Photogalvanic solar conversion and storage by using Thionine as photosensitizer and EDTA as reductant in the presence of CTAB as surfactant

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Uso de Tionina como fotosensibilizador y EDTA como reductor en elementos fotogalvánicos para la conversión y almacenamiento de energía solar, en presencia de CTAB como tensioactivo

Utilització de Tionina com a fotosensibilitzador i EDTA com a reductor en elements fotogalvànics per a la conversió i emmagatzematge d'energia solar, en presència de CTAB com tensioactiu

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RESUMEN

El efecto fotogalvánico del sistema fotosensibilizador - reductor formado por Tionina y EDTA ha sido estudiado en presencia del tensioactivo CTAB (Bromuro de Cetiltrimetilamonio) para la conversión y almacenamiento de energía solar. El fotovoltaje y la fotocorriente generados por esta celda fueron respectivamente 662 mV y 150 μA. La potencia de la celda fue de 53.5 μW en el punto óptimo. La eficiencia de conversión observada fue de 0,5144% y el factor de relleno determinado fue 0.50. La celda fotogalvánica puede ser utilizada en la oscuridad durante 50 min., demostrando que la capacidad de almacenamiento de la celda frente al tiempo de carga fue de 190 min. Se estudió el efecto de diferentes parámetros sobre el rendimiento eléctrico de la celda, y se propone un mecanismo para la generación de fotocorriente en la celda fotogalvánica.

Palabras clave: Bromuro de Cetiltrimetil Amonio, Eficiencia de conversion, EDTA, celda fotogalvánica, Tionina, Capacidad de almacenamiento.

SUMMARY

The photogalvanic effect of photosensitizer – reductant as Thionine and EDTA has been studied in presence of surfactant CTAB (Cetyltrimethyl Ammonium Bromide) for solar energy conversion and storage. The photopotential and photocurrent generated by this cell were 662 mV and 150 μA, respectively. The power of the cell was 53.5μW at its power point. The observed conversion efficiency was 0.5144% and fill factor was determined as 0.50. The photogalvanic cell can be used in dark for 50 min., showing the storage capacity of the cell against charging time was 190 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.

Keywords: Cetyltrimethyl Ammonium Bromide, Conversion efficiency, EDTA, Photogalvanic cell, Thionine, Storage capacity.

RESUM

S'ha estudiat l'efecte fotogalvànic del sistema fotosensibilitzador - reductor format per Tionina i EDTA en presència del tensioactiu CTAB (Bromur de Cetiltrimetilamoni) per a la conversió i emmagatzematge d'energia solar. El fotovoltatge i la fotocorrent generats per aquesta cel·la van ser respectivament 662 *mV i 150 μA. La potència de la cel·la va ser de 53.5 μW en el punt òptim. L'eficiència de conversió observada va ser de 0,5144% i el factor de farciment determinat va ser 0.50. La cel·la fotogalvànica pot ser utilitzada en la foscor durant 50 min., demostrant que la capacitat d'emmagatzematge de la cel·la respecte al temps de càrrega va ser de 190 min. Es va estudiar l'efecte de diferents paràmetres sobre el rendiment elèctric de la cel·la, i es proposa un mecanisme per a la generació de fotocorrent en la cel·la fotogalvànica.

Mots clau: Bromur de Cetiltrimetil Amoni, Eficiència de conversió, EDTA, cel·la fotogalvànica, Tionina, Capacitat d'emmagatzematge.

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1. INTRODUCTION

Energy has been universally recognized as one of the most important inputs for economic growth and human development. Modern life has very high energy demands. Accordingly renewable energy resources are attracting a great deal of attention, and solar energy is one of the most promising future energy resources. Bacquerel[1, 2] in 1839, first observed the flow of current between two unsymmetrical illuminated metal electrodes in sunlight. The photogalvanic effect was first symmetrically investigated by Rabinnowitch[3, 4]. Hoffman and Lichtin[5] have discussed various problems encountered in the development of this field. Jana and Bhowmik[6] reported enhancement in the power output of a solar cell consisting of mixed dyes. Surash and Hercules[7] proved that only negative photopotential should be obtained with carbonyl compounds. Hara et al.[8] investigated design of new coumarin dyes having thiophene moieties for highly efficient organic dye-sensitized solar cells.

A detailed literature survey reveals that different photosensitizers [9–22] have been used in photogalvanic cells, but no attention has been paid to the use of Thionine-EDAT-CTAB 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

Thionine (LOBA), EDTA (S.D. Fine), CTAB (LOBA) and Sodium Hydroxide (S.D. Fine) were used. All the solutions were prepared in doubly-distilled water and stored in amber-colored containers to protect them from light. A mixture of the solution of the Thionine, EDTA, CTAB, and NaOH was filled into an H-shaped glass cell. A platinum electrode (1.0 ×1.0 cm^2) was placed in one compartment of the cell and a Saturated Calomel Reference Electrode (SCE) in the other. The whole system was first placed in dark till a stable potential was obtained, then the Platinum electrode was exposed to a 200W tungsten lamp (Philips) while the SCE was kept in the dark. The temperature of the system was maintained at 303K (±0.1 K).

A water filter was placed between the exposed limb and the light sources to cut-off infrared radiations. A digital pH meter (Systronics model-802) and a microammeter 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.

3. RESULTS AND DISCUSSION

3.1. Effect of Variations

The effects of variation in the concentrations of Thionine, EDTA and CTAB on the electrical output of the cell have been observed and the effects of variation of pH have also been studied. These results are summarized in Tables - 1.

Table - 1 *Effect of Variation on Thionine- EDTA -CTAB System (Temperature = 303K; Light intensity=10.4mW cm^{-2})*

Variations	Concentration	Photopotential(mV)	Photocurrent*(μA)
Thionine ×10^{-6}M	7.2×10^{-6}	618	120
	8.0×10^{-6}	638	135
	8.8×10^{-6}	662	150
	9.6×10^{-6}	632	129
	10.4×10^{-6}	610	110
EDTA×10^{-3}M	3.2×10^{-3}	620	122
	3.6×10^{-3}	641	137
	4.0×10^{-3}	662	150
	4.4×10^{-3}	635	130
	4.8×10^{-3}	612	110
CTAB ×10^{-4}M	3.6×10^{-4}	616	120
	4.0×10^{-4}	643	140
	4.4×10^{-4}	662	150
	4.8×10^{-4}	635	130
	5.2×10^{-4}	607	105
pH	10.2	624	125
	10.4	646	140
	10.6	662	150
	10.8	639	135
	11.0	616	112

Table - 2 *Effect of Variation of Light Intensity on Thionine- EDTA -CTAB System (Temperature = 303K; Light intensity=10.4mW cm^{-2})*

Light Intensity	Photopotential (mV)	Photocurrent (A*)	Log V
3.1	626	130	2.7965
5.2	648	140	2.8115
10.4	662	150	2.8208
15.6	679	155	2.8318
26.0	706	160	2.8488

3.2. Effect of light intensity

The photocurrent shows a linear increasing behavior with increase in the intensity of the light, whereas the photopotential increases in a logarithmic manner. The variation of these electric parameters with light intensity is shown in Table - 2. The number of photons per unit area (incident power) that strike the dye molecules around the platinum electrode increases with the increase in the light intensity. Hence, the photocurrent and the photopotential of the photogalvanic cell are affected favorably (increases). On the other hand, increase in light intensity also raises the temperature of the cell. Therefore, an intensity of medium order (10.4mWcm^{-2}) was used for all investigations.

3.3. 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 dimension. The results are reported in Table - 3. 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 behavior is 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 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.

Table - 3 *Possible Combinations for Electroactive Species*

In Illuminated chamber	In Dark Chamber
TH	Oxidized form of reductant (R^+)
Leuco or Semi – TH^-	Oxidized form of reductant (R^+)
Leuco or Semi – TH^-	TH

3.4. Current–voltage (i–V) characteristics, conversion efficiency and performance of the cell

The open-circuit voltage (V_{oc}) and short-circuit current (i_{sc}) of the photogalvanic cell were measured by means of a digital multimeter (keeping the circuit open) and a microammeter (keeping the circuit closed), respectively. The current and potential between two extreme values (V_{oc} and i_{sc}) were recorded with the assistance of a carbon pot (linear 470 K) that was connected in the circuit of the multimeter and through which an external load was applied. The i–V characteristics of the cell containing a Thionine-EDTA -CTAB System are shown graphically in Fig. 1. The curve for the cell deviates from its ideal regular rectangular shape. A point in the i–V curve, called the power point (pp), was determined where the product of photocurrent and photopotential is maximum. The potential and the current at the power point are represented by V_{pp} and i_{pp}, respectively. With the help of the (i–V) curve, the Fill Factor and Conversion Efficiency of the cell are found to be 0.50 and 0.5144 %, respectively, using the formulae:

$$\textit{Fill Factor} = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}}$$

$$\textit{Conversion Efficiency} = \frac{V_{pp} \times i_{pp}}{10.4 mWcm^{-2}} \times 100 \quad \%$$

The performance of the cell was studied by applying the external load that was necessary to have the current and the potential at the power point after removing the source of light. The cell can be used in the dark at its power point for 60.0 min. Thus, whereas photovoltaic cell cannot be used in the dark even for a second, a photogalvanic system has the advantage of being used in the dark, but at lower conversion efficiency.

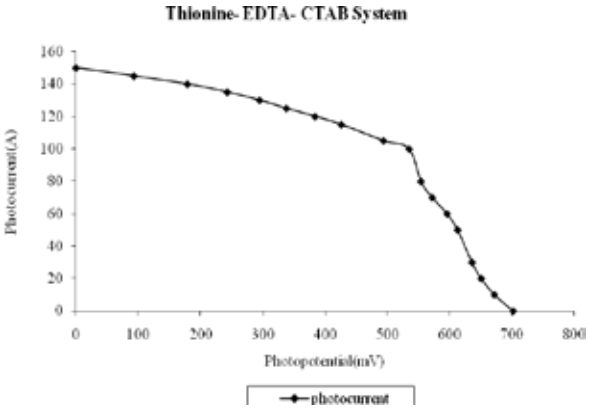

Figure 1 *-Current-potential (i-V characteristic) of the Cell*

3.5. Mechanism

As no reaction is observed between the Thionine and EDTA in the dark, it may be concluded that the redox potential of EDTA is much higher than that of Thionine. A rapid fall in potential is observed when the platinum electrode is illuminated. The potential reaches a steady value after certain period of exposure. Although the direction of the change of potential is reversed on removing the source of light, the potential does not returns to its initial value. This means that the main reversible photochemical reaction is also accompanied by some side irreversible reactions. The electroactive species in this photogalvanic system is thus different from that of the well-studied Thionine–iron (II) system. In the present case, the lecuo- or semi reduced dye is considered to be the electrode active species in the illuminated chamber, and the dye itself in dark chamber. On the basis of the information gained above, the mechanism of photocurrent generation in the photogalvanic cell can be represented as:

Illuminated Chamber

Bulk Solution

$$TH \xrightarrow{h\nu} TH^{*}$$

$$TH^{*} + R\,(EDTA) \longrightarrow TH^{-} + R^{+}$$

At Electrode

$$TH^{-} \longrightarrow TH + e^{-} \quad \textit{(Platinum electrode)}$$

Dark Chamber

At Electrode

$$TH + e^{-} \longrightarrow TH^{-}$$

Bulk Solution

$$TH^{-} + R^{+} \longrightarrow TH + R \quad \textit{(SCE electrode)}$$

Where TH, TH^{-}, R and R^{+} are Thionine, its semi or leuco form, reductant and its oxidized form, respectively.

4. CONCLUSIONS

On the basis of above results, it is concluded that Thionine can be used successfully as a photosensitizer in a photogalvanic cell. The conversion efficiency of the cell is 0.5144% and the cell can be used in dark at its power point for 60 min. Photovoltaic cells have better conversion efficiency than photogalvanic cells, but they lack storage capacity. Photogalvanic cells have the added advantage of having in-built storage capacity. The time is not far off when the conversion efficiency of these cells will be comparable with that of existing solar cells. Thus, photogalvanic cells show good prospects of becoming commercially viable.

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