

Transient current study in safranine-T dye based organic photo-electrochemical cell using exponentially distributed trap assisted charge transport model

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Abstract: In this work we have studied the transient current in safranine-T dye based organic photo-electrochemical cell. We assumed that the traps behave like a potential well which are distributed exponentially in the form $P(V_t) = V_0 \text{Exp}(-V_t/V_0)$, where V_t represents depth of trap. The charge carriers move randomly within these potential wells. With this trap distribution the current-time ($I-t$) behavior is estimated as $I \approx t^{\alpha-1}$ where ' α ' is a parameter. This parameter is related linearly to temperature and inversely to the trap depth. The result is verified experimentally by measuring the transient current in safranine-T dye based solid-state thin film for different bias voltage. Our results indicate that this parameter increases with applied voltage. There are two possibilities for this variation. Due to applied voltage the current increases and as a result the temperature increases and thereby the parameter ' α ' also increases. The other possibility is to expect some rearrangement of the trap distribution with applied voltage which reduces the trap depth. Due to lowering the trap depth this parameter increases.

Keywords: Exponential trap distribution; Disorder solid; Charge transport; Traps

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1. Introduction

The organic/polymeric solids are taking an important role for fabrication of different electronic and optoelectronic devices due to their semiconducting properties [1]. The materials used in these devices have advantages of having relatively excellent film forming properties [2], facile color tunability and adequate mechanical properties [3]. In addition, these and relate materials have been fabricated over a large area on flexible substrate from its solution by various techniques such as sol-gel, dip coating, spin coating, etc. [4-8]. In these applications generally photoconductive dye/polymers are sandwiched between two metallic electrodes, one of which is transparent to allow light to pass. Photo-carriers are generated due to this radiation and the carriers are separated under electric field. To modify this internal field for photovoltaic applications, different device architectures are used such

as single layer, double layer, multi-layer structures as suggested in literatures [9-11]. In our earlier work [12, 13] we have studied on solid state photo electrochemical cell (PEC), the principal of which has been used by Pei et al. [14] to develop organic light emitting diode. In a PEC, a solid electrolyte is used as an 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.

The organic materials are basically disorder in nature and charges are being trapped during transport leading to some unusual transport properties. The rather slow response speed, hysteresis effect in I-V measurement, and power law I-t relation etc. show that the charge carriers are being trapped. The laws used to describe the charge transport mechanism in inorganic or even in disorder inorganic materials are not successful in explaining behavior of organic materials [15, 16]. It is worthwhile to mention here that the charge transport mechanism in these disorder materials are not well understood. During last 25 years

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several attempts have been made by many workers [17–27] to tackle this problem. Among different theories the one proposed by Scher and Montrol [17] for both inorganic (amorphous As_2Se_3) and organic (trinitrofluorenone–polyvinylcarbazole) systems has been widely used to describe the charge transport mechanism in different organic systems. The charge carriers are injected from cathode and reach anode within a certain time. During this transport the carriers are trapped and as soon as one carrier is trapped the internal field within device changes. Hence the different carriers take different times to travel a certain distance. In other words it can be considered that there is a distribution of time to travel from the cathode to anode contributing to the origin of the anomalous effect in conduction mechanism. By using the distribution function of the form $\psi(t) = At^{\alpha-1}$, with $\alpha = k_B T/V_0$ and $0 < \alpha < 1$ Scher and Montrol [17] attempted to describe the charge transport. But this theory has some limitations and cannot successfully predict the experimental results as mentioned by different workers [12, 13, 28]. Moreover the universality factor of ‘2’ as suggested by Scher and Montroll [17] is not valid in many cases. So far there is not much attempt to give any physical interpretation of this parameter, although it is evident that this parameter is related to traps. One of our interests is to see whether the parameter describing the distribution has any sensitivity to the variation of applied voltage, which may not be important for inorganic thin films, but may be relevant for organic thin films, since the number of charge carriers increase with voltage.

In this work, out of many other distributions only an exponential distribution of traps is considered when modeling the decay in current.

2. Theoretical model

Theoretical models, which describes charge transport in inorganic semiconductors are not appropriate for organic solids. It is important to remember that there are large differences between the 3-D crystal lattice of most inorganic semiconductors and the crystalline amorphous structure of conjugated polymers and the molecules are weakly bound together by Van der Waal’s force. The organic solids are disorder solids. Charge carriers are being trapped during transport. The traps act as potential well in which the charge carriers are immobilized for certain time resulting slow charge relaxation process. The charge carriers move randomly within these traps. We consider the traps are distributed exponentially of the form,

$$P(V_t) = V_0 \text{Exp}(-V_t/V_0) \quad (1)$$

where ‘ V_t ’ represents the potential of traps and V_0 is the expected value of V_t . Let us assume that charges perform a random walk on different site and get trapped in these

potential wells for certain time depending on the depth of the potentials.

The probability that the walker exits a well is proportional to the Boltzmann factor

$$w = \text{Exp}(\beta V_t), \quad \text{where } \beta = 1/k_B T. \quad (2)$$

The distribution of transition rates would then be

$$\phi(w) = P(V_t) \frac{dV_t}{dw}$$

which give

$$\phi(w) \approx w^{(1/V_0 - \beta)/\beta} \quad (3)$$

Hence the waiting time, the time spent by the carrier in the potential well, which is proportional to $1/w$ can be calculated from $\phi(w)$.

The waiting time distribution is given by

$$\psi(t) = At^{-(\alpha+1)} \quad (4)$$

where $\alpha = k_B T/V_0$. and A is a constant.

The mean square displacement can be calculated as [29]

$$\langle r^2(t) \rangle = Bt^\alpha \quad (5)$$

where B is a proportionality constant.

The conductivity, using Einstein’s diffusion relation, may be written as

$$\sigma = ne^2 D(t)/k_B T \quad (6)$$

where $D(t)$ is “time dependent diffusion parameter” which changes as diffusion proceeds.

$$D(t) = \langle r^2(t) \rangle / t = Bt^\alpha / t \quad (7)$$

Now the current can be written as

$$I = \sigma ES \quad (8)$$

where ‘ S ’ is the effective area of the sample and ‘ E ’ is the applied electric field.

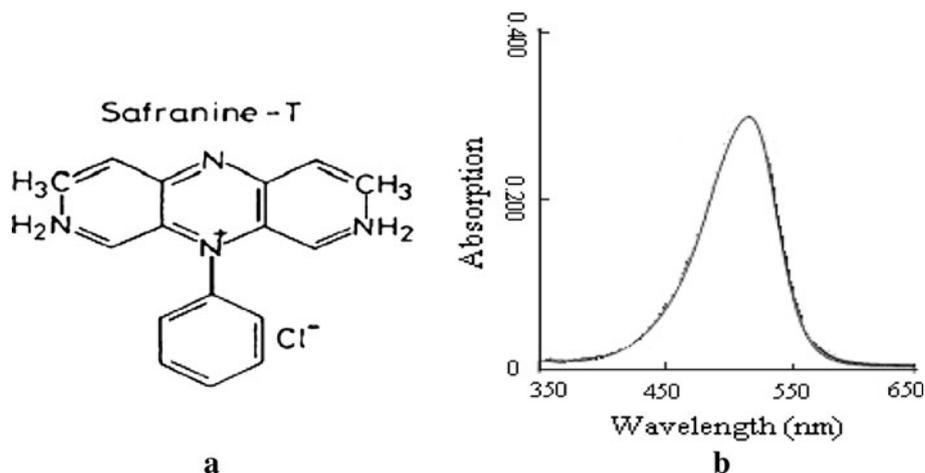
Hence

$$\begin{aligned} I &= ESBne^2 t^{\alpha-1} / k_B T \\ &= Ct^{(\alpha-1)} \quad \text{where } C = ESBne^2 / k_B T \quad \text{i.e., } I \approx t^{\alpha-1} \end{aligned} \quad (9)$$

3. Experimental details

PEC under study contains a blend made of safranin-T (E. Merck, Germany) dye dispersed in transparent polyvinyl alcohol (PVA) (S.D. Fine Chem. Ltd., Boiser; M.W. 125,000), polyethylene oxide (PEO) (BDH, England; M.W. 600,000) complexed with lithium perchlorate (LiClO_4) (Fluka, 99.5 % pure), ethylene carbonate (EC) (Fluka, 99.5 % pure), and propylene carbonate (PC) (Fluka, 99.5 % pure). Safranin-T dye was used as an optical active material and was dispersed in PVA, which acted as

Fig. 1 (a) Structure of safranine-T dye and (b) its absorption spectra with peak absorption at 520 nm



an inert binder. LiClO₄ was mixed with solid polymer matrix PEO to form the solid-state ionic conductor. The ionic conductivity of PEO: LiClO₄ complexes were very low. In this system we used EC dissolved in PC as plasticizers to enhance the mobility of the charge carriers. A solid film of this blend was sandwiched between transparent indium tin oxide (ITO) coated glass plate and aluminium electrodes, which acted as contact electrodes.

The structure of the dye safranine-T and the absorption spectra of its water solution having peak at 520 nm, which corresponds to an optical band gap of the order of 2.39 eV is shown in Fig. 1 and the basic cell structure is shown in Fig. 2. To measure time dependence of dark current the cell was biased with a dc source connecting with a series resistance of 56.7 K. Voltage across this sensing resistance was measured by a high-speed data acquisition system (Agilent, 34970A). It was observed that after application of each bias voltage a sufficient time was required to attain

the steady value of the current. The experiment was repeated for different bias voltages for several times and with different dye concentrations. To check the recovery of charge carriers experiment was performed by changing the polarity of the bias voltage. It was found that there were some residual charges in the system. So to avoid this effect the cell was discharged properly by connecting the two terminals directly. This short circuit condition was maintained for around 15 min prior to application of any bias voltage. Under this situation no residual charge was found in the system. The entire experiment was performed at room temperature (300 K).

4. Results and discussion

After application of bias voltage (1.0–6.0 volt) it is observed that the current decrease from a peak value ($\sim 1 \mu\text{A}$) and attains a steady value after more than 150 s. The variation of current with time is plotted in Fig. 3 which fits the Eq. (9). Careful scrutiny reveals that transient current does not agree well with exponential relation.

From the fitting data with Eq. (9) we get different values of ' α ' (listed in Tables 1–3) for different bias voltage with different dye concentrations. The value of ' α ' ($0 < \alpha < 1$) increases with external bias first and then attains almost a constant value for all dye concentrations as shown in Fig. 4.

The variations of V_0 with bias voltage is shown in Fig. 5. Which shows that V_0 decreases with the increase of bias voltage and then becomes constant.

This effect is of course interesting and unexpected in case of inorganic thin film. In organic thin film it is observed that due to applied bias voltage the current injection increases and as a result the temperature increases [30, 31]. This may be the reason for variation of α with bias voltage according to Eq. (4). But there is also another possibility which can not be ignored. At higher voltages the

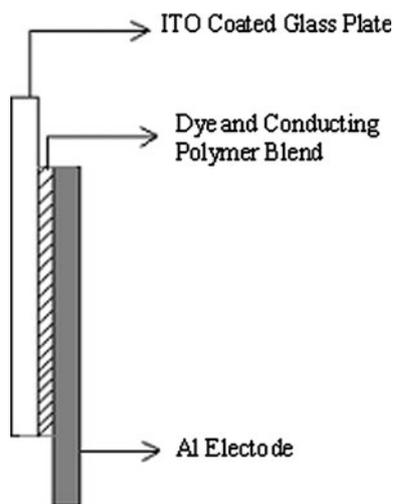


Fig. 2 Schematic diagram of the structure of the PEC

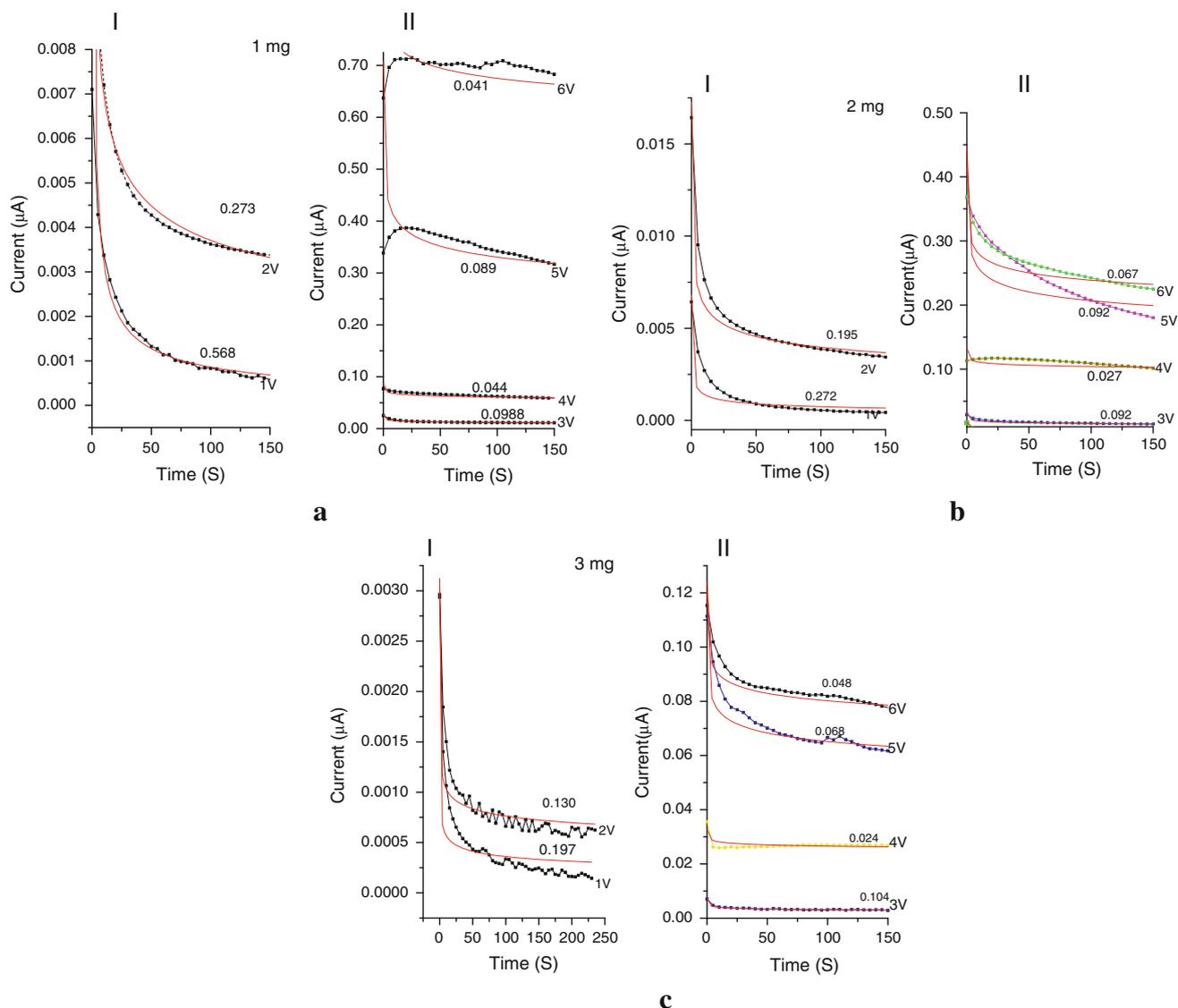


Fig. 3 (a) Variation of current with time for different bias voltage measured for solid state PEC for dye concentration 1 mg. Graph I for low bias voltages and graph II for high bias voltages. The *black dots* are experimental data whereas *solid lines* are fitting curves ($I \sim t^{-\gamma}$) with fitting values (e.g. $\gamma = 0.568, 0.273$ etc.) as shown. **(b)** Variation of current with time for different bias voltage measured for solid state PEC for dye concentration 2 mg. Graph I for low bias voltages and graph II for high bias voltages. The *black dots* are experimental data

whereas *solid lines* are fitting curves ($I \sim t^{-\gamma}$) with fitting values (e.g. $\gamma = 0.272, 0.195$ etc.) as shown. **(c)** Variation of current with time for different bias voltage measured for solid state PEC for dye concentration 3 mg. Graph I for low bias voltages and graph II for high bias voltages. The *black dots* are experimental data whereas *solid lines* are fitting curves ($I \sim t^{-\gamma}$) with fitting values (e.g. $\gamma = 0.197, 0.130$ etc.) as shown

Table 1 Dye concentration: 1 mg ST in 5 g PVA

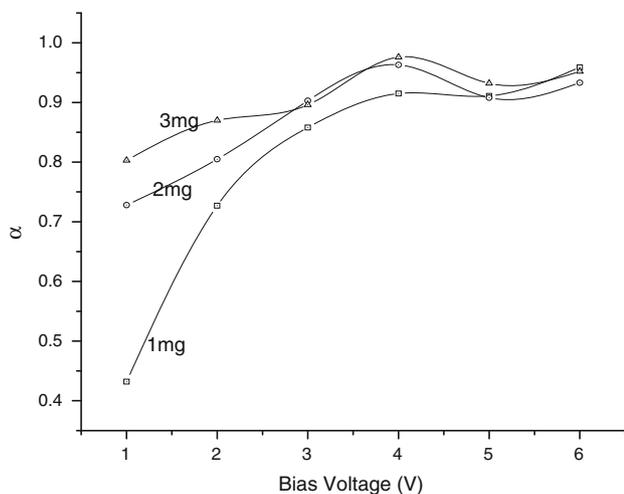
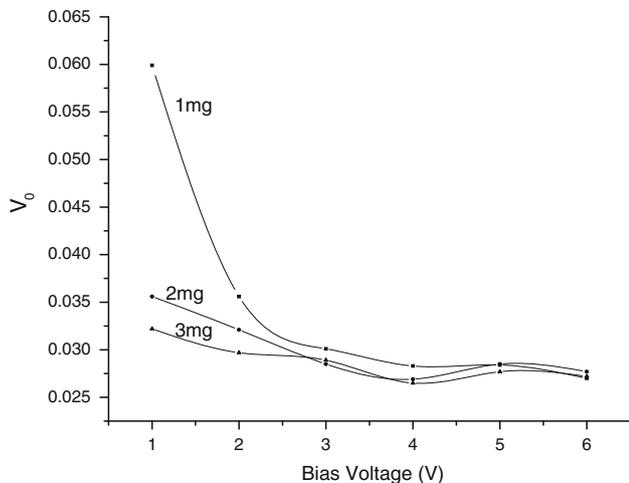
Bias voltage (V)	Value of α	Value of V_0 (eV)
1.0	0.432	0.0599
2.0	0.727	0.0356
3.0	0.858	0.0301
4.0	0.915	0.0283
5.0	0.911	0.0284
6.0	0.959	0.0270

Table 2 Dye concentration: 2 mg ST in 5 g PVA

Bias voltage (V)	Value of α	Value of V_0 (eV)
1.0	0.728	0.0356
2.0	0.805	0.0321
3.0	0.908	0.0285
4.0	0.963	0.0269
5.0	0.908	0.0285
6.0	0.933	0.0277

Table 3 Dye concentration: 3 mg ST in 5 g PVA

Bias voltage (V)	Value of α	Value of V_0 (eV)
1.0	0.803	0.0322
2.0	0.870	0.0297
3.0	0.896	0.0289
4.0	0.976	0.0265
5.0	0.932	0.0277
6.0	0.952	0.0272


Fig. 4 Variation of α with bias voltage for different dye concentrations

Fig. 5 Variation of V_0 with bias voltage for different dye concentrations

higher current can fill some of the traps, effectively leading to a lower number of apparent traps which is commonly observed in thin film organic transistors as the number of charge carriers is increased. Unlike the interactions in

inorganic thin film this organic materials in the present film is dominated by Vander Waal's forces which is much weaker. And as such the organic thin film may respond differently to applied voltage. This will distort the existing arrangement which may be considered to be an assembly of short rods or any other form that gives rise to change in distribution that may be reflected in the value of this parameter. So there is always a possibility to expect some rearrangements of the molecule and also thereby the change in the traps. However, this conjecture need to be experimentally verified further. But the present result shows at the power law behavior of dependence of current stabilizing with time, unlike an exponential one in this complex, multi-component system seems to indicate that different scales are involved. To probe further and to see whether the exponent, which is evidently connected with and contains the relevant information about the distribution of traps, has any sensitivity to variation of applied voltage which may not be important for inorganic thin films, but may be relevant in organic ones. According to our measurements, the change occurs.

5. Conclusions

Characterization of the nature of traps in organic semiconductors is an important, yet unresolved problem although it plays a major role in charge transport mechanism of this system. The nature of these traps are quite different from the inorganic one. In this work we assumed the traps to be distributed exponentially. The current-time $I-t$ behavior is estimated as $I \approx t^{\alpha-1}$. Our results indicate that the parameter ' α ' is evidently connected with the distribution of traps and sensitive to variation of applied voltage. Variation of this parameter with bias voltage seems to show that due to applied bias voltage the current injection increases and as a result the temperature increases. This may be the reason for variation of α with bias voltage according to Eq. (4). There is also another possibility which can not be ignored. At higher voltages the higher current can fill some of the traps, effectively leading to a lower number of apparent traps which is commonly observed in thin film organic transistors as the number of charge carriers is increased. And as a result the traps are redistributed and the trap depth V_0 reduces. Investigation on this parameter ' α ' with bias voltage is informative for study on trap controlled charge transport in disorder organic solid. In our subsequent work we will consider the dependence and variation of traps with temperature.

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