USE OF AZUR-C-NITRILOTRIACETIC ACID AS A NEW SENSITIZER-REDUCTANT SYSTEM FOR ENHANCED SIMULTANEOUS SOLAR POWER CONVERSION AND STORAGE BY PHOTOGALVANIC CELL

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ABSTRACT:

Solar power is energy from the sun that is converted into thermal or electrical energy. A solar cell, or photogalvanic cell, is a device that converts the energy of light directly into electricity by the photogalvanic effect, which is a physical and chemical phenomenon. The present study of the PG cells based on so far unexplored Azur-C-Nitrilotriacetic acid as a photosensitizer-reductant couple in the sodium hydroxide alkaline medium has shown greatly enhanced cell performance over published results. On the basis of the effect of various parameters of performance of the cell, a tentative mechanism for photocurrent generation has been proposed. The maximum photo potential, photocurrent and power of this cell were **3**4*7* MV*, 7*0 µA and 19.84 µW. The observed conversion efficiency was 0.19% and 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.

Keywords- Azur-C, Nitrilotriacetic acid, Fill Factor, Conversion Efficiency, Storage Capacity

INTRODUCTION:

The conventional fuel is limited and their combustion is leading to increase in environmental pollution. In the era of energy crisis, there is an urgent need to find out alternative, non-conventional, harmless, inexhaustible source of energy, and, photogalvanic cell has these qualities. Becquerel [1839a, 1839b] investigation shows the photo effects in electrochemical systems were first reported by on the solar illumination of metal electrodes long back and Studies of the effect of actinic radiation of sunlight by means of electric currents. Surash and Hercules [1962] proved that only negative photopotential should be obtained with carbonyl compounds and Studies on photo-induced electrode potentials. Ameta et al. [1988] reported use of toluidine blue as dye and nitroloacetic acid as reductant (TB-NTA) system in photogalvanic cell for solar energy conversion. Tennakone and Kumara [1998] investigate the sensitization of nanoporous films of TiO2 in the presence of santaline (red sandal wood pigment) used as dye. Jana and Bhowmik [1999] reported enhancement in the power output of a solar cell consisting of mixed dyes for Storage capacity and conversion efficiency of photogalvanic cells. Schwarzhurg and Willig [1999] explored the origin of photovoltage and photocurrent in nanoporous, dye-sensitized solar cell and photoelectrochemical solar cell. Monat and McCusker [2000] reported the femto-second excited state dynamics of an iron (II) polypyridyl photoelectrochemical cell for storage of energy. Hara et al. [2003] investigated design of coumarin used as dyes having thiophene moieties for highly efficient organic dye-sensitized solar cells. Ameta et al. [2006] investigate the use of micelles in photogalvanic cell for solar energy

conversion storage in Bromophenol-EDTA system for Storage capacity and conversion efficiency of photogalvanic cells.Genwa et al[2009] explored the construction of a dye–sensitized solid-state photovoltaic cell was attempted by Photogalvanic solar energy conversion with different systems reported on Toluidine Blue-Malachite Green in presence of Na LS. Yadav et al[2010,2010] reported the conversion and storage by using Thionine as photosensitizer and EDTA as reductant in the presence of CTAB as surfactant for conversion and storage and also Use of Bismarck Brown–Glucose system for generation of Electricity in a Photogalvanic cell. Koli [2014, 2015] investigate the Solar energy conversion and storage using Naphthol Green-B dye photosensitizer in photogalvanic cells and Study of enhanced photogalvanic effect of Naphthol Green-B and result obtained in these study may be due to the very small sized Pt with the SCE component of the combination electrode. Yadav et al [2016,2017] observed the generation of Electricity in a Photogalvanic cell and also report the advance environment successive key for solar energy conversion and storage using Thionine- Glucose-CTAB system, Rose Flower-Mannitol-NTA system and Rose Flower-Ascorbic Acid system. Mahesh Meena [2021]discuss on four systems namely Rh B – EDTA - Tween80, MB – EDTA -NaLS, Rh 6G – EDTA - CTAB &Safranine - EDTA - ALS.

EXPERIMENTAL:

Azur-C (Koch-light), sodium hydroxide (Hi-media) and NTA (Koch-light) were used in present work. A mixture of solutions of Azur C, NTA and sodium hydroxide was taken in a H-type cell. A platinum electrode (1 cm x 1 cm) was immersed in one limb of the H-type cell, which was illuminated with a 200 W tungsten lamp (Sylvania). On the other side, a saturated calomel electrode (SCE) was kept in the other limb of the cell and that too in dark, A water filter was used for cutting infra-red Radiations. Photochemical bleaching of Azur C by Na in alkaline medium was observed using a digital pH meter (Systronics Model 435) and multimeter (Systronics Model 435) to measure potential and photocurrent, respectively, The i-v characteristics of the system Azur C-NTA/OH- /hv in photogalvanic cell was observed with an external load (log 500 K) in the circuit. The experimental set-up of photogalvanic cell is given in Figure 1

RESULTS AND DISCUSSION:

1. Effect of pH on electrical output of the cell

An increase in the electrical output of the cell was observed with the increase in pH values. It was maximum for pH 11.2. Further increase in pH values resulted into decrease in photopotential and photocurrent both. It was observed that the pH for optimum output is much close to pKa value of the reductant. It is because of the fact that the reductant is available in its anionic form at this pH value, which is better donor of electron, at pH slightly higher than pka. Photopotential and photocurrent due to variation in pH are reported in table-1.

2. Effect of reductant and dye concentration

Initially, the output of the cell was low for the lower concentration of the reductant, because less number of reductant molecules was available for electron donation to excited dye molecules. On the other hand, larger concentrations of NTA also cause decrease in the electrical output as larger number of reductant molecules hinder the movement of dye molecules to reach the electrode in desired microtime limit. Here maximum photopotential and photocurrent were obtained at the [NTA] = 2.0×10^{-2} M. During the variation of

dye concentration, the maximum output was obtained at $1,2 \times 10^{-4}$M Azur C. Lower concentrations of dye molecules resulted into poor electrical output because less number of dye molecules were available for excitation and consecutive donation of the electrons to the platinum electrode, Similarly larger concentrations of *A*zur C also decrease the photopotential and photocurrent, as the light intensity reaching the dye molecules near the platinum electrode will decrease due to absorption of major portion of light by dye molecules present in the path. The dependence of photo potential and photocurrent on concentration of NTA and Azur C are summarized in Table 2.

3. Effect of diffusing path length

The effect of diffusing path length on current parameters of the cell (imax, ieq and initial rate of generation of current) using H-cells of different dimensions was studied and the results are given in Table 3. A sharp increase in photocurrent to a maximum (imax) in first few minutes of illumination and then a decrease to a stable value (ieq) was observed. This behaviour of photocurrent indicates an initial rapid reaction followed by a slow rate determining step at a later stage. More knowledge about nature of electrode active species; donating an electron to the electrode or accepting an electron from the electrode, may be obtained by changing diffusing path length. Out of various probable processes for photocurrent generation in photogalvanic cell, the three possible combinations for *v*arious electrode active species are shown in Table 4. If oxidised form of the reductant (R+) is considered as an electrode active species then it must diffuse from the illuminated chamber to the dark chamber of the cell to accept an electron from the dark electrode. It was observed that the initial

rate of generation of photocurrent and the value of imax were proportional to the diffusion length instead of being inversely proportional and the value of ieq. was found to be almost independent to the variation of diffusion length, on basis of the observed data, case I and II i. e. the oxidised form of the reductant to act as an electrode active species in dark chamber, became invalid. Therefore, it may conclude that the leuco or semi reduce form of the dye and dye itself are the main electrode active species at illuminated and dark electrode respectively. However, the reductant and its oxidised form (R+) behave only as an electron carrier in the cell.

4. Effect of electrode area, temperature and light intensity

The values of imax were found to increase with increase in electrode area whereas negligible decrease in ieq was observed and the effect of temperature on photopotential and photocurrent of this cell represented in Figure-2. It is clear from the figure that rise in temperature affects the two parameters in different manners; the photocurrent increase whereas photopotential falls. It is known that increase in temperature causes decrease in internal resistance of the cell and hence a rise in photocurrent was observed. *A*s a consequence, the photopotential of the cell decreases. This rapid fall of the photopotential cannot be compensated with the corresponding rise in photocurrent, so higher temperature should be avoided for better electrical output from the photogal*v*anic cell.

The effect of light intensity on the electrical output of the cell was also studied by using tungsten lamp of different wattage. It was observed that photo potential increase in a logarithmic manner and photo current increases linearly with increasing intensity of light, because higher the light intensity means increase in

number of photons per unit area (incident power) striking the dye molecules around platinum electrode. The temperature of cell al so rises with the increase in light intensity and therefore a*v*erage light intensity (10.4 mw cm^{-2}) was used throughout the present investigations. On a clear day, about 100 mw cm^{-2} solar insolation is falling on the earth and output from the cell in sunlight should be approximately double (because $\log_{10} 100 = 2.0$) of the output with the intensity 10.4 mw cm^{-2}, howe*v*er, this was never achie*v*ed in the present work. This may be due to lower intensity of sunlight or the presence of saturation point, above which increase in light intensity does not affect the electrical output of the cell.

5. Current Voltage (i-V) Characteristics, Conversion Efficienc*y* and Performance of the cell

The short circuit current (is*c)* and the open circuit voltage (Vo*c)* of the photo*g*alvanic cell were measured with the help of a microameter (keeping circuit closed) and a multimeter (keeping the circuit open), respectively. The potential and current values in between these two extremes values (Voc and isc) were obtained using a *c*arbon pot (log 500 K) connected in the circuit, through which an external load was applied.

It was observed that i-V curve of this cell deviated from its ideal rectangular shape. A point on this curve (i-V) called power point (pp) was determined, where the product of potential and current was maximum. The corresponding potential and current at power point are denoted by Voc and isc, respectively. The fill factor and conversion efficiency of the cell was determined as 0.23 and 0. 19% respectively by using the formula:
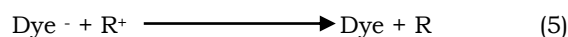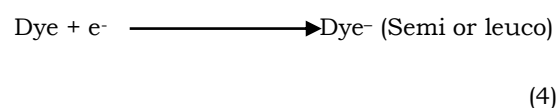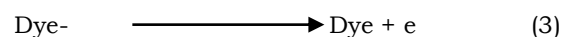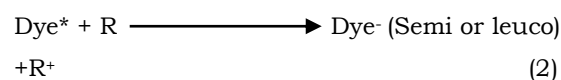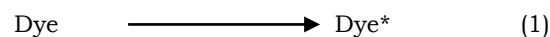
$$\text{Fill Factor} = \frac{V_{pp} \times i_{pp}}{V_{oc} \times i_{sc}} \qquad (1.1)$$

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

$$(1.2)$$

The performance of the cell was also studied by applying the necessary external load to have potential at power point in absence of light. It was observed that this photogalvanic cell can be used in dark for 38 minutes, at its power point. Thus use of photogalvanic cell in dark is an additional advantage.

Mechanism:

On the basis of these observations, a mechanism is suggested for the generation of photocurrent in the photogalvanic cell as:

Dye $\longrightarrow$ Dye* (1)

Dye* + R $\longrightarrow$ Dye$^-$ (Semi or leuco) +R$^+$ (2)

Dye- $\longrightarrow$ Dye + e (3)

Dye + e$^-$ $\longrightarrow$ Dye$^-$ (Semi or leuco) (4)

Dye $^-$ + R$^+$ $\longrightarrow$ Dye + R (5)

Where Dye, Dye*, Dye$^-$, R and R$^+$ are the dye, excited form of dye, semi or leuco form of dye, Reductant and oxidized form of the Reductant, respectively.

CONCLUSION:

Conclusively the NTA as Reductant and Azur C as dye can be used successfully in a photogalvanic cell. The Conversion Efficiency and Fill Factor of the cell is 0.19 % and 0.23 respectively, on irradiation for 38 minutes developed photogalvanic cell. It has been

observed that the Dye has not only enhanced the electrical parameters (i.e. Photopotential, photocurrent and power) but also enhanced the conversion efficiency and storage capacity of photogalvanic cell. The efforts are also successful because of the photogalvanic cells showed good prospects of becoming commercially viable.

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| A = Microammeter |
| K = Key |
| R = Resistance |
| S = Light Source |
| V = Digital pH Meter |
| F = Water Filter |
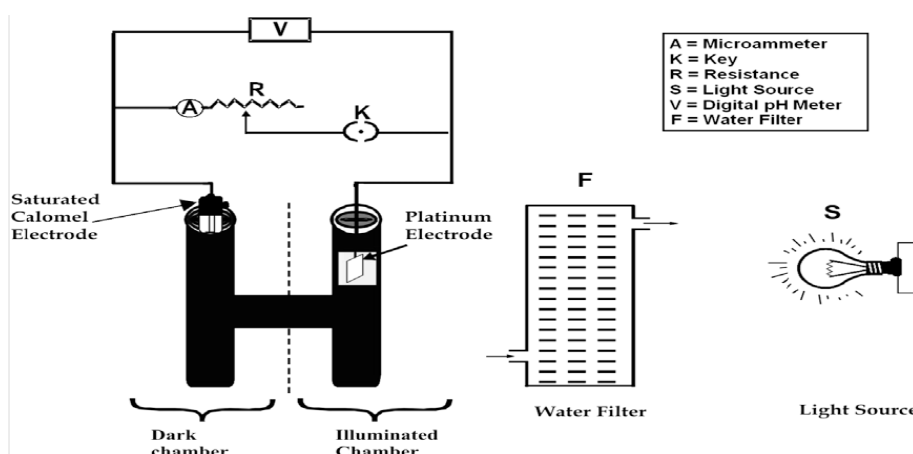
Table 1- Effect of Variation of pH [Azur C] = 2.0×10^{-4}M; [NTA] = 1.2×10^{-2}M Light intensity = 10.4mW cm^{-2}; Temp= 303K		
pH	**Photopotential (mV)**	**Photocurrent (µA)**
10.8	315	25.0
11.0	321	30.0
11.2	330	50.0
11.3	342	40.0
11.4	339	20.0
11.5	325	15.0

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Table 2-Effect of variation of Reductant and Dye Concentration pH = 11.2 ; Light intensity =10.4mW cm^{-2}; Temp= 303K			
[NTA] ×10^{-2}M	[Azur C] ×10^{-4}M	Photopotential (mV)	Photocurrent (μ A)
1.2	2.0	339.0	50.0
1.6	2.0	342.0	60.0
2.0	2.0	347.0	70.0
2.4	2.0	338.0	60.0
1.2	2.0	358.0	50.0
1.2	0.4	335.0	40.0
1.2	0.8	342.0	50.0
1.2	1.2	347.0	70.0
1.2	1.6	331.0	60.0
1.2	2.0	330.0	50.0
1.2	2.4	346.0	30.0

Table 3-Effect of Diffusion length [Azur C] = 2.0 ×10^{-4}M; [NTA] = 1.2 ×10^{-2}M pH = 12.7;Light intensity =10.4mW cm^{-2}; Temp= 303K			
Diffusion path length D$_L$ (mm)	Maximum Photocurrent i$_{max}$ (μ A)	Equilibrium Photocurrent i$_{eq}$ (μ A)	Rate of initial gen. of current (μ A min^{-1})
25.0	110.0	72.0	13.3
30.0	120.0	70.0	15.0
35.0	132.0	69.0	17.6
40.0	138.0	69.0	18.7
45.0	150.0	67.0	20.0

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Table 4 The Probable Electrode Active Species	
In Illuminated Chamber	**In Dark Chamber**
Dye	Oxidised Form of the Reductant (R+)
Semi or Leuco form of Dye	Oxidised Form of the Reductant (R+)
Semi or Leuco form of Dye	Dye

AZUR C-NTA System

Figure-2 Variation of Photopotential with Temperature

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