

Degradation of Safranine T dye-based photo electrochemical organic photovoltaic devices

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Abstract In this work, we studied the degradation of different photovoltaic parameters of Safranine T (ST) dye-doped organic photo electrochemical cell (PEC). Different photovoltaic parameters were measured for as-prepared device. The same measurement was repeated with time at 24-h regular interval for five successive days. During the measurement, the devices were unencapsulated and kept in an open environment. The photovoltaic parameters degraded up to 90% of its initial value. Along with moisture, humidity was the main reason for the degradation considered to be the reduction of work function difference of two electrodes in contact with organic blend.

Keywords Degradation · Dye-doped PEC · Photovoltaic cell

Introduction

Photovoltaics made from organic materials have several potential advantages compared with conventional inorganic solar cells, including lightweight, flexibility, and potential for low cost fabrication over large areas [1]. Dye-doped solid-state photo electrochemical cell (PEC) is an emerging area to develop photovoltaic devices [2, 3]. Out of different limitations, one of the major drawbacks is the stability of these devices. Despite the significant effort being focused on the development of organic solar cells, great progress in both power conversion efficiency and stability is needed for practical device application [4–9]. The organic materials are

very much sensitive to humidity and temperature [7–12]. However, lifetimes of up to 2,000 h continuous operation for the encapsulated devices have been reported [13]. Due to encapsulation, these devices are protected from oxygen and water ingress. The performance of the devices is also affected by these parameters in long-time operation.

In this paper, we studied the stability of Safranine T (ST) dye-based photovoltaic device in PEC structure. The device was prepared by spin coating of active organic blend of poly vinyl alcohol (PVA), ST, poly ethylene oxide (PEO), lithium per chlorate, ethylene carbonate (EC), and propylene carbonate (PC) on Cu plate. Al mesh was taken as other electrode. Different photovoltaic parameters measured with respect to time. The unencapsulated cell was kept in an open environment of our laboratory during the measurement. Measurements were done to see the effect of temperature, moisture, and humidity on the device performance for practical applications.

Experimental details

Sample and cell preparation

Preparation of sample and cell is almost the same as described in our earlier work [14]. The ST dye was recrystallized twice from ethanol–water mixture and mixed with PVA (S. D. Fine Chem. Ltd., Boisar; M. W. 1, 25,000). In a clean test tube, 5 g PVA was mixed with 10 cm³ double distilled cold water and stirred to make a transparent viscous solution of PVA. Two milligrams Safranine T (cationic dye) was mixed with this solution.

A solid electrolyte was prepared in a separate clean beaker by mixing PEO (BDH, England; M. W. 600000), LiClO₄ (Fluka, 99.5% pure), EC (Fluka, 99.5% pure), and

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PC (Fluka, 99.5% pure). The complex of PEO–LiClO₄–EC–PC (30.60–3.60–19.60–46.20% by weight) were mixed and stirred for 4 h. This gel-like solid electrolyte was mixed with the previously prepared dye–PVA solution to form the blend. This blend was stirred properly to mix them well for 6 h. This viscous gel-like solid solution was then spin coated on Cu plate, and Al mesh with mesh diameter 1.0 mm was taken as another electrode. The electrodes were cleaned in chloroform solution and dried under vacuum for 2 h before use. The two electrical leads were taken out from the two ends of the electrodes. The complete cell was vacuum-dried for 6 h before taken for measurement.

Measurement

The prepared and dried cell was then taken out for photovoltaic measurement. Radiation from a polychromatic source was allowed to fall on the active material through Al mesh (1.0 mm diameter and 48 holes/cm²). Intensity of the illuminated radiation was adjusted to 100 mW/cm² and measured by a calibrated Lux meter (Kyoritsu Electrical Instruments Works Ltd. Tokyo, model 5200). Before switching on the light, the cell was not in complete dark environment but rather under a low intensity of almost 10 mW/cm². The measurement in complete dark condition has been done separately. Photo voltage and current is measured by multimeter (Kithley) and high-speed data logger (Agilent, Model No: 34970A), respectively. As stated earlier, the measurements were done for five successive days with the interval of 24 h. In between two measurements, the cell was kept in normal room temperature (~27 °C) and 55–60% humidity. The experiments have been done in an open environment and have stayed connected with the experimental setup.

Results and discussion

Safranine T dye-based photo electrochemical cell shows photovoltaic effect. As soon as the light is allowed to fall on the active material of the freshly prepared device, the current increases. To study the stability of the devices, we measured all the photovoltaic parameters with respect to time.

Figure 1 represents the experimental curve for photovoltaic measurement, which clearly shows three distinct regions. The results before illumination starts, during illumination, and after illumination are represented by Regions 1, 2, and 3, respectively. Before illumination starts, the current is almost constant (Region 1). After radiation is allowed to fall on the cell, the current starts to increase and gets saturated after a few seconds (Region 2). Then, the light is switched off and the current starts to

decrease (Region 3). In Fig. 1, subpanel a represents the data for the fresh cell, and subpanels b–f represent the results after 24-h intervals. As seen from the figure, the photocurrent is higher for fresh cell and reduced for successive measurements. Typical efficiency of the order of $22 \times 10^{-4}\%$ has been observed.

In Table 1, all the measured photovoltaic parameters are listed. The first row of the table gives the values for the as prepared cell. The consecutive rows give the values for successive measurements. Short circuit current (I_{SC} ; 10 mW/cm²) represents the values of currents before light is on. I_{SC} (100 mW/cm²) represents the maximum value of current for corresponding measurements under illumination (100 mW/cm²). Similarly, V_{OC} (10 mW/cm²) is the open circuit voltage for dark condition and V_{OC} (ph) for conventional open circuit voltage under illumination. It is observed that all the parameters degrade with time.

Different parameters are plotted with time separately to see the effect of degradation. Figure 2 represents the decrease of V_{OC} both in dark and under illumination with time (hours). The value of open circuit voltage for fresh measurement was 400 mV. It decreased with time and became 40 mV after 5 days. Although recent research shows that the difference in work functions is not a major factor determining the V_{OC} , generally, open circuit voltage is attributed to difference in work functions of two contact electrodes [15, 16]. The device structure under study (PEC) contains a layer of organic material (ST dye) sandwiched between two electrodes of different work function: one is copper and a low work function material Al. The difference in work function provides an electric field. This field is not sufficient to break up the photo-generated excitons. In the thin film of organic blend, the salt ions of LiClO₄ mixed with PEO act as the solid electrolyte and provide the

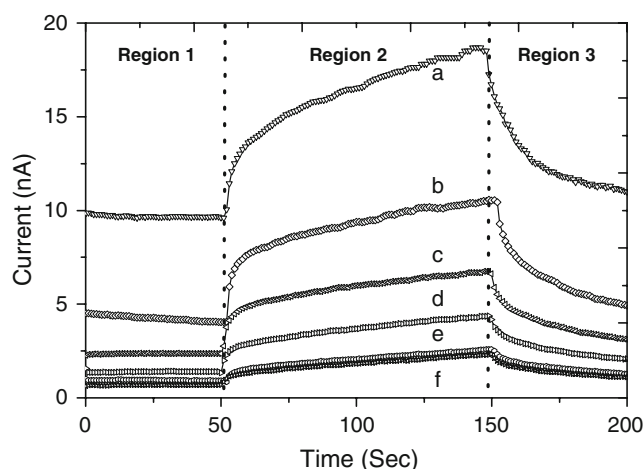


Fig. 1 Photovoltaic current growth and decay of cell. Different curves are for different day measurement. **a** for fresh measurement, **b**, **c**, **d**, **e**, and **f** for 24, 48, 72, 98, and 120 h, respectively. Value of current decreases chronologically

Table 1 The values of photovoltaic parameters I_{SC} and V_{OC}

Measurement	Short circuit current (nA)			Open circuit voltage (mV)		
	Dark	(10 mW/cm ²)	(100 mW/cm ²)	Dark	(10 mW/cm ²)	(100 mW/cm ²)
Fresh cell (0 h)	1.291	9.612	18.520	140.00	143.50	401.06
24 h	0.545	4.074	10.546	71.20	72.38	187.68
48 h	0.508	2.346	6.737	40.80	41.67	119.89
72 h	0.377	1.328	4.356	21.60	23.50	77.39
96 h	0.311	0.913	2.592	15.00	15.40	46.00
120 h	0.280	0.705	2.328	10.10	10.90	41.36

0 first measurement after cell preparation

counter ions and ionic conductivity necessary for the doping [17,18]. Addition of plasticizers EC and PC makes the complexed mixture viscous, which helps easy fabrication of the film and also enhances the carrier mobility. Presence of ions has great effect on photovoltaic parameters particularly in open circuit voltage. Accumulation ions in respective electrodes enhance the charge migration at the electrode–blend interface. Decrease of open circuit voltage may attribute to the lowering of work function difference. Decreasing of work function difference means increase of work function of low work function electrode (i.e. Al). Formation of a blocking layer in between Al and blend takes place in presence of moisture (–OH of PVA attracts moisture) and heat (generated at the time of light exposure). During exposure to radiation, heat produces in the Al–Blend interface. Oxidization of Al may also take place in presence of heat. Thus, oxidization of electrode reduces the effective driving open circuit voltage. However, the identification of actual reason of degradation (of V_{OC}) is not completed, and it needs much research on that particular issue. As this open circuit voltage in the cell is

the key driving force to separate the photo-generated charge carriers, reduction of this force results to decrease of photocurrent.

Similarly, in Fig. 3, I_{SC} is plotted with time which also degrades with time. We analyzed the decay nature of open circuit voltage and short circuit current. The fitting line for both of them is shown by bold dark lines in Figs. 2 and 3, respectively. Fitting equation for V_{OC} can be given as

$$V_{OC} = V_0 + V' \text{Exp}(-t/t') \tag{1}$$

Here, t is time. Fitting parameters are listed in Table 2.

Corresponding fitting equation for I_{SC} can be given as

$$I_{SC} = I_0 + I' \text{Exp}(-t/t') \tag{2}$$

Here, t is time. Fitting parameters are listed in Table 3.

The meaning of t' in both the equations is the same, which is the inverse time constant having the unit of time, but the values are different. At $t=t'$, the argument of the exponent is equal to unity, and it is called relaxation time. In Fig. 4, we plotted the percentage of decrease of open circuit voltage and short circuit current to their initial values

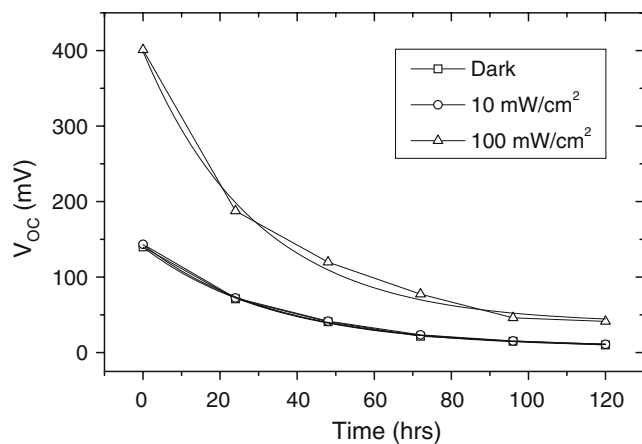


Fig. 2 Degradation of V_{OC} for successive measurement. Three curves are for **a** dark, **b** 10 mW/cm², and **c** 100 mW/cm². Nature of V_{OC} under perfectly dark condition is almost the same as that with 10 mW/cm². Dark bold line indicates theoretical fitting line

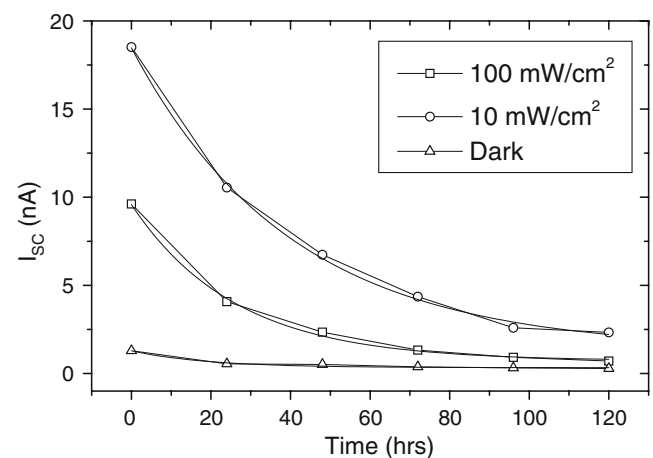


Fig. 3 Degradation of I_{SC} for successive measurement. Three curves are for **a** dark, **b** 10 mW/cm², and **c** 100 mW/cm². Dark bold line indicates theoretical fitting line

Table 2 Fitting parameters of decay of open circuit voltage

Measurement condition	V_0 (mV)	V' (mV)	t' (h)
Dark	6.65	135.20	34.01
Intensity (10 mW/cm ²)	7.67	135.48	33.50
Intensity (100 mW/cm ²)	38.20	360.44	29.62

Data extracted from Fig. 2

with respect to time. All the parameters decreased to almost 10% of their initial values.

From measured values of currents and voltages, we define parameter resistance. Resistance at 10 mW/cm² is the ratio of V_{OC} to I_{SC} for 10 mW/cm², whereas ratio of V_{OC} to I_{SC} for 100 mW/cm² represents the resistance for 100 mW/cm². Figure 5 shows the variation of these two resistances with time. From the figure, it is seen that photo resistance of the cell decreases from 22 M Ω to 18 M Ω in first measurement after 24 h and then it becomes constant, whereas the dark resistance remains constant throughout the measurement with values in the range 15–17 M Ω .

Conclusion

Safranine T dye-based PEC structure shows photovoltaic effect. Here, we investigated the stability of Safranine T dye-based PEC device in open laboratory environment for long-time operation. Different photovoltaic parameters were measured for freshly prepared device, and the same measurement was repeated with time at 24-h regular interval for 120 h. During the measurement, the device was kept in an open environment of our laboratory, which is a dust-free clean room, and the temperature and humidity of the laboratory was 27 °C and 55–60%, respectively. Our measurement shows that all the photovoltaic parameters degrade almost to 10% after 120 h of their initial values. Nature of degradation of V_{OC} and I_{SC} indicates that after 120 h, the values become almost stable. Photo resistance of the cell has been measured in the order of 22 M Ω and became constant after the first measurement at the value 18 M Ω . Degradation of photovoltaic parameters is expected due to the contamination of the organic materials with oxygen and water contains of the atmosphere. Our measure-

Table 3 Fitting parameters of decay of short circuit current

Measurement condition	I_0 (nA)	I' (nA)	t' (h)
Dark	0.327	0.954	19.44
Intensity (10 mW/cm ²)	0.713	8.86	26.25
Intensity (100 mW/cm ²)	1.350	17.12	40.11

Data extracted from Fig. 3

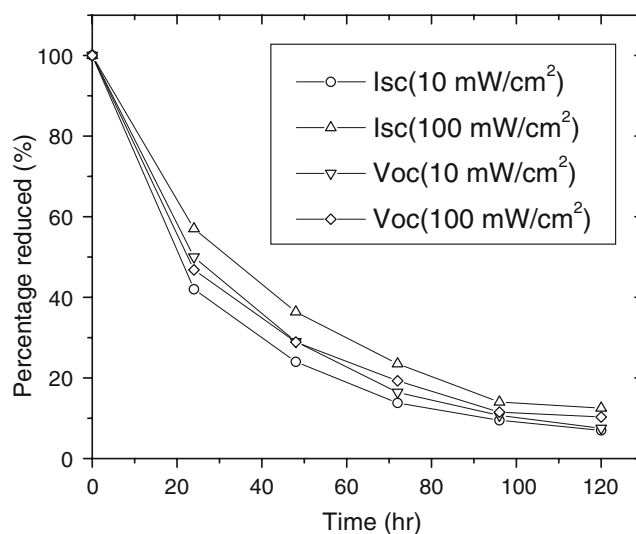


Fig. 4 Percentage reduced from the initials of all measured parameters. Nature of decreasing shows exponential type of decay

ment will be useful for long-term use of the device. Presently, we are trying to encapsulate the devices by using different resin so that the device can be free from the contact of the atmosphere; thereby, the moisture and oxygen contact may be avoided. To understand the details of work function reduction, a more detailed study is needed.

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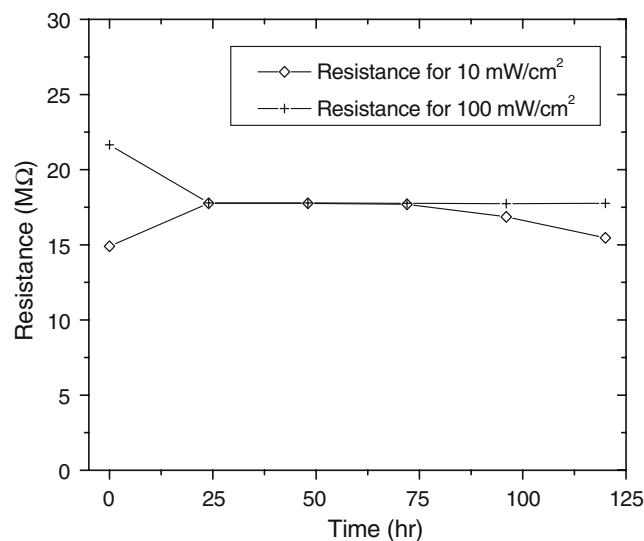


Fig. 5 Figure represents the variation of dark and photo resistance with time. Resistance for low intensity does not have any regular nature, whereas resistance for higher intensity decreases after first measurement and becomes constant after that

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