Solar Energy Conversion and Storage: Rose Bengal-Triton X-100 by Photogalvanic Cell

Sawsan A. Mahmoud Basma S. Mohamed
Processes Development Department, Egyptian Petroleum Research Institute
PO box 11727, 1, Ahmed El-Zomor St., Nasr City, Cairo, Egypt

Abstract

Photogalvanic cells are photoelectrochemical devices involving ions as mobile charges moving in solution through diffusion process. These cells are capable of solar power generation at low cost with inherent storage capacity. This property of photogalvanic cell needs to be exploited as this technology is cleaner and promising for application in daily life. In our work, Rose Bengal is used as photosensitizer with oxalic acid as reductant and triton as surfactant for photoelectrochemical conversion of solar energy into electrical energy. The photopotential and photocurrent generated were 289.0 mV and 29.1 µA, respectively. The maximum power of the cell was 8.409 µW. The observed conversion efficiency was 0.023 % and fill factor was determined as 0.293 against the maximum theoretical value 1.0. The photogalvanic cell can work for 45.0 min in dark after irradiation for 21.0 min, i.e. the storage capacity of the photogalvanic cell is 45 min. The effect of different parameters on electrical output of the cell was studied and a mechanism has also been proposed for the generation of photocurrent in photogalvanic cell.

Keywords: Rose Bengal; Oxalic acid; Triton; Conversion efficiency; Storage capacity; Photocurrent.

1. Introduction

The photogalvanic cells are based on “photogalvanic effect”. This term was first time used by Rabinowitch [1, 2] 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 [3–5] 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 photosensitizer is photo excited to energy rich product, which in turn can lose energy electrochemically to generate electricity involving ions as mobile charges diffusing through solution.

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 [6], 118mV [7]; power 0.038 µW [6]; current 12 µA [8]; and energy conversion efficiency of the order of 0.0022% [9]).

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) [6,8,11].

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 arousing 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 Fe^{2+} as reducing agent. The earlier researcher emphasized more on thionine dye sensitizer with Fe^{2+} as reducing agent. Later on, the researcher [12–30] 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.

2. Experimental

2.1.The structure of chemicals used

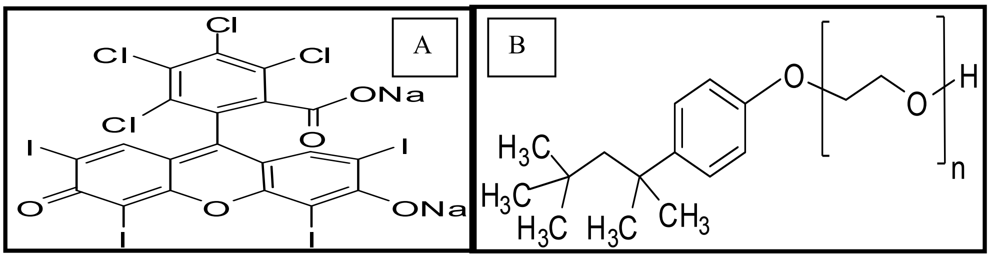

Figure 1A&B: The structure of Rose Bengal (A) and Triton X-100 (B)

2.2. Materials

The structure of Triton X-100 and Rose Bengal are shown in Figure 1A&B. Triton X-100, Rose Bengal and oxalic acid were purchase from Sigme-Aldrich. Sodium hydroxide was provided from Merck.

2.3. Photogalvanic cell

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

A platinum electrode of different area (0.25- 1.0 cm^2) was dipped in one limb having a window and a saturated calomel electrode (SCE) were 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 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 light source. A water filter was placed between the illuminated chamber and the light source to cut-off infrared radiations. The photopotential and photocurrent generated by the system was measured with the help of the digital pH meter and microammeter (Ruttonsha Simpson), respectively. 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 in the circuit through a key to have close circuit and open circuit device. The experimental set-up of photogalvanic cell is given in Figure 2.

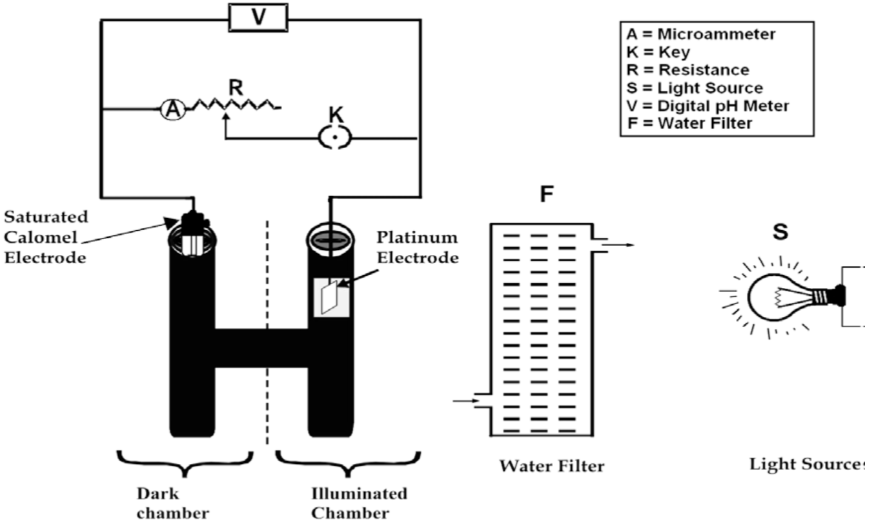

Figure 2. Experimental set-up of photogalvanic cell.

3.Results and discussion

3.1. Effect of pH on the system

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 can be observed from the Table 1 that there is an increase in electrical output of the cell with the increase in pH values. At pH 13.4 a maxima was obtained [31]. On further increase in pH, there was a decrease in photopotential and photocurrent. photogalvanic cells containing the Rose Bengal– Oxalic acid–Triton system were found to be quite sensitive to the pH of the solutions. The effect of variation of pH on photopotential and photocurrent are reported in Table 1.

Table 1 Effect of pH on the system

pH	photopotential, (mV)	photocurrent, (µA)	power, (µW)
13.89	171.5	15.4	2.641
13.74	198.3	19.2	3.807
13.62	216.8	22.5	4.878
13.52	235.2	25.2	5.927
13.40	289	29.1	8.409
13.26	245.8	26.5	6.513
13.11	221.5	23.5	5.205
12.98	196.7	18.4	3.619

3.2. Effect of variation of surfactant concentration

The effect of surfactant (Triton) concentration was also investigated in the present system. The surfactant was used to increase the solubility of photosensitizer. It was observed that electrical output of the cell was found to increase on increasing the concentration of surfactant reaching a maximum value. On further increase in their concentrations, a fall in photopotential, photocurrent and power of the photogalvanic cell was observed. The results are reported in Table 2.

Table 2

Effect of variation of Surfactant (triton) concentration on the system

[Triton]× 10^{-2} M	photopotential, (mV)	photocurrent, (µA)	power, (µW)
6	241.3	22.5	5.249
5.2	265.7	25.2	6.69
4.5	281.5	27.9	7.85
3	289	29.1	8.409
2	273.8	26.8	7.337
1	248	23.6	5.85

3.3. Effect of variation of dye (Rose bengal) concentration

With the increase in concentration of the photosensitizer (Rose Bengal) in present system, the photopotential and photocurrent were found to increase until it reaches a maximum value. On further increase in concentration of photosensitizer a decrease in electrical output of the cell was found. The effect of variation of Rose Bengal concentration on photopotential and photocurrent are reported in Table 3. On the lower side of the concentration range of photosensitizer, there are a limited number of photosensitizer molecules to absorb the major portion of the light in the path and, therefore, there is low electrical output, whereas higher concentration of the photosensitizer does not permit the desired light intensity to reach the molecules near the electrodes and hence, there is corresponding fall in the power of the cell.

Table 3: Effect of variation of dye (Rose bengal) concentration on the system

[Rose bengal] × 10^{-5} M	photopotential, (mV)	photocurrent, (µA)	power, (µW)
10.75	228.5	20.5	4.68
10.47	256.2	24.3	6.225
10.35	271.4	27.5	7.463
10.16	289	29.1	8.409
9.84	267.8	26.7	7.15
9.52	237.2	22.4	5.31
9.00	208.7	20.1	4.19
7.80	188.5	16.5	3.11

3.4. Effect of variation of Oxalic Acid (Reductant) Concentration

With the 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 the electrical output of the cell was observed. The effect of variation of reductant concentration on the photopotential and photocurrent of system are reported in Table 4. The fall in power output was also resulted with decrease in concentration of reductant due to less number of molecules available for electron donation to the cationic form of dye. 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.

Table 4: Effect of variation of reductant (Oxalic acid) concentration on the system

[Oxalic acid] × 10^{-3} M	photopotential, (mV)	photocurrent, (μA)	power, (μW)
1.3	215.8	19.5	4.208
1.5	247.6	22.8	5.645
1.7	262.4	25.9	6.79
1.9	289	29.1	8.409
2.1	278.9	27.5	7.669
2.5	254	23.7	6.019

3.5. Effect of variation of Diffusion length

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 there 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 [8] 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. The results are graphically represented in Figure 3.

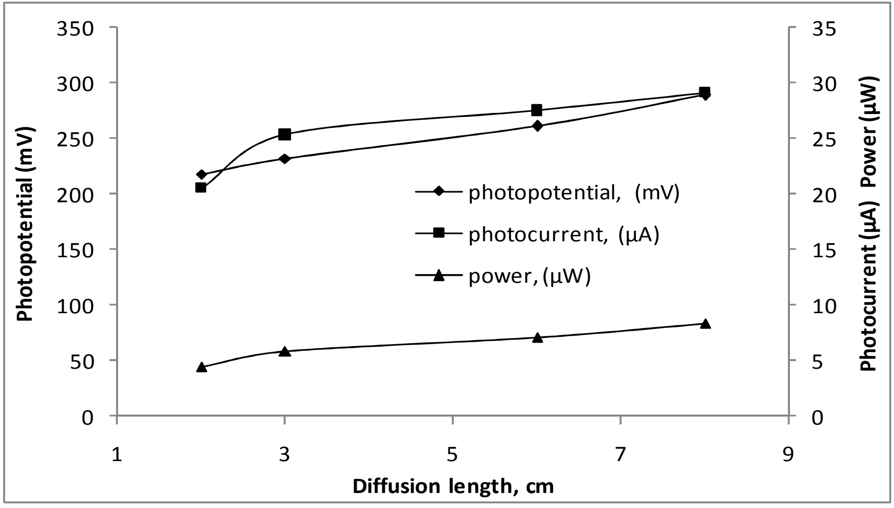

Figure 3. Effect of variation diffusion length on the system

3.6. Effect of variation of Electrode area

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 4. It was observed that with an increase in the electrode area, the power of the cell was found to increase.

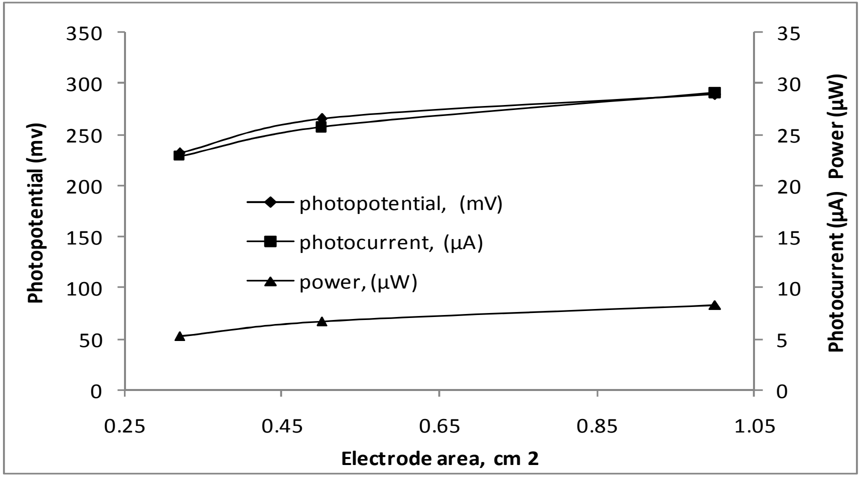

Figure 4. Effect of variation Electrode area on the system

3.7. I–V characteristics of the cell

The short circuit current (isc) 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– Triton system is graphically represented in Figure 6. 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 (Ff) = $v_{pp} \times i_{pp} / V_{oc} \times i_{sc}$

Where as 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 (ff = 0.293) was obtained and the power point of cell (pp) = 2.46 µW was determined on the system.

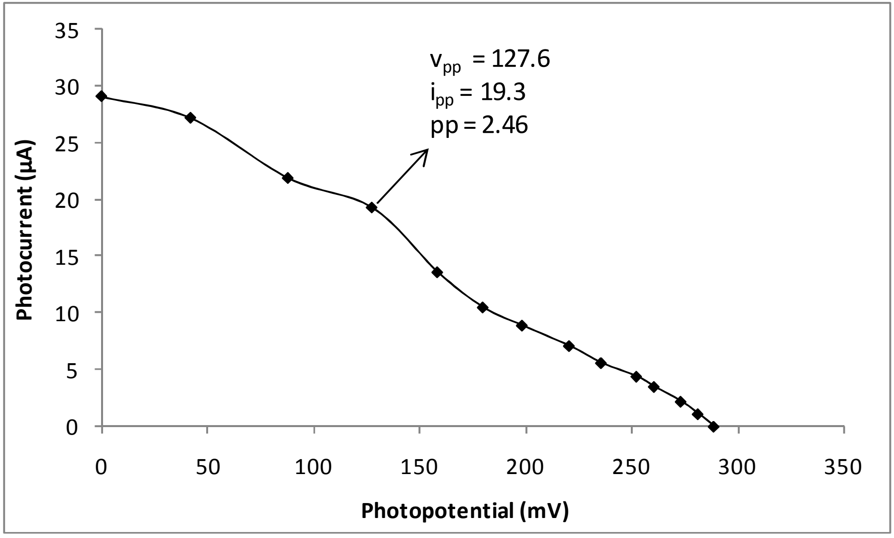

Figure 5. Current – potential (i- V) characteristics of the system.

3.8. Storage capacity 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 45.0 min on irradiation for 21.0 min. The results are graphically represented in Figure 6.

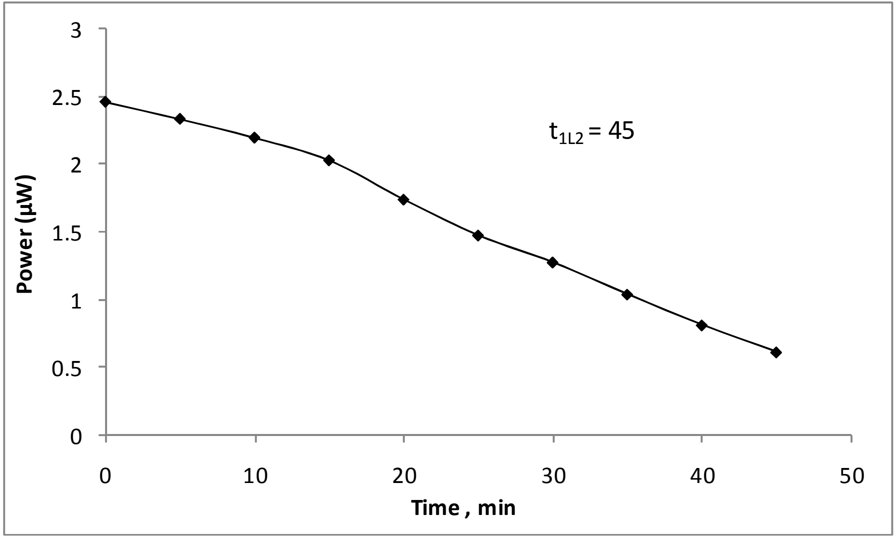

Figure 6: Storage capacity of the photogalvanic cell.

3.9. Conversion efficiency of the photogalvanic cell

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 0.258 % using the following formula:
Conversion Efficiency % = [$v_{pp} \times i_{pp}$ / 10.4 mWcm^{-2} × Electrode area] × 100

3.10. The performance of photogalvanic cell

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–Triton system are summarized in Table 7.

Table 7 The performance of the photogalvanic cell

Parameters	Observed results
Open circuit voltage (V_{oc})	289 mV
Short circuit current (i_{sc})	29.1 µA
Time of illumination	21 min
Storage capacity ($t_{1/2}$)	45 min
Conversion efficiency	0.023 %
Fill factor	0.293
Current at power point (i_{pp})	19.3 µA
Potential at power point (V_{pp})	127.6 mV
Power at power point (PP)	2.46 µW
Maximum power	8.409 µW

4. 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 [8]. 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 [6, 8, 10, 11, 12–15]. 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 [16].

Illuminated chamber (anode)

$$\mathrm{Dye} \xrightarrow{hv} \mathrm{Dye}^{*}(\mathrm{S}) \xrightarrow{\mathrm{ISC}} \mathrm{Dye}^{*}(\mathrm{T}) \qquad \text{(i)}$$

$$\mathrm{Dye}^{*}(\mathrm{T}) + \mathrm{R} \longrightarrow \mathrm{Dye}^{-}(\text{semi or leuco}) + \mathrm{R}^{+} \qquad \text{(ii)}$$

$$\mathrm{Dye}^{-} \longrightarrow \mathrm{Dye} + e^{-}\ (\text{at Pt electrode}) \qquad \text{(iii)}$$

Dark chamber (saturated calomel electrode^{-} SCE as cathode)

$$\mathrm{Dye} + e^{-} \longrightarrow \mathrm{Dye}^{-}\ (\text{semi or leuco})\ \text{at SCE} \qquad \text{(iv)}$$

$$\mathrm{Dye}^{-} + \mathrm{R}^{+} \longrightarrow \mathrm{Dye} + \mathrm{R} \qquad \text{(v)}$$

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 [31]. The reaction is reversible, and the rates of both the forward (light) and reverse (dark) reactions are easily measured [1, 2]. The photogalvanic behavior has been found reversible for several cycles [32].

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

$$D^{-} + S \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} D^{\cdot 2-} + S^{\cdot +}$$

Conclusion

Scientists have been studying the harvesting of solar energy through techniques like photoelectrochemical, photovoltaic and photogalvanic cells. Photovoltaic cells are widely used for solar energy conversion but owing to their lack of storage capacity, the photogalvanic cells have emerged as preferred research field as they have the added advantage of inherent storage capacity. The use of Rose bengal as photosensitizer and Oxalic acid as reductant, have not only enhanced the electrical output but also increased the conversion efficiency and storage capacity of photogalvanic cells. The photogalvanic cells still have enough scope to put efforts to enhance the performance and reduce the cost.

References

[1] E. Rabinowitch, "The photogalvanic effect I. The photochemical properties of the thionine–iron system", J. Chem. Phys. 1940 vol. 8, pp. 551–559, 1940.

[2] E. Rabinowitch, "The photogalvanic effect II. The photogalvanic properties of the thionine–iron system", J Chem. Phys. vol. 8, pp. 560–566 1940.

[3] S. Zhang, A. Islam, X. Yang, C. Qin, K. Zhang, Y. Numata, H. Chen, L. Han, "Improvement of spectral response by co-sensitizers for high efficiency dye sensitized solar cells", J. Mater. Chem. A. vol.1, pp. 4812–4819, 2013.

[4] J. Guo, Y. Shi, Y. Chu, T. Ma," Highly efficient telluride electrocatalysts for use as Pt-free counter electrodes in dye-sensitized solar cells. Chem. Commun. vol. 49, pp. 10157–10159, 2013.

[5] J. Yu, J. Fan, Zhao Li. "Dye-sensitized solar cells based on hollow anatase TiO2 spheres prepared by self-transformation method", Electrochim. Acta. vol. 55, pp. 597–602, 2010.

[6] R. Tamilarasan, P. Natarajan , "Photovoltaic conversion by macromolecular thionine films". Nature, vol. 292, pp. 224–225, 1981.

[7] H. Shiroishi, Y. Kaburagi, M. Seo, T. Hoshi, T. Nomura, S. Tokita, M. Kaneko," Virtual device simulator of bipolar photogalvanic cell", J. Chem. Soft.vol. 8, pp. 47–54, 2002.

[8] M. Kaneko, A. Yamada, Photopotential and photocurrent induced by a tolusafaranine-ethylenediamintetraacetic acid systems, J. Phys. Chem. vol. 81, pp. 1213-1215, 1977.

[9] A. S. N. Murthy, K. S. Reddy, "Studies on photogalvanic effect in systems containing toluidine blue", Sol. Energy, vol. 30, pp. 39–43, 1983.

[10] W. J. Albery, M. D. Archer," Optimum efficiency of photogalvanic cells for solar energy conversion", Nature, vol. 270, pp. 399–402, 1977.

[11] S. Dube, S. L. Sharma, "Studies in photochemical conversion of solar energy: simultaneous use of two dyes with mannitol in photogalvanic cell', Energy Convers. Manage. vol. 35, pp. 709–711, 1994.

[12] S. Dube, S. L. Sharma, S. C. Ameta, "Photogalvanic effect in Azur B-NTA system",
Energy Convers. Manage.vol. 38, pp. 101–106, 1997.

[13] K. M. Gangotri, R. C. Meena, R. Meena, "Use of micelles in photogalvanic cells for solar energy conversion and storage: cetyl trimethyl ammonium bromideglucose-
toluidine blue system", J. Photochem. Photobiol. A: vol. 123, pp. 93–97, 1999.

[14] K. M. Gangotri, R. C. Meena, "Use of reductant and photosensitizer in photogalvanic cells for solar energy conversion and storage: oxalic acid– methylene blue system", J. Photochem. Photobiol. A: vol. 141, pp. 175–177, 2001.

[15] K. M. Gangotri, S. Pramila, "Use of anionic micelles in photogalvanic cells for solar energy conversion and storage NaLS–mannitol–safranine system", Energy Sources Part A: vol. 28, pp. 149–156, 2006.

[16] K. R. Genwa, A. Chouhan, "Role of heterocyclic dye (Azur A) as a photosensitizer in photogalvanic cell for solar energy conversion and storage: NaLS–ascorbic acid system", Sol. Energy, vol. 80, pp. 1213–1219, 2006.

[17] S. C. Ameta, P. B. Punjabi, J. Vardia, S. Madhwani, S. Chaudhary, "Use of Bromophenol Red–EDTA system for generation of electricity in a photogalvanic cell", J. Power Sources, vol. 159, pp. 747–751, 2006.

[18] C. Lal, "Use of mixed dyes in a photogalvanic cell for solar energy conversion and storage: EDTA–thionine–Azur-B system", J. Power Sources, vol. 164, pp. 926–930, 2007.

[19] K. R. Genwa, M. Genwa, "Photogalvanic cell: a new approach for green and sustainable chemistry", Sol. Energy Mater Sol. Cells, vol. 92, pp. 522–529, 2008.

[20] K. M. Gangotri, M. K. Bhimwal, "Study the performance of photogalvanic cells for solar energy conversion and storage: Rose Bengal–D-xylose–NaLS system", Sol. Energy, vol. 84, pp. 1294–1300, 2010.

[21] K. K. Bhati, K. M. Gangotri, "Photogalvanic conversion of solar energy into electrical energy by using NaLS–

xylose–methylene blue system", Int. J. Electr. Power Energy Syst. vol. 33, pp.155–158, 2011.
[22] P. P. Solanki, K. M. Gangotri, "Photogalvanic cell for conversion of solar energy into electricity: safranine–arabinose–sodium lauryl sulphate system. Sol. Energy, vol. 85, pp. 3028–3035, 2011.
[23] K. M. Gangotri, P. Aseri, M. K. Bhimwal, "The use of Tergitol-7 in photogalvanic cells for solar energy conversion and storage: an EDTA–Azur B system. Energy Sources, Part A: vol. 35, pp. 312–320, 2013.
[24] K. R. Genwa, A. Kumar, A. Sonel, "Photogalvanic solar energy conversion: Study with photosensitizers Toluidine Blue and Malachite Green in presence of NaLS. Appl. Energy, vol. 86, pp. 1431–1436, 2009.
[25] P. Koli, U. Sharma, K. M. Gangotri, "Solar energy conversion and storage: Rhodamine B – Fructose photogalvanic cell", Renew. Energy, vol. 37, pp. 250–258, 2012.
[26] U. Sharma, P. Koli, K. M. Gangotri, "Brilliant Cresyl Blue – Fructose for enhancement of solar energy conversion and storage capacity of photogalvanic solar cells", Fuel,vol. 90, pp. 3336–3342, 2011.
[27] S. Yadav, C. Lal, "Optimization of performance characteristics of a mixed dye based photogalvanic cell for efficient solar energy conversion and storage", Energy Convers. Manage.vol. 66, pp. 271–276, 2013.
[28] K. R. Genwa, C. P. Sagar, "Energy efficiency, solar energy conversion and storage in photogalvanic cell", Energy Convers. Manage.vol. 66, pp. 121–126, 2013.
[29] A. Chouhan, K. R. Genwa, "The study of the photogalvanic effect in a photogalvanic cell containing acid fuchsin as a photosensitizer in a benzethonium chloride-EDTA system", Energy Sources, Part A: vol. 35, pp. 685–693, 2013.
[30] M. K. Bhimwal, K. M. Gangotri, "A comparative study on the performance of photogalvanic cells with different photosensitizers for solar energy conversion and storage: d-xylose–NaLS systems", Energy, vol. 36, pp. 1324–1331, 2011.
[31] S. A. Mahmoud, B. S. Mohamed, A.S. El-Tabei, M.A. Hegazy,M. A.Betiha, H.M.Killa, E. K. Heikal, S. A.KHalil, M. Dohium, S. B. Hosney Improvement of the Photogalvanic Cell for Solar Energy Conversion and Storage: Rose Bengal–Oxalic Acid -Tween 80 System Energy Procedia 46, pp. 227 – 236, 2014.
[31] W. J. Albery, A. W. Foulds, K. J. Hall, A. R. Hillman, R. G. Egdell, A. F. Orchard, "Thionine coated electrode for photogalvanic cells", Nature, vol. 282 ,pp. 793–797, 1979.
[32] E. Suresh, J. Pragasam, F. P. Xavier, K. S. Nagaraja, "Investigation of manganese–molybdenum–diethyldithiocarbamate complex as a potential system for solar energy conversion", Int. J. Energy Res. vol. 23, pp. 229–233, 1999.