Study on the Performance of Photogalvanic Cell for Solar Energy Conversion and Storage

Sawsan A. Mahmoud^{*}, Basma S. Mohamed

Processes development department, Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt *E-mail: <u>sawsanhassan2003@yahoo.com</u>

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Solar energy conversion and storage was studied through Photogalvanic effect using photogalvanic cell using Rose Bengal – Oxalic acid – CTAB System. The oxalic acid as reductant, Rose Bengal as sensitized dye and Cetryl hexadecyl ammonium bromide as charge transfer carrier in aqueous solution. The photopotential and photocurrent generated were 550.0 mV and 75.0 μ A respectively. The observed power of the cell was 41. 3 μ W at its power point. The conversion efficiency and fill factor was determined as 0.067% and 0.169 respectively. The cell performance was 175.0 min in dark. A mechanism for the Photogeneration of electricity has also been proposed. The effects of different parameters on the electrical output of the cell and current-voltage (i-V) characteristics of the cell were studied.

Keywords: Rose Bengal; cell performance; ctorage capacity; photocurrent; photopotential.

1. INTRODUCTION

The development of viable and long-term solution to meet our energy needs that also maintains the quality of our environment which remains one of the most critical challenges is being facing by the scientific community. The solution of this challenge increasingly depends on electrochemical processes in solids. The solar energy is easily available, cheaper, environmental friendly source and has the potential to provide energy with almost zero emission. The novel approach for renewable sources of energy has led to an increasing interest in photogalvanic cells because of their reliable solar energy conversion and storage capacity. The theoretical conversion effeciency of a photogalvanic cell is 18% [1] However, this was never achieved due to :a) back electron transfer, b) lower stability and aggregation of dye molecules around the electrode.

The photogalvanic cells are based on "photogalvanic effect". This term was first time used by Rabinowitch [2, 3] to denote a special case of the so-called Becquerel effect, in which the influence of light on the electrode potential is due to a photochemical process in the body of the electrolyte (as distinct from photochemical or photoelectric processes in the surface layer of the electrode, which are the basis of the original Becquerel effect). Therefore, the photogalvanic cells are quite different from other cells [4–6] like galvanic or voltaic cells. Photogalvanic cells use very dilute solution of photosensitizer and reductant. The solution is the absorber phase, and it is contacted by two electrodes with different selectivity to the redox reaction. The photogalvanic cells where the dye undergoing photoexcited state in solution and the products regenerated at inert electrode have been investigated extensively in past, and proven very inefficient due to various reasons. The observed electrical output was very low (like potential 75 mV [7], 118mV [8]; power 0.038 μ W [7]; current 12 μ A [9]; and energy conversion efficiency of the order of 0.0022% [10]).

It is to be noted that the earlier researcher emphasized more on mechanism, kinetics and other insights of photogalvanic cells. This lower electrical output might have been due to some complex and unsuitable cell fabrication parameters like use of light-intercepting black plate between electrode chambers, Pt electrode in both chambers, coated Pt, only visible rays for illumination and acidic medium (low pH like 6) [7,9,11]. But, Albery and Archer forecasted that efficiency of these cells could be as high as 18% [11]. This encouraging forecast has been motivating researchers for working on photogalvanic cells, and it has also resulted into tremendous enhancement in cell performance are using hope that these cells may be the future energy source. With this hope, the later researchers have studied photogalvanics in alkaline medium (high pH) with very simple fabrication involving uncoated Pt in illuminated chamber and saturated calomel electrode (SCE) in dark chamber without intercepting plate. Absence of intercepting plate may be relatively favorable for more diffusion of species between chambers leading to higher performance as these cells are diffusion controlled. And, at high pH, there may be less bleaching and higher electron ejection from dye sensitizers. The earlier researcher emphasized more on thionine dye sensitizer with Fe²⁺ as reducing agent. The earlier researcher Fe²⁺ as reducing agent. Later on, the researcher emphasized more on thionine dye sensitizer with [12-22] started using other dyes with organic reductant. The use of new dyes with organic reductant has led to the tremendous enhancement in cell performance. But, this cell performance further needs to be enhanced to make these cells practicable and efficient. The study of variations of variables likes concentration of dye, surfactant, oxalic acid, etc. was also undertaken to find out their suitable combination for optimum performance of the cell.

A detailed survey of literature reveals that no attention has been paid to the Rose Bengal-CETAB system in a photogalvanic cell for solar energy conversion and, therefore, the present work has been undertaken

2. EXPERIMENTAL

2.1. Structure of the compounds used



Figure 1. A&B: The structure of 4,5,6,7-tetrachloro-2',4',5',7'-tetraiodofluorescein, Rose Bengal (A) and Cetyltrimethylammonium bromide, CETAB (B)

2.2. Materials

The structure of CETAB and Rose Bengal are shown in Figure 1A&B. CETAB, Rose Bengal and oxalic acid were purchase from Sigme-Aldrich. Sodium hydroxide was provided from Merck.

2.3. Experimental set up of the Photogalvanic cell

A glass tube of H-shape was used containing known amount and concentration of the photosensitized dye, Oxalic acid, CETAB and sodium hydroxide. The total volume of the mixture was kept 25.0 ml making up by doubly distilled water. All the solutions were kept in amber coloured containers to protect them from sunlight.

A platinum electrode of different areas $(0.25-1.0 \text{ cm}^2)$ was dipped in one limb having a window and a saturated calomel electrode (SCE) was immersed in another limb of the H-tube. The terminals of the electrode were connected to a digital pH meter (Hanna) and the whole cell was placed in the dark. The potential (mV) was measured in the dark when the photogalvanic cell attained a stable potential. Then, the limb containing platinum electrode was exposed to a 200 W tungsten lamp (Philips) as a light source. A water filter was placed between the illuminated chamber and the light source to cut-off infrared radiation. The photopotential and photocurrent generated by the system was measured with the help of the digital pH meter and microammeter, respectively.

Initially, the circuit is kept open and cell is placed in dark till it attains a stable potential (dark potential, Vdark). Then, the Pt electrode is exposed to light radiation emitted from tungsten bulb. A water filter is put between the cell and lamp to cut off infra-red radiation with the aim of curbing heating effect of cell, to ensure that the produced voltage and current is originate as a result of the irradiation only. On illumination, the photo potential (V) and photocurrent (i) are generated by the system.

After charging of the cell, the cell parameters like maximum potential (V_{max}), open-circuit potential (V_{oc}), maximum current (i_{max}) and short-circuit current (i_{sc}) are measured.

Study of i-v characteristics (which has been done by observing potential at different direct currents by varying resistance) shows the highest power at which cell can be used.

The cell is operated in highest power (i.e., power at power point, p_{pp}) at corresponding external load, current (i.e., current at power point, i_{pp}) and potential (i.e., potential at power point, V_{pp}) for study of its performance by observing change in current and potential with time.

Cell performance is studied in terms of half change time $(t_{0.5})$, conversion efficiency (CE) and fill factor (Ff) in the dark. Time taken for the fall in the power of the cell to its half value of power at power point is called $t_{0.5}$ (which is measure of storage capacity of cell). The CE and Ff are calculated from Equations as below

Fill factor (Ff) = $V_{pp} \times i_{pp} / V_{oc} \times i_{sc}$

Conversion Efficiency % = [$V_{pp} \times i_{pp} / 10.4 \text{ mWcm}^{-2} \times \text{Electrode area}$] × 100

The current–voltage characteristics of photogalvanic cell have been studied by applying an external load with the help of a carbon pot (log 470 K) connected to the circuit through a key to close and open the circuit device. The experimental set-up of photogalvanic cell is shown in Figure 2.



Figure 2. Experimental set-up of photogalvanic cell.

3. RESULTS AND DISCUSSION

3.1. Mechanism of photocurrent generation

The photo-excited dye accepts an electron from reductant to form leuco or semi form of dye. The dye and leuco or semi dye form is the electro-active species in the dark and illuminated chambers, respectively. The reductant and its oxidized form act only as electron carriers in the path [9]. The leuco or semi dye gives electrons to Pt electrode connected through external circuit with SCE at which dye

accepts an electron. Finally, leuco/semi form of dye and oxidized form of reductant may combine to give original dye and reductant molecules in the dark chamber [9, 11, 23, 24, 25–28]. The leuco or semi forms are the two reduced form of the dye. The semi is the one electron reduced state of the dye, and leuco is the two electron reduced state of the dye. The energy stored in the charge separated form-semi or leuco can be converted into the electrical energy. Also, the formation of charge transfer complex between dye and ionic liquid is very important in production of energy.

The mechanism of photocurrent generation in the photogalvanic cell can be schematically represented as follows [29].

Illuminated chamber (anode) $Dye \xrightarrow{hv} Dye^{*}(S) \xrightarrow{ISC} Dye^{*}(T)$ (i) $Dye^{*}(T) + R \longrightarrow Dye^{-}(semi \text{ or leuco}) + R^{+}$ (ii) Dye ____ Dye + e (at Pt electrode) (iii)

Dark chamber (saturated calomel electrodeSCE as cathode)

Dye + e ----- Dye (semi or leuco) at SCE (iv) $Dye + R^+ \longrightarrow Dye + R$ (v)

Where Dye^* , Dye^- , R and R⁺ are the excited form of Rose Bengal (photosensitizer), its semi or leuco forms, Oxalic reductant and its oxidized form, respectively. The S, T and I_{SC} are singlet excited dye, triplet excited dye and inter-system crossing, respectively.

As such, there is no chemical reaction leading to change in the chemical composition. Only electron exchanges take place among electrodes, dye, and reductant. Ideally, the photogalvanic system acts as a (cyclic) light-driven electricity generator [30]. The reaction is reversible, and the rates of both the forward (light) and reverse (dark) reactions are easily measured [2, 3]. The photogalvanic behavior has been found reversible for several cycles [31].

The overall forward (light) and back (dark) reactions in the cell under continuous illumination may be represented as:

$$D^- + S \xrightarrow{\text{light}} D^{-2-} + S^{-+}$$

3.1. Effect of variation of Rose Bengal concentration

In the present system, to study the effect of Rose Bengal concentration on the electrical output, different concentrations of dye was used while the concentration of different components of the cell was kept constant and also the pH. Table 1 shows that with increase in concentration of Rose Bengal, the photopotential and photocurrent were found to increase until it reaches a maximum value. On further increase in concentration of photosensitized dye, a decrease in electrical output of the cell was found.

(i) On the lower concentration range of Rose Bengal; there is a limited number of photosensitized molecules to absorb the major portion of the light and therefore, a few number of electrons can reach the platinum electrode and a low electrical output was obtained;

(ii) Higher concentration of the dye does not permit the desired light intensity to reach the molecules near the electrodes and hence, there is a corresponding fall in the power of the cell;

(iii) Due to the high concentration, there are short lived excited dye states therefore; an excited dye molecule must reach Pt within its short life for electron donation. Given this, only those dye molecules that exist and absorb photons near Pt have greater chance of electron donation to Pt electrode, and

(iv) The increased concentration of dye under operational conditions may also lead to be accelerated recombination between the injected electrons and dye accompanied by losses of photocurrent and photo-voltage and reduced conversion efficiencies.

A reversible dye electro-chemical process is believed to take place here as the ratios of currents (oxidation/reduction) are close to unity for the dye compounds [32].

[Rose bengal] \times 10 ⁻⁵ M	Photopotential	Photocurrent	Power
	(mV)	(µA)	(µW)
10.75	409.0	38.5	15.74
10.47	496.0	58.4	28.96
10.35	520.0	64.5	33.54
10.16	550.0	75.1	41.31
9.84	508.0	55.4	28.14
9.52	471.0	49.7	23.41
9.00	419.0	39.5	16.55
7.80	390.8	30.8	12.04

Table 1. Effect of variation of photosensitizer (Rose bengal) concentration

3.2. Effect of variation of reductant (Oxalic acid) concentration

Figure 3 shows the effect of oxalic acid electrolyte on the electrical output of the system. It is obvious that, with increase in concentration of the reductant (Oxalic acid) in present system, the photopotential was found to increase till it reaches a maximum value. On further increase in concentration of reductant, a decrease in electrical output of the cell was observed. At very low concentration of electrolyte, the fall in power output was resulted with decrease in concentration of reductant due to less number of molecules available for electron donation to the cationic form of dye. As the concentration increase the electrical output increase, this is due to the fact that electrostatic interactions between oppositely charged ions decrease as the concentration decreases. On further increase in concentration of reductant, a decrease in the electrical output of the cell was observed. On the other hand, the movement of dye molecules may be hindered by the higher concentration of

reductant to reach the electrode in the desired time limit and it will also result into a decrease in electrical output. The hydrolysis of oxalic acid occurs in two steps as follows:

$$C_2O_4H_2 \rightarrow C_2O_4H^- + H^+; \ pK_a = 1.27$$

 $C_2O_4H^- \to C_2{O_4}^{2-} + H^+; \ pK_a = 4.27$

The two acid dissociation constants, $pKa_1 = 1.2$ and $pKa_2 = 4.2,38$ suggest that all three forms of oxalate is present in solution. The formed fragments $H_2C_2O_4$, $HC_2O_4^-$, and $C_2O4_2^-$ are known to be e_{aq}^- and OH, scavengers [33-35]

The formed $HC_2O_4^-$ could be meniralized and form CO_2 and H_2O which cause a fall in electerical output.

 $HC_{2}O_{4}^{-} + \frac{1}{2}O_{2} + H^{+} \rightarrow 2CO_{2} + H_{2}O_{2}$

Also upon irradiation there are series of reaction which could be occured and affact the electrical uotput as follows

$$\begin{array}{rcl} H_2O \rightarrow & H^+ & + & ^{\circ}OH \\ HC_2O_4 & + & ^{\circ}OH \rightarrow & HC_2O_4 & + & ^{\circ}OH \end{array}$$

In the presence of oxygen, this radical intermediate undergoes bond cleavage and electron migration leading to the formation of CO_2 and a more stable carboxyl radical, CO_2 .

 $HC_2O_4^{\circ} \rightarrow CO_2+CO_2^{-1}$

Another reaction could be occur in the solution,

$$\mathrm{HC}_{2}\mathrm{O}_{4}^{} + \frac{1}{2}\mathrm{O}_{2}^{} + \mathrm{H} \rightarrow 2\mathrm{CO}_{2}^{} + \mathrm{H}_{2}\mathrm{O}$$



Figure 3. Effect of variation of Oxalic acid concentration on electerical output.

3.3. Effect of variation in surfactant (CTAB) concentration

The effect of CTAB concentration was also investigated in the present system. It was observed that electrical output of the cell was found to increase on increasing the concentration of micelles reaching maximum value. On furthur increase in their concentrations, a fall in electerical output was observed (Figure 4). The reason of the change in in electerical output is that micelles solubilize the dye molecules up to highest extent at or around their micelles concentration.upon increase in CTAB concentration to a value higher than CMC a charge transfer complex between dye and surfactant which is hydrophobic in nature so a fall in electerical output was observed.



Figure 4. Effect of variation of CTAB concentration on photopotential, photocurrent and power.

3.4. Effect of pH

The photogalvanic system is quite sensitive for pH variation. The electrical output of the photogalvanic cell was changed by the variation of pH on the system.

It is well known that the shape, the charge and the size of the micelle depend upon pH of the media, NH₂, -OH show pH sensitivity. Patel et al 2014 [36] stated that, the extent of ionization of these solubilizates depends on pH. Spherical micelles form at concentration, above the critical micelle concentration (CMC) and may grow to rod-like or worm-like structures or even transform into vesicles under different solvent conditions. The spherical, ellipsoidal, rod or worm-like structures may also depend on the presence of additives. Aromatic acids have tendency to deprotonate when the pH is above their pKa value of RB has a pKa value 3.9 [37]. The solution viscosity increased the hydrophobic interaction between the phenyl ring of dye and the nonpolar chain of the surfactant. This association of ionized dye with the polar head group promotes micellar growth. If the solution pH < pKa, equilibrium of dye molecules shifts toward less ionized species having low aqueous solubility and solubilization by hydrophobic effect takes place this resulted in decrease the electrical output.

Figure 5 shows that there is an increase in electrical output of the cell with the increase in pH values. At pH 13.52 a maxima was obtained [38]. On further increase in pH, there was a decrease in photopotential and photocurrent. It is observed that the pH for the ptimum condition has a relation with

pKa of the reductant and the desired pH is higher than in pKa value (pH>pKa). The reasons of increasing in electrical output is:

1) Decreasing in the viscosity drastically but hydrodynamic size consequently increases. This indicates elongated micelles may form a branched network or make entanglements and lead to a decrease in viscosity.

2) The availability of the reductant in its anionic form, which is a better donor form.



Figure 5. Effect of variation of pH on photopotential, photocurrent and power.

3.5. Effect of diffusion length on the system

The effect of the variation of diffusion length (distance between the two electrodes i.e. saturated calomel electrode and Pt electrodes) on the electrical output of the photogalvanic cell was studied using H-cells of different dimensions. It was observed that in the first few minutes of illumination there was a sharp increase in the photocurrent and then here was a gradual decrease to a stable value of photocurrent. This behavior of photocurrent indicates an initial rapid reaction followed by a slow rate determining step. On the basis of the effect of diffusion path length on the current parameters, as investigated by Kaneko and Yamada [9] 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. It was observed that the current increases on increasing the diffusion length. Electroactive species take a bit longer time to reach the electrode surface as the diffusion length increases [39]. This gives ample time for the reaction to take place, causing increase in i max. The results are graphically represented in Figure 6.



Figure 6. Effect of variation of diffusion length on photopotential, photocurrent and power.

3.6. Effect of electrode area on the system

The effect of variation of electrode area of Pt electrode on the electrical output of the photogalvanic cell was studied using different measurements of electrode areas. The results are graphically represented in Figure 7. It was observed that with an increase in the electrode area, the power of the cell was found to increase, whereas photocurrent at equilibrium (ieq) was found to be almost independent with respect to change in electrode area (rather it is affected in reverse manner). In the system, the reaction at the electrode surface is more important. The dye molecules are transported towards the charged illuminated electrode by diffusion and a static layer is gradually developed near the electrode surface. A loose complex between the dye and CETAB is formed on the electrode surface which could be a charge transfer type with increased donor capacity [39].



Figure 7. Effect of variation of electrode area on photopotential, photocurrent and power.

3.7. Current-voltage (i–V) characteristics of the photogalvanic cell

The short circuit current (i_{sc}) and open circuit voltage (V_{oc}) of the photogalvanic cells were measured with the help of a microammeter (keeping the circuit closed) and with a digital pH meter (keeping the other circuit open), respectively. The current and potential values in between these two extreme values were recorded with the help of a carbon pot (log 470 K) connected in the circuit of microammeter, through which an external load was applied. The Current–Voltage (i–V) characteristics of the photogalvanic cell containing Rose Bengal–Oxalic acid–CTAB system is graphically represented in Figure 20. A point in i–V curve, called power point (pp) is determined where the product of current and potential was maximum and the fill factor is calculated using the following formula:

Fill factor (F_f) = ($V_{pp} \times I_{pp}$) / ($V_{oc} \times I_{sc}$)

Where: V_{pp} and i_{pp} represent the value of photopotential and photocurrent at power point, respectively and V_{oc} and i_{sc} represent open circuit voltage and short circuit current, respectively. The value of fill factor (F_f = 0.327) was obtained and the power point of cell (pp) = 4.15 μ W was determined on the system.



Figure 8. Current–potential (i–V) of the cell

3.8 .Storage capacity, Conversion efficiency and performance of the photogalvanic cell

The storage capacity of the photogalvanic cell was observed by applying an external load (necessary to have current at power point) after termination the illumination as soon as the potential reaches a constant value. The storage capacity was determined in terms of $t_{1/2}$, i.e., the time required in fall of the electrical output (power) to its half at power point in dark. It was observed that the photogalvanic cell can be used in dark for 175.0 min on irradiation for 20.0 min. The results are graphically represented in Figure 9.



Figure 9. Storage capacity of the cell

It is also observed that previously reported photogalvanic cells [40-43] have relativly lower storage capacity compared with our system ; EDTA-thionine-azur B (59.0 min), EDTA-safranine-tween-80 (20.0 min), EDTA-safranine-O-DSS (80.0 min), methylene blue-xylose-NaLS (55.0 min) systems.

The conversion efficiency of system containing Rose Bengal as photosensitizer is calculated using the electrical output at power point and the power of incident radiations. The conversion efficiency of the photogalvanic cell is determined as 0.067 % using the following formula:

Conversion efficiency% = $V_{pp} \times i_{pp} / 10.4 \text{ mWcm}^{-2} \times \text{electrode area (cm}^2) \times 100\%$ where the intensity of light was measured in terms of mWcm⁻² with the help of solarimeter.

The overall performance of the photogalvanic cell was observed and reached to remarkable level in the performance of photogalvanic cells with respect to electrical output, initial generation of photocurrent, conversion efficiency and storage capacity of the photogalvanic cell. The results so obtained in Rose bengal –Oxalic acid–CTAB system are summarized in Table 2.

Table 2.	The perfor	mance of pl	hotogalvanic	cell.
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Parameters	Observed results
Open circuit voltage (V _{oc})	550 mV
Short circuit current (i _{sc})	75.1 μΑ
Time of illumination	82 min
Storage capacity $(t_{1/2})$	175 min
Conversion efficiency	0.067 %
Fill factor	0.169
Current at power point (i _{pp})	27.8 μΑ
Potential at power point (V_{pp})	252 mV
Power at power point (pp)	7.005 μW
Maximum power	41.305 μW

[Rose bengal] = 10.16×10^{-5} M; [oxalic acid] = 1.9×10^{-3} M; [CTAB] = 3×10^{-2} M; light intensity = 25.0mWcm⁻²; temperature = 298 K.

4. CONCLUSIONS

The photogalvanic conversion of solar energy has attracted attention of scientists towards solar energy conversion and storage. Considering the limited efforts and the time spent so far on the development of photogalvanic cells, the results appear encouraging and efforts are continuously made in this direction to increase conversion efficiency and storage capacity using different photosensitizers. On the basis of studies and obtained results in developed photogalvanic cell it can be concluded that Rose bengal system is an efficient system and can be use in photogalvanic cell for solar energy conversion and storage.

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