

Effect of plasticizer on safranine-T-dye-based solid-state photo electrochemical cell

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Received: 1 October 2007 / Revised: 3 February 2008 / Accepted: 19 February 2008 / Published online: 27 March 2008
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Abstract Effect of plasticizers on electrical and photovoltaic properties of safranine-T-dye-based solid-state photo electrochemical cell (PEC) is studied. Ethylene carbonate (EC) and propylene carbonate (PC) are used as plasticizers. Dark current–voltage characteristic and different photovoltaic parameters such as open-circuit voltage, short-circuit current, and power conversion efficiency are measured. To understand the effect of plasticizers on charge transport process, we analyze the dark current–voltage characteristics to estimate the trap energy. From detail analysis of dark I–V, it has been observed that there is a crossover voltage called *transition voltage* where the conduction mechanism changes. Above this voltage, the dark current is a space charge limited current (SCLC) in the presence of exponentially distributed traps. Below transition voltage, current is ohmic for the cell without plasticizers and dark current is an SCLC in presence of discrete traps for the cell with plasticizers. From our analysis, it is shown that the transition voltage reduces due to the presence of plasticizers but the characteristic trap energy (E_T) is not changed significantly. From photovoltaic measurements, it is observed that in presence of EC and PC power conversion efficiency of the device increase from $7.319 \times 10^{-4}\%$ to $14.64 \times 10^{-4}\%$ under illumination with polychromatic light of 100 mW/cm^2 . It is expected that the power conversion efficiency depend on transition voltage. Due to the presence of plasticizers, the barrier potentials of the devices reduce which results lowering of transition voltage. Lowering of it assists the migration of charge carriers and as a result power conversion efficiency enhances.

Keywords Disordered systems · Electronic transport · Transition voltage · Optical properties

Introduction

Recently, different organic-dye-based photo electrochemical cells are being widely studied to develop organic photovoltaic devices [1–5]. Safranine-T (ST) is a cationic dye and it shows good optical response in aqueous solution [6, 7]. In our earlier work, we have shown that safranine-T-dye-based solid-state photo electrochemical cell (PEC) may be used to detect light [8, 9] incident on the device. Photovoltaic behavior of this dye in solid-state photo electrochemical cell structure is also observed. But the power conversion efficiency of such devices is quite poor. In a PEC, different ions are present which are accumulated in the respective electrodes due to which the barrier potential and also the transition voltage of the device is reduced which assist the charge migration of the device. Due to incorporation of plasticizers, it is expected that the transition voltage of the device is further reduced and the overall efficiency of the device is enhanced.

In this work, we have studied the effects of plasticizers on ST-dye-doped PEC. Ethylene carbonate (EC) and propylene carbonate (PC) is used as plasticizers for indium tin oxide (ITO)/{polyvinyl alcohol (PVA) + ST + poly ethylene oxide (PEO) + LiClO_4 }/Ag device configurations. To understand the effect of plasticizers on charge transport mechanism of the devices, dark I–V characteristics has been analyzed. Characteristic trap energy for both the cases have been calculated from the model based on exponentially distributed traps. Photovoltaic parameters are estimated and compared for both the cases. Due to incorporation of the plasticizer,

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transition voltage of the device reduced and the power conversion efficiency is enhanced significantly.

Experimental

Sample and cell preparation

Structure of the Safranin-T dye is shown in Fig. 1. To investigate the effect of plasticizer on photovoltaic and electrical properties of Safranin-T-dye-based PEC, two different cells were prepared one of which contains plasticizers. In a cleaned test tube, 2.0 mg of safranin-T and 5.0 g of PVA is taken in 10 ml of cold water to form a viscous gel-like solution of this dye. In another beaker, a solution of PEO and LiClO₄ (weight ratio 60:14.12 mg) was prepared. Two solutions were mixed to have a blend of solid electrolyte mixed with ST dye.

A thin film of this blend is deposited by spin coating technique on transparent ITO-coated glass plate. Metallic silver paste is coated on thin layer of this blend to reduce the preparation cost of the cell, which acts as the counter electrode. This cell marked as cell 1 does not contain any plasticizers. We prepared another cell marked as cell 2 which contains the plasticizers. To prepare this cell, two plasticizers EC and PC is added in the previously prepared blend of the dye with weight ratio of 38:30 mg. In the same process, this plasticized blend is spin coated on ITO-coated glass plate and the layer of this blend is coated with metallic silver paste to get the counter electrode. In Table 1, the cell structure is shown. Both the cells have effective area of 0.2 cm². The complete cell was vacuum dried for 10 h before using it for characterization.

Measurement

Figure 2 represents the optical absorption spectra of the prepared blend in solid form. It is mentioned here that the blend has the same spectral response range as that of the dye in aqueous solution. The absorption occurs from 480 to 550 nm and the absorption peak is located at 520 nm. Optical characterization of the cells has been done for measuring the photovoltaic parameters. Illumination from a polychromatic

Fig. 1 Structure of the safranin-T dye

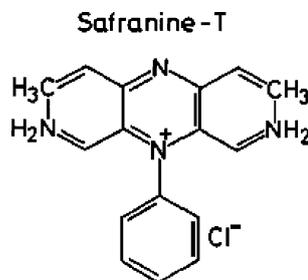


Table 1 Detail of the two cells including their structures

Name of cell	Configuration
Cell 1	ITO/PVA + ST + PEO + LiClO ₄ /Ag
Cell 2	ITO/PVA + ST + PEO + LiClO ₄ + EC + PC/Ag

light source was allowed to fall on the cells from ITO side. A calibrated Lux meter (Kyoritsu Electrical Instruments Works Ltd. Tokyo, model 5200) is used to measure the intensity of incident illumination. All measurements were carried out at room temperature. The photo voltage is measured by a 6 digit multimeter (Kithley, 2000E) and photocurrent by a high-speed data acquisition system (Agilent, 34970A). A monochromator is used to vary the wavelength to measure the photovoltaic action spectra.

To study the dark current–voltage (I–V) characteristics, the film was biased by a direct current (dc) voltage source with a series resistance of 56 K. By varying the dc bias, the steady voltage across the resistance was measured by a computer-interfaced high-speed data logger (Agilent, 34970A). In each case, it is found that the steady-state dark current is not reached immediately after the application of bias voltage. The current takes few seconds to reach its steady value. By dividing the measured voltage by the value of this sensing resistance, the current flowing through the device is calculated.

Results and discussion

The short-circuit photocurrent action spectra for both cell 1 and cell 2 are measured and shown in Fig. 3. Both the cells have the same spectral response range. The action spectra was measured at illumination through the ITO electrode.

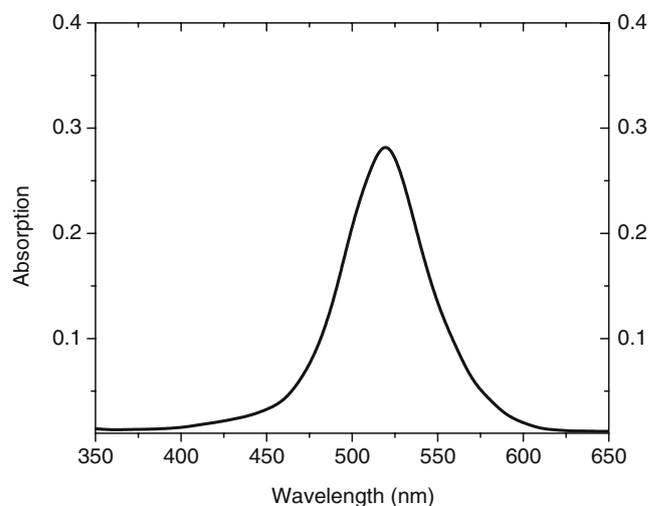


Fig. 2 Absorption spectra of the solid-state PEC cell

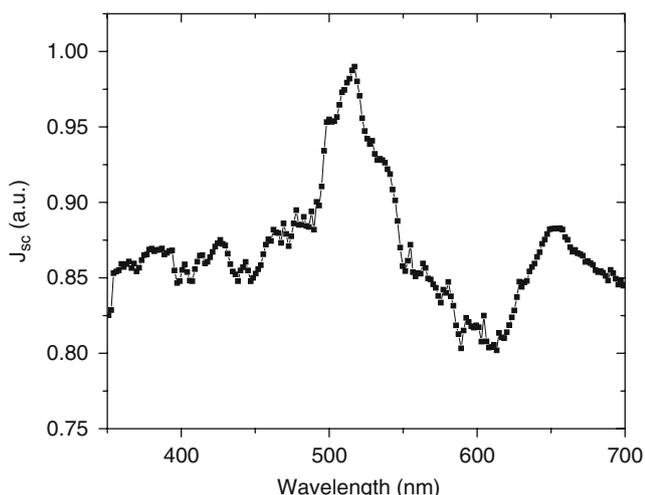


Fig. 3 The photocurrent action spectra of the cells. Both the cells have the same spectral response range

From Fig. 3, it is seen that the photocurrent is generated within the wavelength of 486 to 540 nm and the photocurrent become maximum at 516 nm. This photocurrent action spectrum can be related with the absorption spectra of the dye shown in Fig. 2 where the maximum absorption occurs from 480 to 550 nm and the absorption peak is located at 520 nm. From these two data, it is clear that the photocurrent is generated due to the absorption of photon carriers from the incident radiation by the ST dye.

Figure 4 shows the $J_{ph}-V$ characteristics in the fourth quadrant of $J-V$ diagram of two cells under a polychromatic light. The curves are obtained by varying the load resistance. Several parameters of interest such as open-circuit voltage (V_{oc}), short-circuit photocurrent (I_{sc}), fill factor (FF) and power conversion efficiency (η) can be evaluated from these curves and are listed in Table 2. The power conversion efficiency of the cell is calculated by using the equation

$$\eta\% = \frac{I_{sc} \times V_{oc} \times FF}{\phi_0} \times 100 \tag{1}$$

Where ϕ_0 is the incident intensity of light (100 mW/cm^2) and FF (fill factor) is defined by relation

$$FF = \frac{V_m \times I_m}{V_{oc} \times I_{sc}} \tag{2}$$

Where V_m and I_m represent the voltage and current for maximum power rectangle. Measurements with different intensity of incident illumination have been carried out for the second cell. Maximum power conversion efficiency has been recorded for 100-mW/cm^2 intensity.

Table 2 reflects clearly the effect of plasticizers on photovoltaic parameters. As a result of incorporation of EC and PC, short-circuit current increases from 8.88 to 13.90 nA and open-circuit voltage improves from 250 to 270 mV. Power conversion efficiency enhances from $7.32 \times 10^{-4}\%$ to $14.64 \times$

$10^{-4}\%$, i.e., the power conversion efficiency becomes almost double.

We have studied the effect of plasticizers on the dark current–voltage characteristics of the device also. Dark current–voltage is measured for both the cells. Dark current (I) voltage (V) curve for two cells is shown in Fig. 5. Log I –log V plot is shown in Fig. 6.

It is clear from Fig. 6 that for cell 1 there are two regions of different slopes which meet at 2.0 V. Cell 2 also shows the same type of curve with two different regions and meets at 1.77 V. This particular point can be taken as transition voltage (V_T). Values of the slopes below V_T are 1.15 and 1.75 for cell 1 and cell 2, respectively. Above V_T , the corresponding values are 4.34 and 4.20, respectively. In the next section, we will try to explain this unusual current–voltage nature by suitable theoretical understanding.

The theoretical models developed so far [10–13] for explaining current–voltage characteristic of disorder systems have failed to explain different experimental results as ours. Most of these models have been developed for the devices like organic light-emitting diode (OLED), organic field effect transistor, etc. The dark current–voltage nature for organic PV cells, particularly made from organic semiconducting dyes and pigments have been extensively studied [14–17]. In our earlier work [8], we have shown that dark current–voltage curve for safranine-T-dye-based PEC can be explained using the model used for OLED. In PEC, there are ions along with the electrons and holes that make the system more complicated. Although there are large differences between the working principle and the charge carriers present in OLED and PEC, it is interesting that the

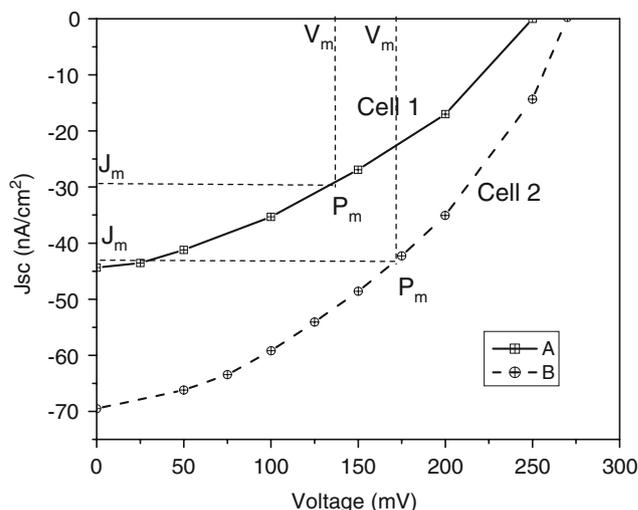


Fig. 4 Photovoltaic current–voltage diagram of the devices A Cell 1 and B Cell 2. Open-circuit voltage and short-circuit current for the cell 2 is higher than that of cell 1. Calculated values of both fill factor and power conversion efficiency clearly reflects the effect of plasticizers on photovoltaic parameters

Table 2 Photovoltaic parameters for cell 1 and cell 2

Cell structure	Area (cm ²)	I_{SC} (nA)	J_{SC} (nA/cm ²)	V_{OC} (mV)	Fill factor	Efficiency ($\times 10^{-4}\%$)
Cell 1	0.2	8.88	44.36	250	0.33	7.32
Cell 2	0.2	13.90	69.50	270	0.39	14.64

model that can be used for OLED is well applicable in case of PEC also.

According to Yang and Shen [18], the space charge limited current (SCLC) in presence of exponentially distributed traps in between lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) governs the superquadratic relation between current and voltage for dark current characteristics. The exponentially distributed trap charge concentration (n_t) may be expressed as

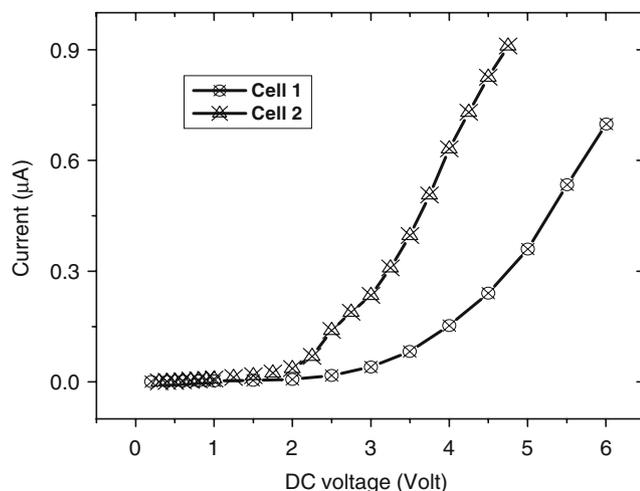
$$n_t = H_n \exp\left(\frac{F_n}{kT_c}\right) \quad (3)$$

Where H_n is the trap density, F_n is the electron Fermi energy, k is Boltzmann constant, and T_c is characteristic temperature of the exponential trap distribution (i.e., $T_c = E_c/k$, where E_c is the characteristic trap energy). Solving the Poisson equation with this form of trap distribution, the current–voltage characteristic is calculated and written in the following form [18, 19]

$$J = N_c \mu q^{1-m} \left(\frac{m\varepsilon}{H_n(m+1)}\right)^m \left(\frac{2m+1}{m+1}\right)^{m+1} \frac{V^{m+1}}{L^{2m+1}} \quad (4)$$

where N_c is the effective density of states in LUMO or HOMO, μ is the mobility of majority carrier, L is the thickness of the layer, ε is equal to $\varepsilon_0\varepsilon_r$ with ε_0 being the permittivity of vacuum and ε_r the dielectric constant, V is the applied voltage and $m = T_c/T$, T_c is a “characteristic temperature” that describe the trap distribution.

The most notable feature in the above equation is the power law dependence of $J \sim V^{m+1}$. Our result is best fitted

**Fig. 5** Dark current–voltage curve of the cells cell 1 and cell 2

with this equation. But the value of the constant ‘ m ’ is different for two cells. Different values as extracted from our experimental data by the above relation are given in Table 3.

From Table 3, it is clear that both the cells have two different charge conduction processes below and above transition voltages. For the first cell, the transition voltage is at 2.0 V. Below this voltage, the value of the exponent is equal to 1.15, i.e., $m_1 = 0.15$. The conduction process below this voltage can be treated as ohmic conduction. Above this voltage, the value of the exponent is 4.34, i.e., $m_2 = 3.34$. This higher value of ‘ m ’ indicates SCLC conduction process with exponentially distributed trap states above transition voltage. Corresponding value of characteristic trap energy as calculated is 0.087 eV (E_{T1}).

For cell 2, the transition voltage is 1.77 V. Below this transition voltage, the value of exponent is 1.75 (~2.0), i.e., $m_1 \sim 1.0$. It indicates that below this transition voltage the conduction mechanism is not ohmic rather it seems to be a SCLC with discrete trap levels in between LUMO and HOMO. Above the transition voltage, the value of the exponent is estimated and found to be 4.20 which gives m_2 is equal to 3.20. So, it is expected that the conduction process is governed by SCLC with exponentially distributed traps. So, it is concluded that in cell 2 ohmic conduction

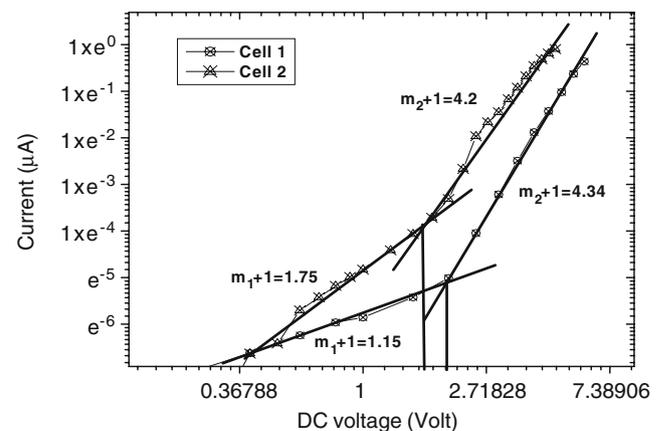
**Fig. 6** Logarithmic curve of dark I–V for cell 1 and cell 2. A crossover voltage, called transition voltage, indicates two different charge transport process of the cells. Decrease of transition voltage for cell 2 indicates that incorporation of plasticizer reduces the barrier potential. Below these voltage, current increases almost linearly and above this it increases, obeying power law relation. Corresponding values of characteristic trap energies are 0.087 eV and 0.084 eV for cell 1 and cell 2, respectively

Table 3 Parameters extracted from experimental results using Eq. 4

Cell	V_T (V)	m_1 (below V_T)	E_{T1} (eV)	m_2 (above V_T)	E_{T2} (eV)
1	2.00	0.15	0.0039	3.34	0.087
2	1.77	0.75	0.0195	3.20	0.084

V_T Transition voltage, m_1 T_c/T for cell 1, m_2 T_c/T for cell 2, E_{T1} characteristic trap energy for cell 1, E_{T2} characteristic trap energy for Cell 2

process does not take place. Below the transition voltage, SCLC with discrete trap states is dominated and this process is continued above the transition voltage with exponentially distributed trap states. The characteristic trap energy is calculated which is of the order of 0.084 eV.

From the above analysis of dark I–V characteristics, it is found that use of plasticizer in PEC structure reduces the value of transition voltage (V_T). It is expected that incorporation of EC and PC increases the ionic conductivity and that may result to reduction of barrier potential of PEC at electrode–material interface. On the other hand, there is not much difference in characteristic trap energy for both the cells which indicates that the characteristic trap energy is not much affected in presence of plasticizers.

In presence of plasticizers, it is expected that the ionic conductivity increases and the barrier potential decreases which are mainly responsible for lowering of transition voltage and enhancement of power conversion efficiency of the device. In a PEC, a 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 multilayered structure. This principle has been used by Q. Pei et al. [20, 21] to develop organic light-emitting diode. Upon illumination from a light source, dye molecules absorb light and photo carriers are generated. These photo carriers are then separated by the external field generated at the contact of the electrodes. The internal field produced by the redistribution of the ion species within the PEC enhances the migration process of these photo carriers. Due to incorporation of plasticizers, the barrier potential in contacts of ITO and polymer materials is lowered [22, 23]. It is expected that the transition voltage largely depends on this barrier potential and the transition voltage will reduce with the lowering of the barrier potential.

Apart from the lowering of transition in presence of plasticizers, the ionic conductivity also enhances. In case of PEC, the mobility of ion in electrolyte has greater importance. Higher mobility of ions can increase overall performance (regeneration of dye, ion, charge collection, etc.) of the device. Using plasticizer, one can enhance the mobility of ions. EC and PC are widely used plasticizers. Ethylene carbonate was chosen because of its high dielectric constant and viscosity, which favors ionic dissociation of the solute and easy ion migration [24]. The plasticized electrolyte has

higher conductivity. The addition of plasticizer decreases the crystallinity and lowers T_g (glass transition temperature), which can be attributed to an enhancement in the amorphous phase and improve flexibility of polymer host [25]. Long-chain polymers like PEO show a tendency to form crystalline phase [26, 27], where the conductivity is negligible compared to the amorphous phase of a polymer electrolyte. An important concern is to minimize the presence of crystalline phases. In cell 2, we introduce EC and PC as plasticizer to increase the ionic conductivity. As it was expected, incorporation of plasticizers in ion sources increases ionic conductivity which ultimately gives lowering of transition voltage and increase of efficiency.

Conclusion

Effects of plasticizer on both electrical and optical properties of safranin-T-dye-doped PEC device have been discussed. In this work, we found that due to the presence of plasticizers the transition voltage of the device has decreased from 2.0 to 1.77 V and the power conversion efficiency is enhanced from $7.32 \times 10^{-4}\%$ to $14.64 \times 10^{-4}\%$. Dark current–voltage characteristics of the cells is analyzed and found that it follows the relation of the form, $I \propto V^{m+1}$, and the value of m is related to the characteristic temperature of the system. For both the cell, there is a transition voltage beyond which the conduction mechanism changes. It is found that in absence of plasticizers the conduction process is ohmic below the transition and above transition the conduction process is governed by SCLC with discrete trap charges. In case of plasticizers, it is found that even below the transition voltage there is no ohmic conduction process. Below the transition voltage, the conduction process is governed by SCLC with discrete trap states and above the transition voltage the conduction process is SCLC with exponential distribution of trap states. By analyzing the I–V relation characteristic, trap energy is estimated for both the cell. Experimental result shows that value of power conversion efficiency increase with lowering of transition voltage. The value of trap energy does not change significantly in presence of plasticizers. Along with the ion source in the presence of plasticizers, it is expected that the barrier potential is reduced and the ionic conductivity increases which are basically responsible for lowering the transition

voltage and enhancing the power conversion efficiency of the device. More measurement and analysis is needed to know the exact reason for the variation of transition voltage and characteristic trap energy for better understanding of the device. This present work also shows that ST-dye-doped PEC structure has enough possibility to develop photovoltaic device. Although the efficiency of the devices is low as compared to the present scenario, the low-cost and easy processing technique and the use of low-cost materials quite encourages work in this area. There are possibilities to do work by varying the concentrations of different materials and changing electrode combinations to enhance the quantum efficiency.

Acknowledgement One of us (S. Maity) would like to thank University Grants Commission, Govt. of India, for providing financial support by funding a project on Organic Solar Cell. We are thankful to Professor A. N. Basu, Emeritus Professor of Department of Physics, Jadavpur University for his valuable suggestions to analyze the experimental data. We are also thankful to Defence Research and Development Organization, Govt. of India.

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