

Electrical and photovoltaic characterisations of methyl red dye doped solid-state photoelectrochemical cell

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Abstract In this work, we have reported the electrical and photovoltaic properties of methyl red dye sensitised photoelectrochemical cell. Here, we have explored the possibility of using methyl red dye in photovoltaic devices. The dye was dispersed in polyvinyl alcohol used as an inert polymer binder and polyethylene oxide complexed with lithium perchlorate ion salt as a solid electrolyte. Ethylene carbonate and propylene carbonate are used as plasticisers. A thin film of this blend is sandwiched between two electrodes, one of which is indium tin oxide coated glass plate and another is aluminium. The active area of the cell is 0.04 cm^2 . By analysing dark I - V characteristics, trap energy is estimated in the order of 0.053 eV . The photovoltaic parameters such as open circuit voltage, short circuit current, fill factor and power conversion efficiency of the cell have been calculated to be 368 mV , 410 nA , 0.349 and 1.24% , respectively. The photovoltaic currents were measured with different intensity.

Keywords Dye-doped photoelectrochemical cell · Photovoltaic parameters · Methyl red dye · Trap energy

Introduction

Recently, organic and polymer materials are widely used to develop different optoelectronic devices such as large area solar cell [1–4], photodetectors [5–7], etc. There are many advantages of using organic materials in solar cell fabrication.

The devices may be fabricated over a large area on flexible substrate from its solution by simple processing techniques such as sol–gel, spin-coating, solvent casting, sublimation, dip coating, etc. The materials used in these devices have some advantages of relatively excellent film forming properties, facile color tunability and adequate mechanical properties. There are still many problems to be addressed for further improvement for commercial exploitation. The preparation of solar cells using organic layers does not compete with the traditional silicon-based p–n junctions. The efficiency of the cells is quite low and shows different unusual properties in its current–voltage, photocurrent-transient measurements. Low conversion efficiency and carrier mobilities, disordered structures and high bulk resistivities are still the main drawbacks when used for commercial application. Moreover, there is also difficulty in understanding the charge transport due to the disordered structure of organic materials. There is no such theoretical model for charge transport which can explain the experimental results. Researchers are trying to improve the efficiency by using different materials with different device architectures like single layer, double layer, blend, etc.

Generally, in these applications, photoconductive dye/polymers including molecularly doped dye/polymers dispersed in a suitable matrix are sandwiched between two metallic electrodes, at least one of which is transparent. Upon application of incident radiation of suitable wavelength, photo carriers are generated and these carriers are separated under electric field. The electric field occurs mainly due to the contact potential within the devices. To maximise this internal field for photovoltaic applications, different device architectures such as single-layer, double-layer and multi-layer structures are suggested in literatures. The solid-state photo electrochemical cell (PEC) has some advantages over other device architectures. In a PEC, a

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solid electrolyte is used as ion source. The ions are separated in respective electrodes. Incorporation of mobile ions changes the operational characteristics of the device drastically with respect to conventional single or multi-layered structure. This principle has been used by Pei et al. [9–10] to develop organic light emitting diode. In our earlier works [11–12], we have also reported that the solid-state dye doped PEC can be used for light detection. But there is no such report on photovoltaic devices based on this principle.

The PEC under study contains a blend made of methyl red dye dispersed in transparent polyvinyl alcohol (PVA), polyethylene oxide (PEO) complexed with lithium perchlorate (LiClO_4), ethylene carbonate (EC) and propylene carbonate (PC). Methyl red dye [8] is used as an optical active material and is dispersed in PVA, which acts as an inert binder. LiClO_4 is mixed with solid polymer matrix PEO to form the solid-state ionic conductor. The ionic conductivity of PEO: LiClO_4 complexes is very low [13–14]. The use of plasticisers is a common technique to enhance the ionic conductivity [5]. In this system, we have used EC dissolved in PC as plasticisers to enhance the mobility of the charge carriers. A solid film of this blend is sandwiched between transparent indium tin oxide (ITO) coated glass plate and Al plate, which acts as two contact electrodes. Upon illumination from a light source, dye molecules absorb light and photocarriers are generated. These photocarriers are then separated by the external field generated at the contact of the electrodes. It is expected that the internal field produced by the redistribution of the ion species within the PEC enhances the migration process of these photocarriers. The barrier potential in contacts of ITO and polymer materials is lowered [14–15] due to the accumulation of these ion species near the respective electrodes leading to enhancement of charge injection through the metal polymer interface layer.

In this work, we have studied the dark current–voltage (I – V) characteristics and other photovoltaic parameters. Photovoltaic parameters such as open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF) and power conversion efficiency (η) have been measured. By analysing I – V characterisation, the trap energy is estimated.

Experimental

(a) Sample preparation

The structure of the dye, methyl red (Fluka) having the absorption peak at 440 nm that corresponds to an optical band gap of the order of 2.82 eV is shown in Fig. 1a. Absorption spectra of methyl red dye are also shown in Fig. 1b. In a cleaned test tube, 1 g of PVA was mixed with

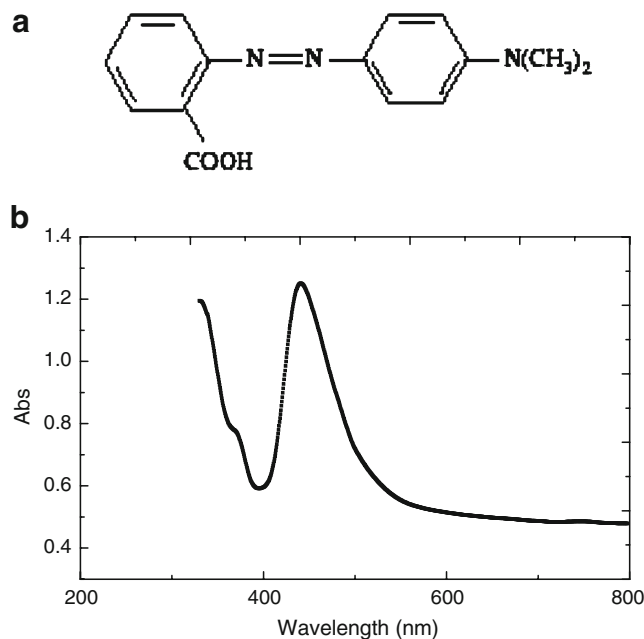


Fig. 1 a Structure of methyl red dye. b Absorption spectra of methyl red in water solution

10 cc of double distilled water, warmed gently and stirred to make a transparent viscous solution of PVA (S. D. Fine Chem. Ltd., Boisar; MW 125,000). Also, 6 mg of methyl red (anionic dye) is mixed with this solution.

A solid electrolyte was prepared in a separate cleaned beaker by mixing PEO (BDH, England; MW 600,000), LiClO_4 (Fluka, 99.5% pure)–EC (Fluka, 99.5% pure) and PC (Fluka, 99.5% pure). The complex of PEO– LiClO_4 –EC–PC (30.60%–3.60%–19.60%–46.20% by weight) were mixed, stirred and heated around a temperature 60 °C for 4 h. This gel-like solid electrolyte is mixed with the previously prepared dye–PVA solution to form the blend. This blend is heated at 60 °C and stirred properly to mix them well for about 2 h.

This viscous gel-like solution is then sandwiched between two electrodes. The electrodes were cleaned in chloroform solution and dried under vacuum about 2 h before use. The two electrical leads are taken out from the two ends of the electrodes. The complete cell is dried in vacuum for about 6 h at around 60 °C before the final measurement. The active area of the cell was 0.04 cm². The structure of the cell is shown in Fig. 2.

(b) Measurements

To measure the dark I – V characteristics, the cell is biased with a dc source with a series resistance of 56 K Ω . The current flowing through the device was estimated by measuring the voltage drop (measured by Agilent data acquisition unit, model no. 34970A) across this sensing resistance. For optical measurement, a tungsten lamp of 200 W is used. Incident light is allowed on the cell. By

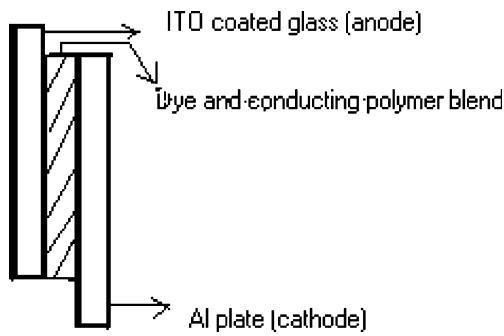


Fig. 2 Structure of photoelectrochemical cell

varying the intensity of incident radiation, voltage drops and hence the photocurrent across the sensing resistance is measured. The intensity is measured by a calibrated lux meter (Kyoritsu Electrical Instruments Works Ltd. Tokyo, model 5200). Photocurrent is measured by varying the intensity of light.

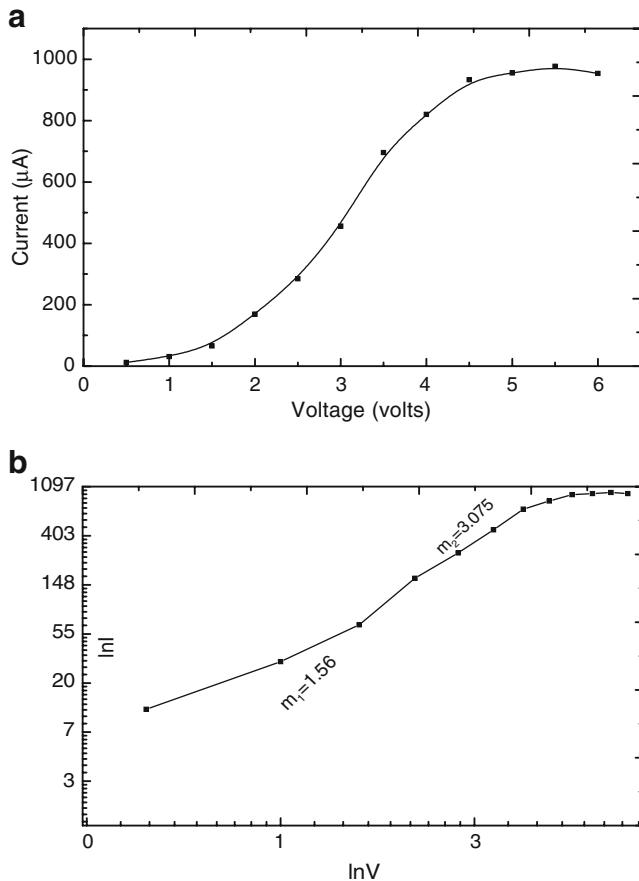


Fig. 3 a Dark I - V characteristic plot. b $\ln I$ versus $\ln V$ plot

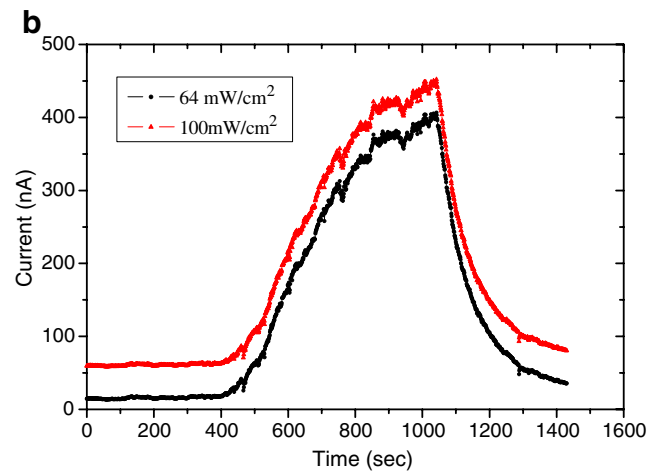
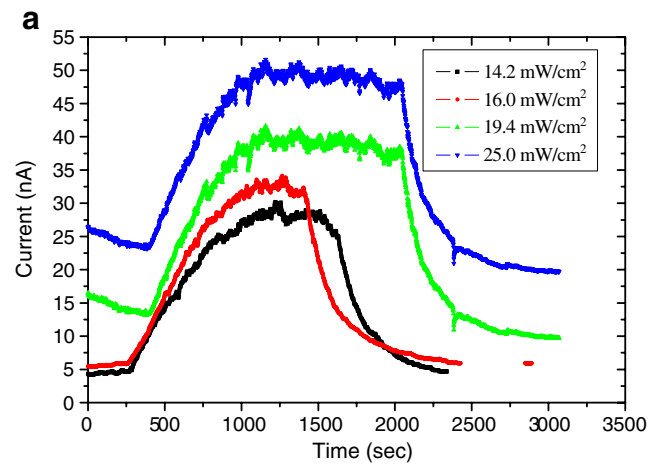


Fig. 4 a Photocurrent at different illumination intensity (up to 25 mW/cm²). b Photocurrent at different illumination intensity (up to 100 mW/cm²)

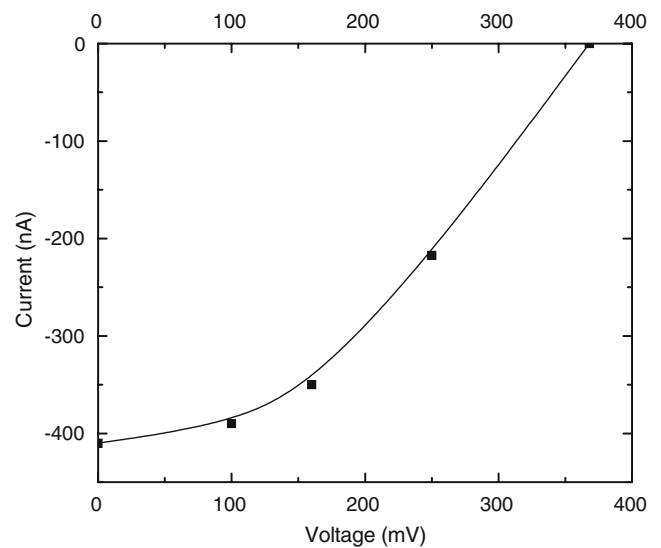


Fig. 5 I - V characteristic at illumination of 100 mW/cm²

Results and discussion

(a) Dark I - V characteristics

Since an ionic salt LiClO_4 is used, it is expected that the positive ions from LiClO_4 salt becomes accumulated near the cathode and the negative ions near the anode upon application of external bias on the device. A depletion layer is formed inside the active layer due to the redistribution of ionic charges in a similar manner as found in the case of light emitting electrochemical cell [10, 15–19] used to develop organic light emitting diodes.

The I - V curve is shown in Fig. 3a. A logarithmic plot of the current versus bias voltage is shown in Fig. 3b. The linear $\ln I$ - $\ln V$ plot shows a transition point at a bias voltage of 2 V, which seems to indicate a change in current conduction mechanism. As the organic materials are disordered solids, there is no well-defined band structure. The molecules are bound together with weak Van der Waals forces and the charge transport occurs through the loosely bound π -conjugated electrons. Here, instead of

conduction and valance band, there are lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels. This energy difference (E_g) between the LUMO and HOMO states is equal to the electrochemical redox potential of the organic material. Application of bias voltage greater than the threshold voltage (V_{ON}) will dope the material of p-type and n-type simultaneously [9, 10]. So, the voltage at which this process occurs is given by

$$E_g = eV_{\text{ON}} \quad (1)$$

where E_g is the band gap.

Here $E_g=2$ eV, whereas the actual value of the band gap of the dye is 2.82 eV. This deviation is quite reasonable within our experimental limit. Though the blend is a mixture of different materials, it is expected that the dye plays a major role in charge conduction mechanism.

$\ln I$ - $\ln V$ relation is linear which shows a power law relation of I - V of the form

$$I \propto V^{m+1} \quad (2)$$

where m is constant.

In our case, m has two values. Below transition, i.e., within the region $V < 2$ V, $m=1.559$ which indicates that the conduction process is ohmic and for the above transition $V > 2$ V, $m=3.075$, which indicates trap charge-assisted conduction process.

The dark I - V curve can be fitted with the assumption that, during conduction, carriers are trapped at different trap levels between LUMO and HOMO. To explain the charge conduction mechanism beyond the ohmic region, a model based on trap charges is considered [20]. The starting equations are one-dimensional single (double) carrier drift current and Poisson equations (e.g., for electron or holes or both of them):

$$J_d = nq\mu E \quad (3(a))$$

$$\frac{dE}{dx} = \frac{q}{\epsilon} (n + n_t) \quad (3(b))$$

where J_d is the current density, μ is the carrier mobility, E is the electric field strength, n and n_t are the free and trapped charge concentrations, respectively, q is the unit charge, ϵ is equal to $\epsilon_0\epsilon_r$ with ϵ_0 being the permittivity of vacuum and ϵ_r is the relative dielectric constant. When traps have an exponential energy distribution, the trap charge concentration (n_t) is given

$$n_t = H_n \exp\left(\frac{F_n}{KT_1}\right) \quad (4)$$

where H_n is the trap density, F_n is the electron Fermi energy, K is Boltzmann's constant and T_1 is characteristic temperature of the exponential trap distribution (i.e., $T_1=E_t/K$, where E_t is

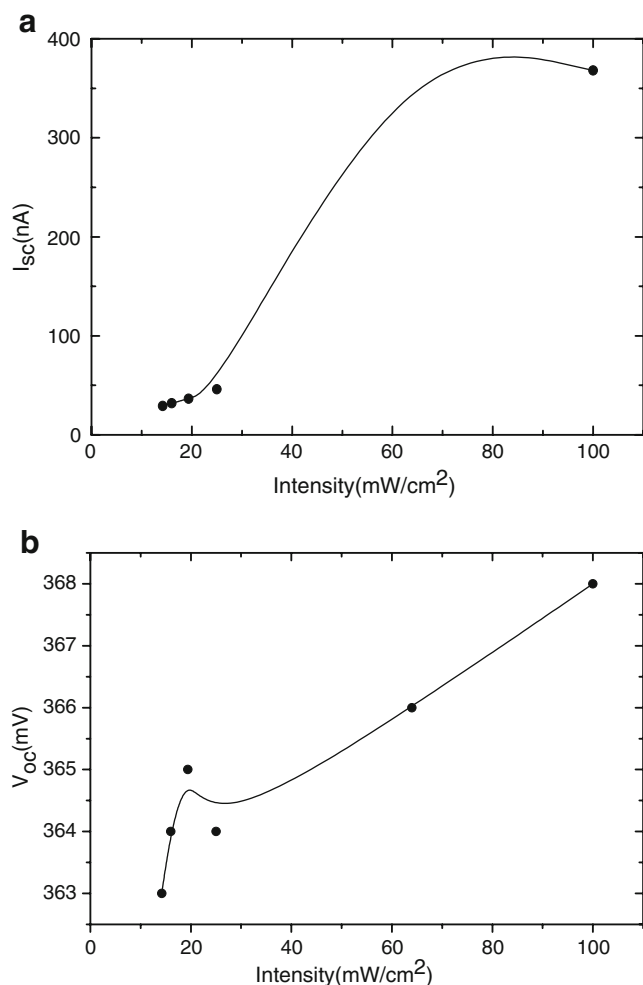


Fig. 6 **a** Short circuit current versus intensity curve. **b** Open circuit voltage versus intensity curve

the characteristic trap energy). Solving Eq. 3(a) and Eq. 3(b) with the above distribution of traps, the current–voltage characteristic has the form,

$$J = N_c \mu q^{1-m} \left(\frac{m\varepsilon}{H_n(m+1)} \right)^m \left(\frac{2m+1}{m+1} \right)^{m+1} \frac{V^{m+1}}{L^{2m+1}} \quad (5)$$

i.e. $I = A \cdot N_c \mu q^{1-m} \left(\frac{m\varepsilon}{H_n(m+1)} \right)^m \left(\frac{2m+1}{m+1} \right)^{m+1} \frac{V^{m+1}}{L^{2m+1}}$ (6)

where $m = T_t/T$ and A is the effective surface area of the film. The most notable feature in the above equation is the power law dependence $I \propto V^{m+1}$.

To calculate this trap energy E_t , we have to calculate characteristics trap temperature T_t , where T is room temperature,

$$\begin{aligned} T_t &= mT \\ T_t &= 622.5 \text{ K} \end{aligned} \quad (7)$$

So $E_t = kT_t = 0.053 \text{ eV}$

(b) Photovoltaic measurements

Measurement of I_{sc} and V_{oc} is done under different intensities of illumination. The variation of short circuit current (I_{sc}) with time (t) for different intensity illumination are shown in Fig. 4a and Fig. 4b, where ITO/dye sensitised polymer layer/Al junction is illuminated through ITO side. The I – V characteristic at 1 Sun incident illumination is depicted in Fig. 5.

Furthermore, experimental evidences of this effect are presented in Fig. 6a and b, where the short circuit current (I_{sc}) and open circuit voltage (V_{oc}) are plotted as function of intensity of incident light.

Various photovoltaic parameters such as V_{oc} and I_{sc} are obtained to be 368 mV and 410 nA, respectively for 1 Sun intensity of illumination. The power conversion efficiency of each cell can be estimated by using the equation

$$\eta\% = \frac{I_{sc} \times V_{oc} \times FF}{\phi_0} \times 100 \quad (8)$$

where ϕ_0 is the incident intensity of light and FF is defined by relation

$$FF = \frac{V_m \times I_m}{V_{oc} \times I_{sc}} \quad (9)$$

where V_m and I_m represent the voltage and current density at maximum power point, respectively.

The estimated values of FF and power conversion efficiency are 0.349% and 1.24% for 1 Sun radiation.

Conclusions

Reports on the photovoltaic property of the device made in PEC band structure are not common. In this work, photovoltaic properties of methyl red dye sensitised solid-state PEC have been described. The film was prepared by spin-coating technique. Analysis of dark I – V characteristic shows the presence of trap energy levels in the device. The amount of trap energy is estimated in the order of 0.053 eV. The cell has a fill factor of 0.349 and a power conversion efficiency in the order of 1.24% under 1 Sun radiation. Our results indicate the possibility of using dye sensitised PEC devices as solar cells.

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