

USE OF AZINE DYE AS PHOTSENSITIZER IN SOLAR CELL: EDTA–SAFRANINE SYSTEM

K. M. Gangotri* and O. P. Regar

*Department of Chemistry
Jai Narain Vyas University
Jodhpur 342005, India*

الخلاصة :

نمحص في هذه الدراسة الظاهرة الفولضونية لخلية تحتوي السافرانين و EDTA كعناصر جاسئة للضوء ومختزلة على الترتيب. وقد أنتجت هذه الخلية جهداً وتياراً ضوئيين قدرهما (٧٦٠) ميلي فولت و(٥٠) ميكروأمبير على الترتيب، وكفاءة التحول قدرها ٠,٢٦١٨٪ وأقصى طاقة للتحلية ٢٨ ميكرو واط. درسنا أيضاً تأثير عوامل مختلفة على تابع الخلية الكهربائي، ومن ثم نقترح ميكانيكية لإنتاج التيار والفولت الضوئيان.

ABSTRACT

The photogalvanic effect was studied in a photogalvanic cell containing safranin and EDTA as photosensitizer and reductant, respectively. The photopotential and photocurrent generated by the system were 760 mV and 50 μ A respectively. The observed conversion efficiency was 0.2618% and the maximum power of the cell was 38.0 μ W. 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.

* Address for correspondence:
C-38, University Jaswant Campus
Jodhpur 342001
Rajasthan, India

USE OF AZINE DYE AS PHOTSENSITIZER IN SOLAR CELL: EDTA-SAFRANINE SYSTEM

1. INTRODUCTION

The photogeneration of electricity has attracted the attention of scientists as a viable medium for solar energy conversion with bright future prospects. Rideal and Williams [1] discovered the photogalvanic effect for the first time but it was systematically studied by Rabinowitch [2, 3]. Later on, Kaneko and Yamada [4], Murthy *et al.* [5–7], Rohtagi Mukherjee *et al.* [8], Ameta *et al.* [9–12], and Gangotri *et al.* [13–15] have reported some interesting photogalvanic systems. Various problems encountered in the development of this field have been discussed by Hoffman and Lichtin [16]. The theoretical conversion efficiency of a photogalvanic cell is about 18% but the observed conversion efficiencies are quite low, due to lower stability of dye, back-electron transfer, aggregation of dye molecules around electrode, *etc.*

A detailed literature survey reveals that different photosensitizers have been used in photogalvanic cells [17–21], *e.g.* riboflavin, brilliant cresyl blue, methylene blue, and toluidine blue, but no attention has been paid to the use of azine dye as photosensitizer in photogalvanic cell for solar energy conversion, and, therefore, the present work was undertaken by selecting EDTA-Safranin system for this purpose.

2. EXPERIMENTAL

Safranin (Loba), EDTA (SISCO), and sodium hydroxide (s.d.fine) were used in the present work. All the solutions were prepared in doubly distilled water. A mixture of the solutions of the dye, EDTA, and sodium hydroxide was taken in an H-shaped glass cell. A platinum electrode ($1.0 \times 1.0 \text{ cm}^2$) was dipped into one limb of the cell and a saturated calomel electrode (SCE) was kept in the other. The platinum electrode was exposed to a 200W 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 infrared radiation. The photochemical bleaching of safranin (Saf.) was studied potentiometrically. The photopotential and photocurrent generated by the system saf./EDTA/OH/ $h\nu$ were measured by the digital pH meter (Agronic Model 511) and microammeter (Sympson), respectively. The i - V characteristics of the cell were studied using an external load (log 470K) in the circuit.

3. RESULTS AND DISCUSSION

3.1. Effect of Variation of pH

The electrical output of the cell was affected by the variation in pH of the system. The results are reported in Table 1.

It is observed from Table 1 that there is an increase in electrical output of the cell with an increase in pH values. At pH 12.8, a maximum was obtained. On further increase in pH, there was a decrease in photopotential and photocurrent. Thus, photogalvanic cell containing the safranin EDTA 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 pK_a of the reductant and the desired pH is higher than its pK_a value ($\text{pH} > pK_a$). The reason may be the availability of reductant in its anionic form, which is a better donor form.

3.2. Effect of Variations of EDTA Concentration

The electrical output of the cell was affected by the variation of reducing agent concentration [EDTA] in the system; the results are summarized in Table 2. Lower concentrations of reducing agents resulted in a fall in electrical output because fewer reducing agent molecules were available for electron donation to dye molecules.

Table 1. Effect of Variation of pH.

	[Saf.] = $4.00 \times 10^{-6} \text{ M}$ Temp = 303 K		[EDTA] = $2.24 \times 10^{-6} \text{ M}$ Light Intensity = 10.4 mW cm^{-2}		
	pH				
	12.0	12.4	12.8	12.9	13.0
Photopotential (mV)	410.0	522.0	760.0	570.0	293.0
Photocurrent (μA)	43.0	52.0	50.0	46.0	31.0

A large concentration of reducing agent again resulted in a decrease in electrical output, because the large number of reducing agent molecules hinder the dye molecules from reaching the electrode in the desired time limit.

3.3. Effect of Variation of Safranin Concentration

Dependence of photopotential and photocurrent on the concentration of dye was studied and the results are summarized in Table 3.

A lower concentration of dye resulted into a fall in photopotential and photocurrent because fewer dye molecules are available for the excitation and consecutive donation of the electrons to the platinum electrode. A greater concentration of dye again resulted in a decrease in electrical output as the intensity of light reaching the dye molecule near the electrode decreases due to absorption of the major portion of the light by dye molecules present in the path.

3.4. Effect of Diffusion Path Length

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

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 a slow rate determining step at a later stage.

Table 2. Effect of Variation of EDTA Concentration.

	[EDTA] × 10 ³ M				
	1.5	1.8	2.2	2.5	2.8
Photopotential (mV)	310.0	486.0	760.0	505.0	285.0
Photocurrent (μA)	30.0	56.0	50.0	43.0	26.0

Table 3. Effect of Variation of Safranin Concentration.

	[Saf.] × 10 ⁶ M				
	3.0	3.5	4.0	4.2	4.5
Photopotential (mV)	245.0	495.0	760.0	610.0	280.0
Photocurrent (μA)	22.0	38.0	50.0	46.0	24.0

Table 4. Effect of Diffusion Path Length.

Diffusion path length D_L (mm)	Maximum photocurrent i_{max} (μ A)	Equilibrium photocurrent I_{eq} (μ A)	Rate of initial generation of current (μ A min ⁻¹)
35.0	74.0	49.0	13.0
40.0	78.0	49.0	15.0
45.0	80.0	50.0	16.5
50.0	82.0	48.0	17.5
55.0	84.0	48.0	18.5

On the basis of the effect of diffusion path length on the current parameters, as investigated by Kaneko and Yamada [4], 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 carries in the cell diffusing through the path.

3.5. Current Voltage ($i - V$) Characteristics of the Cell

The short circuit (i_{sc}) and open circuit voltage (V_{oc}) of the photogalvanic cells were measured with a microammeter (circuit closed) and with a digital pH meter (circuit open), respectively. The current and potential value between these two extreme values (V_{oc}) and (i_{sc}) were recorded with a carbon pot (log 470 K) connected to a microammeter through which an external load was applied.

It was observed that $i-V$ curve deviated from its ideal regular rectangular shape. A point in $i-V$ curve, called the power point (pp) determined, where the product of potential and current was a maximum, and the values are V_{pp} and i_{pp} , respectively. With the help of the $i-V$ curve, the fill factor was determined as 0.58 using the formula:

$$\text{fill-factor } (n) = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}} \quad (1)$$

3.6. Conversion Efficiency and Performance of the Cell

With the help of current and potential values at power point and the incident power of radiations, the conversion efficiency of the cell was determined as 0.2618% by using the formula:

$$\text{Conversion efficiency} = \frac{V_{pp} \times i_{pp}}{10.4(mW/cm^2)} \times 100\% \quad (2)$$

The performance of the cell was studied by applying the external load necessary to have the current and potential at the power point after removing the source of light. It was observed that the cell can be used in the dark at its power point for 19 minutes.

4. MECHANISM

On the basis of the above investigations, the mechanism of photocurrent generation in the photogalvanic cell can be represented as follows:

Illuminated Chamber:



At Pt electrode:



Dark Chamber:

At electrode:



Where Saf, Saf*, Saf⁻, R, and R⁺ are the safranin, excited form of safranin, semi or leuco form of safranin, reductant (EDTA), and its oxidized form, respectively.

Dye molecules will get excited on illumination and the excited dye will accept an electron from the reductant to give its semi-reduced (leuco) form (Saf⁻); during this process reductant (R) is converted to its oxidized form (R⁺), which will move towards the dark chamber. The leuco form of the dye (Saf⁻) will donate its electron to the electrode in the illuminated chamber and will regenerate the original dye molecules. On the other hand, the dye accepts an electron from the electrode and is reduced to its semi or leuco form, which donates its electron back to the oxidized form of reductant (R⁺) to give reductant molecules (R), and the cycle will go on.

ACKNOWLEDGEMENTS

The authors are grateful to Professor and Head, Prof. S. P. Garg, Department of Chemistry, Jai Narain Vyas University, Jodhpur, India, for providing the necessary laboratory facilities and Dr. D. S. Jha, Associate Professor, for reviewing the draft and making his scholarly and helpful comments.

REFERENCE

- [1] E. K. Rideal and D. C. Williams, *Makromol. Chem.*, (1925), p. 258.
- [2] E. Rabinowitch, *J. Chem. Phys.*, **8**(1940), p. 551.
- [3] E. Rabinowitch, *J. Chem. Phys.*, **8**(1940), p. 560.
- [4] Kaneko and A. Yamada, *J. Phys. Chem.*, **81**(1977), p. 1213.
- [5] A. S. N. Murthy and K. S. Reddy, *Int. J. Energy Res.*, **3**(1979), p. 205.
- [6] A. S. N. Murthy, H. C. Dak, and K. S. Reddy, *Int. J. Energy Res.*, **4**(1980), p. 339.
- [7] A. S. N. Murthy and K. S. Reddy, *Solar Energy*, **30**(1983), p. 39.
- [8] K. K. Rohatgi-Mukherjee, M. Roy, and B. B. Bhowmik, *Solar Energy*, **31**(1983), p. 417.
- [9] S. C. Ameta, P. K. Jain, A. K. Janu, and R. Ameta, *The Energy Journal*, **58**(1985), p.8.
- [10] S. C. Ameta, S. Khamesra, A. K. Chittora, and K. M. Gangotri, *Int. J. Energy Res.*, **13**(1989), p. 643.
- [11] S. C. Ameta, S. Khamesra, Manju Bala, and K. M. Gangotri, *Phillips J. Energy Res.*, **119**(1990), p. 371.
- [12] S. C. Ameta, S. Khamesra, N. K. Jain, and K. M. Gangotri, *Pol. J. Chem.*, **65**(1991), p. 1415.
- [13] K. M. Gangotri, Om Prakash Regar, Chhagan Lal, Krishna Ram Genwa, Prashant Kalla, and Rajni Meena, *Arab J. Sc. Engg.*, **22**(1997), p. 115.
- [14] K. M. Gangotri, Prashant Kalla, Krishna Ram Genwa, Chhagan Lal, Om Prakash Regar, and Rajni Meena, *J. Ind. Con. Chem.*, **10**(1994), p. 19.
- [15] K. M. Gangotri, Om Prakash Regar, Chhagan Lal, Prashant Kalla, Krishna Ram Genwa, and Rajni Meena, *Int. J. Energy Res.*, **20**(1996), p. 581.
- [16] M. Z. Hoffman and N. N. Lichtin, *Solar Energy*. ed. R. R. Hantala, R. B. King, and C. Kutal. Clifton: N. J. Publisher, p. 153.
- [17] T. Yamase, *Photochem Photobiol.*, **34**(1981), p. 111.
- [18] T. Tamilarasan and P. Natarajan, *Indian J. Chem.*, **20A**(1983), p. 213.
- [19] Mukhopadhyay and B. B. Bhowmik, *J. Photochem. Photobiol.*, **69**(1992), p. 223.
- [20] B. B. Bhowmik and M. Mukhopadhyay, *J. Photochem. Photobiol.*, **78**(1984), p. 173.
- [21] Prabudh K. Jain, Praveen K. Jain, and Suresh C. Ameta, *Z. Phys. Chem. (Leipzig)* **265**(1984), p. 841.

Paper Received 30 November 1996; Revised 12 May 1999; Accepted June 11, 1997.