

A Novel Photogalvanovoltaic Tandem Cell

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A novel type of photoelectrochemical cell based on a unique combination of photogalvanic (PG) and photovoltaic (PV) effects has been constructed. The improvement of the cell has been brought about by using a polymer-coated platinum electrode instead of a simple Pt electrode. The feasibility of such a photogalvanovoltaic (PGV) cell as a transducer of light energy to electrical energy has been demonstrated.

Attempts to utilize solar energy have led to the development of two main types of photoelectrochemical (PEC) devices: (i) Photogalvanic (PG) cells; and (ii) 'wet' photovoltaic (PV) cells. These are wet devices as against solid PV cells. Interest in wet PV devices mainly arises due to the fact that they may lead to cheap light-to-energy transducers where very well prepared surfaces for electrodes are not required. In PG cells, redox photochemistry occurs in solution and inert electrodes help to separate the reducing and oxidising equivalents. The thionine-ferrous system is the classical example of PG cell¹. On the other hand, in the wet PV cells, electrodes are photoactive semiconductors, inorganic or organic, connected to a counter electrode dipped in an inert solution. The illumination of the electrode by the supra band gap radiation results in photoinduced charge separation at the interface. Mountz and Tien² demonstrated that combination of PG and PV effects could give much improved performance. Instead of inert electrode, metal tetraphenylporphyrin (MTPP) coated Pt or C electrode was used as the counter electrode in iron-thionine PG cell with Pt wire as working electrode and SCE as the reference electrode.

For sometimes past we have been working on two types of cells (A and B) individually: (a) phenosafranine (PSF) + EDTA in PG mode³ which have been found to give large photopotential. The power conversion efficiency of the system was not good, $P = 0.24 \mu\text{W cm}^{-2}$ and $\text{SEE} = 10^{-30}\%$. The current-voltage curve indicated large activation overpotential and a fill factor of only 0.11.

Pt spiral (light)	PSF $1 \times 10^{-5} M$	+ EDTA $0.1 M$	+ KCl $0.1 M$	Pt spiral (dark)
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(A)

(b) Metal tetraphenylporphyrins (MTPP) coated electrodes for which the maximum SEE was only

$10^{-4}\%$ with a fill factor of 0.17 and poor I-V characteristics.

Pt spiral	KCl $0.1 M$	ZnTPP/Pt
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(B)

In this paper we describe the construction of a photoelectrochemical cell based on a unique combination of PG and PV effects.

Materials and Methods

The electrical measurements were made using a Keithley electrometer (model 604). A projector unit with halogen tungsten lamp was used as the light source. Doubly distilled water was used as solvent. EDTA (AR, Glaxo Laboratories) was used as such. PSF (George T Gurr Ltd, London) was purified by chromatography. ZnTPP was prepared following Adler⁴ method.

PGV cell: Photogalvanovoltaic tandem cell with /PSF + EDTA/ + MTPP/system

The two cells, (A) and (B) were combined in a different way than that used by Mountz and Tien². The separate identity of the two cells was maintained and they were connected in tandem as shown in Fig. 1. The PG solution was contained in a partitioned cylindrical cell (6 cm height and 3 cm int. diam). The light and dark compartments were partitioned by a pair of opaque separators with mismatched holes. Platinum spirals served as electrodes in each compartment. The electrode placed in the dark compartment has not been shown in Fig. 1 for clarity of presentation. The solution was deaerated completely by bubbling N_2 gas through a jet inserted into the solution. The PV cell (B) consisting of ZnTPP coated Pt electrode (coated by dip-dry method in CHCl_3) as working electrode and Pt spiral as a counter

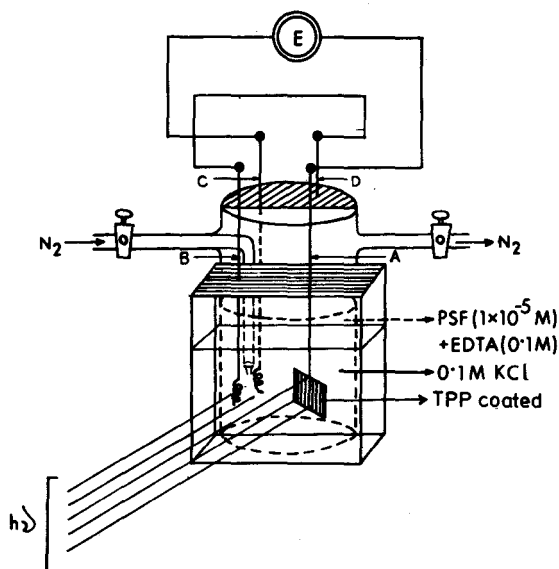


Fig. 1—Rectangular cell—PV cell (—); cylindrical cell—PG cell (---) having two compartments separated by a pair of opaque partition with mismatched holes. The dark compartment containing the spiral counter electrode is not shown for clarity in presentation. [A—PV working electrode (coated with MTTP); B—PV counter electrode (illuminated); C—PG working electrode (in the light half of the PG cell); D—PG counter electrode (in the dark half of the PG cell not fully shown in the figure); E—electrometer. The two counter electrodes B and D are connected in series]

electrode was contained in a rectangular cell ($4\text{ cm} \times 2\text{ cm} \times 1\text{ cm}$) dipped in 0.1 M KCl (not deaerated). The PV cell was juxtaposed in front of the PG cell such that the ZnTPP photocathode of PV cell did not shadow the Pt photoanode of the PG cell. The counter electrodes of the two cells were connected in series (Fig. 1).

Further attempts were made to improve the efficiency of the ZnTPP electrode by surface modification. The polyacrylonitrile was found to be a good polymer for charging the electrode with this dye. The polymer was prepared by polymerisation of acrylonitrile using $\text{KHSO}_3 + \text{K}_2\text{S}_2\text{O}_8$ system as initiator in a nitrogen-saturated solution at 60°C on a water-bath. The polymer precipitated as powder after 30 min and was separated, washed and dried. The platinum foil electrode was cleaned successively in aqua regia and distilled water and burnt in alcohol flame. The electrode was coated by applying a solution of 1% polyacrylonitrile in dimethylformamide (DMF) and allowing the solvent to evaporate. The polymer coated electrode was then soaked for 15 min in chloroform solution of ZnTPP (0.1 mM). The electrode was removed, dried and washed with triply distilled water. The coloration of the polymer film confirmed the incorporation of ZnTPP dye on the film.

Results and Discussion

The combined PGV cell (PSF/EDTA/+ZnTPP system) gave much higher photovoltage and photopotential which were the sum of the photoresponse of the two cells separately. The power factor also increased. Above all the current-potential (I-V) curve showed remarkable improvement, giving a nearly rectangular response. The fill-factor was calculated to be 0.5, a very large value indeed as compared to values obtained so far for any wet solar energy device (Table 1). Furthermore, since the cells were totally illuminated and both the electrodes were participating in the photochemical reaction, better utilization of solar energy was achieved.

Polymer coated dye-loaded ZnTPP electrode in a 0.1 M KCl (aerated) solution with a Pt spiral counter electrode considerably improved the PV characteristics. Both photocurrent and photovoltage increased. When the cell was combined with the PG cell (PSF + EDTA) as before, a further enhancement of V_{oc} and I_{sc} was observed. The fill factor increased to 0.66 (Table 1). Although overall solar energy efficiency is still very low, by bringing about improvement in cell configuration, electrode size and by introducing more compact arrangement to avoid current losses, we hope to improve the efficiency considerably. The I-V curves for various cells, individually and combined, are presented in Fig. 2. The spectacular improvement of fill factor is very evident. A tentative mechanism for this observation can be attempted as follows.

In PSF+EDTA system, photovoltage develops only in unstirred and degassed system. This suggests that the dye layers deposited at the electrode surface contribute to photovoltage generation. This observation could be confirmed by cyclic voltammetric studies⁵. In the presence of EDTA reduction potential of PSF is lowered due to formation of charge transfer complex⁷ and it has been concluded that in the PSF + EDTA PG cell photo-induced redox reaction occurs primarily on the electrode surface with some

Table 1—Characteristics of PSF + EDTA + ZnTPP PGV Tandem Cell Using Modified ZnTPP Electrodes

Cell type	V_{oc} (mV)	I_{sc} (μA)	Fill factor	Power (μW) ^a
PG	550	1.03	0.12	0.24
PV	220	0.4	0.19	0.12
PGV	750	1.62	0.5	0.461
(PV) _{polymer}	350	1.60	0.5	0.272
(PGV) _{polymer}	880	1.84	0.66	1.063

^aPower calculated as $P = V_{oc} \times I_{sc} \times \text{ff}$ only, not divided by the area. Therefore, the values are relative since the same set of electrodes have been used. They, however, indicate nearly two and a half fold increase in power output on using polymer-coated electrode.

contribution from the bulk solution. In the bulk, back recombination of charge carrier lowers the efficiency.

On the other hand, Kawai *et al.*⁶ have discussed the energy level scheme for ZnTPP/Pt electrode. The ZnTPP is a *p*-type semiconductor, and a Schottky barrier is produced at the metal-dye interface. Since the work function of ZnTPP (Fermi level, $E_F = 4.3$ eV) is smaller than that of Pt ($E_F = 6.0$ eV), electrons will flow from MTPP to Pt, creating a band bending at the interface. The system has second interface at the solution side which will be affected by the redox electrolyte in the solution. The initial charge carrier generation occurs due to electron transfer from the excited ZnTPP to an electron acceptor in the solution.

Previous studies⁵ have shown that photo-voltage developed in such a cell is not affected by presence of O_2 but is sensitive to *pH* of the solution. Since it is known that ZnTPP⁷ has high efficiency of inter-system crossing to the triplet state, the lowest triplet will be the probable precursor of the electron transfer to the solution due to its long life.

A cyclic mechanism for operation of the PGV cell is the most reasonable explanation as shown in Scheme 1. In this process there is no net consumption of chemicals excepting EDTA the concentration of which is very large compared to others, and the overall process results in the direct conversion of light energy into electricity. The usual reduction reaction occurs at the PG electrode where EDTA is oxidised irreversibly. At the photocathode excited TPP* donates electrons to H^+ to generate $\frac{1}{2}H_2$ and TPP⁺ cation. The cation is neutralised by the electron flow from the Pt electrode. The OH^- moves over to the counter electrode and donates the electron to form OH , which eventually can lead to formation of O_2 . The redox reaction occurring at photoanode between PSF and EDTA builds up a high electron density which will force the electron to flow through the external circuit to the TPP electrode, thus completing the cycle. The energy conversion efficiencies of the cells are presented in Fig. 2 and the data are given in Table 1.

Recently polymer-coated dye-loaded electrodes have been found to be effective in improving the photovoltage and photocurrent generation^{8,9}. Direct application of the dye on metal electrodes very often causes structural instability on photoexcitation, quenching by electron transfer or energy transfer between dye and electrode system and in the case of semiconductor electrodes, quenching may occur via surface states also. The mode and strength of

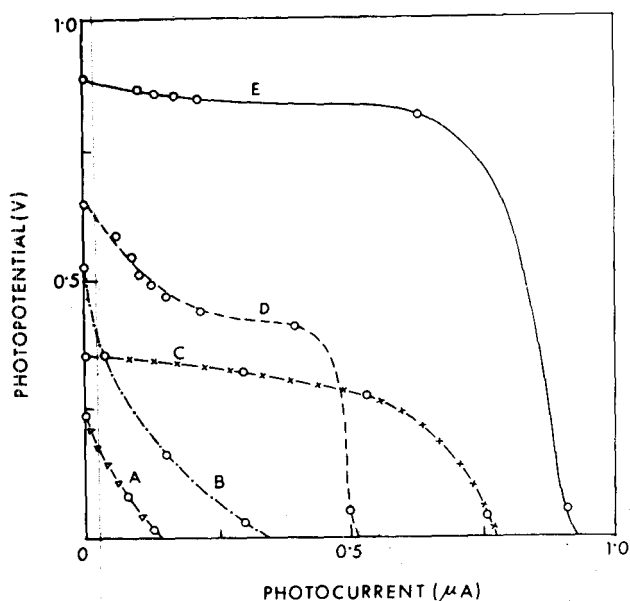
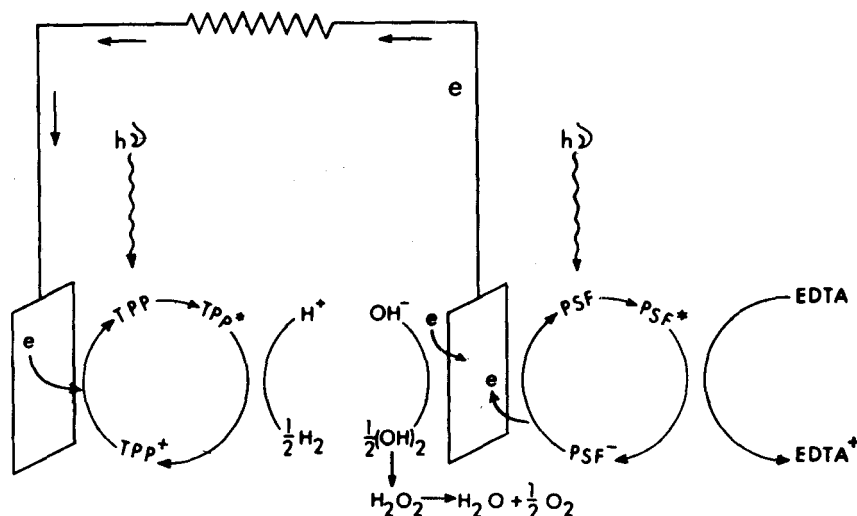


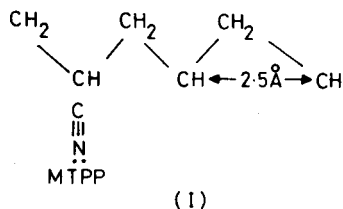
Fig. 2—I-V characteristics of PV (A), PG (B), (PV)_{polymer} (C), PVG (D) and (PVG)_{polymer} (E) cells



Scheme 1—Reaction mechanism at electrode-electrolyte interphase.

adsorption is important and very often activation overpotential may limit the photocurrent generation. More important is the fact that the thickness of the coating may limit the light absorption capabilities.

The ZnTPP is a water insoluble dye which tends to donate an electron and produces ZnTPP^+ cation. The polyacrylonitrile is found to be a good polymer for charging the electrode with this dye. Polyacrylonitriles (PAN) have $-\text{C}\equiv\text{N}$ as pendant groups on a polyethylene chain as shown in structure(I).



In the stretched zigzag configuration of C-chain, the alternate C—C distance is 2.5 Å. Normally one expects a random coil configuration because of steric reasons. ZnTPP is probably intercalated in the cavities formed by the polymer chain and resides near a number of $-\text{C}\equiv\text{N}$ groups. ZnTPP will interact with the polar $-\text{C}^+\equiv\text{N}^-$ ZnTPP^+ by charge transfer interaction imparting photoconductivity to the polymer. Furthermore the point of attachment to the electrode surface by $-\text{C}\equiv\text{N}$ group which acts as a conducting wire reduces the barrier to electron transfer to the electrode surface. Here $-\text{C}\equiv\text{N}$ acts as bridge between Pt surface and TPP layer and the electron transfer from Pt to TPP becomes easier.

In summary, the cell has the following noteworthy features:

(i) Both the electrodes are photoactive, and the total emf produced is the sum of the single electrode potentials. This provides an additional voltage compared to the system in which only one electrode is active (i.e. conventional PG or PV).

(ii) Since both electrodes are photoactive, the resistance at each electrode solution interface is lowered.

(iii) The cell can be used to provide direct conversion of solar energy to electricity.

Since the tandem cell is completely illuminated, two photons appear to be absorbed simultaneously. The PSF is photo-reduced both by EDTA and by MTPP building up a large negative photopotential on the photoanode driving them to the photocathode with reasonable efficiency. There is much scope for improvement of its performance by optimising the conditions and configuration of the cell.

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