

Photoelectrochemical Cell with Phenosafranin Coated Electrode†

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A totally illuminated electrochemical cell has been developed with phenosafranin coated platinum foil as photoanode and bare platinum foil as photocathode dipped in deoxygenated aqueous solution of EDTA. The photovoltage increases with increase in [phenosafranin] on coated electrode. When chlorophyll-coated platinum foil is used as photocathode with phenosafranin ($5 \times 10^{-3} M$) coated platinum foil as photoanode open-circuit photovoltage of 512 mV, short-circuit photocurrent of $17 \mu A/cm^2$, fill-factor of 0.33 and solar energy efficiency of $1.3 \times 10^{-2}\%$ have been obtained corresponding to white light irradiation of light intensity $22 mW/cm^2$, and the quantum efficiency is about 0.5% at 540 nm. The effect of pH on photovoltage generation has also been studied. The mechanism of photochemical reactions leading to photovoltage generation is also discussed.

A fairly large photogalvanic effect was reported in phenosafranin (PSF)-EDTA aqueous system both in light and dark compartments^{1,2} using platinum electrodes. The same system generated appreciable photovoltage in the solid polycrystalline state in a sandwich cell using illuminated semiconductor SnO_2 electrode and dark platinum foil counter electrode³. The solar energy efficiency (SEE) in both the cases^{2,3}, was observed to be about $1 \times 10^{-3}\%$ corresponding to unfiltered light. It was confirmed by cyclic voltammetry⁴ that the photovoltage generation in PSF-EDTA aqueous system is influenced by the adsorption of PSF on the platinum electrode surface. The activation of platinum electrode by dye adsorption was first noted by Miller⁵ and later confirmed by Hall *et al.*⁶. A film of adsorbed dye could be photochemically reduced and electrochemically oxidised without any bulk movement. On the other hand, improved performance in thionine- Fe^{2+} aqueous system due to film formation was ascribed to increase reversibility of thionine/leucothionine couple at the dye-coated electrode and blocking of Fe^{2+}/Fe^{3+} couple^{7,8}.

Recently pigment-based photoelectrochemical cells^{9,10} have been developed to transduce light into electrical and/or chemical energy with higher efficiency. Tien and Higgins¹¹ reported a new type of photoelectrochemical cell consisting of two pigment-sensitized semiconductor electrodes in appropriate redox solutions for photovoltaic electrochemical cells for the conversion of light into electrical energy. A film

of the pigment, *meso*-tetraphenylporphyrin on a tin oxide (SnO_2) substrate acted as a photocathode, and a film of the dye Victoria Blue B also on SnO_2 acted as a photoanode. The characteristics of this cell reported were; photovoltage > IV; photocurrent $100 \mu A$; and quantum efficiency > 1% corresponding to white light irradiation with light intensity of $100 mW/cm^2$.

To increase the SEE of PSF-EDTA system, a novel photoelectrochemical cell based on PSF-coated platinum foil as a photoanode and bare platinum foil as a photocathode has been developed. The efficiency of the above cell has also been investigated using chlorophyll (Chl)-coated platinum foil as a photocathode instead of the bare platinum. All the characteristics of this cell are reported herein along with the mechanism of photovoltage generation.

Materials and Methods

Phenosafranin (3, 7-diamino-5-phenylphenazinium chloride, PSF) (Sigma Chemicals) was recrystallised twice from 50% aq. ethanol. EDTA (disodium salt, dihydrate) and polyvinyl alcohol were of the AR grade (BDH) and were used as such. Chlorophyll (Chl), actually a mixture of chlorophylls (a) and (b) in the ratio of 3:1, was extracted from spinach leaves by the standard method and it was used without separation.

The platinum electrode was coated with PSF by dipping the electrode into a solution of PSF of known concentration containing definite amount of polyvinyl alcohol (0.8 g/5 ml). The dip and dry process was repeated 4-5 times when a film of 30-40 μm thickness was formed. In the case of Chl-coated platinum electrode, the same procedure was followed with a saturated aqueous solution of Chl containing the same amount of polyvinyl alcohol.

The dye-coated platinum electrode and counter

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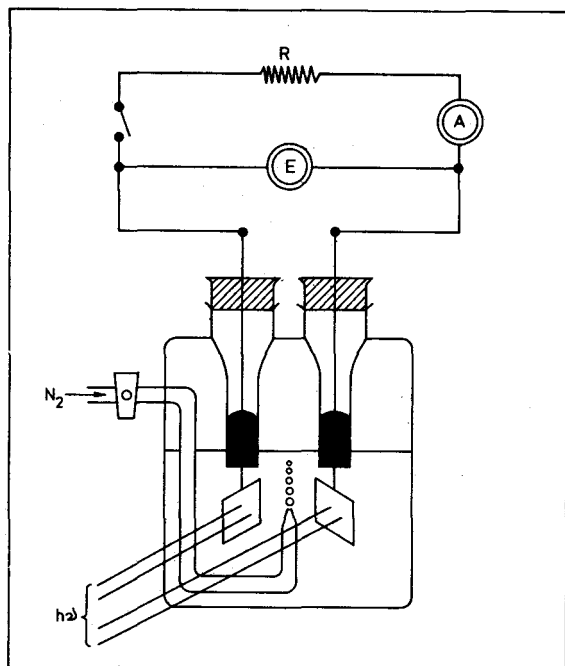


Fig. 1—Schematic diagram of experimental photoelectrochemical cell using coated platinum electrodes each of 1 sq cm area and placed 1 cm apart in the cell [A, multimeter, V, electrometer and R, variable resistance]

platinum electrode, each of 1 sq cm area, were placed 1 cm apart in a cell (Fig. 1) containing aqueous solution of 0.1 M EDTA at pH 4.5. The solution was deoxygenated by bubbling N_2 gas into the cell for 15–20 min before measurement. The light source was a 300 W projector tungsten lamp focussed for 22 mW cm^{-2} . The electrodes were placed at an angle of 45° to the incident light. The photovoltage and photocurrent were measured with a Anadigi model DE 5202 digital electrometer and HIL model 2105 digital multimeter, respectively. The pHs of the solutions were adjusted with dil. acid (HCl) and dil. alkali (NaOH) and checked with Elico pH meter.

The absorption spectra of PSF and Chl in the polyvinyl alcohol film were recorded on a Perkin-Elmer model 200 spectrophotometer. The action spectrum of photovoltage generation of the system was measured at different wavelengths using a 100 W xenon lamp and grating monochromator (Applied Physics) blazed at 500 nm.

Results and Discussion

It is observed that on illumination, a photovoltage develops, which attains a maximum value within a few minutes. When the illumination is stopped, the photovoltage decreases gradually and reaches very nearly the original value in the dark. The growth and decay of photovoltage with time on illumination and in the dark, using photoanode coated with different

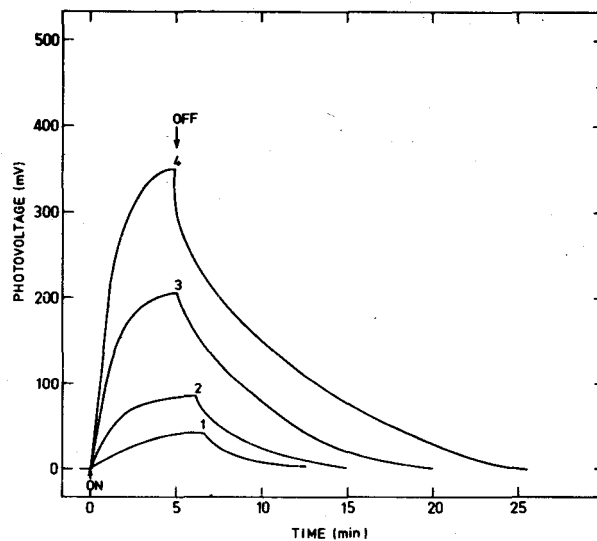


Fig. 2—Growth and decay of photovoltage induced by illumination using PSF-coated platinum as photoanode and bare platinum as photocathode [The concentrations (M) of PSF used in photoanode of the cell are: (1) 1×10^{-5} , (2) 1×10^{-4} , (3) 1×10^{-3} and (4) 5×10^{-3}]

concentrations of PSF are shown in Fig. 2. The maximum open-circuit photovoltages (V_{oc}) developed at different [PSF] of 1×10^{-5} , 1×10^{-4} , 1×10^{-3} and $5 \times 10^{-3} \text{ M}$ are 34, 82, 186 and 342 mV respectively. The V_{oc} generated at different [PSF] follows Freundlich adsorption isotherm type of equation, i.e. $V_{oc} = kC^n$, where k and n are constants, the values being 2.24 and 0.36 V respectively. The characteristic current-voltage curve (Fig. 3, curve 2) of a system containing $5 \times 10^{-3} \text{ M}$ PSF† gives a short-circuit current (I_{sc}) of 8 μA . The I_{sc} values at [PSF] of 1×10^{-5} , 1×10^{-4} and $1 \times 10^{-3} \text{ M}$ are 3.0, 5.0 and 6.5 μA , respectively. The SEE of this cell has been calculated to be about $3.23 \times 10^{-3}\%$ corresponding to the unfiltered light. The results show improvement over the previous work (Fig. 3, curve 1) in this system using only bare platinum electrodes, both in the light and the dark compartments. Thus the PSF-coated electrode acts as a selective electrode to reduced PSF dye and prevents back combination of photoredox species generated during illumination of the cell. It is observed that the efficiency of the cell is further improved by using Chl-coated platinum foil as photocathode instead of bare platinum. The characteristic current-voltage curve is shown in Fig. 3 (curve 3). All the characteristics of the cell are reported

†The solubility of PSF in aqueous solution containing polyvinyl alcohol does not permit concentrations above $5 \times 10^{-3} \text{ M}$. The dark voltage of about 85 mV develops due to asymmetrical electrodes. The photovoltage reported is the net increase of voltage during illumination.

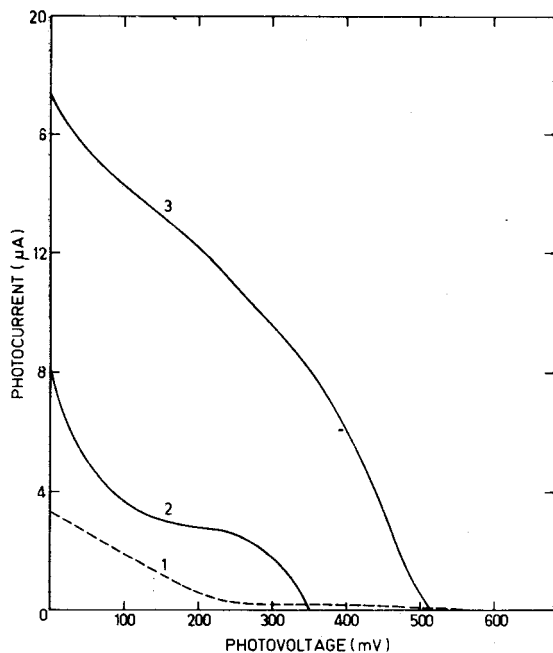


Fig. 3—Photocurrent versus photovoltage characteristic curves of PSF-EDTA system under different conditions [(1) with bare platinum electrodes both in the light and the dark compartments; (2) PSF ($5 \times 10^{-3} M$) coated photoanode and bare platinum electrode; (3) PSF ($5 \times 10^{-3} M$) coated photoanode and Chl-coated photocathode]

in Table 1. When platinum foil coated with Chl is used as photocathode and bare platinum foil as photoanode, both dipped in 0.1 M EDTA solution, the system generates only 20-30 mV photovoltage on illumination under the same condition.

The effect of varying pH on photovoltage generation in this system with PSF and Chl coated electrodes is shown in Fig. 4. Interestingly the photovoltage generation gives two maxima at pH 6.8 and 9.0 while the absorption spectrum of PSF is independent of pH in the range of 3-10. The triplet PSF

Table 1—Characteristics of Cell Consisting of PSF ($5 \times 10^{-3} M$) Coated Photoanode and Chlorophyll (Chl) Coated Photocathode at $30^\circ C^a$

Photo-anode	Photo-cathode	V_{oc} (mV)	I_{sc} (μA)	Fill-factor ff	Power efficiency PE ($\mu W cm^{-2}$)	Solar energy efficiency SEE (%)
PSF	Bare	342	8.0	0.26	0.71	3.23×10^{-3}
PSF	Chl	512	17.0	0.33	2.87	1.31×10^{-2}
Bare	Chl	20-30	—	—	—	—

^aThe characteristics of PSF-EDTA system in aqueous solution using platinum electrodes, both in the light and the dark compartments at $30^\circ C$ are: V_{oc} , 680 mV; I_{sc} , 3.14 μA ; ff, 0.1; PE, 0.24 $\mu W cm^{-2}$; and SEE, $1.1 \times 10^{-3}\%$. These values are taken from ref. 2. There is always small voltage in each case due to asymmetrical electrodes and the photovoltage reported is the net increase of voltage during illumination.

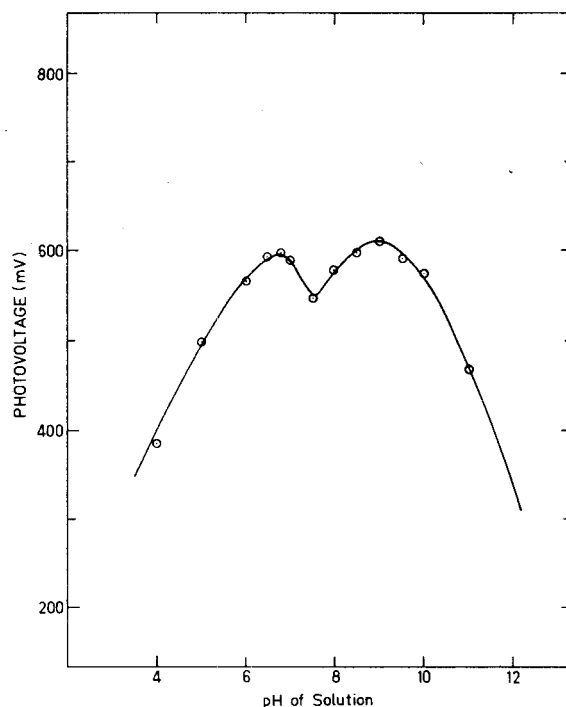
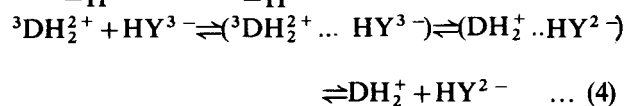
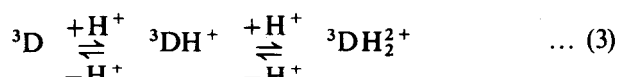


Fig. 4—Plot of photovoltage as a function of pH for cell with PSF and Chl coated platinum electrodes

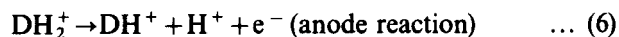
which is an efficient electron acceptor and generates photovoltage in the presence of Triton X-100¹² and EDTA¹³ by charge-transfer (CT) complex formation with them. The transient photochemistry of Safranin-O, a dye very similar to PSF, has been recently reported by Baumgartner *et al.*¹⁴ using ascorbic acid and EDTA as the reducing agents. From flash spectroscopic technique, pH-dependence of generation of semireduced dye has been studied. In the absence of reducing agent three triplet species of the dye, viz. ${}^3DH_2^+$ ($pK_a = 7.5$), ${}^3DH^+$ ($pK_a = 9.2$) and 3D are observed as a function of pH. The order of reactivities of these triplet states are ${}^3DH_2^+ > {}^3DH^+ > {}^3D$ and the life-times are $\tau({}^3DH_2^+) = 277 \mu s$; and $\tau({}^3DH^+) = 44 \mu s$. Because of the longer life-time and more efficient electron accepting property, ${}^3DH_2^+$ is likely to participate in the photoreduction chemistry of Safranin-O. Baumgartner *et al.*¹⁴ observed a pH dependence of semireduced dye formation with maximum between pH 6 and 7. The pK_a values for EDTA (H_4Y)¹⁵ are 2.1, 2.7, 6.2 and 10.3. Bonneau *et al.*¹⁶ have shown that only the species HY^{3-} and Y^{4-} have lone pair of electrons on nitrogen atoms available for donating to suitable acceptors. Therefore, EDTA will act as an efficient electron donor towards triplet PSF above pH 6. While the triplet diprotonated PSF (${}^3DH_2^+$) is prominent electron acceptor among the three triplet PSF species, the fully ionized EDTA (Y^{4-}) is also expected to function as a strong electron donor among the

different species of EDTA. Considering the pK_a values (6.8 and 9.0) of protonated triplet PSF, the CT interaction of ${}^3DH_2^{2+}$ with HY^{3-} at pH 6.8 and of ${}^3DH^+$ with Y^{4-} at pH 9.0 on the PSF-coated electrode surface clearly explains the pH-dependence of photovoltage generation. Since the photochemical reduction and electrochemical oxidation of triplet PSF takes place on the surface of the coated electrode, the photovoltage generation should be independent of the life-times of protonated triplet PSF species. The difference in the pK_a values observed in Safranin-O and PSF may be due to minor difference in their respective structures.

The action spectrum for the photovoltage generation of the system with PSF and Chl coated platinum electrodes, and visible absorption spectra of PSF and Chl in polyvinyl alcohol film, are shown in Fig. 5. The visible absorption spectrum of PSF in polyvinyl alcohol shows a maximum at 540 nm. The close similarity between the photovoltage action spectrum and the visible absorption spectrum of PSF in film indicates that photoactive species are generated at the PSF-coated electrode due to light absorption. The various steps of redox reaction initiated after the light absorption by PSF for photovoltage generation at pH 6.8 are shown in Scheme 1.

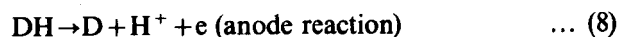


CT interaction



Scheme 1

In Scheme 1 D, DH^+ , DH_2^+ and DH_3^+ represent dye (PSF), protonated dye, protonated semi- and leuco-dye respectively at pH 6.8 whereas HY^{3-} represents triply ionized EDTA. Similarly the photochemical and electrochemical reactions at pH 9 are same except the formation of ${}^3DH^+$ by step (3) and its CT interaction with fully ionized EDTA (Y^{4-}) with the generation of electrode active species DH and Y^{3-} which in turn, react as shown in Eqs (8) and (9)



While the formation of protonated triplet dye in step

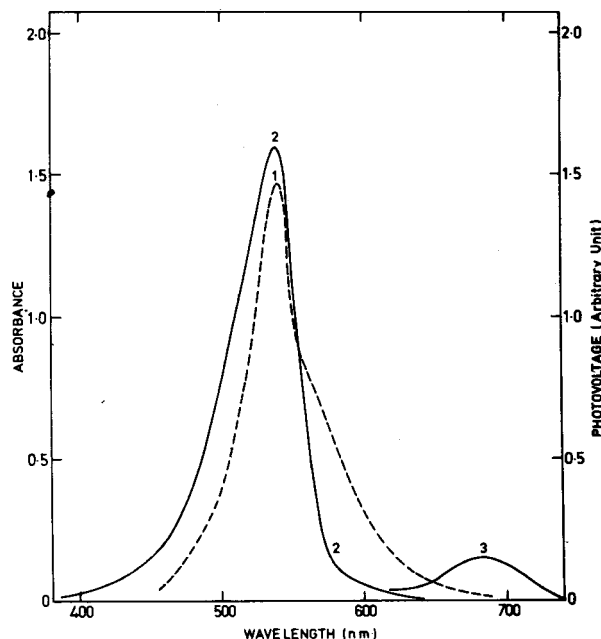
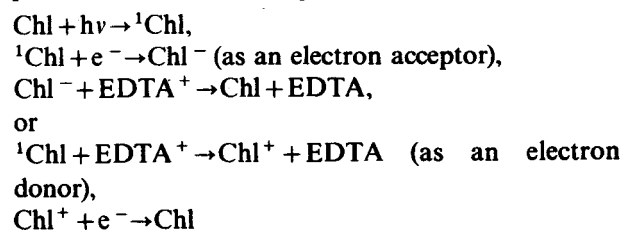


Fig. 5—Action spectrum of photovoltage for the system with PSF and Chl coated platinum electrodes (curve 1), and the absorption spectra of PSF (curve 2) and Chl (curve 3) in polyvinyl alcohol film

(3) is favoured at low pH, the anode reactions (6) and (8) should be favoured at higher pH and the maximum photovoltage generation at pH 6.8 and 9.0 is the balance between the two. In the text, both HY^{2-} and Y^{3-} are represented by $EDTA^+$ which is involved in cathode reaction, a part of $EDTA^+$ may lose CO_2 by side reaction as mentioned earlier¹³. No photovoltage is produced in the absence of EDTA. At the maximum photovoltage, the PSF-coated photoanode appears colourless. Excited PSF in the triplet state reduces to semi- or leuco-form in the presence of EDTA and semi- or leuco-PSF generates electron at the PSF-coated photoanode whereas $EDTA^+$ accepts electron at the cathode. The direct dependence of photocurrent on incident light intensity, observed in this system as well as in an earlier² one, proves the participation of semi-dye at the photoanode. Chlorophyll (Chl) molecule in the excited state can function both as electron donor and acceptor¹⁷ depending on the relative strength of redox compounds which react with the excited Chl molecule. The transfer of electron to $EDTA^+$ at photocathode is facilitated due to the presence of Chl according to Scheme 2:



Scheme 2

It has been found that when PSF-EDTA and Chl-EDTA aqueous solutions are placed in a H-shaped cell separated by sintered disc and only PSF-EDTA aqueous solution is deoxygenated, photovoltage is generated. From this observation one can conclude that PSF in the triplet state and Chl in the singlet state are involved in photochemical redox reactions for the generation of photovoltage.

The quantum efficiency of the cell with both PSF and Chl coated electrodes corresponding to monochromatic light (540 nm) with light intensity of 0.60 mWcm^{-2} is about 0.48% which is very encouraging in this type of cell.

Acknowledgement

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References

- 1 Eisenberg M & Silverman H P, *Electrochim Acta*, **5** (1961) 1.
- 2 Rohatgi-Mukherjee K K, Bagchi M & Bhowmik B B, *Electrochim Acta*, **28** (1983) 293.
- 3 Rohatgi-Mukherjee K K, Roy M & Bhowmik B B, *Solar Energy*, **31** (1983) 417.
- 4 Basu J, Kundu K K & Rohatgi-Mukherjee K K, *Indian J Chem*, **23A** (1984) 630.
- 5 Miller L J, "A Feasibility Study of Thionine Photogalvanic Power Conversion System", Final Report, Contract No: AF 33(616)-7911, Sunstrand Aviation, ASTIA Document No. 282878 (1962).
- 6 Hall D E, Wildes P D & Lichtin N N, *J electrochem Soc*, **125** (1978) 1365.
- 7 Albery W J & Foulds A W, *J Photochem*, **10** (1979) 41.
- 8 Archer M D, Ferreira M I C, Albery W J & Hillman A R, *J electroanal Chem*, **111** (1980) 295.
- 9 Kampas F J, Yamashita K & Fajer J, *Nature*, **284** (1980) 40.
- 10 Jimbo H, Yoneyama H & Tamura H, *Photochem Photobiol*, **32** (1980) 219.
- 11 Tien H T & Higgins J, *Chem Phys Lett*, **93** (1982) 276.
- 12 Rohatgi-Mukherjee K K, Chaudhuri R & Bhowmik B B, *J Colloid Interface Sci*, **106** (1985) 45.
- 13 Rohatgi-Mukherjee K K, Bagchi M & Bhowmik B B, *Indian J Chem*, **24A** (1985) 1002.
- 14 Baumgartner C E, Richtol H H & Alkenes D A, *Photochem Photobiol*, **34** (1981) 17.
- 15 Schwartzbach G & Ackermann H, *Helv Chim Acta*, **30** (1947) 1798.
- 16 Bonneau R, Jousot-Dubien J & Faure J, *Photochem Photobiol*, **17** (1973) 313.
- 17 Tien H T, in *Photosynthesis in relation to model systems*, edited by J. Barber (Elsevier/North Holland Biomedical Press, New York), 1979, pp. 115.