ORIGINAL ARTICLE

Sudan-I dye and Fructose chemicals based photogalvanic cells for electrochemical solar energy conversion and storage at low and artificial sun intensity

Pooran Koli

Department of Chemistry, Jai Narain Vyas University, Jodhpur 342001, Rajasthan, India

Abstract   With the rapid commercialization of wind and solar power generation, the need of power storage capacity is gaining importance. The photogalvanic cells as described in the present manuscript are promising energy devices as they provide for a route for simultaneous solar power generation and its storage. The study of photogalvanics of Sudan-I dye (photo-sensitizer)-Fructose (reductant)-Sodium Lauryl Sulfate (surfactant) has been done in alkaline medium at low and artificial sun intensity with aim of finding relatively better combination of chemicals like photosensitizer, reductant and surfactant for further enhancing the efficiency of these cells. This combination of chemicals has shown very impressive and surprisingly very high improvement in cell performance. The optimum conditions for cell have also been observed for optimal cell performance. The power at power point, solar conversion efficiency, open circuit potential, equilibrium current, charging time, and power storage capacity (as half time) at 10.4 mWcm^{-2} (low and artificial illumination intensity) has been observed of the order of 367.8 μW, 11.49%, 1014 mV, 1350 μA, 21 min, and 30 min, respectively.

1. Introduction

The sustainable energy generation needs to focus mainly on exploitation of the renewable energy sources like wind energy, solar energy, etc. The solar energy is a peculiar renewable energy source as it is most abundant and mother of rest other energy resources (like wind, bio-mass, ocean currents, fossils fuels, etc.). It is only solar energy which can provide electricity as long as life exits on the planet earth. It is also an energy source which can supply power on all planets. It is because we don't know whether life, water, wind, coal, etc. exist on the other planets, but it is certain that all planets have the solar radiations. Therefore, the development of solar energy harvesting techniques (like photovoltaic cell, photogalvanic cell (PG),

etc.) for solar power production is of utmost importance for the future

The PG cells are relatively cheap, clean and potential source of Energy. The PG cells are light sensitive electrochemical devices capable of converting solar energy into solar power with its inherent storage in the form of photo-excited states of the sensitizer molecules. In this solar device, the solution consisting of photosensitizer, reductant and surfactant is a light absorbing phase, which is contacted by two dissimilar electrodes showing different selectivity to the redox processes (Gangotri et al., 1996). A dye sensitizer molecule present in liquid phase of electrolyte is photo-excited to an energy rich species capable of losing energy electrochemically to generate solar electricity. It is is to be noted that three chemicals–sensitizer, reductant, NaOH-are compulsory for harnessing solar energy by photogalvanic cells. The use of surfactant chemical is not compulsory for harnessing solar energy but its use enhances the solar energy conversion efficiency.

The discovery of significance of electrochemistry as solar harvesting technique can be attributed to the Becquerel's pioneering work. In year 1839, Becquerel reported that the illumination of two unsymmetrical metal electrodes causes the flow of electrons (current) from one electrode to other electrode (Becquerel, 1839). The photogalvanic effect was first time observed by Rideal and Williams in year 1925 (Rideal and Williams, 1925). Later on in year 1940, the Rabinowitch reported systematic studied on the photogalvanic effect in Fe (II)-Thionine chemical system with the suggestion that this effect may be exploited for converting solar energy into electricity (Rabinowitch, 1940). To exploit this idea, various PG cells based on various dyes and reductants have been studied. Early studies focused on Thionine photosensitizer- ferrous species reductant based PG cells (Potter and Thaller, 1959; Albery and Archer, 1977). Later on, the role of micelles and range of photosensitizers including and reductants for advancement of photogalvanic cells was studied (Pokhrel and Nagaraja, 2009; Koli and Sharma, 2016; Koli, 2016; Koli and Sharma, 2017; Gangotri and Koli, 2017; Madhwani et al., 2007; Genwa et al., 2009; Pramila and Gangotri, 2007; Koli, 2018; Koli, 2019; Koli et al., 2019; Meena et al., 2004; Gangotri and Gangotri, 2009; Sharma et al., 2011; Bhimwal and Gangotri, 2011). Recently, some studies on the photogalvanics have reported tremendous enhancement in the electrical output of the PG cell (Koli et al., 2012); and have reported conversion efficiency (CE), short-circuit current (i_{sc}), maximum power (P_{pp}), and power storage capacity ($t_{0.5}$) respectively as 7.58%, 972 μA, 244.02 μW, and 216 min for Rhodamine B dye sensitizer-Fructose reductant- NaOH alkaline medium (Koli et al., 2012).

The photovoltaics may be considered as a reference solar technique to judge the state of development of other similar solar techniques as the photovoltaics is presently only solar technique having full commercial application in daily life world over. Thus, to make photogalavanic cells more efficient and practically applicable in daily life, some new gradients have to be exploited for assembling the PG cells. It is reported that alkaline medium and small sized platinum electrode (Koli et al., 2012) with surfactants (Groenen et al., 1984) enhances the efficiency of PG cells. The anionic surfactants are reported as most effective surfactants for solar power generation and its storage through the PG cells (Madhwani et al., 2007; Mukhopadhyay and Bhowmik, 1993). To best of my knowl-

edge, there is no reported focus on use of sensitizer(s) in these cells having absorption below 500 nm.

Therefore, the present research study of the use of Sudan-I dye as photosensitizer- Fructose as reductant-Sodium Lauryl Sulphate (SLS) as surfactant- small Pt as anodic electrode- SCE part of combination electrode as cathodic electrode was undertaken in alkaline medium at 10.4 mW cm^{-2} (a low and artificial sun intensity) to further improve electrical performance by optimization of cell fabrication parameters for optimal performance of the Sudan-I system based PG cells. The observed results in present work clearly establish the novelty, originality and advancement over the already published results of the same photogalvanic chemical system (Koli et al., 2012).

2. Material and methods

2.1. Chemicals

The solutions, i.e., M/500 of Sudan-I (λ_{max} 476 nm, Purity greater than 95.0%), M/100 of Fructose (99.8% Assay), M/10 of Sodium lauryl sulfate (SLS; purity 94% minimum), 1 M of NaOH (98% Assay), 1 M Oxalic Acid, and Phenolphthalein have been used as photosensitizer, reductant, surfactant, alkaline medium, standard solution for standardization of NaOH, and indicator, respectively. Sudan-I shows absorbance in UV–Visible range (mainly in 280 nm–650 nm) with characteristics bands at 480 (ε 14,481 LM^{-1}cm^{-1}), 314 nm (ε 6930 LM^{-1}cm^{-1}), and a shoulder band at 419 nm (ε 982 LM^{-1}cm^{-1}) in ethanol solvent (Supplementary Information-SI, Sec. 1).

2.2. Experimental and calculation method

The photogalvanic cell is fabricated by taking solutions of sensitizer, reductant, surfactant, and alkali NaOH in an H-shaped glass tube having Pt as anodic electrode in one arm and saturated calomel electrode (SCE) in another arm as shown in Figs. 1 and S2 (Koli et al., 2012; Sharma et al., 2011). The
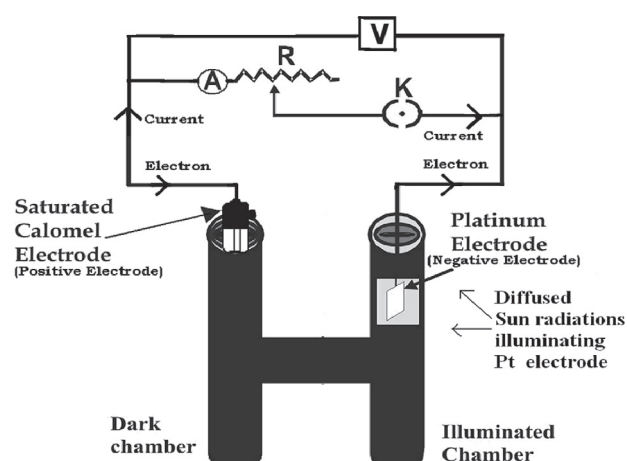
A, Micro-ammeter; K, Key; R, Resistance; V, Digital pH meter

Fig. 1 Photogalvanic cell set–up. A, Micro-ammeter; K, Key; R, Resistance; V, Digital pH meter.

Pt anode area for calculation of the efficiency is also supported by Murthy et al. (Murthy et al., 1980).

3. Results and discussion

3.1. Variation of the photo-potential, current and power

First of all, the photogalvanic cell (SI, Sec. 2) was put in the dark to achieve a stable dark potential. Thereafter, the cell was illuminated through the illuminated window against the Pt electrode. With passage of time, the photo-potential rose continuously to achieve a maximum potential (V_{max}) corresponding to a fast irreversible process in the beginning, and after some time, the establishment of photo-equilibrium of photo-processes led to a quite constant open-circuit potential corresponding to the zero circuit current (Table 1, Fig. 2). It can be explained on the basis of the 2nd law of thermodynamics that establishment of the equilibrium in any process needs time. In the beginning, processes are irreversible and in forward direction only. Later on, once the forward process products are formed causes backward processes. In the beginning, the amount of forward process products are less in quantity, therefore, as per the law of mass action, the extent of rate of backward process is low, and as the amount of forward process product increases, the rate of backward process increases to a equilibrium value at which the rate of both forward and backward processes are equal. As far as the photogalvanic cell is concerned, there are certain photo-processes occurring in the illuminated and dark chambers of the cell. In the beginning, the processes are only in forward direction to produce the product species causing continuous rise of the photo-potential. Thereafter, the establishment of the equilibrium of the photo-process results in generation of the equilibrium potential (open-circuit potential).

It is well known fact that a cell works with maximum power output at a certain characteristics external load. This fact for present cell was determined by the manual i-V characteristics study done by noting potential values at corresponding and varied current values obtained by varied circuit resistance. The i-V curve and table shows that this cell gives maximum power 367.8 μW at current 600 μA and external load resistance 1021.6 Ω (Table 2, Fig. 3).

The extraction of power from the cell in the dark (in absence of light after charging of the cell) has been studied at this external load resistance 1021.6 Ω. The extracted power diminishes with time in the dark to its half value, called half change time ($t_{0.5}$). Even after the half change time, the cell give power in the dark till it is fully discharged (Table 3, Fig. 4). The power storage capacity of the cell and its extraction in the dark may be attributed to the stable and quite long lived semi/leuco reduced ground states of the molecules of the dye sensitizers. The power storage is not as a result of the charge
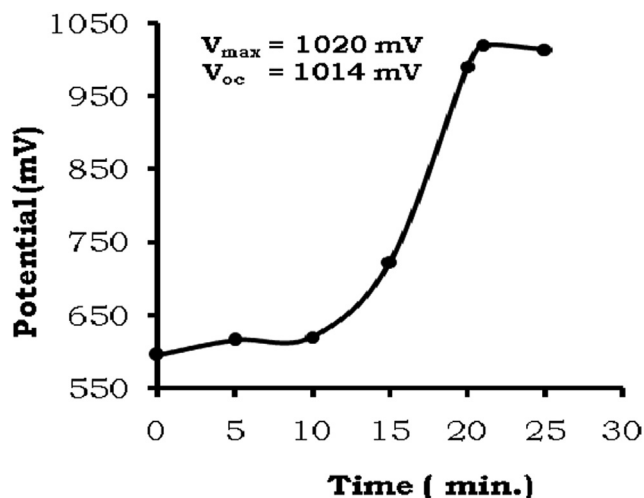

Fig. 2 Variation of potential with time during charging of the cell.

gathering at electrodes. But, it is due to the average life of excited species like singlet and triplet sensitizer molecules, relative stability of the semi and leuco reduced forms of the sensitizer molecule, and inherent current carrying properties of the ionic species (e.g., surfactant and NaOH used in the cell electrolyte). The power storage is not as a result of the charge gathering at electrodes is also proved by the facts that, after removal of electrodes with which the electrolyte was illuminated, the insertion of fresh set of electrodes in the already photo-illuminated electrolyte also give current and power as soon as this new set of electrodes is dipped in solution.

The cell performance at cell parameters (like concentration, diffusion length, etc., See SI, Sec.3) is summarized as dark potential (V_{dark}) 596 mV; maximum potential (V_{max}) 1020 mV; open-circuit potential (V_{oc}) 1014 mV; photopotential (ΔV) 424 mV; charging time (t) 21 min; maximum current (i_{max}) 1800 μA; equilibrium current (i_{eq}) or short-circuit current (i_{sc}) 1350 μA; photo-current (i) 1350 μA; power at power point (p_{pp}) 367.8 μW; potential at power point (V_{pp}) 613 mV; current at power point (i_{pp}) 600 μA; $t_{0.5}$ 30 min; potential at $t_{0.5}$ ($V_{t0.5}$) 358 mV; current at $t_{0.5}$ ($i_{t0.5}$) 510 μA; conversion efficiency (CE) 11.49%; fill factor (FF) 0.26; and rate of change of current over $t_{0.5}$ ($\Delta i/\Delta t$) 3.0 μA min^{-1}.

For all classes of the solar cells like photovoltaic cells, dye-sensitized solar cells, perovskite solar cells, etc., the CE and FF values are concordant (if CE is high then FF is also proportionately high). But, for the photogalvanic cells as in the present study, the CE is high, but FF is not proportionately high. For photogalvanic cells, it may be attributed to
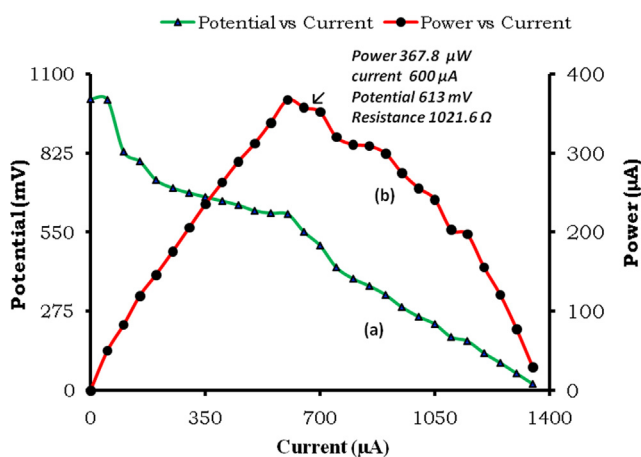
the photo-decay of dye photo-sensitizer, short life of excited states of dye photo-sensitizer, diffusion requirement of photo-

Table 1 Variation of potential with time.

Time (min)	0	5	10	15	20	21	25
Potential (mV)	596	616	620	723	990	1020 (V_{max})	1014 (V_{oc})

Table 2 Variation of current with potential and power (i-V characteristics of cell).

Current (μA)	Potential* (mV)	Power (μW)	Resistance (Ω)
1350	22	29.7	16.2
1300	60	78	46.1
1250	97	121.25	77.6
1200	130	156	108.3
1150	172	197.8	149.5
1100	185	203.5	168.1
1050	230	241.5	219
1000	256	256	256
950	290	275.5	305.2
900	333	299.7	370
850	364	309.4	428.2
800	389	311.2	486.2
750	428	321	570.6
700	504	352.8	720
650	551	358.15	847.6
(i_{pp}) 600	(V_{pp}) 613	(p_{pp}) 367.8	CE = 11.49%, FF = 0. 26, 1021.6
550	616	338.8	1120
500	625	312.5	1250
450	644	289.8	1431.1
400	659	263.6	1647.5
350	674	235.9	1848.5
300	687	206.1	2290
250	704	176	2816
200	732	146.4	3660
150	798	119.7	5320
100	832	83.2	8320
50	1012	50.6	20,240
0	1015	0	∞

(Mosquera et al., 1994). For the photogalvanic cell under study, the calculated R_{sh} is low (of the order of 16.2 Ω cm^2 and calculated Rs is very high (of the order of 20240 Ω cm^2 or even higher).
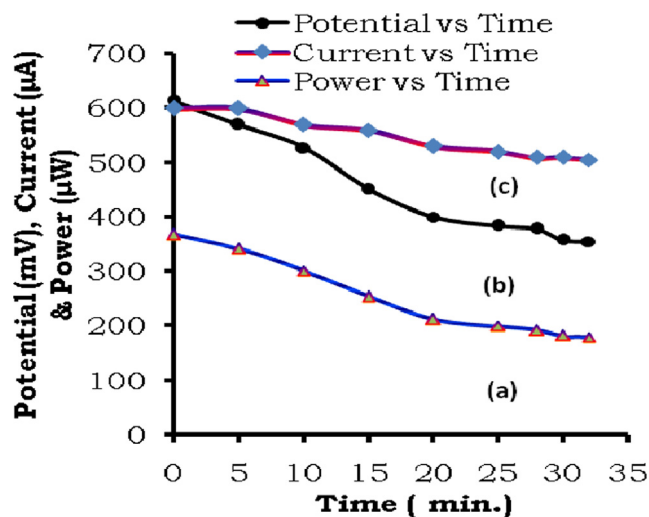
3.2. Mechanism of photocurrent generation and storage capacity

The photo-electrochemistry of fructose reductant solution alone, pure SLS surfactant solution alone, and solution mixture of dye with reductant and alkali was studied in photogalvanic cell to arrive at a proposed mechanism with the help of published literature. The illumination of solution having dye sensitizer along with reductant and alkali shows development of the photo-potential and photo-current.

The dark potential is not due to the dye alone, but as a result of contribution of reductant, and surfactant also. The pure fructose reductant solution showed potential −151 mV (vs SCE) and zero current in the dark. The illumination of this fructose reductant solution showed no change in potential (the potential was still −151 mV) and current (the current was still zero) indicating that the fructose in neutral form is neither an electro-active species at electrodes (it is not giving/accepting electrons to/from Pt/or SCE) nor a charged carrier in the solution. But, the dye sensitizer in the presence of the fructose

Table 3 Change of power with time (study of cell performance).

Time (min)	Current (μA)	Potential (mV)	Power (μW)
0	600	613	367.8
5	600	570	342
10	570	528	300.96
15	560	452	253.1
20	530	400	212
25	520	384	199.6
28	510	378	192.7
30	510	358	($t_{0.5}$ 30 min) 182.5
32	505	355	179.2

Fig. 3 Variation of current with potential and power (i-V characteristics of cell).

Fig. 4 Study of cell performance (a) Power vs Time, (b) Potential vs Time, (c) Current vs Time.

sensitizer molecules, and lower resistance (shunt resistance type-R_{sh}) at i_{sc} point and higher resistance (series resistance type- R_s) at V_{oc}. The photo-decay and deactivation of excited dye molecules are reported to follows non-zero order kinetics

reductant generate photo-potential and photocurrent showing its electro-active nature, and electron exchange between dye and fructose molecules in turn showing formation of the reduced and oxidized states of the fructose. This fact is supported by the published literature that the reductant in its reduced and oxidized form behaves as an electron carriers diffusing through the path in the cell (Albery et al., 1979). The dye with fructose reductant shows photo-potential and current indicating that it is the dye that is an electro-active species. This fact is substantiated by the published work of Kaneko and Yamada (Kaneko and Yamada, 1977) that the leuco/or semi reduced form of the dyes, and the dyes itself are the main electro-active species at the illuminated and the dark electrodes, respectively (Wildes and Lichtin, 1978). The energy stored in the charge separated semi or leuco forms results into the electrical energy by the so-called photogalvanic effect. In the present study of the azo group Sudan-I dye, it should be the dye molecule itself and two electron reduced leuco form (Scheme 1).

This fact of electrode process involving $2e^-$ and $2H^+$ reduction of (–N = N–) group in the Sudan-I molecule into the hydrazo compound is substantiated by the published cyclic-voltammetric study. The dyes Sudan I, II, III, IV shows similar electrochemical behaviors under established conditions (vs Ag/AgCl on use of Pt cathode) with distinguished reductive peaks at potentials of ∼-0.50 V, –0.53 V, –0.57 V and –0.60 V, respectively. It is reported that reduction of the azo group of Sudan-I is a one step process at cathode potential −0.75 V and dependent on the pH and this process is diffusion controlled as indicated by the linear increase in cathode peak current with half potential (Bard, 1974; Kolthoff and Elving, 1976; Lizier et al., 2012; Ming et al., 2008).

From this redox reaction (Scheme 1), it is clear that the redox potential of Sudan-I will be pH dependent, and the 0.7645 V redox potential observed in this photogalvanic study is supported by the literature on cyclic voltammetry (reported redox potential 0.75 V).

In PG cell, the photon energy is not lost and degraded to heat but is involved in the endergonic processes occurring as storing quantum energy in the form of labile intermediates i.e., semi/leuco transition states (Stein, 1977). The higher delocalization of electrons and bulkiness of dye will enhance the stability of the excited states of the dye, and in turn it will lead to higher storage capacity. The recombination processes may lead to the lowering of storage capacity (Genwa et al., 2009).

The solution of anionic surfactant SLS alone shows potential −340 mV (vs SCE) and current 30 μA in both dark and illuminated state. It shows that the current and potential of SLS should be due to its anionic charge diffusion in the cell.

We know that higher the redox potential of a species means higher the tendency of this species to get the electrons to exist in the reduced state. In PG cell technique; the electrodes, sensitizer and reductant are the entities involved in electron exchange process. The current flows from SCE electrode to Pt electrode through the external circuit. It means the electrons will flow from SCE towards Pt in this series in the bulk of the electrolyte. The observed potential (vs SCE) of dye in the presence of reductant and SLS in dark and illuminated conditions are −596 mV (i.e., V_{dark}) and −1014 mV (i.e., V_{oc}), respectively. By adjusting for potential for reductant and surfactant, the ground state and excited potential (vs SCE) of Sudan–I dye comes out to be −105 mV and −523 mV, respectively. With this calculation, the redox potentials (vs standard hydrogen electrode-SHE) of SCE, ground state Sudan-I dye, Fructose reductant, excited state Sudan-I dye, and Pt^{+2}/Pt shall be +0.2415 V, +0.3465 V, +0.3925 V, +0.7645 V, and +1.18 V, respectively. We know that higher the redox potential means higher the tendency to get the electrons to exist in the reduced state. It means the electrons will flow from SCE (+0.2415 V) to ground state Sudan-I dye (+0.3465 V) to Fructose reductant (+0.3925 V) to excited state Sudan-I dye (+0.7645 V) to Pt (+1.18 V) in this series in the bulk of the electrolyte (Figs. 5 and 6). This is why the electron move from lower redox potential (i.e., 0.3925 V of Fructose reductant) to higher redox potential (i.e., + 0.7645 V, excited state Sudan-I dye), but not in reverse direction. It can also be explained in terms of Gibbs' free energy (ΔG), which is defined as ΔG = - zEF, where, 'z', 'E' and 'F' is number of electrons exchanged,
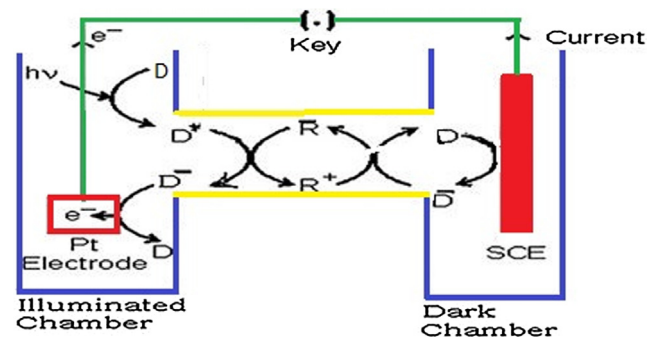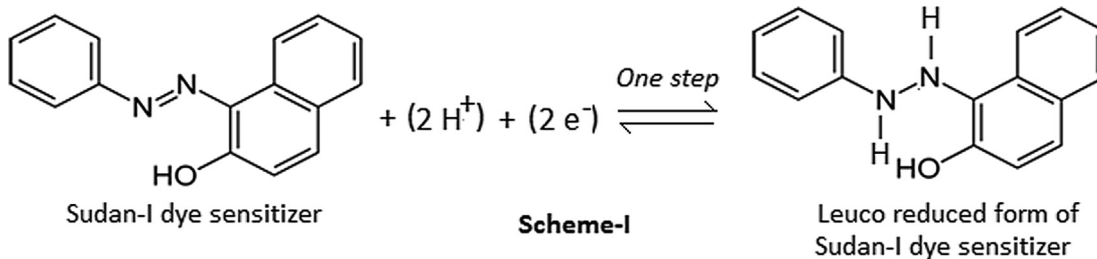

Fig. 5 Mechanism of the photo-generation of the current in photogalvanic cell. *Where SCE, Saturated calomel electrode; D, Sudan-I dye molecule; D^{*-}, oxidised form of the Sudan-I molecule; R^+, oxidised form of the fructose reductant; R, reduced state of the fructose; e-, electron.*

Scheme 1 Reduction of Sudan -I dye sensitizer.

Where, SUD-Sudan-I dye; SCE-Saturated calomel electrode; HOMO-Highest occupied molecular orbital of the dye; LUMO- Lowest unoccupied molecular orbital of the dye; SUD*- Excited dye; 1. Absorption of the light ~ 476 nm; 2. Photo-excitation of an electron from the HOMO to LUMO; 3. Reduction of the excited state dye by the electron transfer to HOMO from the reductant; 4. Transfer of the electron from reduced ground state dye to oxidized state of the reductant; 5. Transfer of the electron to ground state dye from external circuit through SCE.
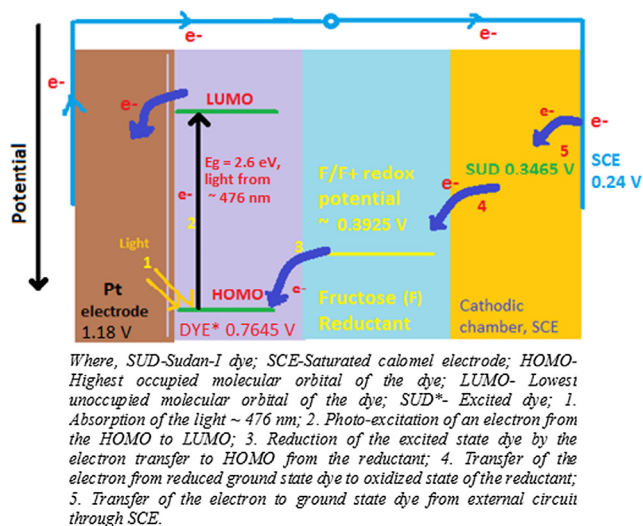
Fig. 6 Energy level diagram for photo-generation of the current in cell.

emf potential, and Faraday constant (96,490 Coulombs/mol), respectively. The free energy change is negative for spontaneous change. The free energy change is negative for one electron shift from reductant Fructose to excited Sudan-I dye [ΔG change = {(-1 × 0.7645 × F) for excited dye - (-1 × 0.3925 V × F) for Fructose reductant} = {- 0.7645 VF + 0.3925 VF} = − 0.372 VF]. Therefore, the electron move from reductant Fructose to excited Sudan-I dye smoothly, but reverse is not true. In summary, the FR^+ (R^+) do not react with SUD^- (D^-) in the light column to convert it back to SUD (D) as it will not be a feasible process owing to associated energy barrier of positive free energy change (i.e., ΔG change = + 0.372F). However, the second law of thermodynamics is natural limitation on every process including the electron shift from reductant to excited dye here. Therefore, this process of electron transfer from reductant to excited dye is also not a 100% efficient process providing some probability of reverse process (recombination or back process) of electron shift from SUD^- to FR^+ leading to formation of SUD and FR.

This recombination process can be stopped by pushing forward process of electron transfer from reductant to excited dye by facilitating interaction between Pt and SUD^- within life time of excited dye. It is ensured by illuminating electrolyte (dye) near the Pt electrode so that the electron excess excited dye molecule within its life reach the Pt and shed its excess electron to working electrode Pt. The increased SUD^- and Pt interaction in turn lowers the number of SUD^- species available for electron shift from SUD^- to FR^+.

In dark chamber, the tendency is of electron movement from ground state SUD^- to FR^+ as the redox potential of FR^+ (+ 0.3925 V) is greater than that of ground state SUD^- (+ 0.3465 V) .

The band gap for Sudan- I is the order of 2.6 eV equivalent to λ_{max} 476 nm required for electron excitation from its highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) (Editorial, 2015). The formation of excited state leaves a vacancy in ground state (HOMO) that can be filled by an electron donor like fructose reductant as redox potential of excited dye state is higher than that of fruc-

tose (electron transfer to HOMO of dye). The net result is that an excess electron is produced in higher energy state of the dye molecule. The excited state dye cannot hold this excess electron for long so this excess electron gets transferred to the Pt electrode. Electrons from the Pt electrode (high potential) flows through the external circuit to SCE (low potential) (Koli et al., 2012; Sharma et al., 2011). At SCE, the ground sate dye molecule in solution accepts electron as redox potential of ground state dye is higher than that of SCE. Excited dye should accept electron in HOMO and ground state dye should accept electron in LUMO. The current carrier in the electrolyte is the diffusion controlled ions. Ideally, the photo-galvanic system behaves as a light-driven cyclic electricity generator (Albery et al., 1979), and it has been found reversible for several cycles (Suresh et al., 1999). This reversible behavior is subject to the limitations imposed by the second law of thermodynamics. The ideal reversibility can be achieved only when the loss of power is zero, and that can be only when the resistance, friction, dissipation, etc., is zero, but such a position is impossible. Therefore, the element of irreversibility in photogalvanics is imminent. And, this is evident from the study done by the scientists Vos and Powels, who have reported that "the *open-circuit operation is a reversible process like Carnot Engine and have zero efficiency, but in operation at maximum power at power point to get maximum efficiency, then the process is not reversible*" (Vos and Powels, 1981). At small photo-potential, the quantum efficiency of the photoreaction is independent of the electrical resistance of the circuit only (Hillson and Rideal, 1953). The reductants may behave both reversibly and irreversibly, and the cyclic voltammograms show that dye reduction is reversible at low pH and quasi-reversible at high pH, where the protonation chemical reaction may be limiting the charge-transfer process (Murthy and Reddy, 1984).

The reversibility of the reductant use was reported in metallic redox couple Fe^{+2}/Fe only (especially in thionine-iron system) in initially studies (Kamat and Lichtin, 1982; Rabinowitch, 1940). Later studies have used organic reductants like EDTA, oxalic acid, mannitol, etc; and Hendrich has used ascorbic acid as an irreversible reductant (Hendrich, 1958). It means the organic reductants may go photo decay leading to its sacrifice and in turn its sacrificial and irreversible use. In present study, the fructose (an organic compound) has been used as reductant, therefore, its use should be sacrificial in nature.

On the basis of afore mentioned facts, the mechanism of photocurrent generation (Figs. 5 & 6) in the photogalvanic cell can be schematically represented as follows (Kamat and Lichtin, 1982; Osif et al., 1978; Wildes and Lichtin, 1978)

Photo-processes occurring in the illuminated chamber containing Pt electrode-

$$SUD \xrightarrow{hv} SUD * (s) \xrightarrow{ISC} SUD * (T) \qquad (i)$$

$$SUD * (T) + FR \rightarrow SUD(semi \ or \ levco) + FR^+ \qquad (ii)$$

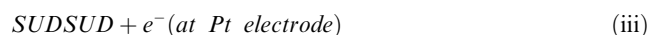$$SUDSUD + e^- (at \ Pt \ electrode) \qquad (iii)$$
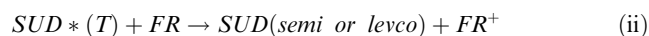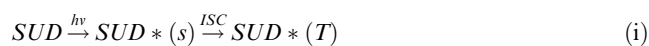
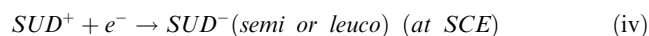*Photo-processes occurring in the dark chamber containing SCE electrode-*

$$SUD^+ + e^- \rightarrow SUD^-(semi \ or \ leuco) \ (at \ SCE) \qquad (iv)$$

$$SUD^- + FR^+ \rightarrow SUD + FR \qquad (v)$$

Here, the FR, $FR^{+\cdot}$ SUD^*, and SUD^- are the Fructose reductant, Fructose's oxidized form, excited form of Sudan-I dye (photo-sensitizer), and its (Sudan-I) semi or leuco form, respectively. The ISC, T, and S are inter-system crossing process, triplet excited dye state, and singlet excited dye state, respectively.

The i_{sc} is the maximum current density achievable on generation of only one electron–hole pair from one photon (Ruhle, 2016).

3.3. Effect of variation of Sudan-I dye photosensitizer concentration

In all, the six photogalvanic cells were constructed for the study of effect of variation of Sudan-I dye photosensitizer concentration on the cell performance (See SI, Sec.4). The optimum cell performance in terms of the i_{sc}, P_{pp}, i_{pp} and CE was observed at optimal dye concentration 3.04×10^{-5} M (Table 4, Fig. 7). This observation may be explained on the basis of the particle nature of the matter and sunlight as both these consists of the discrete particles namely molecules and photons, respectively. At dye concentration below the 3.04×10^{-5} M, the number of the available dye molecules for absorbing the photons shall be less in number than the available number of photons for absorption leading to the lower photo-generation of the current. At dye concentration above the 3.04×10^{-5} M, the available number of photons for absorption by the dye molecule near the Pt electrode shall be less in number as high dye concentration will prevent the photons from reaching to the solution nearby to the Pt electrode. It is to be noted that the photogalvanic cells are diffusion controlled cells requiring the reaching of excited dye molecules within their life time to donate electron to the Pt. Therefore, the dye molecules (absorbing photon) which are very close to Pt will be able to reach to Pt, and high dye concentration will limit such dye molecules leading to the lowering of the cell current. The high dye concentration may also result
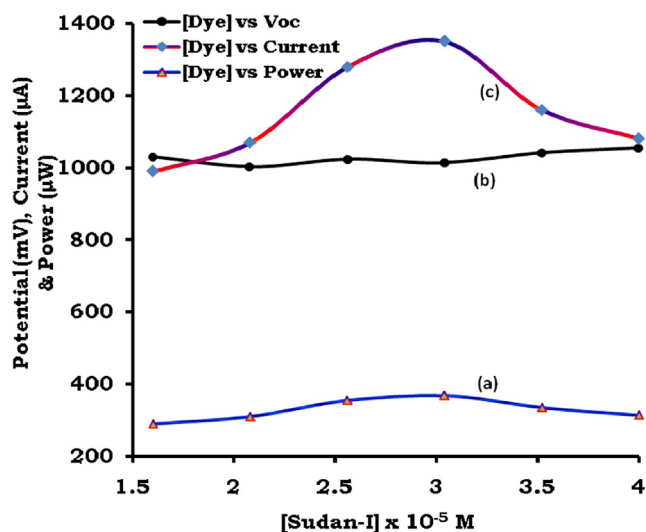

Fig. 7 Effect of variation of dye photosensitizer on power (curve 'a'), potential (curve 'b') and current (curve 'c').

into dye aggregation leading to the reduced current and power generation. The suitability of 10^{-5} M dye concentration range for current generation is supported from the fact reported by the cyclic voltammetric study that the peak current increases linearly with incremental concentration of Sudan I in the range from 6.0×10^{-7} to 7.5×10^{-5} M. (Ming et al., 2008). The Table 4 shows that the characteristic redox potential values of the dye are almost independent of its initial concentration, which is also supported by *Nabar and Shenai* (Nabar and Shenai, 1963).

3.4. Effect of variation of fructose reductant concentration

In all, the six photogalvanic cells were constructed for the study of effect of variation of fructose reductant concentration on the cell performance (See SI, Sec.5). The optimum cell per-

Table 4 Effect of variation of dye photosensitizer*.

Cell parameters	[Sudan-I dye concentration] $\times 10^{-5}$ M					
	1.60	2.08	2.56	3.04	3.52	4.0
V_{dark} (mV)	589	570	623	596	606	670
V_{max} (mV)	1040	1007	1028	1020	1050	1063
V_{oc} (mV)	1030	1003	1023	1014	1041	1055
ΔV (mV)	451	437	405	424	444	393
t (min)	11	27	14	21	34	53
i_{max} (μA)	1280	1180	1310	1800	1690	1270
i_{sc} (μA)	990	1070	1280	1350	1160	1080
P_{pp} (μW)	289.1	309.5	353.8	367.8	334.8	313.7
V_{pp} (mV)	590	543	580	613	598	592
$t_{0.5}$ (min)	18	32	22	30	23	13
$v_{t0.5}$ (mV)	401	368	421	358	406	423
$i_{t0.5}$ (μA)	360	420	420	510	410	370
CE (%)	9.71	10.38	11.47	11.49	10.85	10.17
FF	0.28	0.28	0.27	0.26	0.27	0.27
$\Delta i/\Delta t$ (μA min^{-1})	7.2	4.6	8.6	3.0	6.6	12.3

*At [Fructose] = 6.4×10^{-4} M, [SLS] = 4×10^{-3} M, Temp. = 310 K, Pt electrode area = 0.4×0.2 cm^2, light intensity = 10.4 mWcm^{-2}, diffusion length (D_L) = 5.6 cm, pH = 13.15.

formance in terms of the i_{sc}, P_{pp}, i_{pp} and CE was observed at optimal fructose reductant concentration 6.4×10^{-4} M (Table 5, Fig. 8). This observation may be explained on the basis of the particle nature of the matter and sunlight as both these consists of the discrete particles namely molecules and photons, respectively. At fructose reductant concentration below the 6.4×10^{-4} M, the number of the available fructose reductant molecules shall be less in number for donating electrons to the dye molecules leading to the reduced cell current and power. At fructose reductant concentration above the 6.4×10^{-4} M, the increased back electron combination reaction (electron coming back from dye to reductant) coupled with the increased hindrance by the reductant molecules in the diffusion path of the dye molecules may be the reason for lowering of the cell power and current.

3.5. Effect of variation of surfactant (SLS) concentration

In all, the six photogalvanic cells were constructed for the study of effect of variation of SLS surfactant concentration on the cell performance (See SI, Sec.6). The optimum cell performance in terms of the i_{sc}, P_{pp}, i_{pp} and CE was observed at optimal fructose reductant concentration 4×10^{-3} M (Table 6, Fig. 9). This trend of effect of SLS on PG cell can be explained on the basis of certain reported and observed facts. It is a reported fact that the SLS and other surfactants have good solubilizing effect on the azo group Sudan-I as it (Sudan-I) can rotate around the azo bond to have more conformational freedom (Lang, 2009). The effect of surfactant can be explained in terms of Critical micelle concentration (CMC). The CMC of a surfactant is its concentration value below which no micelles is formed and above which it forms micelles. All the added amount of surfactant over and above CMC goes to form micelles. Before CMC, the surfactant changes surface tension of the solvent strongly, and above CMC, the change in surface tension remains nearly constant with a lower slope. The CMC value is affected by pressure, temperature, and by also the
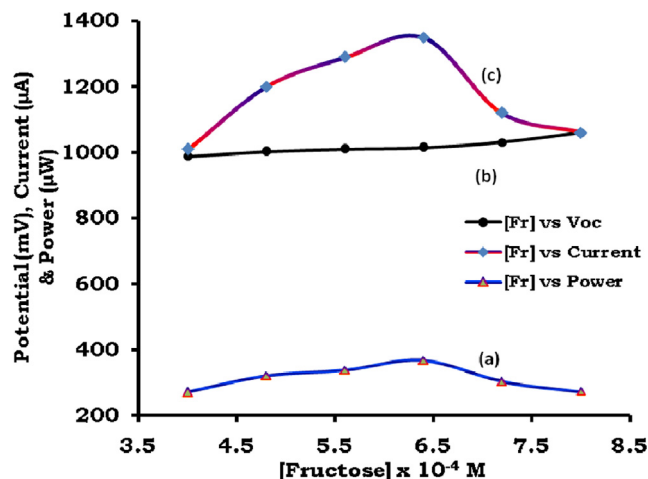

Fig. 8 Effect of variation of Fructose (reductant) concentration on power (curve 'a'), potential (curve 'b') and current (curve 'c'); [Fr] is Fructose concentration.

presence and concentration of other surface active substances and electrolytes.

It is a well known fact that the surfactant over its critical micelles concentration (CMC) solubilizes the dye, and this dye solubility increases linearly with rise in surfactant concentration. But, it holds good for moderate concentrations of the majority of the surfactants. It is because of the fact that at very high surfactant concentration the rod like micelles are formed leading to the rise in viscosity The reported CMC value of the SLS for the Sudan-I solubility is of the order of 10^{-3} M. The surfactant like SLS with a straight alkyl tail gives better solubilization. It is also a reported fact that in absence of any surfactant, the solubility of hydrophobic dye like Sudan-I is almost negligible in the pH interval 3–12, but addition of SLS causes dye solubility in the range of 0.2–0.3 mM. At higher pH over the 12, the increasing pH has positive impact

Table 5 Effect of variation of Fructose (reductant) concentration*.

Cell parameters	[Fructose concentration] $\times 10^{-4}$ M					
	4.0	4.8	5.6	6.4	7.2	8.0
V_{dark} (mV)	609	591	624	596	600	690
V_{max} (mV)	1005	1011	1017	1020	1042	1065
V_{oc} (mV)	988	1002	1010	1014	1030	1060
ΔV (mV)	396	420	393	424	442	375
t (min)	51	45	19	21	16	36
i_{max} (μA)	1140	1260	1130	1800	1380	1290
i_{sc} (μA)	1010	1200	1290	1350	1120	1060
P_{pp} (μW)	270.0	320.9	338.2	367.8	302.9	273.7
V_{pp} (mV)	600	544	604	613	541	595
$t_{0.5}$ (min)	49	13	25	30	41	17
$v_{t0.5}$ (mV)	419	363	426	358	388	402
$i_{t0.5}$ (μA)	320	440	340	510	390	340
CE (%)	8.74	10.01	10.54	11.49	9.46	7.87
FF	0.27	0.26	0.25	0.26	0.26	0.24
$\Delta i/\Delta t$ (μA min^{-1})	2.6	11.53	5.6	3.0	4.1	7.0

*At [Dye] = 3.04×10^{-5} M, [SLS] = 4×10^{-3} M, Temp. = 310 K, Pt electrode area = 0.4×0.2 cm^2, light intensity = 10.4 mWcm^{-2}, diffusion length (D_L) = 5.6 cm, pH = 13.15.

Table 6 Effect of variation of SLS (surfactant) concentration*.

Cell parameters	[SLS concentration] $\times 10^{-3}$ M					
	2.4	3.2	4.0	4.8	5.6	6.4
V_{dark} (mV)	623	544	596	670	702	567
V_{max} (mV)	1043	1023	1020	1027	1070	1060
V_{oc} (mV)	1034	1008	1014	1023	1061	1053
ΔV (mV)	420	479	424	357	368	493
t (min)	11	34	21	45	12	27
i_{max} (μA)	1190	1310	1800	1700	1440	1260
i_{sc} (μA)	1070	1280	1350	1300	1270	1150
P_{pp} (μW)	294.7	332.9	367.8	361.9	320.9	308.8
V_{pp} (mV)	578	574	613	635	563	572
$t_{0.5}$ (min)	23	34	30	46	55	70
$v_{t0.5}$ (mV)	398	405	358	427	400	367
$i_{t0.5}$ (μA)	370	410	510	420	400	420
CE (%)	9.20	10.00	11.49	11.71	8.80	9.27
FF	0.26	0.25	0.26	0.27	0.23	0.25
$\Delta i/\Delta t$ (μA min^{-1})	6.0	5.0	3.0	3.2	3.0	1.7

*At [Fructose] = 6.4×10^{-4} M, [Dye] = 3.04×10^{-5}M, Temp. = 310 K, Pt electrode area = 0.4×0.2 cm^2, light intensity = 10.4mWcm^{-2}, diffusion length (D_L) = 5.6 cm, pH = 13.15.
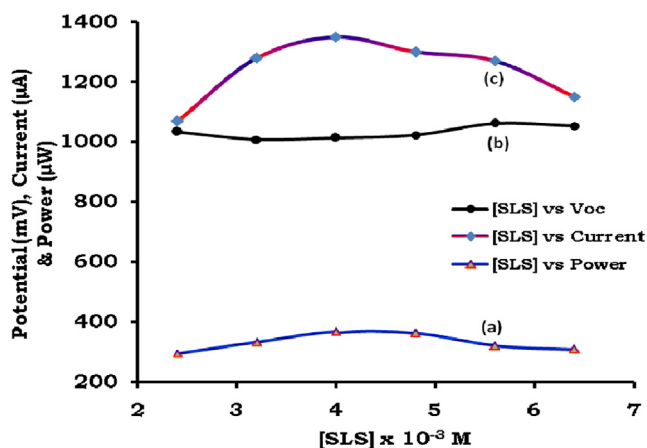

Fig. 9 Effect of variation of Sodium Lauryl Sulfate (surfactant) concentration on power (curve 'a'), potential (curve 'b') and current (curve 'c'); [SLS] is Sodium Lauryl Sulfate concentration.

on the dye solubility in inner, hydrophobic part of the micelle (Tehrani-Bagha et al., 2013; Tehrani-Bagha and Holmberg, 2013).

It is also a reported fact that once the micelles have grown to a certain size the solubilization of dyes is not further facilitated by the micelles becoming even more extended, ultimately often reaching a worm-like or thread-like structure (Ozeki and Ikeda, 1985).

On the basis of these characteristics of the surfactants, the effect of SLS on cell performance may be explained. In present study, the used concentration of SLS is of the order of its CMC 10^{-3} M. Therefore, the use of SLS enhances the solubility of the Sudan-I dye which in turn enhances available numbers of dye sensitizer for photogalvanics leading to an increase in the cell power. The cell power increases with rise in SLS concentration as the dye solubilization increases almost linearly with increasing surfactant concentration beyond the CMC. At very high SLS concentration, the higher viscosity

of the electrolyte may be attributed the reasons behind the lowering of the diffusion of ions leading to the decrease in the cell performance. Thus, the lower electrical output may be attributed to the less number of available SLS molecules (at its lower concentration side) for facilitating electron transfer by enhancing solubility and stability of dye molecules. At higher concentration side of the SLS, the increased number of SLS molecules may hinder the diffusion of the dye molecules leading to the decreased cell current and power.

The SLS solution alone also shows a potential value ~ (-) 300 mV and current ~ 30 μA in the dark as well as in illuminated state. This nature of contribution of SLS to the current may also be one of the reasons for enhancement of the cell power in presence of the SLS.

3.6. Effect of variation of pH

In all, the six photogalvanic cells were constructed for the study of effect of variation of pH on the cell performance (See SI, Sec.7). The optimum cell performance in terms of the i_{sc}, P_{pp}, i_{pp} and CE was observed at optimal pH 13.15 (Table 7, Fig. 10).

To understand the effect of pH on the cell performance, the possible chemical structures (Scheme 2) (Tehrani-Bagha and Holmberg, 2013), and solubility of the azo group neutral Sudan–I at low and high pH with certain other reported facts have to be taken in to consideration.

At higher pH, the dye will be in anionic form and in a more strong position to give electrons to the Pt electrode and reduced reductant while it is in its (dye) excited state and ground state, respectively, leading to an enhancement in the cell current. The dyes are also solubilized strongly at very high pH of the order of 12–14 leading to the enhancement in the cell output.

The anionic nature of the dye at higher pH coupled with anionic SLS may retard the aggregation behavior of the dyes in solution causing higher diffusion and current as PG cells are diffusion controlled. It is reported that the dyes' photo-

Table 7 Effect of variation of NaOH (pH) concentration*.

Cell parameters	pH					
	12.98	13.07	13.15	13.22	13.28	13.33
V_{dark} (mV)	578	586	596	621	633	649
V_{max} (mV)	1020	1020	1020	1036	1045	1078
V_{oc} (mV)	1015	1010	1014	1034	1039	1071
ΔV (mV)	442	434	424	415	412	429
t (min)	38	33	21	23	16	12
i_{max} (μA)	1310	1550	1800	1400	1210	1090
i_{sc} (μA)	1170	1200	1350	1250	1130	1080
P_{pp} (μW)	336.0	344.5	367.8	320.6	310.8	297.0
V_{pp} (mV)	600	584	613	509	536	487
$t_{0.5}$ (min)	34	11	30	61	41	19
$v_{t0.5}$ (mV)	420	419	358	356	361	313
$i_{t0.5}$ (μA)	400	410	510	450	430	470
CE (%)	11.28	11.59	10.97	9.24	9.69	8.90
FF	0.28	0.28	0.26	0.24	0.26	0.25
$\Delta i/\Delta t$ (μA min^{-1})	4.7	16.3	3.0	2.9	3.65	7.3

*At [Fructose] $= 6.4 \times 10^{-4}$ M, [SLS] $= 4 \times 10^{-3}$ M, Temp. $= 310$ K, Pt electrode area $= 0.4 \times 0.2$ cm^2, light intensity $= 10.4$ mWcm^{-2}, diffusion length (D_L) $= 5.6$ cm, [Dye] $= 3.04 \times 10^{-5}$ M.
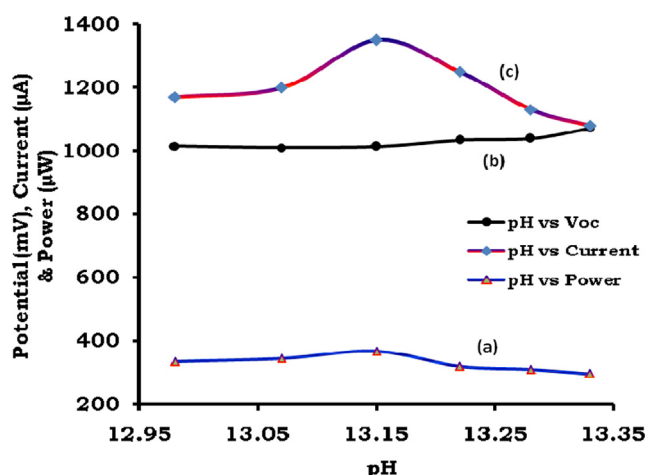

Fig. 10 Effect of variation of pH on power (curve 'a'), potential (curve 'b') and current (curve 'c').

reduction with different reductants in different pH depends on the dyes' reduction potential and reductants' oxidation potential. The redox potentials of the dyes becomes more negative with increasing pH as shown by the cyclic-voltammetric data as dye reduction will be difficult at higher pH due to less favorable protonation of the dye owing to protonation states of the leuco dyes and dyes change over the pH range (Murthy and Reddy, 1984), and preferential reduction of hydrogen cation at cathode will leads to the reduction in cell power.

This is also reported that minimum pH (12–14) is necessary for dyes to be reduced and solubilized completely supporting use of very pH 13 in present study (Nabar and Shenai, 1963).

3.7. Effect of variation of diffusion length

In all, the six photogalvanic cells were constructed for the study of effect of variation of pH on the cell performance (See SI, Sec.8). The optimum cell performance in terms of the i_{sc}, P_{pp}, i_{pp} and CE was observed at optimal pH 13.15 (Table S1).

As explained previously, the photogalvanic cells are diffusion controlled cell devices in which the molecules including the dye carry the current inside the cell solution. The excited dye molecule must reach within its life time to Pt for electron transfer from the dye to the Pt. At higher diffusion length, the excited dye molecules are not able to reach the Pt within their life time leading to the reduced current. At higher diffusion length, the increased concentration gradient also diminishes the potential difference between the two electrodes leading to the reduced photo-potential. At lower diffusion length, the favorable conditions exist for excited dye molecules for reaching the Pt within life time, but in totality the number of such
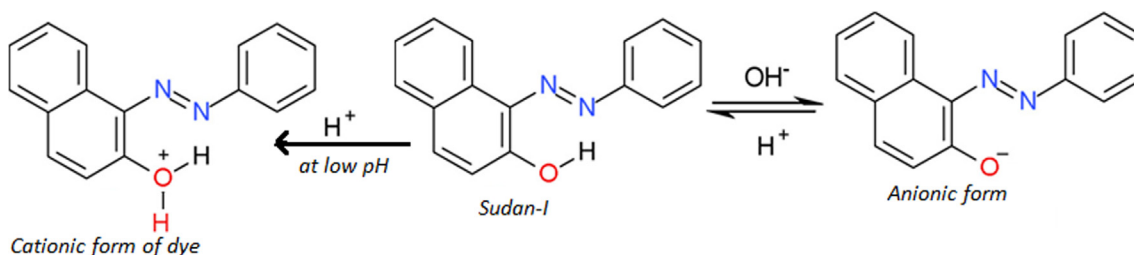
Scheme 2 Deprotonation of Sudan-I dye sensitizer under alkaline conditions.

dye molecules will be less in number as there will be less volume of the solution between the electrodes, leading to the reduced current.

3.8. Effect of variation of temperature

In all, the six photogalvanic cells were constructed for the study of effect of variation of temperature on the cell performance (See SI, Sec.9). The optimum cell performance in terms of the i_{sc}, P_{pp}, i_{pp} and CE was observed at an optimal temperature (Table S2). The temperature rise favors the photocurrent (i_{max}) as a result of increased diffusion, and disfavors the photo-potential (V_{oc}) as a result of disturbance in the double layer at electrode. The potential change is much higher than the current change. The rise in temperature (temperature range under observation) invariably leads to slight rise in the power output irrespective of the fall in photopotential.

The effect of temperature may be explained on the basis of certain reported and observed facts. It is a reported fact that the rise in temperature increases the solubility of hydrophobic dye like Sudan-I in the presence of the ionic surfactants due to increased (i) thermal agitation in the system, (ii) available space for solubilization in the micelle, and (iii) enthalpy term (Datyner, 1978; Rosen, 2004). From this fact, it is also clear that increased temperature will also increase the diffusion of dye molecules leading to the increased electrical performance of the diffusion controlled PG cell.

In the PG cell, the stock solutions which are used are stored at room temperature (~25 °C to 30 °C). On illumination of the cell with illuminating source (incandescent 200 Wattage tungsten bulbs), the average 8 °C to 20 °C rise in the temperature of the electrolyte is observed. The magnitude of the rise in temperature depends on the duration of illumination (7 °C rise in about seven minutes and 20 °C rise in about 60 min). In sun, the rise in temperatures is very low (~3 °C in 10 min). In the case of PG cells, temperature effect on efficiency is not expected adverse at high temperature range as highest achievable temperature of the cell electrolyte is 50 °C. But, there is loss of water and that can be tackled by safe sealing.

The temperature behavior of the dye based PG cells can also be understood with the help of the dye sensitized solar cells (DSSC). It is reported that the efficiency of the DSSC remains highest in the temperature range 30 °C−40 °C, and lowering in efficiency above this temperature. It is reported that the recombination kinetics in the cell is the same between −7 °C and 40 °C leading to the virtually constant efficiency and small differences in the FF associated with changes in the series resistance. Further rise in the temperature above 40 °C favors recombination kinetics lowering photo-potential and cell performance (Raga and F. F-Santiago, 2013).

3.9. Effect of variation of Pt electrode area

In all, the five photogalvanic cells were constructed for the study of effect of variation of Pt electrode on the cell performance (See SI, Sec.10). Under the observed effect of electrode area, the optimum cell performance in terms of the i_{sc}, P_{pp}, i_{pp} and CE was observed at 0.30 cm × 0.25 cm (Table S3). For the observed effect of electrode area, the small Pt electrodes favors higher cell performance owing to relatively less hindrance to the diffusion of ions.

3.10. Discussions

Thus, we see that cell performance is found to be affected by variables like dye concentration, reductant concentration, pH, diffusion length, temperature, light intensity, electrode area, etc. The optimum performance of the cell can only be obtained by carefully selecting the best values for all these variables.

On the basis of optimization of cell fabrication variables (like concentrations, pH, etc), the optimal cell performance in terms of the current, power, etc. has been observed at Sudan-I dye concentration 3.04×10^{-5} M, Fructose reductant concentration 6.4×10^{-4} M, SLS surfactant concentration 4×10^{-3} M, pH 13.15, 0.4 cm × 0.2 cm Pt electrode area, 10.4 mW cm^{-2} light Intensity, 310 K temp., and 5.6 cm diffusion length. The observed optimal cell performance is as V_{oc} 1014 mV, i_{max} 1800 µA, i_{sc} 1350 µA, P_{pp} 367.8 µW, CE 11.49%, FF 0.26, current density ~ 17 mAcm^{-2} and $t_{0.5}$ 30 min.

The photogalvanic cells based on various dyes has been reported. The P_{pp} 14.75 µW, i_{sc} 45 µA, CE 0.14%, FF 0.31, and $t_{0.5}$ 40 min is reported for Azur B dye photosensitizer with EDTA reductant andTergitol-7 surfactant (Gangotri et al., 2013). The P_{pp} 29.8 µW, i_{sc} 93 µA, CE 0.31%, and $t_{0.5}$ 65 min is reported for brilliant green and celestine blue mixed dyes with EDTA reductant (Yadav and Lal, 2013). The P_{pp} 162.96 µW, i_{sc} 240 µA, CE 0.70%, and $t_{0.5}$ 85 min is reported for Eosin dye photosensitizer with Arabinose reductant reductant system (Gangotri and Bhimwal, 2010).

The P_{pp} 244.02 µW, i_{sc} 972 µA, CE 7.58%, and $t_{0.5}$ 216 min is reported for Rhodamine B dye photosensitizer with Fructose as reductant in NaOH as alkaline medium (Koli et al., 2012).

The present photogalvanics reports advancements over the already reported work. This advancement may be attributed to the combined and cumulative effects of use of anionic SLS surfactant, small Pt electrode, relatively small MW and sized Sudan-I dye molecules, and C_2H_5OH alcohol as solvent for solubilization of Sudan-I dye.

The anionic surfactant leads to the increased solubility and electron donation power of the dye molecules. The small sized Pt electrode favors dye diffusion leading to the increased cell performance. The diffusion is inversely proportional to MW (Polson and Reyden, 1950), and size of the molecules and viscosity of the solvent. The MW and size of the Sudan-I (MW 248.28 gmol^{-1}) is lower than that for Rhodamine-B (MW 479.02) (Scheme-I of SI). The viscosity of alcohol (1.1 centipoises at 25 °C) used to dissolve Sudan-I in present work is higher than that for water (0.91 centipoises at 25 °C) used to dissolve Rhodamine-B dye in reported work.

Thus, the present study on Sudan-I dye-Fructose-SLS surfactant photogalvanic system is promising for fabricating applicable and affordable PG cells (workable in natural sunlight) in the future. The present study (using Sudan-I photosensitizer) is different than earlier studies which are based on different photosensitizers Rhodamine B (Koli, 2019) and Brilliant Cresyl Blue (Koli et al., 2018).

A research field has a particular set of materials, method, experiments, observed variables, explanations, etc. The present manuscript reports advancement in photogalvanic cells by modifying cell fabrication at sensitizer, reductant, surfactant, conc., Pt electrode, etc. In present work, in addition to

Sudan-I photosensitiser, the all means reported in literature for increasing cell performance have been used in combination at a time to claim change in the routine cells. The changes are use of anionic SLS surfactant (Groenen et al., 1984; Madhwani et al., 2007; Mukhopadhyay and Bhowmik, 1993) with very small Pt electrode (Koli et al., 2012), use of SCE terminal of combination electrode (Koli et al., 2012), high pH (Koli et al., 2012), well cleaned and scratched Pt electrode (Koli et al., 2012), etc. It is well known fact that the anionic SLS surfactant facilitates cell performance by increasing dye solubility and discouraging back reaction. The Gangotri (Gangotri and Gangotri, 2013) has shown more than two times increase in cell efficiency by use of this anionic SLS surfactant (CE 0.72% with SLS, and CE 0.33% without SLS). Thus, the increase in CE in present work on use of SLS is expected and justified.

It is reported in the Arabian Journal of Chemistry (AJC) (Koli, 2017) that the Sudan-I dye photo-sensitiser with fructose reductant and SLS surfactant combination is a very good photogalvanic system for fabrication of highly efficient PG cells workable in the natural sunlight. The study reported in AJC is based on illumination of photogalvanic cells with natural sunlight intensity. The present work is based on a different set of experiments with different results (different than that in AJC). The experimental conditions used in present work distinguish it from already published work. The already published work was studied in daily life natural conditions like the natural sunlight ~ 1000 Wm^{-2}. Whereas, the present study has been done at the artificial and low sunlight intensity ~ 10.4 mWcm^{-2}.

The set of experiments used in published work of AJC is natural sunlight intensity 100 mW cm^{-2}, Sudan-I dye photosensitiser concentration 10.37×10^{-5} M, Fructose reductant concentration 2.37×10^{-3} M, SLS surfactant concentration 1.48×10^{-2} M, 36.0 mL of 1 M NaOH (pH 13.72), and 6.3 cm diffusion length.

The set of experiments used in present work is artificial and low sunlight intensity (10.4 mW cm^{-2}), 0.38 mL of M/500 Sudan-I dye (resultant concentration 3.04×10^{-5} M), 1.6 mL of M/100 Fructose (resultant concentration 6.4×10^{-4} M), 1.0 mL of M/10 SLS (resultant concentration 6.4×10^{-3} M), 3.6 mL of 1 M NaOH (resultant pH 13.72), and 5.6 cm diffusion Length.

The results reported in AJC are 1081.1 µW maximum powers, 4200 µA short-circuit current, and 1048 mV open-circuit. The results in present work are different (367.8 µW maximum powers, 1350 µA short-circuit current, and 1014 mV open-circuit).

The study reported in Arabian Journal of Chemistry (AJC) was done in Jodhpur (Latitude 26.2389, Longitude 73.0243) situated in western part of the Rajasthan. Rajasthan has more than 325 sunny days in a year with solar radiation of about 6–7 Kwhm^{-2}day^{-1}. Jodhpur in Rajasthan is receiving maximum solar radiation (up to 1250 Wm^{-2}) which is known as Sun City of India. The sky in Jodhpur is clear almost round the year, and it was also during the study reported in AJC. So, the natural sun intensity was ~ 1000 Wm^{-2} for the location of the study reported in the AJC.

But, it is to be noted that the global distribution of natural sun intensity is not same. Some places like California, Jodhpur, etc. receives highest sun intensity, and some places like north and south poles of Earth receives very less intensity.

At a given place like Jodhpur, the sun intensity may vary from morning to evening hours. Therefore, the photogalvanic cells should be shown to work at high as well as low illumination intensity to meet energy needs of whole global community. Therefore, the present study of Sudan I- Fructose has been done at low sunlight intensity ~ 10.4 mWcm^{-2} to explore the Photogalvanic cells for use in area receiving low sun intensity. There were mainly two assumptions/anticipations, (a) the cell performance should be enhanced if best possible reported cell fabrication variables are put together using Sudan- I photosensitizer; and (b) cell based on Sudan-I photosensitizers should also be workable in low illumination intensity. On both these counts, the observed results have been on expected lines of assumptions/anticipations. The chosen chemical system of Sudan-I dye sensitizer-anionic surfactant SLS- alkaline medium in present work has not only shown workability in low intensity illuminating source, but also very impressive optimal cell performance (i.e., i_{sc} 1350 µA, P_{pp} 367.8 µW and CE 11.49%). The observed results in present work clearly establish the novelty, originality and advancement over the already published PG cell performance (i_{sc} 972 µA, P_{pp} 244.02 µW, CE 7.58%) (Koli et al., 2012).

It is reported by Albery & Archer that the maximum power is unlikely to be greater than 10^{-6} Wcm^{-2} under some conditions like that both the electrodes are of same material and same area, all diffusion coefficients are same, etc. (Albery and Archer, 1977). Here it is clarified that the Albery & Archer have actually talked about the power density (i.e., $W_{max}/A \sim 10^{-6}$ Wcm^{-2}) with the remark that the most real PG systems shall not be able to fulfill the necessary conditions assumed for this conclusion of maximum power density. The power is reported by Albery & Archer to be affected by interplay of various factors like photochemistry, homogeneous kinetics, mass transport, electrode kinetics, reaction kinetics and concentrations. In present manuscript, author has reported power, but not power density. Author has reported power 367.8 µW, but not power 367.8 W. Further, the present manuscript has used two different electrodes, i.e., Anodic Pt in illuminated chamber and cathodic SCE in dark chamber, whereas the Albery & Archer used identical electrodes. Present manuscript is based on chemicals of different diffusion coefficients, whereas the Albery & Archer assumed of identical diffusion coefficients. Therefore, the conditions in present manuscript are different than that described by Albery & Archer, and these scientists have himself remarked that power output is result of interplay of various factors. Therefore, the experimentally observed power 367.8 µW in present work is realistic and justified by the concepts of Albery & Archer and also by our own previously published works (Koli, 2019; Koli et al., 2012; Koli and Sharma, 2016; Sharma et al., 2011).

According to Albery, the realistic CE is 5%−9%. It is pertinent to note here that Albery himself has estimated CE 18%, if all necessary conditions could be met. Therefore, the CE $\sim 11\%$ observed in present study by using at a time all favorable cell fabrication variables and conditions necessary for optimal cell performance is well within the limit laid down by the Albery. It be noted that this efficiency $\sim 11\%$ is repetitive any number of times under optimal conditions and method as described in this paper. This efficiency is validated by reputed photochemistry lab of one of the eminent photogalvanicist.

The efficiency has also been estimated by using method as "cell illuminated by the light for a defined period of time to calculate the received optical energy by the cell (integration of power over time) then transferring the stored energy to an external load and measuring the total delivered energy". The estimation of power extracted from cell in dark (Power output) and power (sunlight) absorbed is ~ 1.015128 J and ~ 12.43176 J, respectively. The estimated efficiency from formula [(Power output × 100%)/ (power absorbed)] is ~ 8.165%. Actual power output will be higher than estimated 1.015128 Joule because actual area under power *vs* time will be higher than estimated, and accordingly estimated efficiency will be as high as the calculated efficiency ~ 11.49 (from Eq. (2). Present estimation of power is limited on the basis of already available research data (SI, sec.3).

In literature, various formulas are reported for the calculation of the solar energy conversion efficiency of the photogalvanic cells (Koli et al., 2020). *Potter and Thaller* (Potter and Thaller, 1959) have defined the power efficiency as [(ø E_c^0 I_c/ (εN)], where E_c^0 is zero current voltage, I_c is the short circuit current, Є is the energy per absorbed photon and N is the number of photons absorbed per second. *Clark and Eckert* (Clark and Eckert, 1975) have defined Sunlight Engineering Efficiency as [(maximum Power × 100)/(incident sunlight power)]. *Murthy et al.* (Murthy et al., 1980) have defined conversion efficiency as [(V_{oc} × i_{sc} × fill factor × 100)/(cross sectional area of electrode × Incident Sunlight Power)]. A review paper on photogalvanic cells have reported calculation of conversion efficiency as [(electrical power output (in watts) at its maximum power point × 100)/(input light in Wm^{-2} × electrode area of the photogalvanic cell in m^2)] (Malviya and Solanki, 2016). The fill factor of photogalvanic cells is disproportionately low in comparison to conversion efficiency. Both the parameters (fill factor and efficiency) are indicator of solar energy conversion capacity of the photogalvanic cells. Therefore, the solar efficiency of cell as without linked to fill factor and linked to fill factor has also been defined as [(power at power point in mWm^{-2} × 100%)/(illuminating intensity in mWm^{-2} × Pt working electrode area in cm^2], and [(power at power point in mWm^{-2} × fill factor × 100%)/(illuminating intensity in mWm^{-2} × Pt working electrode area in cm^2)], respectively (Koli et al., 2012; Koli and Sharma, 2017). In present research work, the cell efficiency has been calculated as [(power at power point in mWm^{-2} × fill factor × 100%)/(illuminating intensity in mWm^{-2} × Pt working electrode area in cm^2]. The justification of using this formula is explained as follows. The size of the open window has not been used for calculating the efficiency as- (i) the sunlight strike at illuminating window of the cell. The sunlight being of wave nature has phenomenon of scattering as well the diffraction at hole/barrier. The photogalvanic cells use very dilute solution of dye/pigments. The light diffraction effect and edge effect effectively illuminate the larger solution area, (ii) the PG cell is diffusion controlled, and therefore, only those dye molecules which are nearer to Pt anodic electrode shall be able to reach the electrode within their excited life time. It means that the number of such dye molecules shall be determinable with respect to Pt area, but not the illuminating area of the cell window size; (iii) the illuminating natural sunlight is free and available naturally leading to no change in cost and environmental pollution on account of illumination of the small or large area of the cell. The Pt size matters for the economic and ecological

cost as use of its small size will be less costly and more eco-friendly; (iv) The Pt anode area (instead of cell illumination area) for calculation of the efficiency is also supported by Murthy et al. (Murthy et al., 1980), who have used cross sectional area of the anode for the calculation of solar engineering efficiency; and (v) The photogalvanic cells can also be charged at low illuminating efficiency (Koli et al., 2012). Therefore, the small or large sized illuminating window hardly matters for charging of the cell. The surface area of the window used to illuminate the cell is 1 cm × 1 cm.

The theoretically highest possible V_{oc} for band gap of 2.6 eV is 2.24 V. In present case, the observed V_{oc} for Sudan-I (band gap 2.6 eV) is only 1.01 V. However, it may be noted that for dye sensitized solar cells like PG cells, the low V_{oc} may be one of the factor for their relatively low efficiency in comparison to that for PV cells. The low Voc may be attributed to the non-optimized energy levels of the dye sensitizers with respect to the redox potential of the electrolyte (Ruhle, 2016).

With these discussions for the optimization of cell performance at optimal cell fabrication parameters, the results and advancement of present study may be compared with already reported work on PG cell. The work reported in recently published papers (Gangotri et al., 2013; Gangotri and Bhimwal, 2010; Yadav and Lal, 2013) has not used the all means reported in literature for increasing cell performance. The present study involves the use of anionic SLS surfactant (Groenen et al., 1984; Madhwani et al., 2007; Mukhopadhyay and Bhowmik, 1993) with very small Pt electrode (Koli et al., 2012), use of SCE terminal of combination electrode (Koli et al., 2012), high pH (Koli et al., 2012), well cleaned and scratched Pt electrode (Koli et al., 2012), low molecular weight, etc. Whereas, the recently published papers are based on large Pt, normal SCE, low pH, surfactant other than SLS (Gangotri et al., 2013), and no surfactant use (Gangotri and Bhimwal, 2010; Yadav and Lal, 2013).

In the present study, there is no confusion regarding the effect of light intensity and dye material. For the given concentration of chemicals used in a cell, the optimum cell performance is at optimum illumination intensity. Keeping this concentration constant, any upward or downward change in intensity will decrease electrical output of the cell. But, if higher illumination intensity is used with higher optimal concentration of chemicals then the electrical output of the cell will be high (Mosquera et al., 1994). Regarding the dye nature, the light dye molecules have been found to show better cell performance (Koli et al., 2012).

Among the all techniques like photogalvanic cells (Gangotri and Lal, 2014), photovoltaic cells (PV), dye-sensitized solar cells (Guo et al., 2013; Yu and Fan, 2010; Zhang et al., 2013), etc., the PV technique is commercially popular world over for solar electricity generation. The use of solar techniques during odd hours like during the night time and no wind time requires inherent power storage capacity. It is because use of the external power storage devices shoots up prices. It is here, the photogalvanic cell has potential for inherent storage capacity in a cheaper manner as these cells are fabricated using very dilute solutions of cheap chemicals like photo-sensitizers, reductant, NaOH and surfactant.

The eco-friendly nature of the use of Sudan-I based PG cells can be enhanced by removal of exhausted cell solution

containing this dye by decolorization process using *Shewanella Oneidensis MR-1 method* which removes 66.8% of the Sudan-I in 104 h, by reducing it to aniline. In this method, the higher lactate or biomass concentration was found most efficient electron donor for Sudan-I reduction (Ji et al., 2012). This dye removal method also gives hint for the use of lactate as reducing agent in Sudan-I based PG cells for future research.

4. Conclusion

The use of Sudan-I dye photosensitizer-Fructose reductant-SLS surfactant combination in photogalvanic cell was planned with the aim of further enhancing performance of these cells. The results obtained for this combination have been found very encouraging according to aim of the present work as results are significantly better than reported results in the field of photogalvanics. The Sudan-I dye - Fructose-SLS combination based photogalvanic cells also shows optimum performance in optimal conditions.

Therefore, the Sudan-I dye-Fructose-SLS combination is a good alternative for use in fabrication of highly efficient photogalvanic cells.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2020.102918.

References

Albery, W.J., Archer, M.D., 1977. Optimum efficiency of photogalvanic cells for solar energy conversion. Nature 270, 399.

Albery, W.J., Archer, M.D., 1977. Photogalvanic cells: II. current-voltage and power characteristics. J. Electrochem. Soc. 124, 688.

Albery, W.J., Foulds, A.W., Hall, K.J., Hillman, A.R., Egdell, R.G., Orchard, A.F., 1979. Thionine coated electrode for photogalvanic cells. Nature 282 (5741), 793.

Albery, W.J., Bowen, W.R., Fisher, S., Turner, A.D., 1979. Photogalvanic cells: Part IX. Investigations using the transparent rotating disc electrode. J. Electroanal. Chem. 107 (1), 11.

Bard, A.J., 1974. Encyclopedia of electrochemistry of the elements. New York;Marcel Dekker, 174.

Becquerel, E., 1839. On electron effects under the influence of solar radiation. Comptes Rendues de 'l', Academic Science Paris 9, 561.

Bhimwal, M.K., Gangotri, K.M., 2011. A comparative study on the performance of photogalvanic cells with different photosensitizers for solar energy conversion and storage: D-Xylose-NaLS systems. Energy 36 (2), 1324.

Clark, W.D.K., Eckert, J.A., 1975. Photogalvanic cells. Sol. Energy 17, 147.

Datyner, A., 1978. The solubilization of disperse dyes by dispersing agents at 127 °C. J. Soc. Dyers Colour. 94, 256.

Editorial, Solar Energy Materials & Solar Cells, 133 (2015) A1–A6.

Gangotri, K.M., Lal, M., 2014. Use of trypan blue-arabinose system in photogalvanic cell for solar energy conversion and storage. Int. J. Eng. Sci. Res. Technol. 3, 447.

Gangotri, K.M., Regar, O.P., Lal, C., Kalla, P., Genwa, K.R., Meena, R., 1996. Use of tergitol-7 in photogalvanic cell for solar energy conversion and storage: Toluidine blue-glucose system. Int. J. Energy Res. 20 (7), 581.

Gangotri, K.M., Aseri, P., Bhimwal, M.K., 2013. The use of tergitol-7 in photogalvanic cells for solar energy conversion and storage: An EDTA–azur B system. Energy Sources Part A 35 (4), 312.

Gangotri, K.M., Bhimwal, M.K., 2010. The photochemical conversion of solar energy into electrical energy: Eosin-Arabinose system. Int. J. Electr. Power Energy Syst. 32, 1106.

Gangotri, P., Gangotri, K.M., 2009. Studies of the micellar effect on photogalvanics: solar energy conversion and storage in EDTA−safranine O−tween-80 system. Energy Fuels 23 (5), 2767.

Gangotri, P., Gangotri, K.M., 2013. Studies of the micellar effect on photogalvanics: solar energy conversion and storage-EDTA-safranine O-NaLS system. Energy Sources Part A 35, 1007.

Gangotri, P., Koli, P., 2017. Study of the enhancement on photogalvanics: solar energy conversion and storage in EDTA-safranine O-NaLS system. Sustainable Energy Fuels 1, 882.

Genwa, K.R., Kumar, A., Sonel, A., 2009. Photogalvanic solar energy conversion: Study with photosensitizers Toluidine Blue and Malachite Green in presence of NaLS. Appl. Energy 86 (9), 1431.

Groenen, E.J.J., De Groot, M.S., De Ruiter, R., De Wit, N., 1984. Triton X-100 micelles in the ferrous/thionine photogalvanic cell. J. Phys. Chem. 88 (7), 1449.

Guo, J., Shi, Y., Chu, Y., Ma, T., 2013. Highly efficient telluride electrocatalysts for use as Pt-free counter electrodes in dye-sensitized solar cells. Chem. Commun. 49, 10157.

Hendrich, W., 1958. The photovoltaic effect in the chlorophyll–ascorbic acid system. Roczniki Chemii 32, 107.

Hillson, P.J., Rideal, E., 1953. The Becquerel effect in the presence of dyes and the action of light on dyes. Proc. Royal Soc. London A 216, 458.

Ji, Q., Liu, G., Zhou, J., Wang, J., Jin, R., Lv, H., 2012. Removal of water-insoluble Sudan dyes by Shewanella oneidens MR-1. Bioresour. Technol. 114, 144.

Kamat, P.V., Lichtin, N.N., 1982. Electron transfer in the quenching of protonated triplet thionine and methylene blue by ground state thionine. J. Photochem. 18 (3), 197.

Kaneko, M., Yamada, A., 1977. Photopotential and photocurrent induced by a tolusafranine ethylenediaminetetraacetic acid system. J. Phys. Chem. 81 (12), 1213.

Koli, P., 2016. Sodium lauryl sulphate enhanced solar energy conversion by photogalvanic effect of Rhodamine B-fructose in artificial light. Chem. Select 1 (15), 4624.

Koli, P., 2017. Surfactant and natural sunlight enhanced Photogalvanic effect of Sudan I dye. Arabian J. Chem. 10 (8), 1077.

Koli, P., 2018. Photogalvanic effect of natural photosensitizer (crude Spinach extract) in artificial light for simultaneous solar power generation and storage. Environ. Prog. Sustainable Energy 37 (5), 1800.

Koli, P., 2019. Enhancing efficiency of Fast Green FCF –Fructose photogalvanic solar cell by using surfactant in natural sunlight. Int. J. Ambient Energy 40 (8), 868.

Koli, P., Sharma, Urvashi, 2016. Energy conversion in electrolyte under artificial light: Fast Green FCF–Fructose-Surfactant- small Pt electrode photogalvanic cell. Appl. Solar Energy 52 (2), 76.

Koli, P., Sharma, U., Dayma, Y., Pareek, R.K., 2018. Photogalvanic effect of Brilliant Cresyl Blue-Fructose-surfactant-small Pt electrode-artificial light: Simultaneous solar energy conversion and storage. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 40, 2163.

Koli, P., Sharma, U., Gangotri, K.M., 2012. Solar energy conversion and storage: Rhodamine B - Fructose Photogalvanic cell. Renewable Energy 37 (1), 250.

Koli, P., Sharma, U., 2017. Photochemical solar power and storage through Photogalvanic cells: Comparing performance of dye materials. Energy Sources Part A 39 (6), 555.

Koli, P., Dayma, Y., Pareek, R.K., 2019. Simultaneous electrochemical solar power and storage by using the alkaline Metanil Yellow-Formic acid as a new sensitizer-reductant couple in the photogalvanic cells. RSC Adv. 9, 7560.

Koli, P., Dayma, Y., Pareek, R.K., Jonwal, M., 2020. Use of Congo red dye-formaldehyde as a new sensitizer-reductant couple for enhanced simultaneous solar energy conversion and storage by photogalvanic cells at the low and artificial sun intensity. Sci. Rep. 10, 19264.

Kolthoff, I.M., Elving, P.J., 1976. Treatise on analytical chemistry, II; New York. Wiley 15, 465.

Lang, A.R., 2009. Dyes and Pigments. New Research Nova Science Publisher, New York.

Lizier, T.M., Zanoni, T.B., de Oliveira, D.P., Zanoni, M.V.B., 2012. Electrochemical reduction as a powerful tool to highlight the possible formation of by-products more toxic than Sudan III dye. Int. J. Electrochem. Sci. 7, 7784.

Madhwani, S., Ameta, R., Vardia, J., Punjabi, P.B., Sharma, V.K., 2007. Use of fluoroscein-EDTA System in photogalvanic cell for solar energy conversion. Energy Sources, PartA: Recovery, Utilization, and Environ. Effects 29 (8), 721.

Malviya, A., Solanki, P.P., 2016. Photogalvanics: A sustainable and promising device for solar energy conversion and storage. Renew. Sustainable Energy Rev. 59, 662.

Meena, R.C., Singh, G., Tyagi, N., Kumari, M., 2004. Studies of surfactants in photogalvanic cells-NaLS-EDTA and azur-B. J. Chem. Sci. 116 (3), 179.

Ming, L., Xi, X., Chen, T., Liu, J., 2008. Electrochemical determination of trace sudan I contamination in chili powder at carbon nanotube modified electrodes. Sensors 8, 1890.

Mosquera, M.I.M., Rojas, B.G., Mosquera, J.M., 1994. Mechanism and kinetics of the degradation of chlorophylls during the processing of green table olives. J. Agric. Food. Chem. 42 (5), 1089.

Mukhopadhyay, M., Bhowmik, B.B., 1993. Kinetics of photoinduced electron transfer in a photoelectrochemical cell consisting of thiazine dyes and Triton X-100 surfactant. J. Photochem. Photobiol., A 69 (3), 363.

Murthy, A.S.N., Dak, H.C., Reddy, K.S., 1980. Photogalvanic effect in riboflavin–ethylenediaminetetraacetic acid system. Int. J. Energy Res. 4, 339.

Murthy, A.S.N., Reddy, K., 1984. Cyclic-voltammetric studies of some phenothiazine dyes. J. Chem. Soc. Faraday Trans. I (80), 2745.

Nabar, G.M., Shenai, V.A., 1963. Reduction potentials of vat dyes and their relation to the ease of reduction and tendering behavior. Text. Res. J., 471

Osif, T.L., Lichtin, N.N., Hoffman, M.Z., 1978. Kinetics of dark back reaction of products of the photoreduction of triplet thionine by iron (II). Evidence for association of leucothionine and semithionine with iron (III). J. Phys. Chem. 82 (16), 1778.

Ozeki, S., Ikeda, S., 1985. The difference in solubilization power between spherical and rodlike micelles of dodecyldimethylammonlum chloride in aqueous solutions. J. Phys. Chem. 89, 5088.

Pokhrel, S., Nagaraja, K.S., 2009. Photogalvanic behaviour of $[Cr_2-O_2S_2(1-Pipdtc)_2(H_2O)_2]$ in aqueous DMF. Sol. Energy Mater. Sol. Cells 93 (2), 244.

Polson, A., Reyden, D.V.D., 1950. Relationship between diffusion constants and molecular weight. BBA 5, 358.

Potter Jr., A.E., Thaller, L.H., 1959. Efficiency of some iron-thionine photogalvanic cells. Sol. Energy 3 (4), 1.

Pramila, S., Gangotri, K.M., 2007. Use of anionic micelles in photogalvanic cells for solar energy conversion and storage dioctylsulfosuccinate-mannitol-safranine system. Energy Sources Part A 29 (13), 1253.

Rabinowitch, E., 1940. The photogalvanic effect I. The photochemical properties of the thionine-iron system. J. Chem. Phys. 8 (7), 551.

Raga, S.R., -Santiago, F.F, 2013. Temperature effects in dye-sensitized solar cells. Phys. Chem. Chem. Phys., 15, p. 2328.

Rideal, E.K., Williams, E.G., 1925. The action of light on the ferrous iodine iodide equilibrium. J. Chem. Soc., Trans. 127, 258.

Rosen, M.J., 2004. Surfactants and Interfacial Phenomena. Wiley, New York.

Ruhle, S., 2016. Tabulated values of the Shockley-Queisser limit for single junction solar cells. Sol. Energy 130, 139.

Sharma, U., Koli, P., Gangotri, K.M., 2011. Brilliant Cresyl Blue - Fructose for enhancement of solar energy conversion and storage capacity of photogalvanic solar cells. Fuel 90 (11), 3336.

Stein, G., 1977. Photochemical conversion and storage of solar energy. Solar Power Fuels. (Proc Int. Conf.) 1st, 1–25.

Suresh, E., Pragasam, J., Xavier, F.P., Nagaraja, K.S., 1999. Investigation of manganese-molybdenum-diethyldithiocarbamate complex as a potential system for solar energy conversion. Int. J. Energy Res. 23 (3), 229.

Tehrani-Bagha, A.R., Holmberg, K., 2013. Solubilization of hydrophobic dyes in surfactant solutions. Materials 6, 580.

Tehrani-Bagha, A.R., Singh, R.G., Holmberg, K., 2013. Solubilization of two organic water-insoluble dyes by anionic, cationic and nonionic surfactants. Colloids Surf., A 417, 133.

Vos, A. De, Powels, H., 1981. On the thermodyanamic limit of photovoltaic energy conversion. Applied physics 25, 119.

Wildes, P.D., Lichtin, N.N., 1978. Correlation of open-circuit voltage and short-circuit current of the totally illuminated, thin-layer iron-thionine Photogalvanic cell with photostationary composition. J. Am. Chem. Soc. 100 (21), 6568.

Yadav, S., Lal, C., 2013. Optimization of performance characteristics of a mixed dye based photogalvanic cell for efficient solar energy conversion and storage. Energy Convers. Manage. 66, 271.

Yu, J., Fan, J., 2010. Li Zhao, Dye-sensitized solar cells based on hollow anatase TiO_2 spheres prepared by self-transformation method. Electrochim. Acta 55, 597.

Zhang, S., Ashraful, I., Xudong, Y., Chuanjiang, Q., Zhang, K., Numata, Y., Chen, H., Han, L., 2013. Improvement of spectral response by co-sensitizers for high efficiency dye-sensitized solar cells. J. Mater. Chem. A 1, 4812.