path.

Table 5. Possible combinations for electroactive species

In illuminated chamber	In dark chamber
Dye	Oxidized form of reductant (R^+)
Leuco– or semi – Dye	Oxidized form of reductant (R^+)
Leuco– or semi – Dye	Dye

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 Fig. 1. A point in i-V curve, called the power point (pp) was determined where the product of potential and current was maximum. With the help of i-V curve, the fill factor and conversion efficiency of the cell were determined as 0.46 %and 0.8990 %, respectively using the following formula : -

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

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

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.

Cell performance : The performance of the cell was studied by applying an external load necessary to maintain current and potential at the power point after removing the source of light until the output (power) falls to its half value at the power point in the dark. It was observed that cell can be used in the dark at its power point for 38 minutes.

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

Illuminated chamber

Bulk solution

$$\mathrm{BB} \longrightarrow \mathrm{BB}^{*} \qquad \text{....(3)}$$

$$\mathrm{BB}^{*} + \mathrm{R} \longrightarrow \mathrm{BB}^{-} + \mathrm{R}^{+} \qquad \text{....(4)}$$

At electrode

$$\mathrm{BB}^{-} \longrightarrow \mathrm{BB} + e^{-} \qquad \text{...(5)}$$

Dark chamber

At electrode

$$\mathrm{BB} + e^{-} \longrightarrow \mathrm{BB}^{-} \qquad \text{...(6)}$$

Bulk solution

$$\mathrm{BB}^{-} + \mathrm{R}^{+} \longrightarrow \mathrm{BB} + \mathrm{R} \qquad \text{....(7)}$$

Where BB, BB^{-}, R and R^{-} are the bismarck brown and its leuco– or semi– leuco forms, reductant and its oxidized form, respectively.

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