

# Study of the effect of trap levels on steady-state dark $I$ – $V$ characteristics in Safranin-T-based solid-state thin film photoelectrochemical cell

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In this work we describe the steady-state current–voltage ( $I$ – $V$ ) characteristic of solid-state photoelectrochemical cells (PEC). The cell contains a blend made of Safranin-T dye dispersed in polyvinyl alcohol (PVA), polyethylene oxide (PEO) complexed with ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ), ethylene carbonate (EC) and propylene carbonate (PC). A thin film ( $20\ \mu\text{m}$ ) of this blend is sandwiched between two transparent indium-tin-oxide (ITO)-coated glass plates, which act as the two contact electrodes. Addition of ion salt in the active materials alters the device characteristics in a significant way. In the present work we have concentrated on the steady-state dark  $I$ – $V$  characteristics of the device. The trap-assisted charge carrier transport model is used to satisfactorily describe the  $I$ – $V$  characteristics. The experimental results are explained by the transport of carriers having traps with exponential distribution. The characteristic temperature of the traps and trap energy level have been estimated to be 1164 K and 0.1 eV, respectively, within the experimental limit. The present experimental data will be helpful to understand the steady-state operation of a photoelectrochemical cell.

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## 1. Introduction

Recently, organic and polymer photoconductors have been widely used for large-area optoelectronic devices, such as xerographic photoreceptors, photodetectors, solar cells, etc. In these applications, generally, photoconductive amorphous thin films including molecularly doped polymers dispersed in a polymer matrix are sandwiched between two metallic electrodes, at least one of which is a transparent conductor. Pei *et al.* [1] in 1995 demonstrated a new type of device called light-emitting electrochemical cells (LEC) to develop organic light-emitting diode (OLEDs). Studies in these areas have been extended by different workers in recent times [1–10]. In LECs [1–10] basically a blend of an emissive conjugate polymer mixed with an ion conductive polymer with suitable ion salt is sandwiched between two metallic electrodes, at least one of which is transparent. LEC-based light-emitting devices have certain advantages over conventional OLEDs due to their low operating voltage, high electron/proton conversion efficiency, and high power efficiency. Moreover, the device performance in LECs is independent of the nature of the contact electrode and the thickness of the active layer, which is not so in the case of OLEDs [11, 12]. Some theoretical models have been developed to describe the device model of the LECs [13–15]. Since its discovery there has been a growing interest for the fabrication of light emitting devices in a LEC structure.

The electrical characteristics have been studied theoretically by Smith [13] who has developed the theory based on the junction formation model and explained the current–voltage characteristics. Another study by Sampietro *et al.* [15] is also found in the literature where the current–voltage characteristics have been explained. They showed that the current–voltage dependence can be divided into three different regimes. The first regime is the thermionic emission over a barrier whose height is lowered by the Schottky effect. At higher voltage in the range of the optical band gap, the current following through the LEC increases strongly due to field-induced tunneling injection of charge carriers from the electrode through the thin potential barrier at the interfaces into the active layer. A third regime, called the ohmic regime, is observed if the applied voltage is increased above the electrochemical redox potential of the active conjugated polymer layer, where an electrochemical doping of the polymer occurs.

In our earlier studies [16–18] we have shown that the same structure of a LEC can be used as a photodetector. In all these LEC structures made by different workers the contribution of the trap center is not considered. Due to weak molecular bonds and structural disorder, it is expected that in almost all organic materials trap centers [19, 20] play a major role in the current conduction mechanism. These traps introduce energy levels inside the energy gap between the highest occupied molecular

orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the organic material. The distribution of these trap levels may decrease exponentially with increasing energy below the LUMO. Charging and discharging of these trap levels play an important role in the operation of the device. Due to the crystalline-amorphous nature of the polymer, and the delocalization of the electric field along the  $\pi$ -conjugated segments of the polymer backbone, the charge transport and the semiconducting property of the organic materials are quite different from their conventional inorganic counterpart. To gain a better insight into the performance of these devices we have studied the dark  $I$ - $V$  characteristics. In our system we have found that our experimental results do not completely fit with any of the above theories [13–15]. The  $I$ - $V$  characteristics show that, like other organic-material-based devices [19, 20] a trap-assisted model is used to govern the same. By assuming an exponential trap distribution [20] we have explained the results quite satisfactorily.

## 2. Sample and cell preparation

In our work, the PEC consists of a thin film of blends of organic dye Safranin-T (dispersed in transparent polyvinyl alcohol used as an inert polymer matrix) having an absorption peak at 520 nm, which corresponds to an optical band gap 2.39 eV, as the optical active material, and polyethylene oxide (PEO) complexed with ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) ion salt as the solid electrolyte with ethylene carbonate (EC) and propylene carbonate (PC) as plasticizers. The cell consists of this blend in the form of a thin film as an active material and two transparent indium-tin-oxide (ITO)-coated glass plates as the contact electrodes. It is expected that the salt ions of  $\text{NH}_4\text{ClO}_4$  mixed with PEO act as the solid electrolyte and provide the counter ions and the ionic conductivity necessary for the doping. Addition of plasticizers EC and PC makes the complexed mixture viscous, which assists the fabrication of the film and also enhances the carrier mobility. In our studies [16–18] we have shown that, upon illumination from a tungsten lamp source onto the biased cell, a change in photocurrent is observed.

Safranin-T dye (structure shown in Fig. 1) is mixed with polyvinyl alcohol (PVA). In a cleaned test tube, 5 gm of PVA is mixed with  $10 \text{ cm}^{-3}$  of doubly distilled water, warmed gently and stirred to make a transparent viscous solution of PVA. 1 mg of Safranin-T is mixed with this solution. PVA is used here as an inert transparent binder to form the stable film of the dye.

In a separate beaker, cleaned by regular processes, a solid electrolyte is prepared by mixing polyethelene



Figure 1 Structure of Safranin-T dye, which is a cationic dye soluble in water with an absorption peak at a wavelength 520 nm.

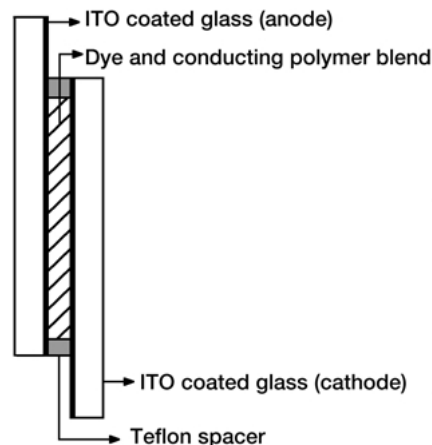


Figure 2 Structure of the photoelectrochemical cell. A  $20 \mu\text{m}$  thin film blend made of organic dye Safranin-T, PEO complexed with  $\text{NH}_4\text{ClO}_4$ , EC and PC, is sandwiched between two ITO-coated glass plate electrodes.

oxide (PEO) – ammonium perchlorate ( $\text{NH}_4\text{ClO}_4$ ) – ethylene carbonate (EC) – and propylene carbonate (PC) (30.60%, 3.60%, 19.60%, 46.20% by weight). The mixture is stirred and heated to a temperature of  $80^\circ\text{C}$  for 5 h. This gel-like solid electrolyte is mixed with the previously prepared dye-PVA solution to form the blend. This blend is heated at a temperature of  $80^\circ\text{C}$  and stirred, to mix them well, for about one hour.

The viscous gel-like solution is sandwiched between two transparent ITO-coated glasses. The glass plates were cleaned in chloroform solution and dried under vacuum for about 5 h before use. The uniform film thickness is controlled by placing two teflon spacers of thickness about  $20 \mu\text{m}$  near the edges of the ITO-coated glass plate and two spring clips were fixed at a moderate pressure at the ends of the electrodes as shown in Fig. 2. The two electrical leads are taken out from the two ends of the ITO-coated glass. The complete cell is vacuum dried for about 12 h at around  $60^\circ\text{C}$  before the final measurement.

## 3. Experimental

The cell is biased with a d.c. source making one of the ITO contacts the anode and with a series resistance of 47 K. The current flowing through the device is estimated by measuring the voltage across this sensing resistance. By varying the d.c. bias, the steady voltage across the resistance is measured by a Philips  $4\frac{1}{2}$  digit Multimeter. Dividing the measured voltage by the value of this sensing resistance the current flowing through the device is calculated. The value of this current together with the d.c. bias voltage is plotted and shown in Fig. 3. It is observed that the current takes time (about 20 min) to reach the steady-state value after application of each bias voltage. The  $I$ - $V$  characteristics are nearly symmetric about the origin for both forward and reverse bias. The  $I$ - $V$  characteristic by changing the polarity of the d.c. bias is not shown in this figure.

## 4. Results and discussions

The  $\log I$ - $\log V$  plot shown in Fig. 4 shows a transition point at a bias voltage around 2.2 V, which seems to

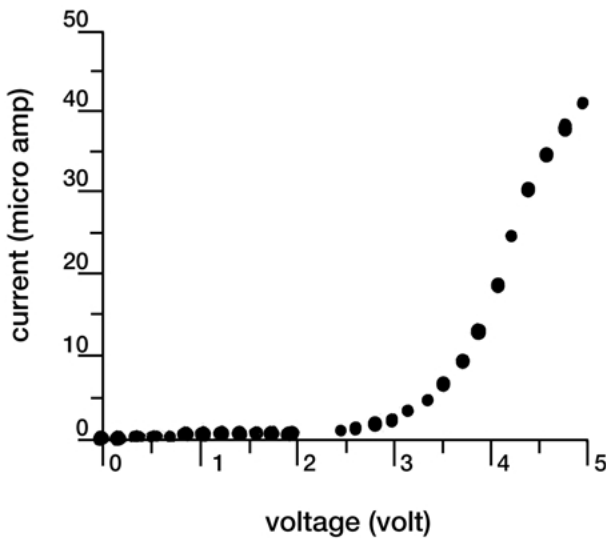


Figure 3 Linear plot of the current versus bias voltage in the dark. The ITO-coated glass plates are connected to the external voltage source.

indicate a change in the conduction mechanism at this bias voltage. By using [2] the relation  $E_g = e \cdot V_{on}$  we get  $E_g = 2.2$  eV, whereas the actual value of the band gap (energy difference between  $\pi$  and  $\pi^*$  bond) of the dye is 2.39 eV.

The  $I$ - $V$  relation as found from this figure can be written as,

$$\begin{aligned} I &\propto V^{1.00} & \text{for } V < 2.2 \text{ V} \\ &\propto V^{4.88} & \text{for } V > 2.2 \text{ V} \end{aligned}$$

As found in the literature [19, 20] the dark  $I$ - $V$  characteristics can be fitted with the assumption that the carriers during conduction through the device may be trapped in different trap levels between the lowest unoccupied molecular orbital (LUMO) states, i.e., bottom of the  $\pi^*$  bond, and highest occupied molecular orbital (HOMO) states, i.e., top of the  $\pi$  bond. To explain the change of the conduction mechanism a model based on trap charges is considered. The starting equations are one-dimensional single (double) carrier drift current and Poisson equations (e.g., for electron or holes or both of them):

$$J = nq\mu E \quad (1)$$

$$\partial n / \partial x = -q / \epsilon (n + n_t) \quad (2)$$

where  $J$  is the current density,  $\mu$  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, and  $\epsilon$  is equal to  $\epsilon_0 \epsilon_r$ , with  $\epsilon_0$  being the permittivity of vacuum and  $\epsilon_r$  the relative dielectric constant.

When traps have an exponential energy distribution the trap charge concentration ( $n_t$ ) is

$$n_t = H_n \exp(F_n k T_t) \quad (3)$$

where  $H_n$  is the trap density,  $F_n$  is the electron Fermi energy,  $k$  is Boltzmann's constant and  $T_t$  is the characteristic temperature of the exponential trap distribution (i.e.,  $T_t = E_t / k$ , where  $E_t$  is the characteristic trap energy) solving Equations 1 and 2 with the above

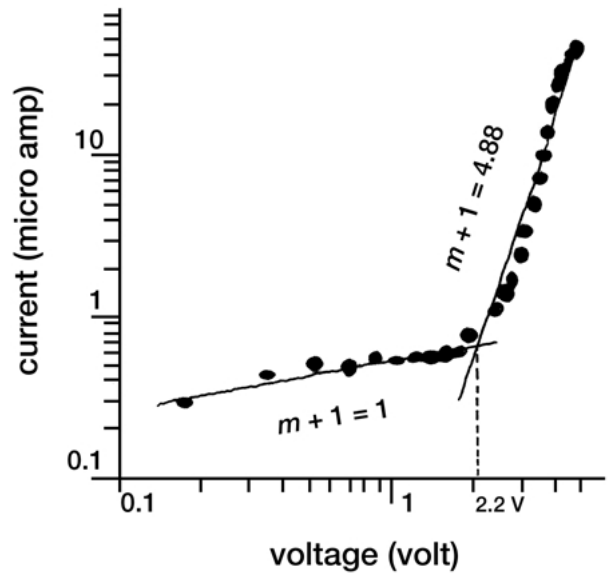


Figure 4 Logarithmic plot of current versus bias voltage in the dark. The  $I$ - $V$  characteristics can be found to have the form  $I \sim V^{m+1}$  where  $m = T_t / T$ ,  $T_t$  is the characteristic temperature of the traps and  $T$  is room temperature. With a best fit to our experimental data the values of  $m$  are found to be 0 and 3.88 below and above bias voltages of 2.2 V.

distribution of traps the current-voltage ( $J$ - $V$ ) characteristics has the form [20];

$$J = N_c \mu q^{(1-m)} \{ \epsilon m / H_n (m+1) \}^m \{ (2m+1) / (m+1) \}^{m+1} V^{m+1} / L^{2m+1} \quad (4)$$

where  $m = T_t / T$ . The most notable feature in Equation 4 is the power-law dependence  $J \sim V^{m+1}$ .

Fitting the experimental data for the dark  $I$ - $V$  curve, as shown in Fig. 4, of our system with Equation 4 we find that above the voltage 2.2 V the current-voltage is fitted with the trap-charge limited model and the value of  $m$  is equal to 3.88 and hence  $T_t$  is estimated to be 1164 K and  $E_t$  is calculated to be 0.1 eV.

## 5. Conclusions

Recently, the solid-state electrolytic cell has been widely used for the fabrication of solar cells photodetectors, LEDs etc. Incorporation of ion salts alters the electrical characteristics of the device in a significant way. In the literature, several attempts have been made to describe the steady-state  $I$ - $V$  characteristics of PEC. Among the existing literature there exists a controversy to describe the internal field distribution within the device. The effect of trap centers is not considered in these models, though it is expected that the organic materials are very much prone to traps arising from structural disorder, defect states, etc. In the present work we have concentrated on the steady-state dark  $I$ - $V$  characteristics of the device and observed the effect of trap centers. Up to a threshold voltage of 2.2 V the conduction is ohmic and above 2.2 V the conduction is governed by an exponential distribution of trap centers. The trap-assisted charge carrier transport model is used to satisfactorily describe the  $I$ - $V$  characteristics. The experimental results are explained by the transport of carriers having traps with exponential distribution. In our system, the trap levels are not located in a single energy level because the

transition is not sharp, but rather a smeared one. The characteristic temperature of the trap and trap energy level have been estimated to be 1164 K and 0.1 eV, respectively, within the experimental limit. The present experimental data will be helpful to understand the steady-state operation of a photoelectrochemical cell.

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